

DISTRIBUTION OF HYDROCARBONS IN WATER AND MARINE SEDIMENTS AFTER THE AMOCO CADIZ AND IXTOC-I OIL SPILLS

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INTRODUCTION

—The shipwreck of the Amoco Cadiz supertanker on the rocks of the Brittany coast in France (March 1978) and the blowout of Ixtoc-I well in the Gulf of Mexico (June 1979) were the most important oil spills ever recorded. The crude oils discharged in the marine environment from both accidents were light petroleum and their chemical compositions were similar (Table 1). After these two oil spills we examined the hydrocarbon pollution in the marine environment. Our chemical studies were limited to an overall estimate of the oil content to assess the importance of and the extent of the pollution at the seawater surface and into the water column plus the sediment contamination. The analytical techniques used were UV spectrofluorometry for the seawater samples and IR spectrophotometry for the sediment samples. The Ixtoc-I study was less important than the Amoco Cadiz one, and was limited to the analysis of samples collected during only one oceanographic cruise. —

Table 1. Characteristics of Amoco Cadiz and Ixtoc-I Oil Spills

| Oil Spill | Amoco Cadiz | Ixtoc-I |
|-----------------------|--|--|
| Nature of incident | stranding of a tanker | blowout (drilling well) |
| Location | Brittany coast, Portsall (France) | Gulf of Mexico (Mexico) 19° 24.5' N - 92° 12.5' W |
| Date | March 16, 1978 | June 3, 1979 to March 20, 1980 |
| Crude oils | "Arabian Light" and "Iranian Light" (about 1:1) | Ixtoc-I |
| Quantities discharged | 223,000 ton | ~600,000 ton |
| Density | 0.85 | 0.84 |
| Chemical composition | | |
| Saturated | 39% (Ref. 1) | 50% (Ref. 3) |
| Aromatics | 34% | 32% |
| Resins and Asphaltens | 27% | 18% |
| Nickel | 14 ppm (Ref. 2) | 10.5 ppm |
| Vanadium | 45 ppm | 55 ppm |

EXPERIMENTAL

Seawater

Subsurface seawater samples (2 liters) were collected at 1-m depth with a glass bottle held in a metal frame. The bottle was closed with a Teflon^{*®} cylindro-conical stopper, the opening and the closing of which were controlled by the manipulator when the sampler was at the sampling depth. The collection of seawater samples at different depths was carried out with sterile plastic bags fixed on a "Butterfly" model sampler. The bags also were opened and closed at the sampling depths. Comparative analysis of two water samples collected with the glass bottle and plastic bag did not show any significant difference [4].

Immediately after collection, the seawater sample was extracted successively with 100 mL of chloroform and 100 mL of hexane. The two organic extracts were set in a glass flask and kept for analysis at the laboratory. The

*Registered trademark of E. I. Du Pont de Nemours & Company, Inc., Wilmington, Delaware.

organic phase (chloroform-hexane mixture) was then reduced by evaporation to about 5 mL. The traces of water were removed with anhydrous sodium sulfate. The extract was then concentrated to dryness under a nitrogen stream and finally rediluted to 5 mL with hexane.

Hydrocarbons were measured by UV spectrofluorometry (Turner apparatus, model 430), according to the method previously described [5-8]. The excitation wavelength was fixed at 310 nm. The emission spectra were set from 500 to 320 nm and maxima of fluorescence appeared between 390 and 360 nm. The spectrofluorometer was calibrated with a solution of emulsified crude oil in hexane, collected respectively near the Amoco Cadiz shipwreck* and Ixtoc-I well.** For comparison, we give the responses of the spectrofluorometer with the two calibration solutions (Table 2). Although only the aromatic compounds are detected by spectrofluorometry, the data are expressed in total hydrocarbons related to calibration crude oil solution. Nevertheless, the data reported are not necessarily representative of absolute hydrocarbon concentrations in seawater.

Immediate Analysis of Seawater on Board

During oceanographic cruises we collected duplicate seawater samples (1 liter) which were extracted with only 20 mL of hexane. The organic extracts were immediately measured on board ship by UV spectrofluorometry under identical conditions. Thus we were able to obtain during these cruises preliminary and immediate information about oil pollution in seawater. A comparison of the results of duplicate water samples analyzed either on board ship or later in the laboratory is illustrated by Figures 1 (Amoco Cadiz) and 2 (Ixtoc-I). For most of the data compared, the correlation is good (85%). So, the spectrofluorometry technique can be used as an operational analytical method to rapidly observe, while still on board the ship, the extent of oil pollution in the marine environment.

Table 2. Spectrofluorometer Responses, Expressed in Arbitrary Units
 $\lambda_{\text{Excitation}}: 310 \text{ nm}; \lambda_{\text{Emission}}: 360 \text{ nm}$

| Solution at 1 $\mu\text{g}/\text{mL}$ in Hexane | Spectrofluorometer Responses (arbitrary units) |
|---|---|
| Amoco Cadiz emulsion | 760 |
| Ixtoc-I emulsion | 465 |

*Emulsion sample given by Dr. Calder (NOAA-USA).

**Emulsion sample given by Ing. Teyssier (IMP-Mexico).

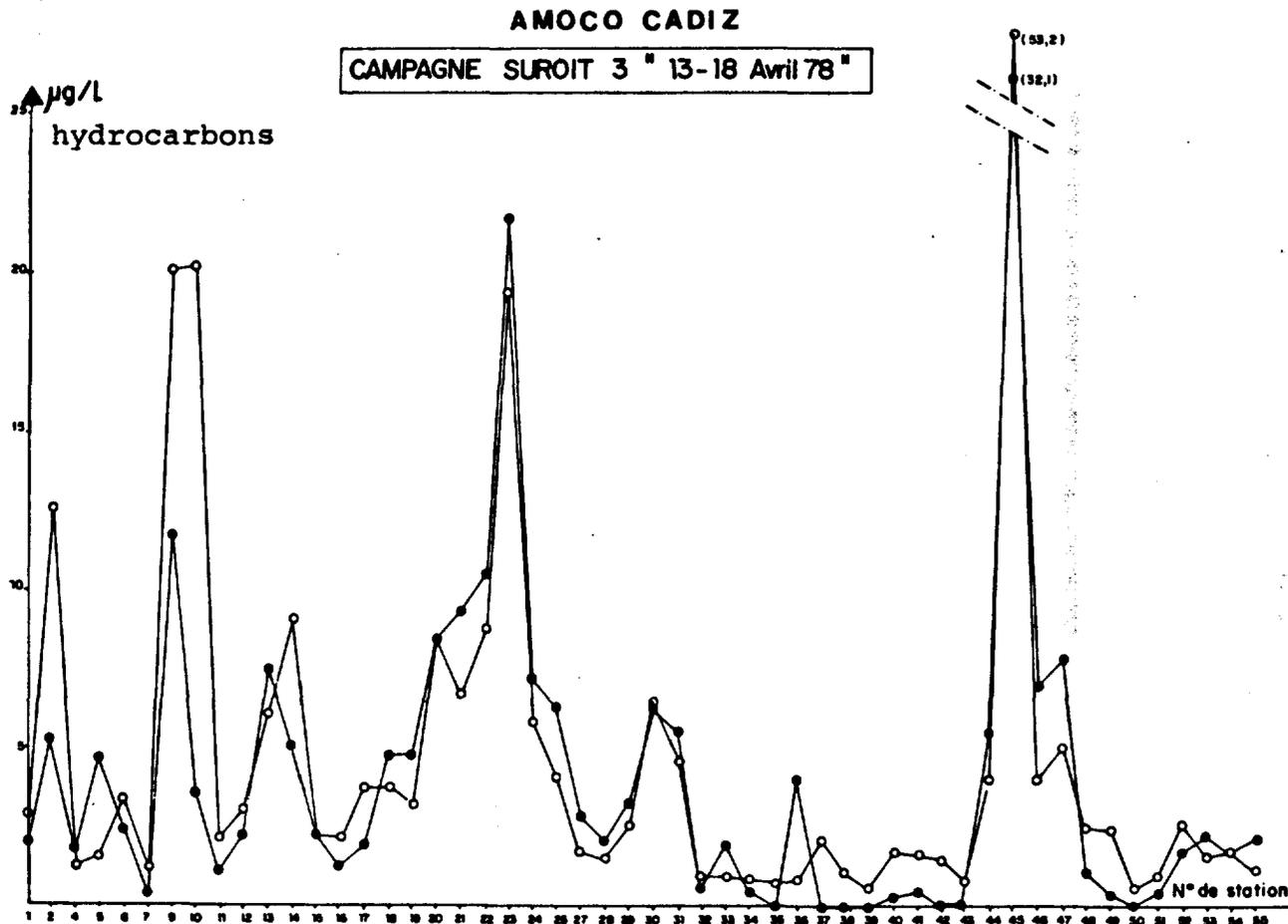


Figure 1. Estimation by UV spectrofluorometry of hydrocarbons in seawater. Comparison of results of duplicate analysis in the Amoco Cadiz study.

- ——— ● On board analysis
- ——— ○ Laboratory analysis

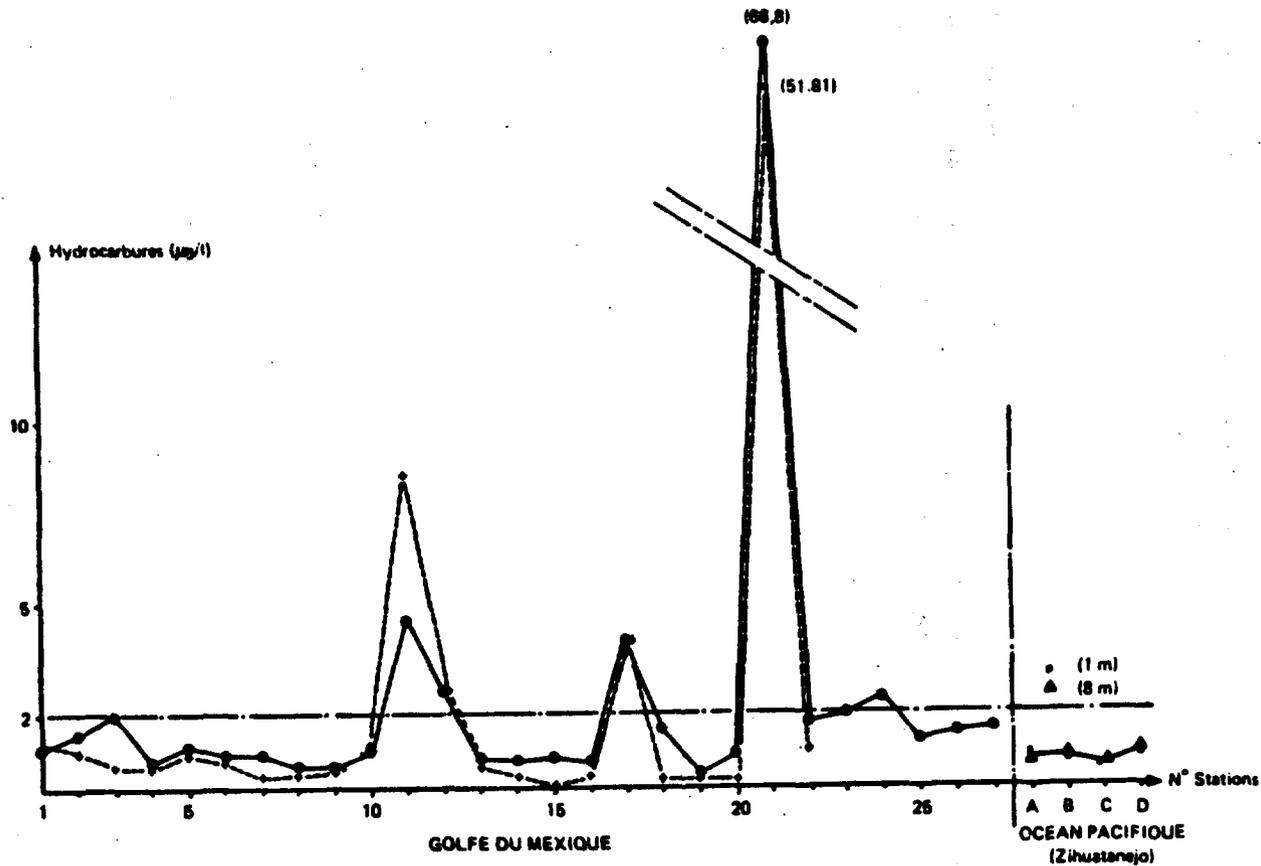


Figure 2. Estimation by UV spectrofluorometry of hydrocarbons in seawater. Comparison of results of duplicate analysis in the Ixtoc-1 study.

+ — + On board analysis
 • — • Laboratory analysis

Sediment

Surface marine sediments were collected with a Shipeck grab device. In coastal areas for the Amoco Cadiz study, we also used the little Ekman grab and Hamon grab devices. The samples, stored in a congelator, were either dried in an oven (70°C) or freeze-dried before analysis. The dried sample (100-200 g) was extracted in a Soxhlet apparatus or by stirring with chloroform or carbon tetrachloride. The organic extract was concentrated to dryness, then dissolved back in 10 mL of carbon tetrachloride.

A first indication of petroleum pollution in sediments was obtained with direct analysis of nonpurified extracts by IR spectrophotometry (Perkin Elmer Model 397). Quantitative measurements were carried out at 2920 cm^{-1} and correspond to the presence of hydrocarbons and polar compounds. The results are overestimated because of the response of coextracted natural substances (fats, fatty acids, etc.) from sediments. The IR spectrophotometer was calibrated with either a mixture of Arabian and Iranian light crude oils or Ixtoc-I crude oil.

Hydrocarbon analysis was performed by IR spectrophotometry after cleanup of organic extracts on activated alumina (200°C) in a glass column (i.d. = 0.6 cm, h = 15 cm). The hydrocarbons were eluted with 15 mL of carbon tetrachloride.

AMOCO CADIZ OIL SPILL

On the night of March 16, 1978 the Amoco Cadiz oil tanker became stranded on shallow rocks off Portsall (North Brittany), 1.5 miles from the coast. From March 17 to March 30, 223,000 tons of a mixture of Arabian light crude oil (100,000 ton) and Iranian light crude oil (123,000 ton) flowed into the sea without interruption. During this period the wind direction (W, NW, SW) induced a large drift of the spill eastward. The slicks successively reached the Aber-Wrac'h (March 19), Roscoff (March 20), the Bay of Lannion (March 21), the Sept-Iles (March 22) and the Sillon du Talbert (March 23). In April, the wind direction changed, thus reversing the slick drift that got to le Conquet and Ouessant Island (April 11), the Raz de Sein zone (April 13) and Douarnenez (April 22). A few hydrocarbon traces reached the coast in the Bay of Audierne at the beginning of May. The maximum extent of the oil slicks is presented in Figure 3. A chemical follow-up of the hydrocarbon pollution was made during several oceanographic cruises [4] (Figure 4) to assess the size and extension of the seawater pollution at the surface and in various water depths and in the sediment.

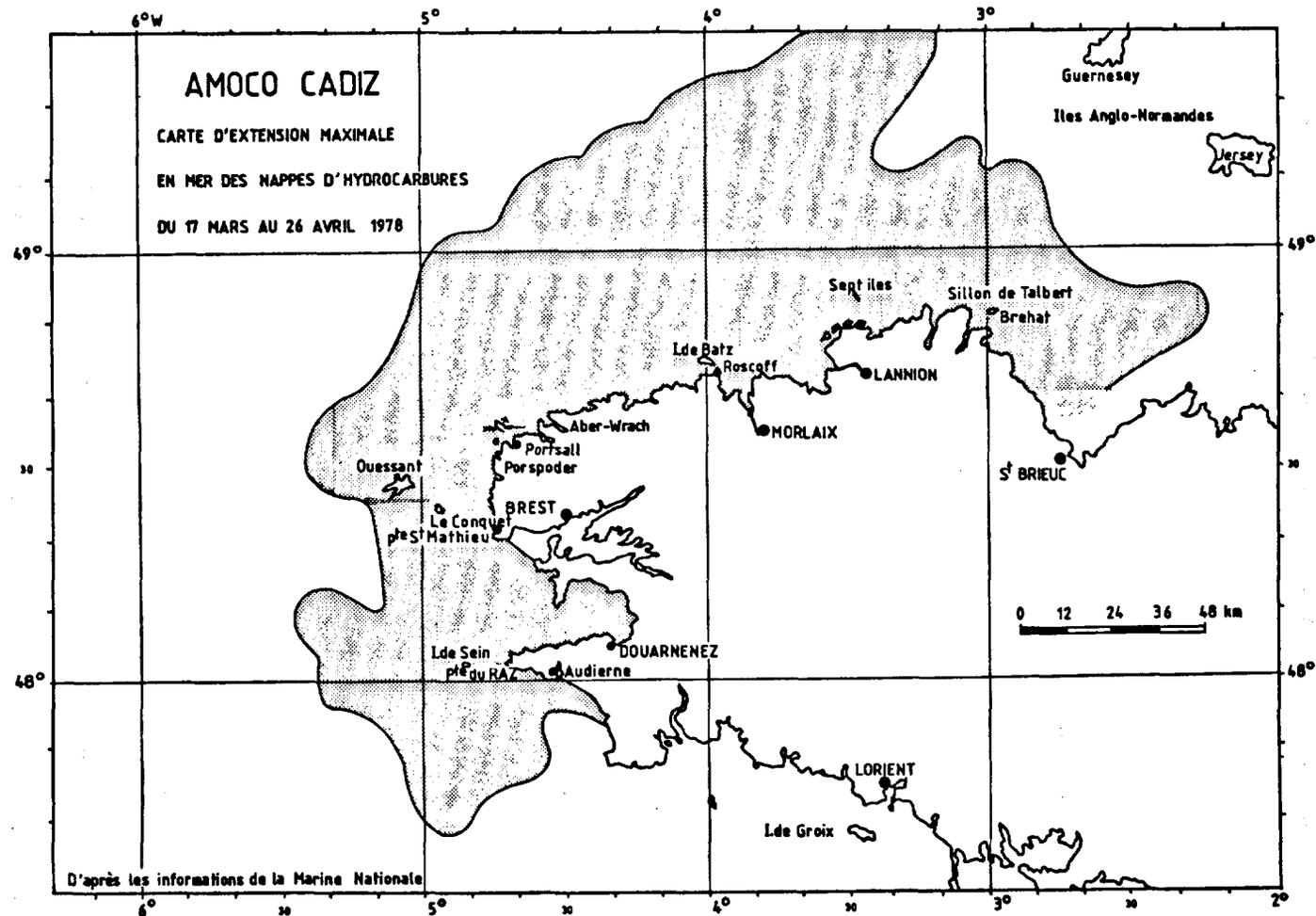


Figure 3. Amoco Cadiz. Maximum extent of oil slicks into the sea from March 17 to April 26, 1978.

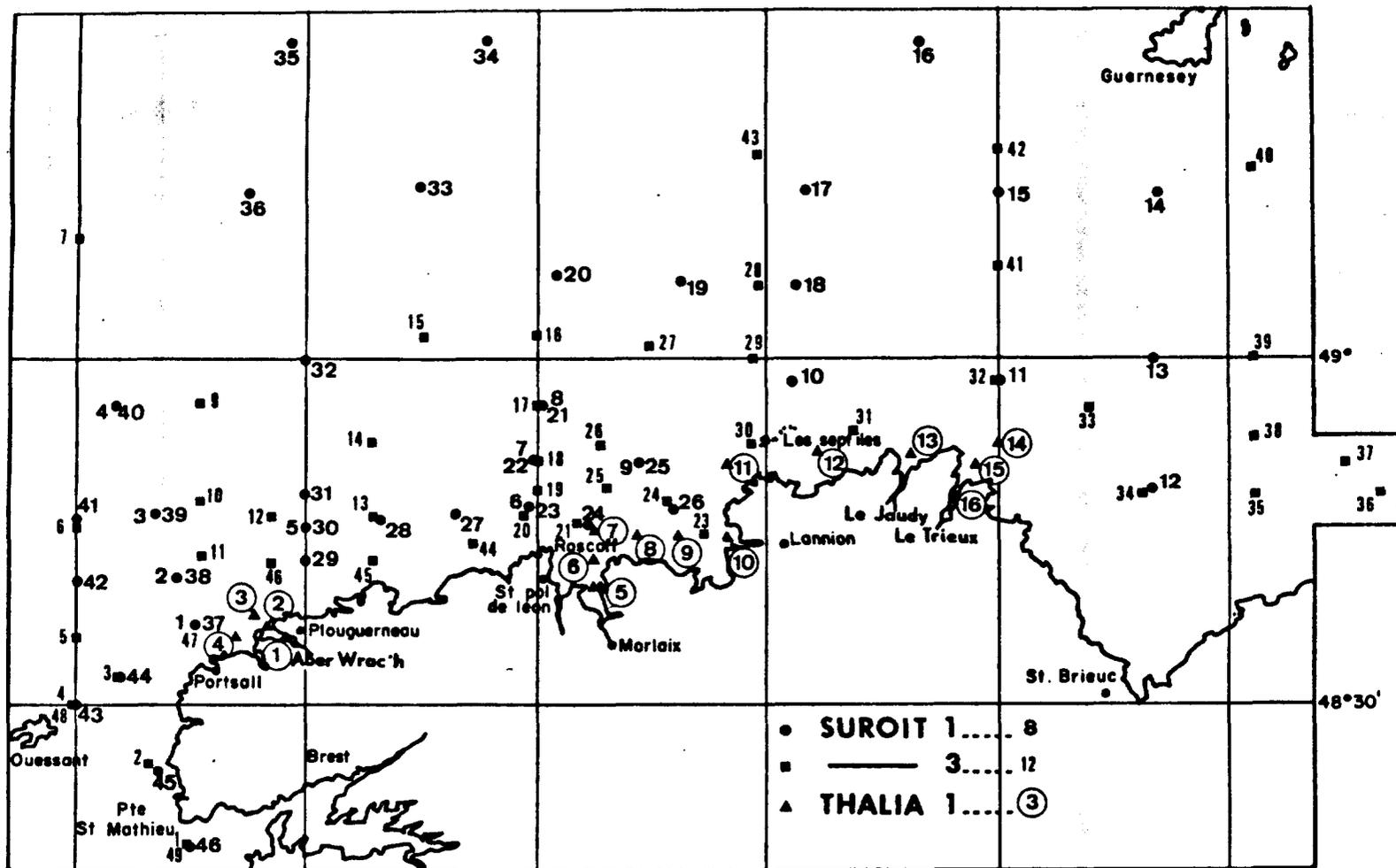


Figure 4. Amoco Cadiz. Sampling stations in the western English Channel during several oceanographic cruises.

Seawater

The chemical study by UV fluorescence geographically determined the spread limits of the oil pollution a fortnight and one month after the stranding. It also determined the diffusion of hydrocarbons into the water column and the evolution of the hydrocarbon contents. The first data showed that the Amoco Cadiz oil spill affected a very large section of the western English Channel. The range of hydrocarbon concentrations in seawater was found to be from 0.5 $\mu\text{g/L}$ to more than 100 $\mu\text{g/L}$. The lowest concentrations were ranged from 0.5 to 1.0 $\mu\text{g/L}$ and were very similar to those reported by other authors [9-10] in unpolluted areas from the NW Atlantic basin ($< 1.0 \mu\text{g/L}$). Like Keizer and Gordon [6], we adopted the limit of 2.0 $\mu\text{g/L}$ as a criterion of oil pollution in seawater. The main conclusions of this study were the following:

Spreading of the Pollution

A fortnight after the Amoco Cadiz stranding, the water pollution, under the action of winds from the West, spread eastward to the Bay of St. Brieuc. The western limit was found at the level of the 5°W meridian and the northern one along the 49°20'N parallel.

One month later (April 13-18) a change in wind direction reversed the drift of the oil spill. The average hydrocarbon concentrations in subsurface seawater, collected in different marine and coastal areas, are presented in Figure 5. The Bay of St. Brieuc did not show any significant pollution ($1.2 \pm 1.0 \mu\text{g/L}$) and the eastern limit could be located approximately at the Sillon du Talbert. A slight increase of the hydrocarbon content was recorded west of Portsall ($2.2 \pm 0.9 \mu\text{g/L}$). The 49°N parallel roughly constituted the northern limit, beyond which no more oil pollution was observed ($1.6 \pm 0.5 \mu\text{g/L}$). The most polluted areas were located in the sheltered coastal zones such as the Abers area ($38.9 \pm 6.7 \mu\text{g/L}$), Bay of Morlaix ($11.5 \pm 5.1 \mu\text{g/L}$) and Bay of Lannion ($10.7 \pm 3.0 \mu\text{g/L}$).

Diffusion of Hydrocarbons into the Water Column

The hydrocarbon concentrations were determined in seawater samples collected at various depths (1, 2, 5, 20 and 50 m above sea bottom), in the western English Channel, during several oceanographic cruises. The data, reported in Table 3, showed that the entire water column was contaminated by the oil slick drift. The in-depth diffusion of the hydrocarbons might be due to the dynamic mixing of water masses (hydrological conditions, sea state), the type of oil spilled (light crude oils facilitating the natural disso-

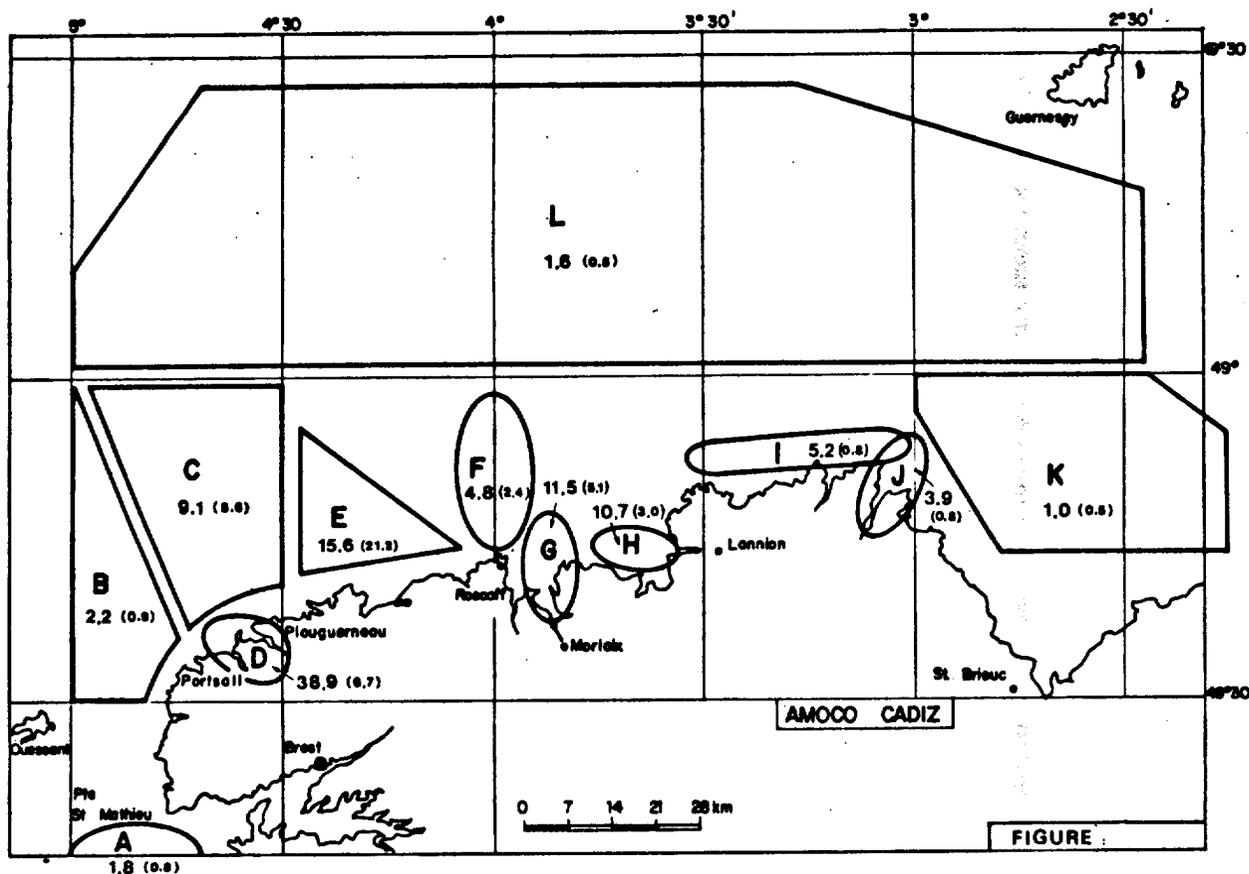


Figure 5. Amoco Cadiz. Chemical follow-up of oil pollution in the seawater. Average concentrations in subsurface seawater collected in different areas (April 13-18, 1978). Concentrations determined by UV spectrofluorometry and expressed in $\mu\text{g/L}$. () is standard deviation.

$< 1.0 \mu\text{g/L}$: no oil pollution

$> 2.0 \mu\text{g/L}$: oil pollution.

Table 3. Diffusion of Oil into the Water Column (Amoco Cadiz Study)
(Hydrocarbon concentrations in seawater expressed in $\mu\text{g/L}$)

| Stations, N ^o | Oceanographic Cruises | | | | | | | | | | | | |
|--------------------------|-------------------------------------|------------|-----------|-----------|-----------|-----------|--------------------------------|-----------|-----------|-----------|-----------|------------|-----------|
| | "Suroit 1" (March 30-April 4, 1978) | | | | | | "Suroit 3" (April 13-18, 1978) | | | | | | |
| | 1 | 3 | 6 | 7 | 9 | 16 | 1 | 4 | 10 | 19 | 21 | 23 | 24 |
| Latitude (N) | 48°37' | 48°45'6 | 48°46'6 | 48°49'2 | 48°52'5 | 49°27'4 | 48°17'6 | 48°29'7 | 48°47' | 48°49'8 | 48°46' | 48°44'8 | 48°44'1 |
| Longitude (W) | 04°42'5 | 04°49'2 | 04°00'7 | 03°57'7 | 03°49'3 | 03°10' | 04°46'5 | 05°01'7 | 04°44'2 | 03°59'8 | 03°55'1 | 03°38'7 | 04°09'1 |
| Depths (m) | | | | | | | | | | | | | |
| 1 | 138.0 | 14.3 | 46.4 | 15.6 | 17.9 | 1.0 | 2.9 | 1.3 | 20.2 | 3.2 | 6.7 | 19.4 | 4.0 |
| 2 | - | 19.7 | 36.4 | 9.9 | 8.3 | 0.6 | 2.3 | 0.9 | 3.7 | 2.5 | 5.9 | 15.0 | 4.9 |
| 5 | 152.9 | 19.9 | 38.6 | 12.1 | 13.8 | 1.1 | 1.9 | 0.8 | 4.5 | 3.3 | 6.9 | 20.3 | 3.3 |
| 20 | 84.1 | 18.6 | 51.1 | 16.6 | 19.8 | - | 2.3 | 1.3 | 4.2 | 7.5 | 12.2 | 39.2 | 4.1 |
| bottom + 5 m | 102.7 | 42.3 | 27.7 | 18.3 | 26.6 | - | 10.7 | 1.8 | 9.6 | 4.9 | 11.0 | - | 4.5 |
| (depth) | (44) | (95) | (40) | (70) | (70) | | (28) | (80) | (95) | (75) | (45) | | (65) |
| Average, \bar{m} | 122.8 | 23.0 | 40.0 | 14.5 | 17.3 | 0.9 | 4.0 | 1.2 | 8.4 | 4.3 | 8.5 | 23.5 | 4.2 |
| $\pm \sigma$ | ± 28.3 | ± 11.0 | ± 9.1 | ± 3.4 | ± 6.8 | ± 0.3 | ± 3.7 | ± 0.4 | ± 7.0 | ± 2.0 | ± 2.8 | ± 10.7 | ± 0.6 |
| (%) | (23%) | (48%) | (23%) | (24%) | (39%) | (29%) | (94%) | (33%) | (83%) | (46%) | (33%) | (46%) | (14%) |

lution process), its physical and chemical evolution (emulsification, natural sinking) and the use of dispersant products. This dispersion process into the water column should have been quick because each water mass maintained some vertical homogeneity of the oil content observed from one site to the other.

Evolution of Surface Seawater Pollution

We observed a general and rapid decrease of the hydrocarbon concentrations in seawater. From March to June 1978, the half-time of hydrocarbons in subsurface water was given at 11 days in the oceanic zone east of Portsall, 14 days in the coastal area near the Abers, and 28 days in the bays of Morlaix and Lannion (Figure 6). Other data reported [1] gave a half-time of oil in water of 40 days in the sheltered estuary zone of Aber-Wrac'h.

Marine Sediments

Pollution of the Sea Bottom in April 1978

One month after the stranding of the Amoco Cadiz, we collected marine sediments samples during an oceanographic cruise (R/V Suroit) to assess the sea bottom contamination in the western English Channel. The sediments sampled were coarse to medium calcareous sands ($> 70\%$ CaCO_3). In coastal areas, the organogen calcareous content decreased ($50\text{--}70\%$ CaCO_3) in sands collected in the bays of Morlaix and Lannion and near the Abers. Organic carbon content generally was low, from 0.02 to 0.6% ($\bar{m} = 0.18 \pm 0.13\%$). The hydrocarbon concentrations in sediment samples ranged from 10 to 1100 ppm. Pollution of the sedimentary phase was observed in the coastal and offshore areas reached by the drifting slicks (Figure 7). The diffusion of the oil into the water column seems to show that the seawater had been a transfer agent of the oil pollution from the surface to the bottom. Off the Sept-Iles, a gradient was observed from the coast to the open sea (219, 52, 42 and 34 ppm). At the level of the 49°N parallel, from west to east, one could observe an increasing and then decreasing gradient: 21, 19, 48, 102, 54, 52 and 24 ppm. The high petroleum accumulations in marine sediments were located in the coastal zones, in the Abers (100 to $> 10,000$ ppm) and in the bays of Morlaix and Lannion (10 to > 1500 ppm) (Figure 8).

Evolution of Oil Pollution in Coastal Sediments

We have followed the oil pollution in sediments collected from the two Abers (Aber-Benoit, Aber-Wrac'h) which are small estuaries, 10 to 15 km

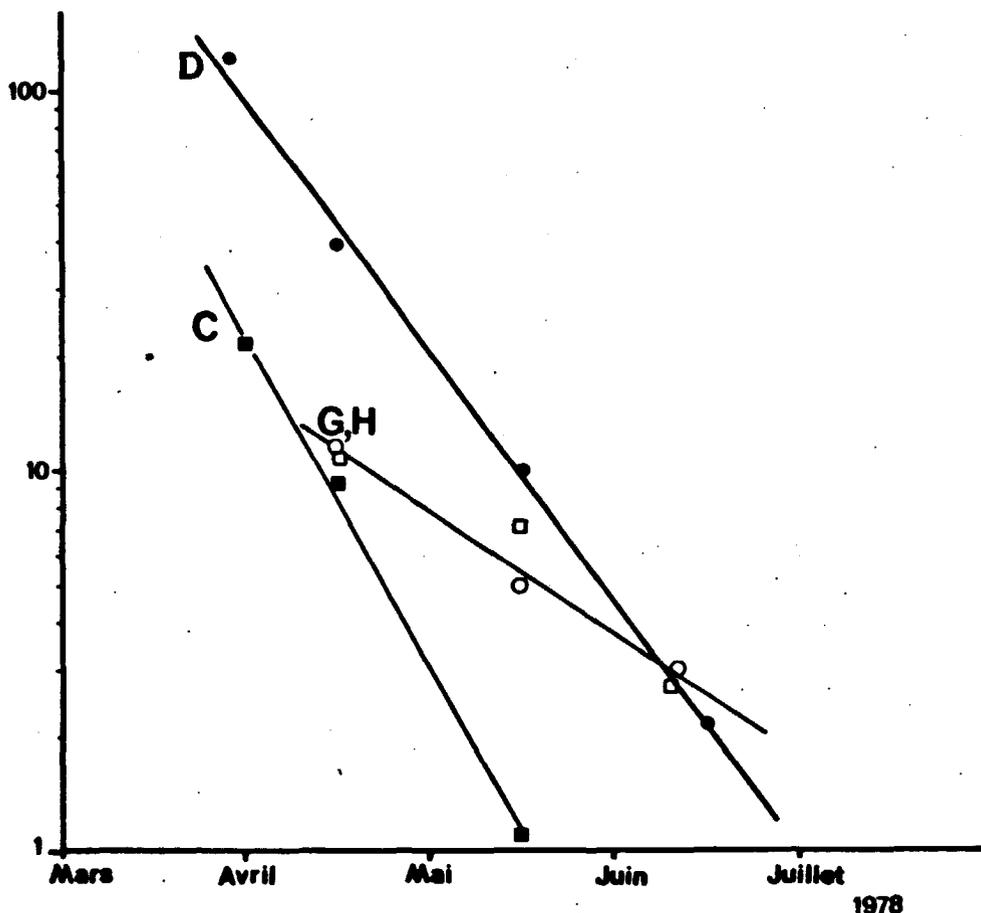


Figure 6. Evolution of hydrocarbon concentrations in subsurface seawater from March to June 1978 in different areas of the western English Channel (cf. Figure 5).

long and 1 km wide, including sandy and muddy areas. The study also was carried out in the bays of Morlaix and Lannion [4]. The chemical follow-up showed that the natural decontamination process was related to two essential factors: the type of sediment and the energy level of the geographic zone. Table 4 shows the main facts we observed during one year of study, and the results are briefly summarized here:

- **Aber-Benoit:** In the mud zone the sediments acted as an oil trap (oil contents >10,000 ppm) and the decontamination process was not observed. However, the medium to fine sands sampled from the downstream part of the estuary were well decontaminated after one year.
- **Aber-Wrac'h:** On the downstream part the decontamination process, activated by the sea nature of the environment, was considerably reduced by the muddy consistency of the polluted sands. On the upstream part, low energy zone, the decontamination of the muddy sands was not observed in any significant manner.

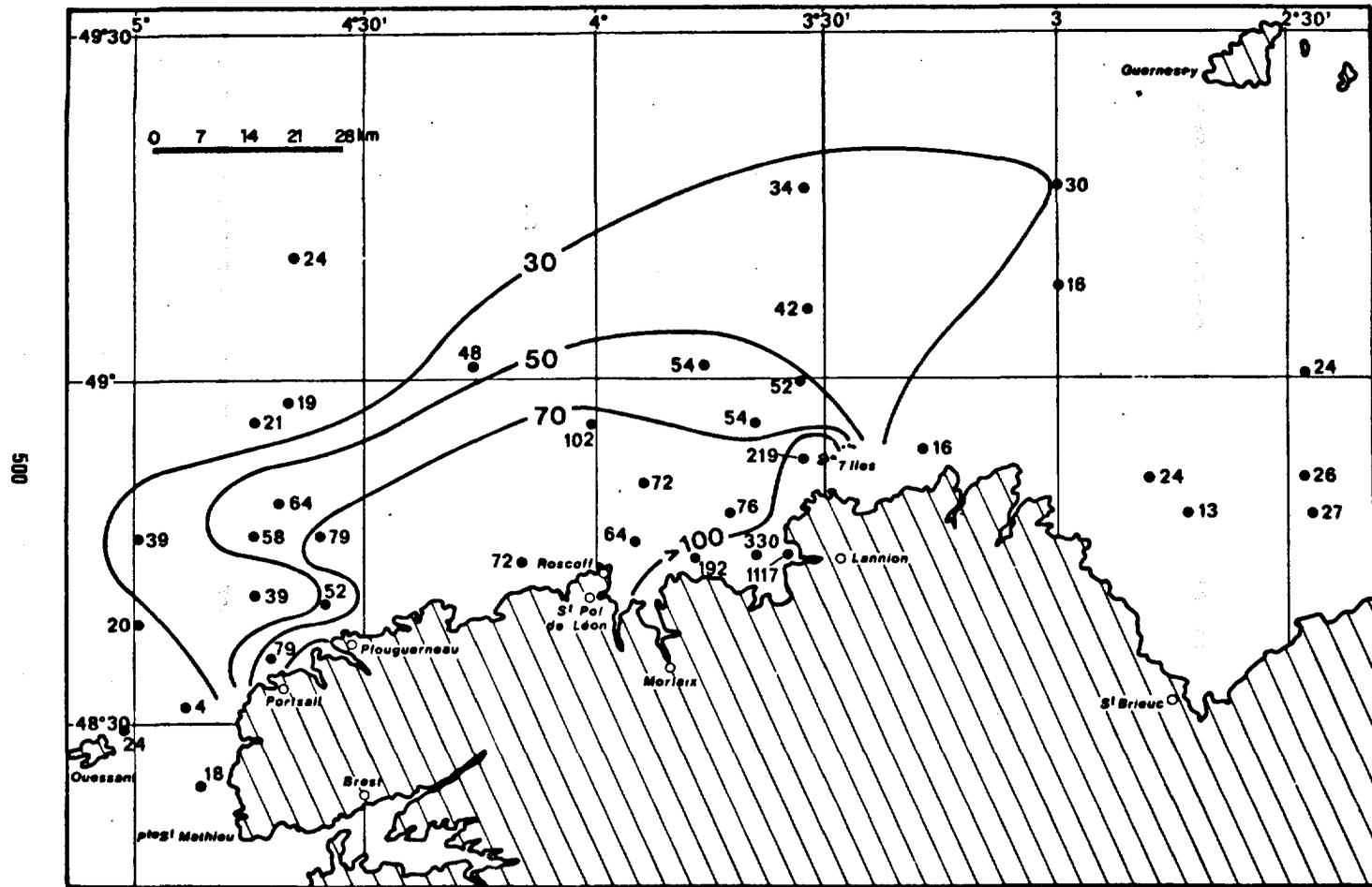


Figure 7. Amoco Cadiz. Petroleum pollution of marine sediments in April 1978. Concentrations expressed in ppm.

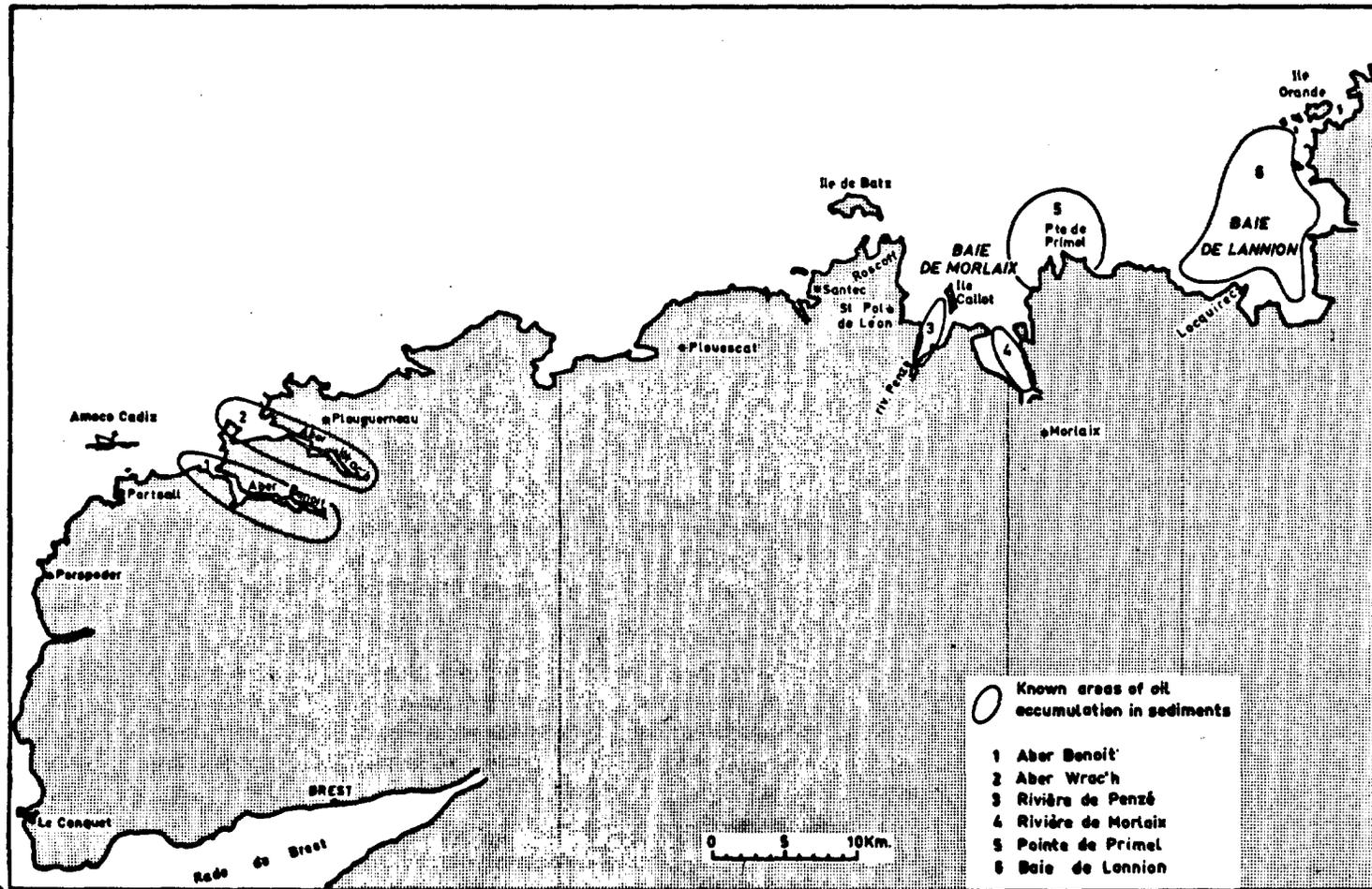


Figure 8. Amoco Cadiz. Known coastal areas of oil accumulation in sediments.

Table 4. Evolution of the Pollution Caused by Oil on the Coastal Sea Floors

| | Coastal Zone | Description | Type of Sediments | Hydrocarbon Content (mean values) | | Decontamination Process |
|---------------------|--------------------------------|---------------------------------------|-----------------------------|--------------------------------------|---------------|----------------------------|
| | | | | April 1978 | March 1979 | |
| Sheltered Area ↓ | 1. The Two Abers | | | April 1978 | March 1979 | |
| | Aber-Benoit | loc majan (mud) | muddy | >10,000 | >10,000 | no |
| | Aber-Wrac'h | upstream part | muddy sands | 1,500 | 1,700 | no |
| | Aber-Wrac'h | downstream part | muddy sands | 4,200 | 1,700 | low |
| | Aber-Benoit | upstream part | no muddy sands | 700 | 27 | yes |
| Exposed Area | 2. Bays of Morlaix and Lannion | | | July 1978 | February 1979 | |
| | Morlaix River | bottom of the bay | sandy mud | 311 | 172 | low |
| | Bay of Lannion | bottom of the bay | fine sands | 281 | 126 | low |
| | Prinel Area | sector exposed to winds and storms | fine to coarse sediments | 600 | 19 | yes |

- Bays of Morlaix and Lannion: In the bottom of these bays, the decontamination process of muddy sands and fine sands was observed but remained low. In the eastern part of the bay of Morlaix, located around Primel, an area more exposed to winds and storms than the bottoms of bays, we observed that the coarse and fine sands were well decontaminated.

So, one year after the Amoco Cadiz stranding, the long-term evolution of oil pollution in the marine environment was focused in the sediments from low-energy level coastal zones, such as estuaries and bays.

IXTOC-I OIL SPILL

The blowout of Ixtoc-I in the Gulf of Mexico occurred on June 3, 1979 and the oil pollution continued until March 20, 1980. The exact quantities of oil spread into the sea will never be known, but according to some information the oil spill was ~4000 ton/day during the first weeks, then decreased to ~2000 ton/day. We can thus estimate an oil spill of more than 600,000 ton of light crude oil with the blowout on the Ixtoc-I well. A significant quantity of oil was burning at the sea surface in a flame field, but the remainder drifted and was dispersed in the marine environment.

During an oceanographic cruise with R/V Oceanográfico HO2 (Mexican Navy), August 16-21, 1979, from Vera Cruz to Ixtoc-I and Ciudad del Carmen (Figure 9), we collected seawater and sediment samples to determine the extent of the oil pollution from this source and to determine the dispersion of hydrocarbons in the ocean.

Seawater

During the cruise, we observed oil pollution on the surface of water as droplets, pancakes of emulsified petroleum, and oil slicks near stations 8-10, 12 and 21. The hydrocarbon concentrations, determined by UV spectrofluorometry in subsurface seawater (1 m), were on the whole low, generally $< 2.0 \mu\text{g/L}$ (Table 5). To compare these data, we also analyzed some seawater samples collected in unpolluted areas in the Pacific Ocean, off Zihuatanejo; the results ranged from 0.6 to $1.0 \mu\text{g/L}$. In this study, we again kept the limit of $2.0 \mu\text{g/L}$ as a criterion of oil pollution in water. Pollution of the seawater was observed only at some stations but was not very important (2.0 - $4.6 \mu\text{g/L}$). The highest level recorded ($66.8 \mu\text{g/L}$) was found at station 21, the nearest to the Ixtoc-I well.

In the *water column*, at stations 5, 9 and 20, where the oil pollution was not observed on the surface, the hydrocarbon concentrations determined along the depth profile were homogeneous and $< 2.0 \mu\text{g/L}$ (Table 6). The

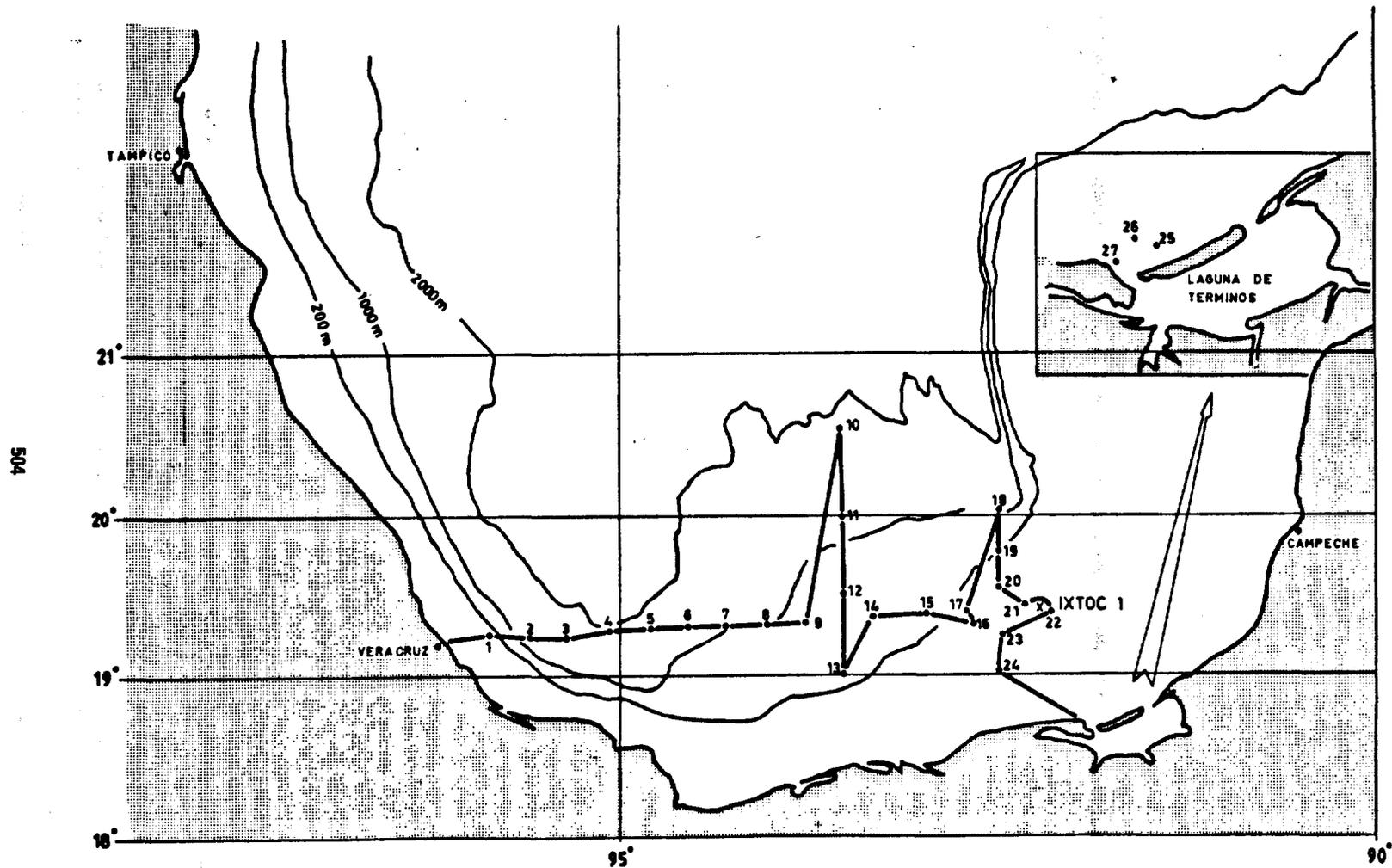


Figure 9. Ixtoc-I. Sampling stations in the Gulf of Mexico during the oceanographic cruise (R/V Oceanográfico H-02), August 16-21, 1979.

Table 5. Spectrofluorometric Determinations of Total Hydrocarbons ($\mu\text{g/L}$) in Seawater Collected in the Gulf of Mexico (August 16-21, 1979)

—Subsurface seawater (1 m)

| Station Number | Position | | Depth (m) | Hydrocarbon Concentration |
|----------------|---|---------------|-----------|---------------------------|
| | Latitude (N) | Longitude (W) | | |
| 1 | 19°15.3' | 95°51.9' | 180 | 1.1 |
| 2 | 19°13.5' | 95°36.4' | — | 1.5 |
| 3 | 19°13.9' | 95°20' | 1640 | 2.0 |
| 4 | 19°15.1' | 95°04' | 2180 | 0.7 |
| 5 | 19°08' | 94°45.9' | 2180 | 1.1 |
| 6 | 19°16.3' | 94°32.4' | 2350 | 0.9 |
| 7 | 19°16.9' | 94°17.1' | 900 | 0.9 |
| 8 | 19°17.9' | 94°01' | 1115 | 0.6 |
| 9 | 19°19.9' | 93°44.9' | 820 | 0.6 |
| 10 | 20°30' | 93°29.9' | 1800 | 1.0 |
| 11 | 20°00' | 93°30' | 1200 | 4.6 |
| 12 | 19°30' | 93°30' | 600 | 2.6 |
| 13 | 19°00' | 93°30' | 485 | 0.8 |
| 14 | 19°21.2' | 93°13.4' | 540 | 0.7 |
| 15 | 19°21.8' | 92°57.7' | — | 0.8 |
| 16 | 19°18' | 92°38.2' | 130 | 0.7 |
| 17 | 19°22' | 92°42.1' | 176 | 4.0 |
| 18 | 20°00' | 92°30' | 1080 | 1.6 |
| 19 | 19°44.9' | 92°30' | 205 | 0.4 |
| 20 | 19°30.8' | 92°31.2' | 110 | 0.9 |
| 21 | 19°24.7' | 92°18.8' | 52 | 66.8 |
| 22 | 19°22.7' | 92°08' | 58 | 1.8 |
| 23 | 19°15.3' | 92°30' | 75 | 2.0 |
| 24 | 19°00.1' | 92°30' | 36 | 2.4 |
| 25 | | | — | 1.3 |
| 26 | } Ciudad del Carmen Laguna de Terminos | | — | 1.5 |
| 27 | | | — | 1.6 |

**Table 6. Spectrofluorometric Determinations of Total Hydrocarbons ($\mu\text{g/L}$) in Seawater Collected in the Gulf of Mexico (August 16-21, 1979)
-Diffusion of Oil into the Water Column**

| Depths (m) | Station Number | | | | | |
|---------------|-------------------------------------|-----------|-----------|-----------|------|------|
| | 5 | 9 | 12 | 20 | 21 | 22 |
| | Hydrocarbons ($\mu\text{g/L}$) | | | | | |
| 1 | 1.1 | 0.6 | 2.6 | 0.9 | | |
| 5 | 1.3 | 1.3 | 3.5 | 1.1 | | |
| 20 | 1.9 | 1.0 | 1.3 | 1.6 | | |
| 100 | 1.2 | 1.0 | 1.7 | 1.8 | | |
| 300 | - | 1.3 | - | - | | |
| \bar{m} | 1.4 | 1.1 | 2.3 | 1.3 | | |
| $\pm\sigma$ | ± 0.3 | ± 0.3 | ± 1.0 | ± 0.4 | | |
| (%) | (26%) | (28%) | (43%) | (31%) | | |
| 1 | | | | | 66.8 | 1.8 |
| 5 | | | | | 2.9 | - |
| 20 | | | | | 3.9 | 10.9 |
| 50 | | | | | 73.1 | - |

water sampling at stations 12 and 21 was made under oil slicks. At station 21, near the Ixtoc-I well, the subsurface water was polluted ($66.8 \mu\text{g/L}$) but the diffusion of oil into the water column remained very low: $2.9 \mu\text{g/L}$ at 5 m and $3.9 \mu\text{g/L}$ at 20 m of depth. At station 12, located about 60 miles from Ixtoc-I, the oil content was low in the subsurface ($2.6 \mu\text{g/L}$) and was only observed down to a depth of 5 m ($3.5 \mu\text{g/L}$); beyond that the hydrocarbon concentrations were $<2.0 \mu\text{g/L}$. At station 8, where emulsified petroleum was observed in surface, the oil content in subsurface water remained at a background level ($0.6 \mu\text{g/L}$).

Two anomalies were observed in the vicinity of the well. At station 21, a very important oil content in water was found at a depth of 50 m ($73.1 \mu\text{g/L}$). At station 22, we noticed a significant contamination of water at a depth of 20 m ($10.9 \mu\text{g/L}$) but not in the subsurface water ($<2.0 \mu\text{g/L}$).

These observations showed that oil pollution in the seawater, at surface and in-depth, appeared especially in the vicinity of the Ixtoc-I well. These data contrast with those obtained during the Amoco Cadiz chemical study. The absence of diffusion of oil in the water can be explained by the unruffled state of the sea during the oceanographic cruise, the burning of volatile hydrocarbons (which are the more easily dissolved compounds in the water) above the well, and the local hydrological conditions. The mixing layer of

waters was thin, at least during our observations, and there was a strong thermocline which restricted the diffusion process to the bottom.

Sediments

Sediments were collected on the continental shelf, near the Ixtoc-I well (calcareous muds) and near Ciudad del Carmen (muddy to fine sands). Results of these analyses are summarized in Table 7. The organic extracts ranged from 26 to 116 ppm ($\bar{m} = 59 \pm 28$ ppm). As a comparison, the average value of the organic extracts measured on coarse to muddy sediments collected in coastal Atlantic waters (Brittany, France) was 53 ± 39 ppm. The IR spectrophotometric analysis of nonpurified extracts gave values from 16 to 76 ppm ($\bar{m} = 36 \pm 19$ ppm). In a first approximation these results did not show any significant oil pollution in sediments. This information was confirmed with IR spectroscopic analysis of total hydrocarbons after clean-up of organic extracts on activated alumina. The hydrocarbon concentrations reported in muddy sediments sampled in the vicinity of the Ixtoc-I well were in a range of 9.7 to 20.9 ppm ($\bar{m} = 15.9 \pm 3.6$ ppm), and in sandy sediments collected near Ciudad del Carmen, in a range from 2.8 to 6.1 ppm ($\bar{m} = 5.8 \pm 2.9$ ppm). These data show that the sea bottom investigated was not polluted by the Oxtoc-I oil spill. As a comparison, total hydrocarbons in sandy sediments from the Brittany coastal area in the Atlantic Ocean (France) were found from 3.6 to 31.3 ppm ($\bar{m} = 11 \pm 8$ ppm) [11]. In the Northeast part of the Gulf of Mexico total hydrocarbon concentrations in shelf sediments ranged from 1.5 to 11.7 ppm [12]. The absence of contamination in the sediments sampled in the vicinity of the Ixtoc-I well indirectly confirmed the lack of diffusion of oil into the water column.

Table 7. IR Spectrophotometry Analysis of Sediments Collected in the Gulf of Mexico (Ixtoc-I)

| Station Number | Type of Sediments | Water (%) | Extract ^a (ppm) | Index of Oil Pollution ^{a,b} (ppm) | Total Hydrocarbons ^a (ppm) |
|----------------|-------------------|-----------|----------------------------|---|---------------------------------------|
| 16 | mud | 60.4 | 82.7 | 61.5 | 16.6 |
| 17 | mud | 64.0 | 115.8 | 76.1 | 20.9 |
| 20 | mud | 62.4 | 29.8 | 23.0 | 9.7 |
| 21 | mud | 59.8 | 52.2 | 29.4 | 15.8 |
| 22 | mud | 58.7 | 57.0 | 32.5 | 15.6 |
| 23 | mud | 60.9 | 43.3 | 31.4 | 16.6 |
| 25 | muddy sand | 31.3 | 73.0 | 28.1 | 6.1 |
| 26 | fine sand | 21.0 | 26.4 | 16.3 | 8.5 |
| 27 | sandy mud | 43.5 | 50.6 | 28.8 | 2.8 |

^aConcentrations expressed in dry weight.

^bIR spectrophotometry analysis of nonpurified organic extracts.

CONCLUSION

These two chemical studies carried out after the Amoco Cadiz and Ixtoc-I oil spills show a difference in behavior of the crude oil spilled in the ocean, in regard to the oil diffusion into the water column and the pollution of the sediments. These differences can be related to the characteristics of the oceanic region polluted, the type of crude oil spilled and the conditions of the discharge of oil in the marine environment.

REFERENCES

1. Calder, J. A., and P. D. Boehm. "The Chemistry of "AMOCO CADIZ" Oil in the Aber-Wrac'h," in *Colloque: AMOCO CADIZ. Conséquences d'une pollution accidentelle par hydrocarbures* (Paris: CNEOX, 1981) pp. 143-158.
2. Ducreux, J., and M. Marchand. "Evolution des Hydrocarbures Présents dans les Sédiments de l'Aber-Wrac'h," in *Colloque AMOCO CADIZ: Conséquences d'une pollution accidentelle par hydrocarbures*. (Paris: CNEOX, 1981), pp. 175-216.
3. IFP. Personal communication from Institut Français du Pétrole, Service Analytique (1979).
4. Marchand, M., and M. P. Caprais. "Suivi de la pollution de l'AMOCO CADIZ dans l'eau de mer et les sédiments marins," in *Colloque AMOCO CADIZ: Conséquences d'une pollution accidentelle par hydrocarbures*, (Paris: CNEOX, 1981) pp. 23-54.
5. Levy, E. M. "The presence of petroleum residues off the east coast of Nova Scotia in the Gulf of St-Lawrence and the St-Lawrence river," *Water Res.* (1971), pp. 723-733.
6. Keizer, P. D., and D. C. Gordon. "Detection of Trace Amounts of Oil in Sea Water by Fluorescence Spectroscopy," *J. Fish Res. Bd. Can.* 30(8):1039-45 (1973).
7. Levy, E. M. "Fluorescence Spectroscopy: Principles and Practice as Related to the Determination of Dissolved and Dispersed Petroleum Residues in Sea Water," Bedford Institute of Oceanography, Report Series BI-R-77 (1977), 17 pp.
8. UNESCO. "Manuel sur la surveillance continue du pétrole et les hydrocarbures en mer et sur les plages," Supplément aux manuels et guides n°7. IOC-WMO-UNEP/MED-MRM/3, Supp. 2 (1977), 21 pp.
9. Gordon, D. C., P. D. Keizer and J. Dale. "Estimates Using Fluorescence Spectroscopy of the Present State of Petroleum Hydrocarbon Contamination in the Water Column of the Northwest Atlantic Ocean," *Mar. Chem.* 2:251-61 (1974).
10. Keizer, P. D., D. C. Gordon and J. Dale. "Hydrocarbons in Eastern Canadian Marine Waters Determined by Fluorescence Spectroscopy and Gas Liquid Chromatography," *J. Fish Res. Bd. Can.* 34:347-53 (1977).

11. Marchand, M. and J. Roucaché. "Critères de pollution par hydrocarbures dans les sédiments marins. Etude appliquée à la pollution du Böhlen," *Oceanol. Acta* 4(2): 171-183 (1981).
12. Gearing, P., et al. "Hydrocarbons in 60 North-East Gulf of Mexico Shelf Sediments: A Preliminary Survey," *Geochim. Cosmochim. Acta* 40:1005-17 (1976).