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Determine Fates of Several Oil Spills in Coastal and Offshore Waters and Calculate a Mass Balance Denoting Major Pathways for Dispersion of the Spilled Oil.

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The ultimate fate of oil spilled in the ocean has received much scientific and public attention and still remains inadequately understood. Conceptionally, numerous mass-balance models have been offered to illustrate the various pathways associated with spilled oil. The purpose of this paper is to analyze the results of scientific investigations of some of the major oil spills of the past to determine the level of our quantitative understanding of these oil dispersal and reaction pathways.

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FINAL REPORT

Project Title:
DETERMINE FATES OF SEVERAL OIL SPILLS IN
COASTAL AND OFFSHORE WATERS AND
CALCULATE A MASS BALANCE DENOTING MAJOR PATHWAYS
FOR DISPERSION OF THE SPILLED OIL

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PROJECT SUMMARY

Understanding the dispersal and reaction processes taking place after an oil spill is of prime importance in predicting the short- and long-term effects of that spill. In this paper, we analyze six major oil spills (Santa Barbara, ARROW, ARGO MERCHANT, AMOCO CADIZ, TESIS, and IXTOC I) in an attempt to quantify major dispersal pathways, these being oil incorporation in the water column, oil deposited on the bottom, oil stranded on the shoreline, and biodegradation.

We found that the data were usually difficult to place into a mass-balance format since sampling was inadequate or only representative of a single time which then had to be integrated over the duration of the spill. Realizing these problems, we were able to account for a maximum of 50 percent of the total oil spilled using data from the AMOCO CADIZ spill. Evaporation determined from laboratory studies accounts for an additional 20-40 percent. Derived component values ranged greatly between spill cases, from 0.02 to 9 percent for oil incorporated in the water column, from 0.1 to 8 percent for oil deposited in bottom sediments, from none to 28 percent for shoreline-stranded oil, and from none to at least 4.5 percent for water column microbial degradation. The information derived at the AMOCO CADIZ oil spill offers, by far, the most usable and complete data, and represents the maximum values presented above.

Future work toward quantifying oil dispersal components should focus on determining the quantity of oil microbially degraded and the amount included as part of the surface slick.

INTRODUCTION

The ultimate fate of oil spilled in the ocean has received much scientific and public attention and still remains inadequately understood. Conceptually, numerous mass-balance models have been offered to illustrate the various pathways associated with spilled oil (Fig. 1); however, few laboratory and field data are available to quantitatively define even the most obvious pathways. The purpose of this paper is to analyze the results of scientific investigations of some of the major oil spills of the past to determine the level of our quantitative understanding of these oil dispersal and reaction pathways. For details of the chemical degradation products associated with oil spills, refer to the original papers or to Butler (Harvard Univ., in press).

Modeling Efforts

Numerous papers have been written concerning the fate of spilled oil. Table 1 presents a brief summary of some of the major oil-spill model components. Kolpack (1977), in an attempt to create a mathematical model defining each mechanism, clearly has the most complex model. Mackay (1980) presents the only one that attempts to quantify primary model components (Fig. 2); however, few supporting data are offered. Boehm et al. (1981), using specific data taken at the IXTOC I blowout site, have quantitatively defined two major weathering pathways, evaporation and dissolution. Ongoing studies by Huanz (Raytheon Ocean Systems Company, pers. commun.) and by Johnson (1981) are developing an updated computer model to reflect realistic, spilled-oil dispersion processes.

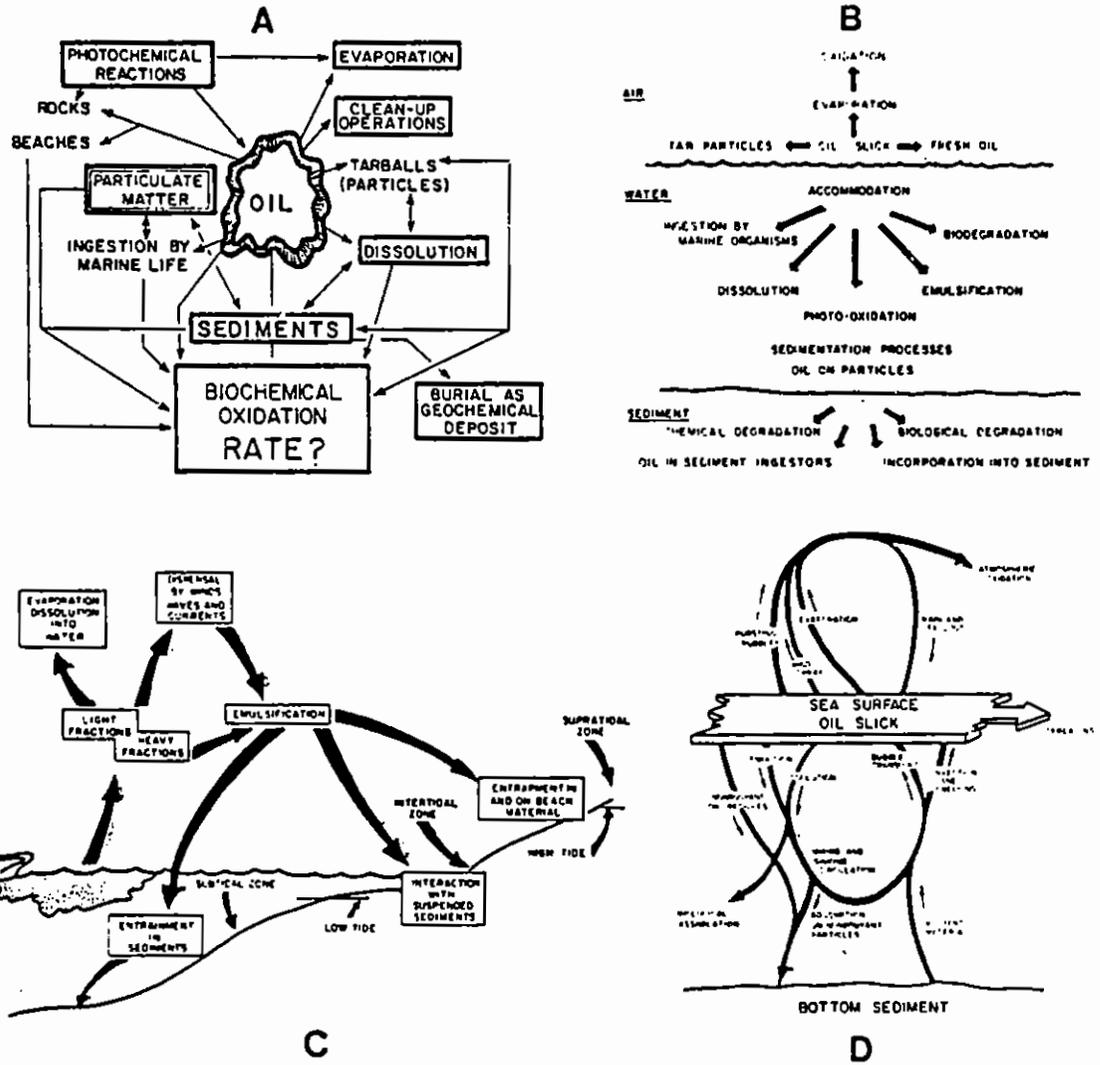


FIGURE 1. Diagrammatic examples of general oil fate models: A is from Farrington (1977); B is from Lee (1977); C is from Exxon Corp. (1979); D is from Kolpack (1977). Another good stylistic model is presented by Clark and MacLeod (1977).

TABLE 1. Examples of spilled oil pathway components. Clark and MacLeod (1977) offer similar components, primarily dissolution, emulsification, evaporation, photochemical modification, biological ingestion and excretion, tar ball formation, agglomeration and sinking, and microbial modification.

KOLPACK (1977)	FARRINGTON (1977)	LEE (1977)	MACKAY (1977)
WATER SURFACE RESERVOIR			
Biodegradation Dissolution Emulsification Mixing Evaporation Photochemical oxidation Adherence Bubble bursting & spray Molecular diffusion	Biodegradation Dissolution Evaporation Photochemical oxidation	Biodegradation Dissolution Emulsification Photochemical oxidation	Dissolution Emulsification Evaporation Photolysis Aerosol formation
WATER COLUMN RESERVOIR			
Biodegradation Dissolution Particle distribution Settling Dispersion	Biodegradation (ingestion) Dissolution Tar ball formation Interaction with sediments	Biodegradation Dissolution Particle adsorption Dispersion	Biodegradation & release Dissolution Tar ball formation Dispersion (spreading, drifting)
ATMOSPHERIC RESERVOIR			
Diffusion			Horizontal & vertical diffusion
BOTTOM RESERVOIR			
Transport & deposition Biodegradation Dissolution Mixing	Burial Biodegradation Dissolution	Sinking or sedimentation Microbes, fauna Dissolution	Uptake and release Dissolution
NEARSHORE RESERVOIR			
Deposition Evaporation Mixing Biodegradation	Shoreline stranding		Stranding

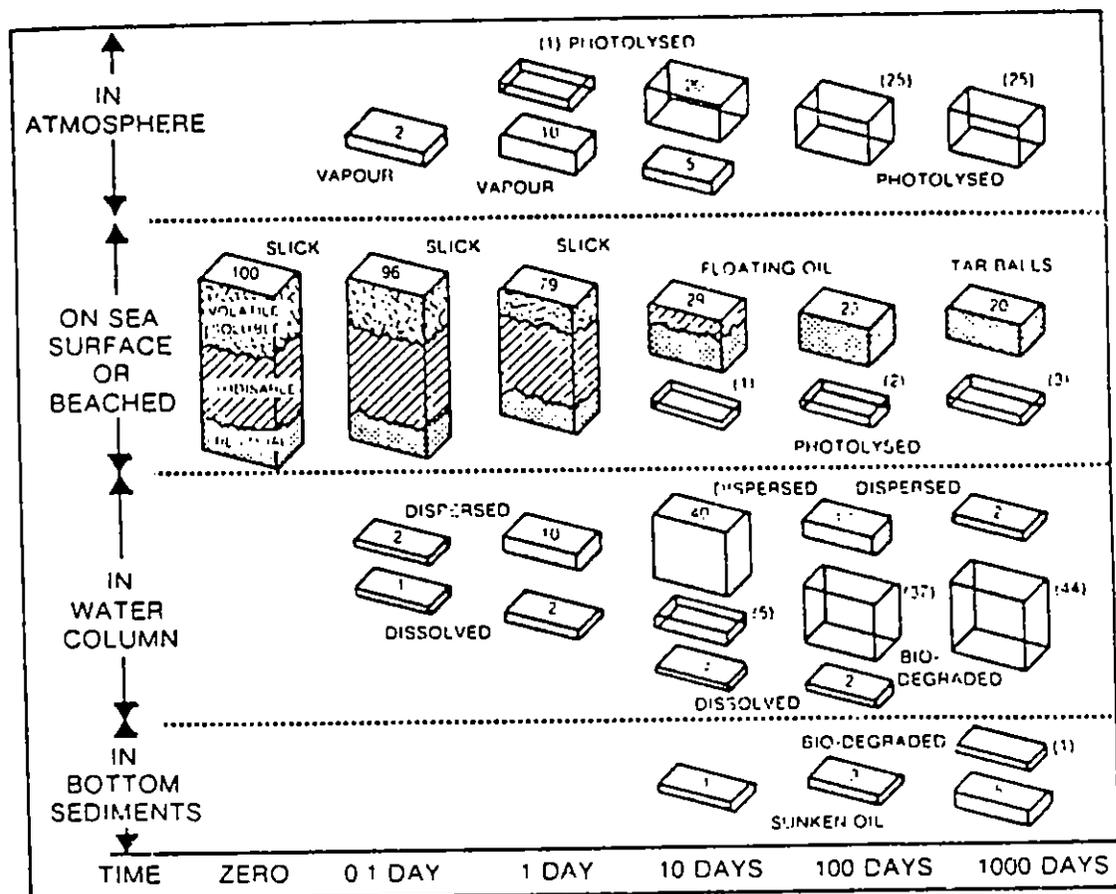


FIGURE 2. Generalized mass balance model beginning with 100 units of spilled oil (from Mackay, 1980; based on a similar diagram by J. N. Butler, Harvard University). Unshaded boxes represent oil converted to another chemical form. This is one of the few models estimating oil degradation over time; however, little supporting data are offered to support these rates.

CASE HISTORIES

The following case histories represent our understanding of oil fate derived from "spills of opportunity." Information from each spill is synthesized from available literature augmented by personal communications with several of the principal authors. All units are converted to metric tons, assuming that 42 U.S. gallons (35 U.K. gallons) equal one barrel and seven barrels equal one metric ton. Unfortunately, there is little consistency of cargo units between spills.

The Santa Barbara Blowout

Blowout of a Union Oil Company platform 10 km off Montecito, California, occurred on 28 January 1969. The proximity of several public and private research institutions enabled a fairly intensive study of the spill site (Kolpack, 1971; Straughan, 1971). However, several major problems are encountered in developing a mass-balance model for this spill; the foremost being not knowing how much oil was spilled. Since estimates vary by an order of magnitude, from 11,290 tons to 112,900 tons (Foster et al., 1971), all comparisons back to the amount spilled are suspect.

Had the amount spilled been better known, the information provided by certain published reports would be more applicable. These available data include the quantity of shoreline oil, as derived by Foster et al. (1971); 4,500 tons spread over 90 km of shoreline by 8 February 1969), and infrared chemical analyses of numerous, bottom-sediment samples from the Santa Barbara Channel (Kolpack et al., 1971). The latter study is particularly interesting in that it indicates a large quantity of oil was carried to the bottom by a massive influx of sediment during a major flood at the time of the spill. Unfortunately, follow-up studies were not performed to determine normal background levels, nor was the infrared technique capable of differentiating between blowout oil and oil from natural seeps or anthropomorphic sources (e.g., urban runoff). Kolpack (pers. commun.) is continuing work along these lines as part of a long-term interest in this problem, but as yet no additional information is available.

ARROW Spill

This oil spill began on 4 February 1970 as the tanker ARROW grounded on rocks in Chedabucto Bay, Nova Scotia. At the time of the accident, some 15,520 tons of Bunker C oil were being transported. Eventually, after rupture and partial loss of cargo, 5,270 tons were offloaded while another 160 tons were thought to still be left on board (MOT, 1970). Although the published range of estimates of total oil lost varies from 9,500 tons to 19,600 tons, the source of the discrepancy seems to be a misquote of the Canadian government (MOT, 1970) figure of 10,090 tons.

Aside from the initial problem of how much oil was lost, scientific literature about this spill offers very useful information concerning the fate of spilled oil. Data presented on oil incorporation into the water column are particularly interesting. In addition, since the effects of the spill lasted almost ten years, several shoreline sites were monitored for long-term persis-

tence (Rashid, 1974; Owens and Rashid, 1976; Owens, 1978; Vandermeulen and Gordon, 1976; Vandermeulen, 1977; and Vandermeulen et al., 1977) or biological effects (Gilfillan and Vandermeulen, 1978; and Thomas, 1972, 1973, 1977, and 1978).

During the spill, 240-300 km of shoreline were oiled (Owens, 1971; Vandermeulen and Gordon, 1976; Keizer et al., 1978). A determination of how much oil initially went onshore is lacking. However, 2.5 months after the spill (and after cleanup had begun), MOT (1970) estimated that 1,800 tons (18% of the total) still remained onshore.

Offshore investigations are primarily reported by Levy (1971), Forrester (1971), and Conover (1971). In a survey during May 1970, Levy (1971) measured the total oil in the water column at two stations in Chedabucto Bay, finding a variation of 16-41 ppb. If an average of 25 ppb is integrated over the entire volume of Chedabucto Bay ($670 \times 10^6 \text{ m}^2 \times 60 \text{ m}$ depth; Conover, 1971), then only 0.01 tons of oil were incorporated into the water column at this time. By winter 1971, oil concentrations were at background levels of 1.5 ppb (Gordon and Michalik, 1971; Levy, 1972).

Forrester (1971) also analyzed oil in the water column, but concentrated on the amount of oil particles present from 15 February to 28 March 1970. Particles ranged from 5 to 2 mm in size. Identification was based on color, texture, and solubility in chloroform. This survey found particles distributed as far as 250 km away and 80 m deep. Forrester (1971) estimates that as of 19 February, there were 50 m^3 of less than 1 mm particles inside the Bay and 25 m^3 outside the Bay. This represents about 75 tons of oil assuming a 1 g/cm^3 density for the oil. There was no increase in particles after this date. Since particles were probably more plentiful immediately after the spill, Forrester (1979) estimates that the maximum at any given time was 100 m^3 . The rate of particle production was placed at $6 \text{ m}^3/\text{day}$ for the first 15 days and $1 \text{ m}^3/\text{day}$ thereafter. So, during the first 1.5 months after the spill, possibly 120 tons of particles were formed.

Conover (1971) also looked at oil in the water column, but from a biological rather than a chemical standpoint. He found that zooplankton grazing on oiled particles passed feces containing up to 7 percent Bunker C oil. Presumably, the passed material then sank to the bottom and was removed from the system. Conover (1971) projects that if the entire stock of zooplankton is considered, then an oil sedimentation rate of 0.21 tons was likely. In the first 1.5 months, this could place some 9.5 tons of oil on the bottom. Unfortunately, bottom sediment samples were not collected during the spill, although Keizer et al. (1978) reported only background levels in bottom sediments collected six years later.

So, in summary, it appears that of the 10,090 tons of oil that were spilled, some 120 tons (1.2% of the total) entered the water column as particulate matter, and nearly 10 tons (0.01% of the total) were sent to the bottom by biological processes. Two and one-half months after the spill, it was estimated, with no supporting data, that 1,800 tons (18% of total) still remained stranded onshore. In the water column, an average value of 25 ppb was found three months after the spill, representing only 0.01 tons of oil in Chedabucto Bay. By April 1971, oil concentrations were at background levels (1.5 ppb).

ARGO MERCHANT

The ARGO MERCHANT oil spill of 15 December 1976 was the first major U.S. oil spill to be investigated by a large multidisciplinary group of university and government scientists. The ARGO MERCHANT ran aground and broke up 53 km southeast of Nantucket Island, Massachusetts, releasing a total of 26,190 tons of No. 6 fuel oil and cutter stock. Fortunately, no oil came ashore. Summary reports of the spill incident are presented by Grose and Mattson (1977), COMS (1978), and Morson (1979).

Results of studies analyzing the hydrocarbon content of the water column and bottom sediments are particularly germane to mass-balance efforts. Bottom sediments taken by box cores and grab-sampler showed minor contamination (\bar{x} = 22 ppm) of an area 10-15 km² located immediately around the wreck site (Hoffman and Quinn, 1978). Oil penetration extended to at least 8-13 cm deep, but may have been deeper. Based on a 15 cm depth and on average sediment specific density of 3 g/cm³, Hoffman and Quinn (1978) estimate that 150 tons or 0.5 percent of the total cargo resided on the bottom. However, since a specific density of 1.5 g/cm³ is probably more accurate, 75 tons or 0.3 percent of the total may be more realistic. The small quantity of oil found on the bottom is attributed to: (1) the low specific gravity of the oil indicating that most of it would float, (2) the active dynamics of the area which would rework and remove most deposited oil, and (3) the generally coarse-grained nature of the bottom (or lack of fine-grained material to adsorb oil particles).

Analysis of the oil content in 12 water column samples showed an elevated hydrocarbon content (\bar{x} = 44 ppb) over some 2,700 km² of the Georges Bank - Nantucket Shoals region (Boehm et al., 1978). This was approximately 40 times the petroleum values noted one year later. It is unlikely that the elevated hydrocarbon concentrations resulted solely from the ARGO MERCHANT as it would include far more oil than the ship carried. Follow-up studies indicate a decline and eventually low background concentrations by the next winter (Boehm, 1980). In addition to the ARGO MERCHANT, the high values in February 1978 may be attributable to winter shipping and/or the GRAND ZENITH which sank in an unknown location off New England. Thus, a complete mass-balance model for this spill is nonquantifiable.

TSESIS

The TSESIS oil spill occurred on 26 October 1977 as the tanker entered Sodertalje ship channel about 50 km south of Stockholm, Sweden. Approximately 1,100 tons of oil, primarily No. 5 with some Bunker C, were lost in total. Shortly after the spill, a joint scientific study was undertaken by the Askö Laboratory of the University of Stockholm, the Swedish Water and Air Pollution Research Institute, and the U.S. National Oceanic and Atmospheric Administration Spilled Oil Research Team (Kineman et al., 1980).

Although the emphasis of study was primarily biological, interesting results were obtained concerning oil fate models. Three sediment traps were placed where the bottom collected substantial quantities of oil (\bar{x} = 43 mg per m²/day) one week after the spill. The extrapolation of these results over the 42 km² that was oiled indicates that 19 tons of oil (2% of the total) may have been deposited on the bottom (Johansson, 1980). Unfortunately, no oil

was found in any of the bottom samples taken during the same period, indicating either inadequate sampling techniques or that the oiled material remained in a flock just above the sediment surface. Other aspects of the fate model (including oil in the water column or on the shoreline) could not be evaluated due to inadequate sampling. Approximately 600-700 tons of oil were removed from the shoreline during cleanup operations.

AMOCO CADIZ

During the night of 16 March 1978, the supertanker AMOCO CADIZ grounded on rocks a few kilometers offshore of the fishing village of Portsall, France. Over the next few days, the entire cargo of approximately 223,000 tons of light Arabian Gulf crude oils and a small amount of Bunker C oil were lost to the sea. Because of the enormous size of the spill and close proximity of several renowned French marine laboratories, the spill attracted great scientific attention from France, the United States, Canada, and the United Kingdom.

Under financial support of several governmental as well as private agencies, numerous 2-3 year studies were undertaken. Summary volumes covering these investigations are Conan et al. (1978, 1981), Hess (1978), and Spooner (1978). Other reports which include preliminary mass balance models of the AMOCO CADIZ are Marchand et al. (1979) and Michel et al. (1979). Presently, a NOAA-sponsored research group (R. Atlas, P. Boehm, E. Gundlach, and D. Ward) is preparing a paper for publication detailing the physical, chemical, and microbiological degradation of AMOCO CADIZ oil, including additional data on oil chemistry. Major components of the spill model discussed herein include oil in the water column, oil in subtidal sediments, and oil in the intertidal zone. Microbial degradation is discussed throughout.

Oil in the Water Column

As oil left the breached ship, high wave activity quickly formed a stable oil-in-water emulsion ("chocolate mousse") containing 30-70 percent water (Ducreux, in press). The oil initially spread rapidly eastward due to storm winds and tidal currents until a shift in wind direction two weeks into the spill caused a strong oil movement to the southwest. Altogether, some 15,000 km² of offshore waters showed some surface oiling during this period.

Several offshore cruises were conducted during March/April 1978 and June 1978 to characterize the surface and subsurface oil distribution (Calder et al., 1978; Calder and Boehm, 1981; Law, 1978; Mackie et al., 1978; Marchand and Caprais, 1981). Obtained water samples were extracted and analyzed by standard UV fluorometric methods (IOC/WHO, 1976). Oil concentrations ranged from 3-20 µg/l in the offshore zone (49°-49°30' N), from 2-200 µg/l in the nearshore zone (shoreline to 49° N), and from 30-500 µg/l in the Aber Wrac'h and Aber Benoit estuaries. By mid-April, hydrocarbon concentrations in offshore regions decreased to background values (less than 2 µg/l), while it took until mid-May and September for the nearshore and estuarine areas, respectively, to reach background levels.

During the first three weeks, approximately 20,000 tons of oil became incorporated into the water column based on average concentrations and four complete water changes (Table 2). Indirect evidence (oxygen depletion) indicates that an additional 10,000 tons of oil was degraded by microorganisms (Aminot, 1981). This would then raise the oil content in the water column to some 30,000 tons (13.5% of the total spilled).

TABLE 2. Calculation of total hydrocarbons incorporated into the water column during the first three weeks of the spill. The specific gravity of the oil assumed to be 1 g/cm³ (derived from Law, 1978; Mackie et al., 1978; and Marchand and Caprais, 1981).

ZONE	DEPTH ^a	AREA (km)	AVG. CONC. ^b (µg/l)	STANDING OIL CROP (tons)	TOTAL ^c (tons)
Offshore (49°-49°30')	30	150 x 30	10	2,250	9,000
Nearshore (shore-49°N)	30	150 x 30	20	2,700	10,800
Estuaries (Benoit & Wrac'h)	30	12 x 0.3	120	120	<u>16</u>
				Total after 3 weeks	19,816

^aDepth of mixing.

^bAbove background.

^cBased on 4 complete water changes.

Oil in Subtidal Sediments

Oil was transported to subtidal sediments located in three regions: (1) offshore areas composed of coarse-grained calcareous sediments and exposed to high current velocities, (2) the more sheltered Bays of Lannion and Morlaix composed of finer-grained sediments, and (3) the very sheltered estuaries at Abers Wrac'h and Benoit which contain mostly silts and clays. Sampling in each region began a short time after the beginning of the spill and continued until June 1978 in offshore areas (Law, 1978), until August 1980 in the Bays of Morlaix and Lannion (Beslier, 1981), and until June 1981 in Aber Wrac'h (Marchand et al, in press).

During the first month of the spill, approximately 18,200 tons of oil were incorporated in subtidal sediments (Table 3). Sampling in offshore areas

TABLE 3. Calculation of oil deposited in subtidal sediments.^a

	AREA (km ²)	AVG. CONC. (ppm)	DEPTH (cm)	TOTAL (tons)
Nearshore	1,806 ^b	35 ^c	10 ^d	7,111
Bays of Morlaix and Lannion	322	210 ^e	10 ^d	7,607
Aber Wrac'h	2.6	1,887-12,000 ^f	20 ^g	1,919
Aber Benoit	2.1	746-28,475 ^h	20 ^g	<u>1,558</u>
		Total during first month		18,195

^aBased on an oil-specific gravity of 1.0 g/cm³ and a sediment density of 1.5 g/cm³.

^b75 percent of the 70 ppm nearshore of Marchand and Caprais (1981); 25 percent considered to be nonoiled rocky area based on grabbing.

^c70 ppm (nonpurified extract) of Marchand and Caprais (1981) is halved to account for petroleum hydrocarbons (purified extract) only (Marchand, in press).

^dSamples taken by grabbing.

^eAverage of 10 sites (Marchand and Caprais, 1981).

^fTwo zones: 2.5 km² x 1,887 ppm, and 0.14 km² x 12,000 ppm (Marchand and Caprais, 1981).

^gFrom Allen et al. (1978).

^hThree zones: 0.9 km² x 746 ppm, 1.12 km² x 3,021 ppm, 0.04 km² x 28,475 ppm (Marchand and Caprais, 1981).

three months later revealed much lower oil concentrations, although exact station comparisons to earlier surveys are difficult to make. A detailed analysis (293 sites) of the Bays of Morlaix and Lannion revealed a decrease from an initial 7,600 tons to 1,800 tons by July/August 1978, and to 800 tons by August 1979 (Beslier, 1981). Cleansing was attributed to storm processes (Beslier et al., 1981). A similarly rapid decrease in bottom sediment contamination was noted in an exposed offshore site at the mouth of Aber Wrac'h (Marchand et al, in press). In contrast, sheltered interior stations containing fine-grained sediments still showed elevated values (600 ppm), only slightly lower than initial levels, three years after the spill (Marchand et al, in press). Oil retention in bottom sediments was related to the physical energy of the geographic area and to sediment type.

Oil in the Intertidal Zone

Based on detailed measurements at 19 stations and extrapolation over the entire oiled zone using ground analysis and aerial photographs, some 62,000 tons of oil came onshore during the first weeks of the spill (Finkelstein and Gundlach, 1981). However, by the end of April, this quantity had decreased to approximately 10,000 tons, although the extent of oiled shoreline increased from an initial 72 km to over 320 km as the larger slicks broke up and spread (Gundlach and Hayes, 1978). The most efficient shoreline cleansing process resulted from wave and tidal action. Cleanup operations, during which thousands of workers participated until September 1978, removed approximately 25,000 tons (Laubier, 1978). Microbial activity, although not acting at a comparable short-term rate, was responsible for the degradation of oil persisting after cleanup or in sheltered areas.

One year after the spill, oil was still obvious along 77 km of shoreline. By November 1979, oil remained along only 50 km (D'Ozouville et al., 1981). This trend of slow decrease would have continued were it not for the occurrence of the tanker TANIO, which spilled 7,000 tons of oil over roughly half of the shoreline previously impacted by AMOCO CADIZ oil (Gundlach et al., 1981; Berne, 1980).

Several intertidal sites were monitored to determine oil degradation rates and products. Analysis by gas chromatograph revealed overall decreases with depth (up to 20 cm) and over time. By 1981, concentrations varied from near background (but weathered beyond chemical recognition) as at Aber Wrac'h to over 11,000 ppm at sheltered areas such as Ile Grande marsh. The behavior of oil in Aber Wrac'h upper intertidal sediments contrasts strikingly with that observed in adjacent low intertidal and subtidal areas. Whereas the analyzed upper intertidal site was virtually free of oil by June 1981 (Boehm, in press), oil in low intertidal to subtidal sediments still showed very high levels (600 ppm) probably due to its greater oiling and anoxic conditions.

Although oil concentrations decreased with depth up to 20 cm, fine-sectioning of some cores indicated variability with this trend, especially among individual hydrocarbon components (Boehm, in press). The physical movement of sand as part of the natural erosional/depositional cycle of the beach in many cases was responsible for much deeper burial (up to 1 m) as compared to chemical migration alone. In addition to variability with depth, the severe patchiness of the distributed oil, as well as the secondary input of

AMOCO CADIZ and/or TANIO oil at several stations, severely complicates the short-term interpretation of the chemical data. Even though physical processes were the major cleansing agent at moderate- to high-energy beaches, and cleanup was responsible for the superficial removal of oil at nearly all heavily oiled locations, microbial activity played a principal role for the degradation of oil in sheltered or stable environments. Based on the measurement of oil degradation rates using radio-labeled trace hydrocarbons, it was estimated that microorganisms would be capable of degrading some 0.5 ug oil per day per gram sediment (Atlas and Bronner, 1981). Superimposing this rate over a 100 m average intertidal zone for the 320 km that was oiled, then some 880 tons of oil could have been degraded by March 1980, the time of additional oil inputs from the TANIO spill. However, in many areas oil became incorporated in subsurface anoxic zones where these rates would not be achieved. Although oil analyzed from these zones appeared less degraded than oil from toxic layers, the potential for anaerobic degradation (40-300x slower) is indicated by the depletion of certain hydrocarbon aromatic families (Ward, in press).

Summary

It is a best-guess estimate that during the first month, the 223,000 tons of AMOCO CADIZ oil was dispersed as follows: 30,000 tons (13.5%) incorporated into the water column, 18,000 tons (8%) deposited in subtidal sediments, and 62,000 tons (28%) deposited onshore. Evaporation remains a major unmeasured component; however, indirect evidence from chemical measurements revealing the loss of the light ends, as well as several laboratory studies (Mackay and Paterson, 1980a), indicates losses range from 20-40 percent. An average of 30 percent is reasonable, raising the total accounted for to 79 percent. The remaining 21 percent or 46,000 tons may be accounted for as drifting slicks and tar balls/particles that were carried through the English Channel by tidal currents.

IXTOC I

The IXTOC I well blew out at a site some 80 km offshore of Ciudad Del Carmen, Mexico, on 3 June 1979. By the time of its final capping on 23 March 1980, it had become the largest oil spill in history. Reports of the actual total conflict slightly. OSIR (1980) quotes PEMEX (Petroleos Mexicanos) in saying that 476,000 tons or 140 million gallons of oil were lost (30,000 bar/day from 3 June to 12 August; 10,000 bar/day from 13 August to 15 November; 2,000 bar/day from 1 December to 5 March; 400 bar/day from 6 March to 14 March; and a negligible amount thereafter). However, in the official Mexican report of the spill (Anon., 1980), a total of 443,000 tons or 130 million gallons was presented as the total lost with somewhat different values for the flow rate. It should be noted that a subsurface marine blowout is a substantially different case than a surface ship-derived spill in terms of spilled oil pathways. The quantity of oil going into the water column, in particular, can be greatly increased.

The major component of the fate model for this spill seems to be evaporation and burning. PEMEX indicates (although unsupported by data) that some 58.1 percent (257,400 tons) of the total burned or evaporated, 3.4 percent (15,100 tons) was cleaned off the water's surface, and 5.5 percent (24,300

tons) was captured by the Sombrero-funnel placed over the blowout during October, leaving 33 percent (146,200 tons) on the ocean surface. Actual evaporation, as indirectly determined by density changes in the oil, was 30-40 percent (Boehm, pers. commun.).

In addition to the Mexican scientific effort (Anon., 1980), the United States supported a research cruise to the well site during September 1979 (Atwood, 1980). Results of the analytical work done on water column and bottom sediment samples are very interesting. Based on analyses from 13 stations, Boehm and Fiest (1980b) characterized the water column in terms of the petroleum content in the surface microlayer, as well as subsurface whole-water, dissolved and particulate fractions. The water column whole-water fraction ranged up to almost 7,000 ppb within 30 km of the well site, much higher than the maximum values observed previously at major, but surface spills including EROFISK (30 ug/l; Grahl-Nielsen, 1978), ARGO MERCHANT (450 ppb; Grose and Mattson, 1977), and the AMOCO CADIZ (350 ug/l; Calder et al., 1978).

By far, most of the water column petroleum was in the particulate form (roughly 90% particulate vs 10% dissolved) which is compositionally different than the dissolved form. Most of the particulates were concentrated in the upper zone of the water column under the slick. In fact, a zone of particulate oil from 5 to 15 m depths was apparently visible by acoustical reflectance (Walter and Proni, 1980). Below 20 m, hydrocarbon concentrations decreased substantially. Physical/chemical weathering, and not microbiological activity, seems to be the primary degradational process.

Boehm and Fiest (1980b) go on to calculate that some 70-80 tons of oil were present in the 20 m of oil under the slick (0.1-1 km wide; 100-1,000 ug/l concentrations) in the 25 km zone around the well site. If it takes 2 days to cover this area with oil (based on 0.5 knot currents), then the amount in the water column within 25 km of the spill site represents some 3 percent of the 20,000 barrels of oil lost in that 2 day period. If it is assumed that PEMEX estimates for the amount actually on the surface represents only 38.5 percent of the total lost (Sombrero not in position yet), then the quantity included in the water column could be as high as 7.3 percent of the surface slick.

In another paper presented at the same symposium, Boehm and Fiest (1980a) present results of their bottom sediment studies. Sampling was completed using a Smith-McIntyre grab sampler at ten stations augmented by sediment traps at three stations. The top 3-4 cm of sediments taken by the grab were removed for analysis. Unfortunately, the closest station to the well site was still 30 km away. Total hydrocarbon contents (gravimetric) varied between 15.1 and 143.3 ug/g, but with notable biogenic inputs. Boehm and Fiest (1980a) go on to estimate the amount of oil in the sediments by making several assumptions:

- 1) All measured oil was concentrated in the top 0.5 cm of sediment--essentially a surface flock as seen initially at AMOCO CADIZ (Cabioch et al., 1978) and postulated for the TSEISIS spill (Johansson, 1980; Boehm et al., 1980).
- 2) All oil was concentrated within a 30 km radius of the well site.
- 3) Average concentrations were 150 ug/cm³.

4) The dry density of sediment equaled 4 g/cm^3 .

The reported result is some 8,700 tons of oil; however, the dry density of sediment is notably too high, thereby lowering the estimated quantity to some 3,200 tons should 1.5 g/cm^3 be used. Again, if PEMEX spill quantity figures are accepted, then this represents some 0.9 percent of the total lost and 2.8 percent if the estimated burned or evaporated fraction is eliminated. The amount of particulates captured in the sediment traps (8 hours on the bottom) was not measured, but estimated quantities ranged from 10 to 15 mg with absolute oil quantity ranging from 50 to 250 μg . Based on the size of the trap opening, the vertical flux of oil per day was roughly estimated at $1\text{-}5 \mu\text{g/cm}^2$.

CONCLUSIONS

In all the cases analyzed, a maximum of 50 percent of the total oil lost can be directly accounted for. A summary of each spill is presented in Table 4. Oil incorporation into the water column varied between 0.02 to 13 percent of the total. The type of oil and the extent of physical mixing are probably the prime determinants of the quantity of oil that will become incorporated in the water column. Oil deposition in subtidal sediments ranged from 0.1 to 8 percent of the total. Sediment type and localized physical processes (primarily currents) influence oil deposition and persistence. Oil stranding on the shoreline varied from none (ARGO MERCHANT) to 28 percent (AMOCO CADIZ). Microbial degradation varied greatly, from minimal at the IXTOC I site, to very significant (possibly up to 4.5 percent in the first few weeks alone) at AMOCO CADIZ. All in all, the information derived at the AMOCO CADIZ spill offers, by far, the most complete data toward quantifying major spilled oil pathways.

Major problems inhibiting our understanding of this topic are based on inadequate sampling at the time of the spill or, as in the case of AMOCO CADIZ, difficulty in integrating single-time standing crop (oil) measurements over the duration of the spill. In the latter case, the rate at which the quantity of oil within each component is replaced is not known even though sampling was quite extensive. Unfortunately, this extra stage of analytical work, including additional shiptime, etc., is most demanding and costly.

A major component not studied directly in the field, but extensively studied in the laboratory, is evaporative losses. Mackay and Paterson (1980a, b, Fig. 3) indicate that up to 40 percent of crude oil may be lost rapidly to the atmosphere. This compares favorably to indirect observations of 30-40 percent evaporative loss based on density changes of IXTOC I oil (Boehm, pers. commun.). Other components include photooxidation, which may be a significant process but remains unsubstantiated, and the surface slick, which is biodegraded or physically broken into tar particles and tar balls.

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TABLE 4. Summary of spill case histories.

OIL SPILL DATE LOCATION	BLOWOUT	ARGON	ARGO MERCHANT
28 January 1969 Santa Barbara Channel, U.S.A.	Blowout	4 February 1970 Chedabucto Bay, Canada	15 December 1976 53 km SE of Nantucket Island, U.S.A.
QUANTITY LOST	11,290-112,900 tons	9,500-19,600 tons (but 10,090 is probably accurate)	26,910 tons
OIL TYPE	Crude	Bunker C	No. 6 oil + cutter stock
SPILL COMPONENT IN THE WATER COLUMN	No data	16-41 ppb (4 samples) representing 0.01 tons during May 1970. 120 tons (1.2% of total) of oil particles formed during first 1.5 months.	12 water column analyses indicate elevated values (\bar{x} = 44 ppb) over some 2,700 km ² of Georges Bank region. Concentrations were at normal levels by the next winter.
OIL IN BOTTOM SEDIMENTS	IR analyses indicate substantial deposition by storm-runoff sediment; however, analyses could not separate oil from natural seeps or biogenic sources.	No bottom sampling done during spill, but based on zooplankton studies, an oil sedimentation rate of 0.21 tons daily or 9.5 tons total (0.01% of total lost) was likely.	Minor contamination (\bar{x} = 22 ppm) was found around wreck site. Oil penetration was at least 8-13 cm. Total quantity was 75-150 tons (0.3-0.6% of total).
OIL ON THE SHORELINE	4,500 tons along 90 km measured two weeks after blowout. Persistence was only short-term due to a major storm.	240-300 km oiled, but quantity not reported. 2.5 months after the spill, 1,800 tons estimated still on shore. In sheltered areas, oil remained almost 10 years.	No oil went onshore.
COMMENTS	Preliminary calculations of Kolpack (pers. comm) indicate a large quantity of oil incorporated in bottom sediments, thereby supporting the higher value for spill loss.	Problems concerning the quantity lost seem partly due to conversions of imperial gallons to barrels and tons.	Water column analyses are puzzling since more oil than was being transported is indicated by using oil values superimposed over the oiled volume. Other sources such as the lost vessel GRAND ZENITH and winter shipping traffic have been postulated.

TABLE 4. Summary (cont.)

OIL SPILL	DATE	LOCATION	QUANTITY LOST	OIL TYPE	SPILL COMPONENT IN	TITLE WATER COLUMN	BOTTOM SEDIMENTS
RESIS	26 October 1977	50 km S of Stockholm, Sweden	1,100 tons + Bunker C	No. 5 + Bunker C	Inadequately sampled.		<p>Results from 3 sediment traps show $x = 43$ mg/m²/day of oil transported to bottom. Extrapolation over the 42 km² area that had surface oil indicates 19 tons (2% of total) may have been deposited. However, no oil was found in bottom sediments by direct sampling.</p>
AMOCO CADIZ	17 March 1978	Biscaya, France	223,000 tons + Bunker C	Arabian and Iranian light crudes + Bunker C			<p>37 offshore samples taken during spill (IR-analysis) reveal concentrations of 4-1,100 ppm. Pollution was restricted to depths of less than 50 m. Concentrations up to 24,457 ppm were found in the sheltered, fine-grained estuaries. Penetration was 10 cm deep in estuaries, 12 cm deep offshore. Follow-up surveys of the estuaries revealed elevated oil levels through July 1981. Detailed sampling of offshore areas beginning March 1978 indicated a total of 18,200 tons incorporated in bottom sediments (8% of total); 14,700 tons offshore, 1,500 in the estuaries.</p>
ITOC 1 (blowout)	3 June 1979 - 23 March 1980	Gulf of Campeche, Mexico	443,000-476,000 tons	Crude			<p>37 offshore samples taken during spill (IR-analysis) reveal oil content 15.1-14.3 mg sediment but include biological inputs. At the time of the survey (Sept. 1979), approximately 3,200 tons were present on the bottom within a 30-km radius. The vertical flux of particulate oil as captured in sediment traps was 1-5 mg/cm² per day.</p>
							<p>Limited sampling indicates whole shore waters revealed concentrations of 153 µg/l. Oil was well mixed throughout the water column. Extrapolation of oil content over the entire spill site indicates that 30,000 tons (13.5% of the total) were present in the water column 3 weeks after the spill. The half-life of oil ranged from 11 to 28 days. Normal concentrations were present by March 1979.</p>
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TABLE 4. Summary (cont.)

TESTS (cont.)	No data	OIL ON THE SHORELINE	COMMENTS
AMOCO CADIZ (cont.)	<p>Detailed survey of 18 stations and extrapolation to adjacent areas using aerial photographs and rapid ground-survey techniques indicate that approximately 62,000 tons of oil (28% of the total lost) initially washed onto 72 km of coasting and 51 km of offshore rocks. A repeat survey one month later revealed a rapid decline in oil quantity to 10,000 tons (primarily due to wave action), but a large increase in the amount of oiled shoreline (320 km) and offshore rocks (55 km).</p>	<p>Approximately 3,900 tons washed ashore along 252 km of shoreline in south Texas; however, no data are available for impact along the Mexican coast.</p>	<p>Indirect evidence (0, depletion) indicates that some 17,000 tons of oil was degraded in offshore waters by microbiological processes during the first three weeks of the spill. Onshore, microbes were found to degrade oil at the rate of 0.5 mg/g sediment per day. For the first two years, this could have resulted in some 880 tons degraded.</p>
IXTOC I (cont.)	<p>The official Mexican report indicates that 58.13 barrels were evaporated, 1.44 cleaned up, and 5.58 was captured by the sombrero. This leaves 338 or 146,200 tons on the ocean surface.</p>		

Bottom oil is thought to be composed of flocks resting lightly on the bottom. Standard sampling techniques do not capture this flock.

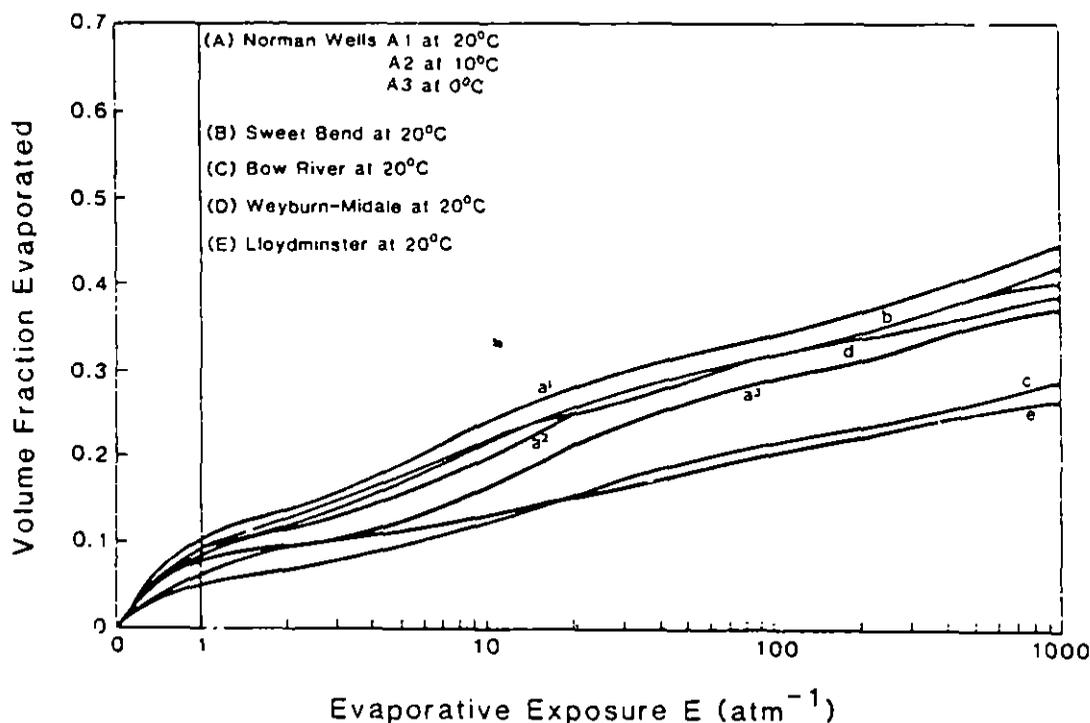


FIGURE 3. Evaporative exposure versus volume fraction evaporated for different Canadian crude oils (from Mackay and Paterson, 1980b). $E = KAvt/(VRT)$ where E is the exposure (atm^{-1}), K is the mass transfer coefficient (m/s), A is the oil area (m^2), V is the initial oil volume (m^3), t is the time, V is molar volume of oil (assumed to be $200 \times 10^{-6} \text{ atm m}^3/\text{mol}$), R is the gas content ($82 \times 10^{-6} \text{ atm m}^3/\text{mol K}$), and T is temperature (K). Typically, K is 0.05 to 0.02 ms. For a 1 cm thick oil layer, (V/A) is 0.01 m. At 0° (273 K) and a wind speed of 32 km/hr ($K = 0.01 \text{ m/s}$), the exposure function becomes $E = 8.9 \times 10^{-3}t$. Thus, E becomes 1.0 when $t = 112 \text{ s}$, 10 when $t = 1,120 \text{ s}$ (19 mins.), 100 when $t = 1,120 \text{ s}$ (3.1 hrs), and 1,000 when $t = 112,000 \text{ s}$ (31 hrs). For example, in the above diagram, Norman Wells' crude oil is 29 percent evaporated by volume at 0° when $E = 100$ (3.1 hrs).

FUTURE STUDIES

Unfortunately, the costs associated with the full range of investigations at a major oil spill can rapidly reach several million dollars. In addition, since "spills of opportunity" occur without warning, the time necessary to reach the spill site with the proper, scientific sampling equipment is often too late. Rather than recommending that water column and bottom sampling intensity be increased, it seems better to focus on a more limited program that yields information concerning the major, but relatively unknown spill-pathway components.

Evaporation is one of the major components not verified in the field; however, laboratory studies have at least presented a plausible range of potential losses. On the other hand, microbial degradation at sea is thought to be a major pathway, but remains largely unverified. By indirect evidence, 10,000 tons were biodegraded at AMOCO CADIZ, but at IXTOC I, biodegradation was severely limited (Atlas et al., 1980a, b). A series of field and laboratory experiments of spill and nonspill conditions may help define potential microbial degradation rates as well as limiting factors. By measuring the maximum amount of oil degraded under optimal nutrient and temperature conditions in the laboratory, an upper limit of degradation could be established. Then, by measuring the real conditions at a spill site, the extent of actual degradation could be estimated. This type of study seems particularly relevant considering microorganisms play a major role in degrading the several millions of tons of oil pollution which enter the ocean every year (NAS, 1975).

Lastly, since surface oil remains totally unquantified as yet, spill assessment utilizing remote sensing augmented with ground trucking could yield surface oil dispersion rates over time. Commonly, surface slicks are determined by low-flying (less than 2,000 m) aircraft; however, resultant photographs only show small parts of the spill. This type of analysis needs high-altitude flights revealing the entire spill site in a limited number of photographs. The thickness of observed colored slicks (or black and white intensities) would have to be initially verified by a sea-surface sampling program. Together, the overflights augmented with surface sampling would aid our understanding of the rate of slick breakup and how it varies under differing sea states and oil types.

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