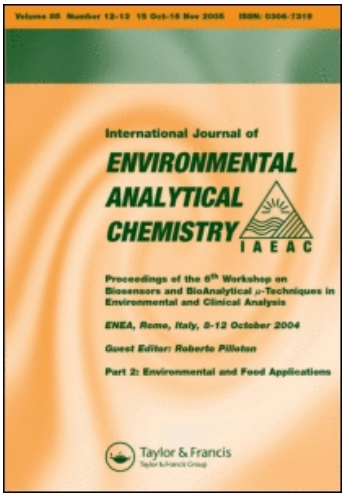

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Distribution and Characterization of Tar Ball Pollution on Beaches in Brittany (France) and Indonesia

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Stranded tar along the Brittany coast and four test sites in Indonesia (Jakarta Bay, Malacca and Makassar Straits, Central South Java) were surveyed in 1982 in order to quantify and identify the possible origin of oil pollutants. The estimation of tar pollution was determined by a statistical methodology based on a stratified random sampling. Western Brittany and Jakarta Bay must be regarded among the areas most vulnerable to chronic oil pollution with respectively gross weight values of 76.9 $\pm$115.6 g/m and 812.7$\pm$219 g/m, comparable to those of other coasts along major tanker routes such as Kuwait or Bermuda. The levels on the other sampled sites were relatively low in spite of such dense maritime traffic as in Malacca straits (15.4 $\pm$5.4 g/m) or near the mouth of La Loire (12.2$\pm$15.9 g/m and less than 0.5 g/m in the Bay of Saint-Brieuc).

Hydrocarbons in tar samples were examined by liquid and gas chromatography for a classification in crude oil residues, sludge residues and fuel oil. A multimethod approach combining GC, IR, SFUV and sulfur content was used for a characterization of oil extracts and their tentative matching with the physico-chemical parameters of some reference oils.

KEY WORDS: Stranded tar pollution, quantitative assessment, possible sources and origins, coastal pollution in Brittany and Indonesia.

INTRODUCTION

The presence of petroleum residues on beaches is becoming a widespread phenomenon in every coastal country. The oil entering the marine environment comes from various sources: Accidental or intentional oil spillages resulting from offshore activities and tanker traffic, natural submarine oil seepages, domestic and industrial petroleum waste discharges from coastal rivers or factories and atmospheric fall-out. Among these sources, the oil spillages from tank washing and deballasting operations at sea seem to be the main contributory factor in the extensive damage to marine life and seaside resorts through the accumulation of tar balls on account of their heavy and punctual inputs. The growing amount of petroleum products carried by tankers or produced may increase the level of coastal pollution. The National Academy of Science[1] has shown that there exists a very close correlation between the density of tar residues washed ashore and the maritime lanes used by tankers. The most sensitive zones are located in areas of oil production and near tanker routes especially in enclosed seas: Persian Gulf, Red Sea, Mediterranean Sea, Gulf of Mexico, or near some important straits and capes. Most particularly the shorelines of Brittany (France) and Indonesia are characterized by an intense tanker traffic in the direct vicinity of the coastline. An average of 180 freighters including 15 tankers are indexed every day at the English Channel western entrance. A similar tanker traffic could be expected near Indonesian coasts since more than 90% of the oil supply for the Pacific countries, particularly Japan and the United States is shipped from the Middle East through the Malacca and Makassar Straits (Indonesia). So the shorelines of Indonesia and Brittany could be among the areas most exposed to oil pollution. It could be interesting to compare the level and the source of tar contamination in these two areas characterized by differences in the geographical location, hydrographical and topographical features.

This paper deals with the two following objectives; firstly to quantify the tar pollution level on different Breton and Indonesian test sites, secondly to identify the possible origin of coastal oil pollution through the characterization of tar residues.

EXPERIMENTAL

Description of the studied sites

The coast of Brittany is characterized by a succession of protruding headlands, large bays and sheltered salt marshes. Tides, strongly prograding on the northern coast from west to east, have a range of 6 to 9 m disengaging large tidal flats. So under the actions of both tidal currents and N.W. winds tar residues and other litters discharged at sea are generally accumulating in the upper part of the foreshore open to the west. On account of a dangerously jagged coastline, severe weather conditions and high level of marine transportation, the northern coast of Brittany has recently been heavily polluted with several oil spills: *Bolhen* 1976, *Olympic Bravery* 1976, *Amoco Cadiz* 1978, *Gino* 1979, *Tanio* 1980. Since all these tanker accidents occurred in winter, our tar ball survey was carried out from October 1982 to February 1983. More than 80 field stations stretching from the mouth of La Loire to Saint-Malo were sampled (Figure 1).

Indonesia is situated between 95° and 141° longitude and between 6° North and 11° South latitude. It is composed of 13,677 islands with a total coastline length of approximately 81,000 km. The climate is completely controlled by monsoon with westerly winds from April to October and northeasterly winds during the remainder of the year. Winds and surface currents play the major role in the direction of oil slicks and floating tar drift.[2] The tide is mainly semi-diurnal with mean range of about 2 m. Based on considerations about prevailing currents, oil activities location and shipping routes, four test sites, namely Kepulauan Seribu, Kepulauan Riau, the southern-west coast of Sulawesi (Langga beach) and the south coast of Java near Jogjakarta were observed and surveyed in August 1982 (east monsoon) and in May 1984 (west monsoon). The location of the test sites is indicated in Figure 2. Kepulauan Seribu is an archipelago located in the Java sea at about 40 km to the northwest of Jakarta. Two islands: Pulau Pari and Pulau Tikus were selected in this archipelago during our 1982 and 1984 surveys. Kepulauan Riau is an archipelago situated south of Singapore island in the Malacca Straits. Numerous oil terminals and refineries with some productive offshore fields located on both sides of the Straits could be, with

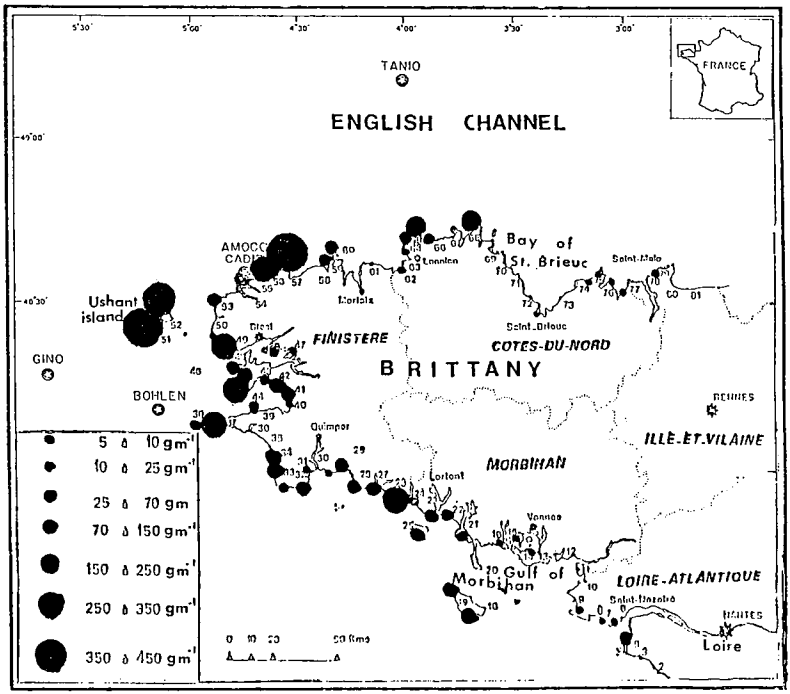

FIGURE 1 Localisation of studied sites and distribution of tar pollution on Brittany (France).

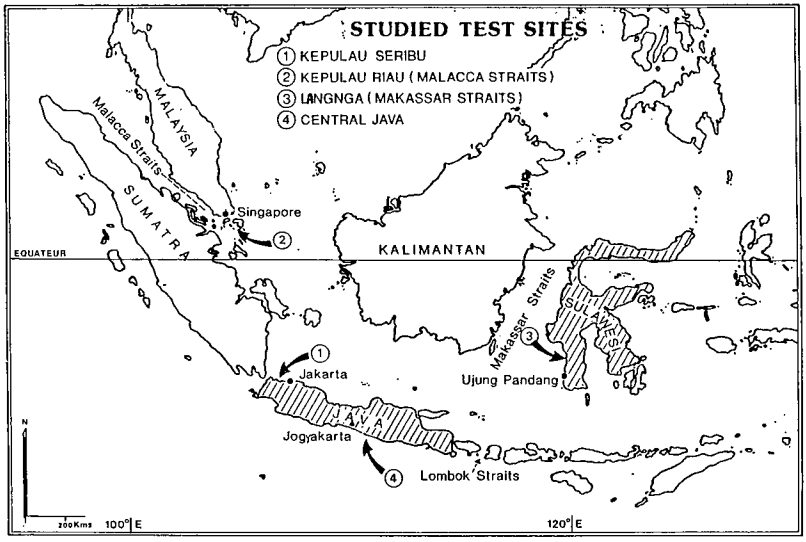

FIGURE 2 Studied test sites along shores in Indonesia.

their intense traffic, regarded as oil and tar pollution sources. Five islands were sampled in the main strait. Langga beach located about 180 km north of Ujung Pandang was the only test site surveyed on the south-western coast of Sulawesi. This sandy beach is an area representative of chronic tar pollution from oil transportation in the Makassar Straits. The test sites on the south coast of Java are composed of two beaches Krakal and Kukup (near Jogjakarta) well exposed to the open ocean swell.

Quantitative assessment of tar pollution

The aim of the developed methodology is to obtain an estimation as precise as possible of the quantity of stranded tar over a determined test site, taking into account that the tar loading is not homogeneous. The stratified random sampling adopted in this study has the advantage of giving a good precision of the estimated mean and of notably minimizing the variance of this mean. Briefly the sampling methodology could be divided into two steps.

- The first step is made up of a rapid reconnaissance of the test area in order to divide it into strata representative of a type of accumulation (i.e. very high, medium, low) each of which is internally homogeneous.
- The second consists in selecting, in each stratum, a random sampling composed of n beach profiles in which all surface tars are collected in a 1-m wide strip of beach extending from the waterline at the time of sampling to the extreme upper line of the investigated zone. Tar concentrations are expressed in grams per linear metre of beach (g/m). This unit has the advantage of being independent of beach width and tide level. Usually tar is concentrated in distinct bands parallel to the water line, which facilitates cleanup but makes the usefulness of expressing its concentration in units of g/m^2 (as it is advocated in the IGOSS methodology[3]) questionable.

For data processing the following formulas were used in a computerized program in order to estimate tar concentration and confidence limits of the sampled area.

$N = N_1 + N_2 + \cdots N_L$ = total number of units (L strata). The suffix h denotes the stratum h with total length N_h.

nh = value of the ith unit in the stratum h.

Y_{hi} = value of the ith unit in the stratum h.

$w_h = \dfrac{N_h}{N}$ = stratum weight. $f_h = \dfrac{n_h}{N_h}$ = sampling fraction in the stratum.

Estimation of the mean per unit over the whole population

$$\bar{y}_{st} = \sum_{h=1}^{L} \frac{N_h \bar{y}_h}{N}. \qquad \text{Sample mean: } \bar{y}_h = \sum_{i=1}^{n_h} \cdot \frac{y_{hi}}{n_h}.$$

Estimation of the standard deviation s_h in stratum h

$$s_h = \sqrt{\frac{1}{n_h - 1} \sum_{i=1}^{n_h} (y_{hi} - \bar{y}_h)^2} \quad \text{or} \quad s_h = \sqrt{\frac{1}{n(n-1)} n \sum y^2 - (\sum y)^2}.$$

Estimation of the whole population

$$y_{st} = \sum_{h-1}^{L} N_h \bar{y}_h.$$

Estimation of the variance of $\bar{y}_{st}$

$$V(\bar{y}_{st}) = s^2(\bar{y}_{st}) = \sum_{h=1}^{L} W_h^2 \frac{s_h^2}{n_h}(1 - f_h).$$

Estimation of the variance of the whole population

$$V(y_{st}) = N^2 \cdot V(\bar{y}_{st}).$$

Approximation of the number of degrees of freedom of $s(\bar{y}_{st})$

$$n_e = \frac{\left(\sum_{h=1}^{L} g_h s_h^2 \right)^2}{\sum_{h=1}^{L} \dfrac{g_h^2 s_h^2}{n_h - 1}} \quad \text{with} \quad g_h = N_h \frac{(N_h - n_h)}{n_h}.$$

Estimated mean

$$\bar{y}_{st} \pm t_p \times s(\bar{y}_{st})$$

with t_p obtained from Student's tables for the probability p and the number of degrees of freedom ne.

Analytical methods

The analytical procedure used in this study has been described elsewhere.[4,5] Briefly after extraction with chloroform in a Soxhlet and complete removal of solvent, some physical parameters (specific gravity, sulfur and metal contents, infrared analysis) could be done on the raw extract. However the analyses carried out by gas chromatography (GC) and UV spectrofluorimetry (SF UV) could be performed once the oil extract had been broken down into paraffinic and aromatic hydrocarbon fractions via conventional adsorption liquid chromatography. The IR spectrum was scanned between 2,000 cm^{-1} and 600 cm^{-1} on a Perkin Elmer 399B using absorbance mode and a KBr cell. UV fluorescence was measured on a Perkin Elmer spectrofluorimeter 3,000 equipped with synchronous excitation and emission monochromator modules. The experimental conditions were as follows: Excitation slit 10 nm, emission slit 5 nm, scan speed 60 nm per minute, synchronous scanning of emission and excitation wavelength with 15 nm, a 10 nm simple quartz sample cell, scanning between 250 and 500 nm. All samples were analysed with the same conditions (10 mg/l) and instrument setting to minimize quenching errors.

Gas chromatographic analyses were carried out on a Hewlett Packard 5840A model equipped with a flame ionization detector, splitless injection and a CP Sil 5 capillary column. The analytical conditions were similar to those described by Calder *et al.*[5] for the analysis of crude oils and petroleum residues by GC.

RESULTS AND DISCUSSION

Tar pollution in Brittany

Assessment of pollution level The geographical location of the 81 test sites surveyed along the shoreline of Brittany is represented on Figure 1 by a circle characterizing its level of tar contamination. Each site was sampled on a beach length between 150 and 2,000 m (m: 603 ± 340 m). The total sampled coast is about 50 km. The

beaches surveyed were regrouped by "regions" based on coastal geology and exposure (Table I). Tar concentrations on the survey area display high variability according to the geographical location and exposure of the site to prevailing winds and currents. Usually the standard deviation for a series of test-sites exceeds the mean. The most polluted areas include mainly west-facing beaches situated near the Channel western entrance as Sta 52 at Ushant (760 g/m), Sta 56 (242 g/m) and Sta 57 (387 g/m) at Plouguerneau while the coastline

TABLE I

Tar pollution on beaches in Brittany
(October 1982–January 1983 survey)

Survey area (test site no.)	Total length sampled (km)	Tar concentration (g/m)		Tar/other litter (% gross weight)
		Range	Mean ± S.D.	
Loire Atlantique				
Sta 1–Sta 10	5.6	0–49	12.2 ± 15.9	1.7 ± 2.2 max Sta 5: 5.8%
Morbihan				
Sta 11–Sta 20	4.4	0–82	7.9 ± 27.3	2.3 ± 1.4 max Sta 18: 3.8%
Sta 21–Sta 26	3.5	10–208	57 ± 72	4.9 ± 4.3 max Sta 26: 12.5%
Finistère				
Sta 27–Sta 32	3.3	0–88	42.1 ± 46.7	4.8 ± 1.6 max Sta 32: 6.5%
Sta 33–Sta 38	5.3	0–203	72.2 ± 75.2	11.4 ± 13.4 max Sta 37: 33.9%
Sta 39–Sta 44	5.2	15–235	91 ± 84	10.0 ± 56 max Sta 39: 16.8%
Sta 45–Sta 50	3.6	0–142	35.2 ± 54.2	11.2 ± 15.2 max Sta 49: 37.5%
Sta 51–Sta 56	3.4	12–760	197 ± 296	35.0 ± 30.2 max Sta 56: 87.4%
Sta 57–Sta 61	3.6	0–387	65 ± 160	36.9 ± 30.6 max Sta 57: 75.6%
Côtes-du-Nord *Ille-et Vilaine*				
Sta 62–Sta 71	4.3	0–130	36 ± 49	32.1 ± 40.4 max Sta 65: 94.8%
Sta 72–Sta 81	7.1	0–4	0.5	

of Bay of Saint-Brieuc and Gulf of Morbihan were not or less polluted. The Breton N.W. coast looked more vulnerable to chronic tar pollution than the S.W. side as a result of the fact that tank washing and deballasting operations could be regarded as the main source of tar pollution along this area. Along the western part (Sta 18 to Sta 68) the mean and standard deviation were estimated to the values in gross weight: 76.9 ± 115.6 g/m during our 1982–1983 survey. Tar distribution is strongly depending on the coastal geomorphology and time of sampling. A follow-up study on the accumulation of stranded tar was carried out at Portsall (Sta 53) between September and June 1982. Tar concentration was between 130.4 g/m and 251.6 g/m with a maximum value in March.[3] Tar was one of the most common pollutants on the beaches and corresponded on some sites: Ushant Island (59%), at Sta 56 (87%), Sta 57 (76%) or at Sta 68 (87%) to the most important pollutant (in weight) found on the test.

Chemical characterization of samples collected in Brittany The main results on the chemical analysis of 21 samples collected in Brittany are summarized in Table II. The oil content in stranded tars generally represents more than 60% ($62 \pm 23\%$) of the tar's dry weight. The percentage of sulfur ranges between 0.99 and 3.98% with an average value of $2.38 \pm 0.71\%$ while the nitrogen content was roughly similar (mean $0.14 \pm 0.05\%$). The oil extract was fractionated by liquid chromatography into saturated hydrocarbons, aromatic hydrocarbons and heavy products (polar compounds, resins and asphaltens). The relative amount of heavy products in comparison with the hydrocarbon content is represented in Table II by the ratio A = heavy products/saturated and aromatic fractions. The values of this parameter ranged from 0.16 to 0.89 (mean: 0.40 ± 0.25) indicating a low degree of weathering in comparison with the average value 0.22 ± 0.06 given by Middle East and North Africa oils.

This fact was confirmed by GC. The first *n*-alkane detected was in most samples below nC_{12}. The volatile fraction defined by the ratio $B = \sum_{10}^{25} n\text{-alkanes} / \sum_{17}^{25} n\text{-alkanes}$ ranged from 1.02 to 2.78. The mean (1.67 ± 0.55) was lower than the value measured in reference oils[4] topped at 150°C (2.01 ± 0.65).

According to the *n*-alkane distribution and the shape of the unresolved envelope, the chromatograms of the samples have been classified in four patterns: A, B, C, D.[6] Chromatogram A shows a

TABLE II

Summary of chemical data for tar samples collected in Brittany

Sampling site	Station site no.	Oil content (%)	Sulfur content (%)	A (1)	Gas chromatography: Profile type	B (2)	$\frac{nC_{17}}{Pt}$	$\frac{nC_{18}}{Ph}$	$\frac{Pt}{Ph}$
Pornichet	7	40.2	2.08	0.16	A	0.99	0.92	0.77	1.78
Erdeven	21	42.5	2.02	0.70	B	2.70	1.76	0.73	1.21
Graves	22	92.5	2.09	0.47	B	2.28	1.60	0.79	1.78
Kerfriant	29	70.5	2.36	0.43	B	2.06	1.50	0.83	2.78
Sables Blancs	32	56.9	2.06	0.19	B	1.61	3.02	2.02	2.73
Kervellec	33	39.7	2.45	0.86	A	1.91	1.50	0.71	1.21
La Torche	34	18.9	2.38	0.78	C	0.14	0.20	1.01	1.29
Pors Peron	39	86.4	2.05	0.36	A	2.38	2.20	1.03	1.58
Plage du Ris	40	74.4	0.99	0.18	C	0.44	0.83	1.98	1.22
Trez-Bellec	42	53.4	3.21	0.25	C	0.59	0.50	0.63	1.25
Aber	43	82.9	1.49	0.89	B	2.45	1.80	0.71	1.69
La Palud	44	89.8	2.27	0.43	B	1.53	1.29	0.74	1.21
Toulinguet	46	71.3	1.78	0.55	B	1.90	1.60	0.76	1.80
Plougastel	48	86.2	3.20	0.25	B	2.13	0.91	0.42	1.46
Posmilin	49	80.7	2.80	0.60	B	1.44	1.17	0.71	1.10
Blancs Sablons	50	72.8	3.98	0.78	C	0.19	0.20	1.30	1.02
Portsall	53	89.0	3.28	0.58	A	3.2	2.60	0.89	2.11
Bouenou	54	50.7	2.22	0.85	B	2.02	1.23	0.70	1.49
Vougeot	56	50.7	2.82	0.36	A	2.30	2.68	0.86	2.37
Roscoff	59	24.6	3.07	0.30	B	1.08	0.90	0.77	1.80
Trozoul	64	28.5	1.48	0.25	A	2.51	2.35	1.09	2.45

(1) A = Heavy products (%)/saturated + aromatic hydrocarbons (%).

(2) $B = \sum_{10}^{25} n\text{-alkanes} / \sum_{17}^{25} n\text{-alkanes}$.

regular distribution of *n*-alkanes from C_{11} to C_{40} (and more) characteristic of a slightly weathered paraffinic crude oil or light fuel oils. Chromatogram B displays a bimodal *n*-alkane distribution with two maxima at approximatively nC_{17} and nC_{32} characteristic of crude and gas-oil sludges (i.e. tanker wall washings). Chromatogram C with an unimodal alkane distribution from C_{16} to more than C_{40} illustrates the profile of heavy fuel oil similar to refined No. 6 fuel or grease with high wax content. Chromatogram D shows only a few detectable GC signals emerging from an unresolved envelope (UCM) characteristic of a highly weathered residue of indetermined

origin. Half of the tars samples on the Breton coast showed a bimodal profile (type B) while a third had a unimodal *n*-alkane distribution similar to weathered crude oils (type A) and the remaining portion looked like heavy fuel oils (type C). These data strongly support transportation activities as the major sources of tar precursors at the western English Channel entrance. This may result from discharges of oily ballast water by small tankers without load on top equipments on inward-bound voyages to north European countries terminals or productive oil fields in the North Sea. Local fishing activities seemed to be a minor contributor since no relationship could be found on the polluted areas between tar loadings and fishing gear (plastic boxes and ropes) lost or discharged at sea. The fact that most samples showed a bimodal *n*-alkanes distribution was likewise determined along the Mediterranean coast[8,9] but usually an unimodel distribution was observed.[10-13]

In this study GC identifying parameters has been used only on the case of slightly weathered samples ($A < 0.7$) showing an unimodal or bimodal *n*-alkane distribution (types A or B) with a light hydrocarbon content ($B > 1.2$). In these conditions, the ratio nC_{17}/Pristane, nC_{18}/Phytane, Pristane/Phytane and biological makers such as the C_{20}–C_{40} acyclic isoprenoids C_{27} steranes and triterpanes[14,15] could be matched with reference oil samples. Yet pinpointing sources of the stranded beach tars requires in most cases, additional data as sulfur, trace element content or other informations obtained by other analytical techniques. In particular Figure 3 illustrates the relation between Pristane/Phytane ratio and sulfur content values. On account of the weathering processes, a rough correlation was expected with the data from the possible pollutant sources. No analysed tar sample looked like North African oils (Algeria and Libya) or North Sea oil (Ekofisk). On the other hand, a good similarity could be observed with compositional parameters of originating Middle East or Mexico oils for almost all the tar samples. One explanation of this possible origin of tar samples could be the relatively low European consumption of other crudes and the difficulty for some North African crudes to form oil patches because of their low asphaltene and paraffin contents.[16] Presumptions that some samples (Sta 32, 40, 64) could be originating from U.S. crude oils are given by GC and sulfur measurements and the observation of barnacles (lepas anatifera) living on them. It may be that floating tars are

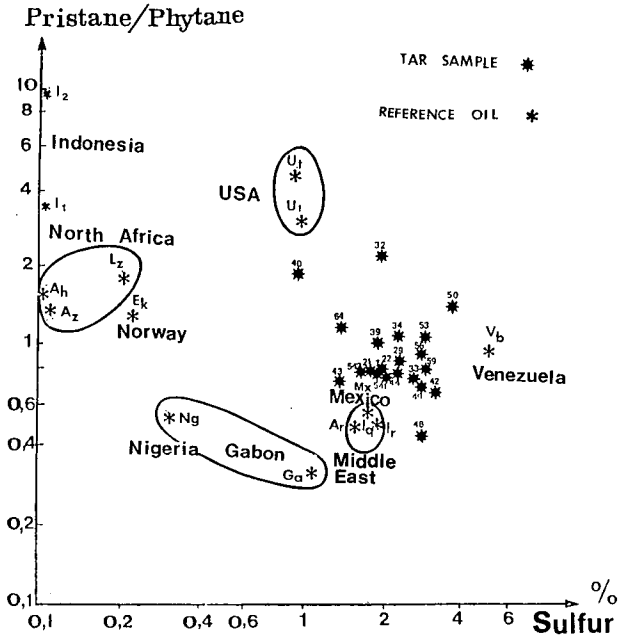

FIGURE 3 Relationship between pristane/phytane ratio and sulfur content in tar samples collected in Brittany (France).

colonized soon after they enter the marine environment and that the type of organisms found on them indicates the kind of environment to which they are first exposed. The size of these barnacles (max 15 mm long) is probably not a reliable measure of the residence time of the tar in the water, until more is known about the factors influencing the growth rates of organisms associated with the tars. However the presence on tar samples of these mollusks unknown on temperate climate should indicate that the discharges occurred far in the open Atlantic ocean before before washing ashore in Brittany under the action of current (Gulf Stream) and westward winds (common in this area).

Tar pollution on the Indonesian test sites

Assessment of pollution level The general estimation of stranded tar ball pollution on the sites surveyed in 1982 and 1984 is indicated on

Table III. The data (mean and confidence limits) are expressed in gram per unit beach length (g/m) of the residues collected before (values in gross weight) and after removal of nonpetroleum compound (values in net weight). Oil contents in tar samples was determined by the chemical analyses (Soxhlet extraction) of about 50 samples randomly distributed on each studied test site. The data expressed in net weight represent about 30% of the values in gross weight. So looking only on the data expressed in gross weight may lead to incorrect evaluation and comparison between the pollution level on two sites when the values are very close together. In this study the results expressed in gross or net weight do not change the order in the pollution level of the studied sites and only the values expressed in gross weight will be discussed.

Kepulauan Seribu in Jakarta Bay appeared to be about 100 times (1984 survey) and 22 times (1982 survey) more polluted than the average level measured on Malacca and Makassar test sites. In the case of Malacca Straits test sites it was very surprising to find that

TABLE III

Tar pollution on Indonesian beaches in August 1982 and May 1984 (data expressed in g/m)

	1982 survey		1984 survey	
Geographical location	Mean in gross weight	Mean in net weight	Mean in gross weight	Mean in net weight
Pulau Pari South	102±45	25.9±11.4	542±394	112.3±85.8
Pulau Pari North	2867±840	189±55	9554±5979	1880±1224
Pulau Tikus	61.1±49.4	18.1±10.8	86±37.8	19.8±9.8
General estimation at Kepulauan Seribu	812.7±219	67±15.3	2460±1349	494±270
Pulau Takong	29.8±18.2	8.14±7	53.6±77.6	13.7±19.8
Pulau Pelampong	15.2±16.5	7.6±8.2	6.57	0.95
Pulau Nirup	11.3±13.1	8.5±9.9	5.21±9.64	1.68±3.10
Pulau Labon Kecil	9.6±13.7	5.5±7.9	2.85±1.88	1.02±0.67
Pulau Kapal Besar	24.1±20.7	11.3±10.1	41.2±37.8	18.3±16.8
General estimation at Kepulauan Riau	15.4±5.4	7.8±3.4	16.03±12.4	4.80±2.95
Makassar Straits (Langga)	56.8±36.5	30.7±21.1	22.6±9.3	9.08±3.32
Central Java coast (Kukup)	<1		7.5±2.7	3.13±2.53

the area in front of Singapore harbour was among the lowest contaminated zones. This fact could be explained by the presence of strong currents. In this case there is no accumulation of tar but only transit. This was observed in Pulau Takong in the middle of the straits. Fresh tar were coming with the flood tide and going back with the ebb tide and the strong drift associated to it. The same portion of the island shore showed a complete redistribution of tar depositions in 24 h although the level of pollution in weight had not changed.

We observe between August 1982 and May 1984 an increase of tar concentration in Kepulauan Seribu by a factor of about three times. On the other sites no characteristic fluctuations in tar loading are noted when compared to the two surveys. The increase of deposition in May could be due to changes in coastal circulation patterns and wind direction during the north-western monsoon.

Chemical characterization of samples collected in Indonesia More than 50 tar residues were randomly sampled during our 1982 field survey and analysed as previously described. The results are represented in Table IV by the average values (mean $\pm$ standard deviation) of oil extract's composition in samples collected in the same area. A strict comparison between the data is difficult because the samples are in different stages of weathering. On the same sampling site we observe that the ratio heavy products/hydrocarbon fractions (A values) has a coefficient of variation (CV%) between 5 and 62% (mean: $32 \pm 18\%$). However each site showed a particular aspect of tar pollution. For example, on the south coast of Pulau Pari (Kepulauan Seribu area) oil pollution was in form of small tar balls and oil patches often lying on the sea bottom at low tidal zone level. The oil content represented about 30% of the sample's weight. The oil extract had low values of sulfur content ($0.6 \pm 0.7\%$) and $n\mathrm{C}_{17}$/Pristane (0.4 ± 0.5) in comparison with the high Pristane/Phytane value (7.5 ± 2.2). The northern coast of Pulau Pari was polluted by discontinuous large oily patches lying at the upper beach zone. The contamination seemed to result from the same oil slick. The oil content was very low ($6.6 \pm 0.9\%$). The organic extract was characterized by relatively high values for sulfur content ($2.4 \pm 0.9\%$) and $n\mathrm{C}_{17}$/Pr (1.6 ± 0.9) and a low Pr/Ph value (1.5 ± 0.8). These data pointed out that the sources and the origin of oil

TABLE IV

Summary of chemical data for Indonesian tar samples

Test site	No. of samples	Oil content mean ± s.d.	Sulfur (%) mean ± s.d.	A (1)	G.C. parameters mean ± s.d.		UV SF (2) I 405/I 350
					nC_{17}/Pr	Pr/Ph	
Kepulauan Seribu area							
Pulau Pari South	13	25.4 ± 10.4	0.6 ± 0.7	0.7 ± 0.4	0.4 ± 0.5	7.5 ± 2.2	0.7 ± 0.1
Pulau Pari North	6	6.6 ± 0.9	2.4 ± 0.9	0.5 ± 0.2	1.6 ± 0.9	1.5 ± 0.8	0.5 ± 0.1
Pulau Tikus	5	48.7 ± 40.9	0.3 ± 0.1	0.8 ± 0.5	1.2 ± 1.0	3.5 ± 0.8	0.4 ± 0.2
Kepulauan Riau area							
Pulau Takong	5	24.1 ± 11.4	0.6 ± 0.4	0.2 ± 0.02	0.7 ± 0.1	6.7 ± 1.0	0.9 ± 0.2
Pulau Pelampong	2	50 ± 30	1.1 ± 1.1	0.4 ± 0.1	1.1 ± 0.4	5.8 ± 0.5	—
Pulau Nirup	8	69.5 ± 16.2	0.4 ± 0.3	0.3 ± 0.1	0.7 ± 0.1	6.6 ± 0.6	0.7 ± 0.1
Pulau Labon Kecil	3	67.1 ± 17.2	0.3 ± 0.2	0.4 ± 0.02	1.8 ± 0.2	3.7 ± 0.5	0.6 ± 0.1
Pulau Kapal Besar	3	46.9 ± 6.2	0.5 ± 0.2	1.0 ± 0.3	—	—	—
Makassar Straits (Langga)	4	53.4 ± 17.9	0.3 ± 0.3	0.6 ± 0.2	1.1 ± 0.5	3.2 ± 0.4	0.4 ± 0.1
Central Java coast	2	81.2 ± 11.7	0.3 ± 0.1	0.9 ± 0.2	1.3	2.6	0.7 ± 0.1

(1) As defined in Table II.
(2) As defined in this paper.

contamination on the northern coast seemed different from those found at the southern part. The majority of the tar samples collected there (54%) displayed a gas chromatogram with a bimodal paraffinic distribution while about 10% looked like a slightly weathered crude, and 16% were similar to a heavy fuel oil. All the samples from Pulau Pari North had an unimodal chromatographic profile characteristic of a weathered crude oil.

Oil in Indonesia produced by Pertamina and its 79 contractors has reached a total amount of 488 million barrels in 1982 including the offshore production of 44% coming mainly from continental shelves located in the N.E. and N.W. Java, Kutei and Natuna basins.[17] Oil found in these reservoirs is paraffin based from medium to high gravity with a low sulfur content. The main characteristic parameters of analysed Indonesian crude oils may be separated in two groups (Table V). Oil samples coming from offshore fields located in the northwestern part of Kepulauan Seribu, labelled I_1, was characterized by a high value of C_{17}/Pr and C_{18}/Ph ratios while the others (I_2 to I_5) had a high Pr/Ph (9.2 ± 0.3) and a low value nC_{17}/Pr (0.33 ± 0.12) values.

The values of Pr/Ph ratio with sulfur contents measured in Kepulauan Seribu tar samples are represented in Figure 4. We observed on this graph that the data of samples labelled 1, 2, 4, 5, 7 were grouped with oils I_2 to I_5 while samples 14, 16, 17, 18, 19 seemed to be similar to reference oils from Middle East, Africa or Mexico. In order to get better identifying proofs about the possible origin of tar samples, analyses by infrared spectrometry and synchronous spectrofluorimetry were carried out. Various nonlinear combination of IR absorbance ratios are possible.[18] A determination limited to the absorbance at the frequences $1600\,cm^{-1}$, $810\,cm^{-1}$ and $720\,cm^{-1}$ provides an additional tool for oil identification. In particular an interesting recognition of tar samples probably coming from Indonesian crude oil I_1 could be noticed on Figure 5.

The aromatics extracts from tar balls were analysed using synchronous fluorescence spectroscopy. Aromatic ring number designations were made according to Wakeham[19] and Ostvold.[20] Scanning of fluorescence from 250 to 500 nm revealed quantitative differences in the spectra of samples from different locations. The relative contribution to fluorescence by five rings and larger aromatic compounds was determined by expressing the peak height at 405 nm

TABLE V

Physico-chemical and chromatographic characteristics of some reference oils

Sample	Code no.	Sulphur content	A (1)	G.C. parameters			UV SF (2)
				C_{17}/Pr	C_{18}/Ph	Pr/Ph	I 405/I 350
Indonesian crudes							
IIAP	I1	0.10	0.28	3.55	8.20	3.30	0.92
AR PT #2	I2	0.13	0.26	0.40	4.47	9.20	0.39
AR DST #3	I3	0.16	0.25	0.48	4.66	8.78	0.32
AR DST #4	I4	0.30	0.18	0.25	3.09	9.40	0.36
AR DST #5	I5	0.12	0.18	0.20	2.51	9.45	0.41
Middle East oils							
Arabian light (+150)	Ar	1.82	0.44	5.66	2.44	0.46	0.55
Iranian light (+150)	Ir	1.85	0.29	5.92	2.81	0.55	0.55
Iraq (crude)	Iq	1.81	0.27	6.96	2.98	0.50	0.50
Other countries							
Nigeria	Ng	0.30	0.07	0.61	2.19	0.55	0.34
Gabon (Mandji)	Ga	1.10	0.11	1.06	0.69	0.35	0.32
Mexico (Ixtoc)	Mx	1.80	0.16	3.64	2.28	0.61	0.40
North Sea (Ekofisk)	Ek	0.22	0.16	2.53	2.72	1.23	0.18
Algeria (Hassi Messaoud)	Ah	0.13	0.19	2.75	3.40	1.40	—
Algeria (Zarzetine)	Az	0.08	0.21	3.03	3.49	1.44	—
Libya (Zueitina)	Lz	0.23	0.13	2.58	1.60	1.68	—
Venezuela (Boscan)	Vb	5.5	1.08	0.62	0.51	0.83	0.33
U.S.A. (Texas)	Ut	1.0	0.07	1.25	4.40	4.80	—
U.S.A. (Louisiana)	Ul	1.1	0.07	1.10	3.0	2.73	—

(1) Defined as Table IV.

(2) Spectrofluorescence data defined by the ratio of fluorescence intensity at 405 nm and at 350 nm.

in relation to the value at 350 nm (I 405/I 350). A rough correlation could be expected between the values in tar balls and in its possible oils sources considering the relative solubility of light aromatic hydrocarbons in sea water before lump and tar ball formation from the spilled oil. However these analytical data seemed roughly in agreement with the other identifying parameters to assess the possible source and origin of the pollution in each studied site.

Oil pollution on the south Pulau Pari coast could be mainly attributed to local shipping and fishing activities. Most samples displayed a gas chromatogram with a bimodal paraffinic distribution and analytical parameters similar to Indonesian oils labelled I_2 to I_5.

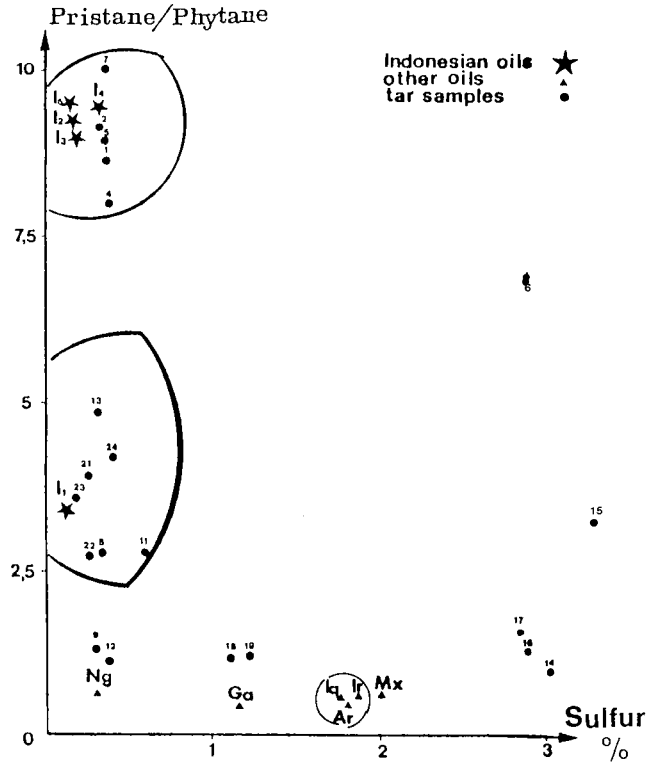

FIGURE 4 Relationship between pristane to phytane ratio and sulfur content in Kepulau Seribu samples.

About 10% of samples looked like weathered crude oil (I_1 type) probably coming from offshore exploitation in N.W. Kepulauan Seribu area while 20% of collected tar could be assigned to oils similar to weathered Middle East (M.E.) crude oils.

The level of tar accumulation at the Kepulauan Riau area was relatively low (16 g/m) in spite of the important traffic across the Straits of Malacca. Based on sulfur content, GC and IR data, the collected samples were arranged in two main groups. About one-third of them were grouped around the reference oil I_1 while the others could be correlated with oils from other Indonesian or South Asia oil fields similar to I_2 to I_5.

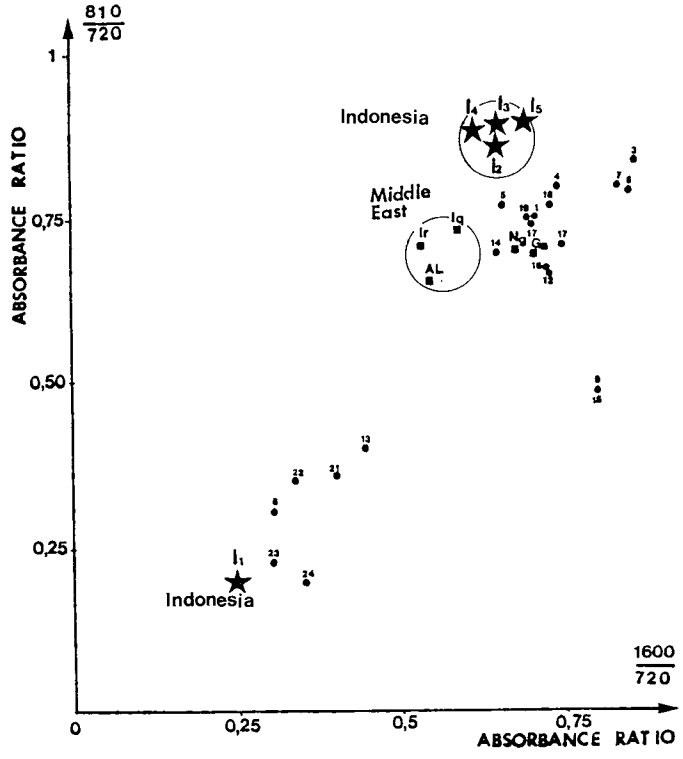

FIGURE 5 Relationship between infrared absorbance ratios in Kepulau Seribu samples.

The two other pilot areas: Langga beach on the western coast of Sulawesi (Makassar Straits) and Kukup beach on the Central Java coast were characterized by a low tar pollution. All the analysed tars had a low sulfur content (mean: 0.3 ± 0.3). One sample showed a bimodal *n*-alkane distribution while the others seemed to be weathered crude oils of indetermined origin.

CONCLUSION

This paper gives a first assessment and characterization of tar depositions on some sites in French Brittany and Indonesia vul-

nerable to chronical oil pollution. The main results are compared in Table VI with data obtained on some areas more extensively studied as Mediterranean, Gulf of Mexico or Kuwaiti coastline. Stranded tar pollution on Kepulauan Seribu (Jakarta Bay) during our 1982 and 1984 surveys was among the highest values found on coastal areas of major tanker routes such as Kuwait, Bermuda or Israel. Pollution levels observed along Malacca and Makassar Straits are comparable with the less polluted coastlines such as Trinidad and Tobago coasts. With an estimation of about 80 g/m, the western part of Brittany is notably subjected to oil contamination.

TABLE VI

Estimation of stranded pollution on some geographical areas

Location	Beach profiles nos.	Tar concentration (g/m) mean ± s.d.	Reference
The Netherlands (North Sea)	10	0.2 ± 0.3	21
Australia (Darwin and vicinity)	8	0.4 ± 1	21
Mauritus (regional average)	46	5.5 ± 9.7	21
Indonesia (Sumatra Sibolga)	12	1.4 ± 4.7	21
Indonesia (Central Java coast)	5	7.5 ± 2.7	this study
Seychelles (Mahi)	32	10.1 ± 12.3	21
Singapore (regional average)	19	10.0 ± 1.2	21
India (West coast)	35	13.1 ± 15.6	21
Indonesia (Malacca Straits)	32	16.0 ± 12.4	this study
Thailand (gulf average)	38	17.8 ± 36.6	21
South Africa (Cape Town/ Durban vicinity)	43	27.8 ± 15.6	21
Indonesia (Makassar Straits)	12	22.5 ± 9.3	this study
Saudi Arabia (Jedda)	3	29.8 ± 27.4	21
Kenya (regional average)	14	42.8 ± 40.8	21
Sri Lanka (regional average)	38	46.4 ± 51.4	21
Trinidad and Tobago	—	54	22
Sudan (Port Sudan vicinity)	10	107.1 ± 87.8	21
France (W. Brittany)	50	76.9 ± 115.6	this study
Malaysia (Gulf of Thailand)	43	125.1 ± 129.4	21
Kuwait (regional average)	58	155.1 ± 87.1	23
Bermuda	—	700	24
Indonesia (Kepulauan Seribu)	47	813 ± 219	1982 survey
Indonesia (Kepulauan Seribu)	47	2460 ± 349	1984 survey
Israel (Mediterranean coast)	—	3625	25

The characterization of tar samples is important in order to define the possible pollutant sources and origin. The classification of samples was based on sulfur content, gravimetric and molecular compositions (gas chromatography), IR and fluorescence spectra. Tar samples collected in Brittany looked very fresh; so that sulfur content and gas chromatographic data were a good approach for identifying oil pollutants. Middle East oils seemed to be the main contributors to beach tar pollution. On the other hand, most tars collected in Indonesia exhibit significant signs of degradation and it was necessary to use other fingerprinting methods such as biological markers (triterpanes and steranes[15]) or infrared and fluorescence spectra.

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