

# EXXON VALDEZ OIL WEATHERING FATE AND BEHAVIOR: MODEL PREDICTIONS AND FIELD OBSERVATIONS<sub>1</sub>

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**ABSTRACT:** *Outdoor flow-through seawater wave tank studies and model predictions on the chemical and physical fate of Prudhoe Bay crude oil in subarctic waters are compared with field observations from the Exxon Valdez oil spill in Prince William Sound, Alaska. Excellent agreement is obtained between predicted and observed parameters, including evaporative loss of lighter distillate cuts, water content in mousse, density, viscosity, oil/water and oil/air interfacial surface tension, and chemical composition. As predicted from wave tank studies, water column samples of dispersed and dissolved oil and suspended particulate material collected from several heavily oiled sheltered coves and bays in Prince William Sound indicate that little oil reached the near-shore benthic environment during the first few weeks after the spill.*

When crude oil or refined petroleum products are released to the marine environment, weathering processes include spreading, evaporation, dissolution, dispersion of whole-oil droplets into the water column, photochemical oxidation, water-in-oil emulsification, microbial degradation, absorption onto suspended particulate material (spm), ingestion by organisms, sinking, and sedimentation. Numerous mathematical and computer-based models have been developed to predict the fate and weathering of spilled oil. Many of them have been reviewed by Huang and Monastero,<sup>4</sup> with an update by Spaulding.<sup>23</sup> Under contract to the National Oceanic and Atmospheric Administration (NOAA), Science Applications International Corporation (SAIC) has developed a computer-driven oil weathering model that has been updated to run on IBM DOS-compatible personal computers.<sup>13,15</sup>

What makes the SAIC approach unique is the fact that the model is based on measured bulk-oil physical properties that are readily available for most produced oils and many refined products.<sup>2,12</sup> In addition, in developing the model, outdoor flow-through wave tank experiments were performed to validate model predictions and provide data for adjusting user-selected parameters and coefficients utilized in execut-

ing the model computer code.<sup>14</sup> The model characterizes the oil by separation into distillate cuts (pseudocomponents) and generates a material balance for each cut, considering the following weathering processes: evaporation, dispersion into the water column, water-in-oil emulsification, and slick spreading. Additional experimentation and model development has made possible prediction of oil weathering behavior in the presence of sea ice,<sup>5,18</sup> and quantification of dispersed oil/SPM interactions.<sup>6,19,21</sup>

## Model design and wave tank validation

**Oil weathering model input data requirements.** Details on the open ocean oil weathering model development and data input requirements have been published.<sup>13,15</sup> To illustrate the use of the model, Figure 1 presents actual input data used to predict the weathering behavior of North Slope (Prudhoe Bay) crude oil for the *Exxon Valdez* oil spill. Note that the only input characterization data required are the true boiling point distillation temperatures, the API gravity, and the volume percent of each cut. These limited data requirements provide maximum flexibility for a variety of crudes and refined products because they are generally available from several sources and are widely used in the petroleum industry.<sup>2,12</sup> In addition, during the response to a real spill, such data generally can be obtained from the owner or shipper of the spilled product when the model is being used to predict weathering behavior.

The use of this distillate cut (or pseudocomponents) approach is also the only practical way to write an overall material balance for the slick. In this regard, component-specific approaches to the same problem will not work because only a small fraction of the individual components in any crude or refined product are generally known. Furthermore, component-specific approaches do not consider the nondistillable residuum (boiling point > 850° F). From a biological standpoint, when it is important to know what compounds may reside within each distillate cut, such data are available from capillary gas chromatographic analyses. Figures 2 and 3 present selected chromatograms of distillate cuts from Prudhoe Bay crude oil.<sup>15</sup> Thus, with computer-generated output that specifies which cuts remain in the slick as a

1. The opinions or assertions herein are those of the authors and do not necessarily represent the views of the Minerals Management Service or the National Oceanic and Atmospheric Administration.

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Ok
LOAD CUTVPO1.BSAAS
Ok
RUN
HIT THE CAPS LOCK KEY
YOU CAN READ AN EXISTING OIL-COMPARISON FILE OR ENTER THE DATA
YOURSELF AND THEN SAVE IT. ENTER 1 TO READ A FILE OR 2 TO ENTER DATA
? 1
ENTER THE OIL-COMPARISON FILE NAME? PBDAT1.ASC
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1 167 72.7 2.1
2 212 64.2 2.6
3 257 56.7 3.5
4 302 51.6 3.6
5 347 47.6 3.7
6 392 45.2 3.5
7 437 41.5 4.4
8 482 37.8 4.9
9 527 34.8 5.1
10 580 30.6 2.8
11 638 29.1 6.6
12 685 26.2 6.9
13 738 24.0 6.1
14 790 22.5 7.5
15 850 11.4 36.7
WANT TO CHANGE ANY? N
1. BULK API = 27
2. BULK VISCOSITY = 35
3. VIS-TEMPERATURE CONSTANT = 9000
4. VIS-FRACTION-OIL-WEATHERED CONSTANT = 10.5
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1. MAXIMUM WEIGHT FRACTION WATER IN OIL = .7
2. MOUSSE-VISCOSITY CONSTANT = .65
3. MOUSSE WATER INCORPORATION RATE CONSTANT = .001
WANT TO CHANGE ANY? N
OIL/WATER SURFACE TENSION, DYNES/CM = 30
WANT TO CHANGE THE SURFACE TENSION? Y
ENTER THE OIL/WATER SURFACE TENSION, DYNES/CM, TRY 30? 27
OIL/WATER SURFACE TENSION, DYNES/CM = 27
WANT TO CHANGE THE SURFACE TENSION? N
CHARACTERIZING THE CUTS NOW
ENTER THE TEMPERATURE IN DEG F FOR THE VAPOR PRESSURE CALCULATION
? 38
THE CUTS HAVE BEEN CHARACTERIZED
DO YOU WANT TO WEATHER THIS CRUDE? Y
ENTER THE SPILL SIZE IN BARRELS? 250000
ENTER THE NUMBER OF HOURS FOR WEATHERING TO OCCUR? 600
ENTER THE WIND SPEED, KNOTS? 8
WANT THE SLICK TO SPREAD? Y
WANT WEATHERING WITH DISPERSION? Y
1. SPILL SIZE, BARRELS = 2.50E+05
2. DURATION OF WEATHERING, HOURS = 600.0
3. WIND SPEED, KNOTS = 8.0
4. THE SLICK SPREADS
5. DISPERSION OCCURS
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ENTER THE DISK FILE NAME FOR THE 132-COLUMN OUTPUT FILE? EKVALIB.ASC
Ok
    
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Figure 1. Example of the input oil characterization parameters and environmental conditions required for initiating the oil weathering program for North Slope (Prudhoe Bay) crude oil from the Exxon Valdez spill—Note the use of the existing oil characterization file PBDAT1.ASC.

function of time, the chromatograms in Figures 2 and 3 can be used to provide component-specific data on individual compounds. All that is required is a knowledge of the relative retention time or Kovats Retention Index for the components of interest.<sup>7,14,15,22</sup>

After a crude oil or refined product data set has been entered into the program, the user must specify a temperature for the calculations

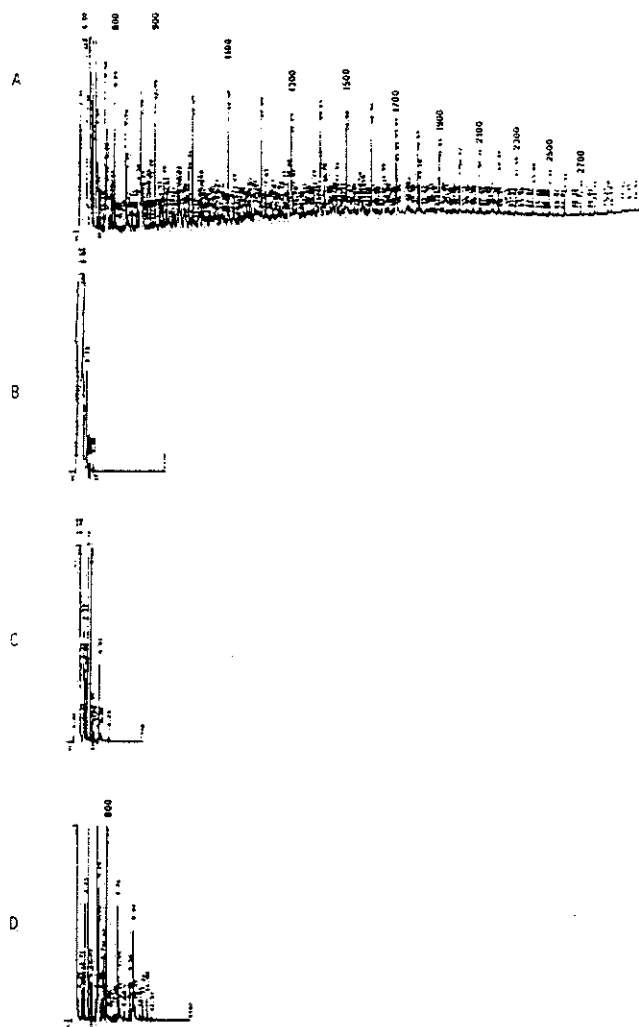


Figure 2. FID gas chromatograms of distillate cuts of fresh Prudhoe Bay crude oil: (A) fresh oil before distillation, (B) cut 1 (107–151° F), (C) cut 2 (186–209° F), and (D) cut 3 (233–259° F)

of physical properties such as vapor pressure and viscosity. The user is then queried for the spill size in barrels and the number of hours for weathering to occur. Mousse formation constants and oil-water interfacial surface tension values then can be adjusted.<sup>8</sup> The computer code asks for a wind speed, whether or not the slick is to spread over the water surface (versus oil trapped within a boom), and whether or not oil droplet dispersion (for oil spills on water versus land) is to occur.

The mass transfer coefficient for evaporation of chemical components from a slick is derived from a correlation value from Mackay and Matsugu,<sup>9</sup> which is a function of wind speed, slick size, and Schmidt number. The spreading equation is based on observations by Mackay et al.,<sup>8</sup> and is not based on the published descriptions of oil spreading due to gravity-viscosity surface tension. The bulk oil viscosity is calculated at 25° C based on the fraction weathered oil composition and scaled with respect to temperature according to the Andrade equation.<sup>3,24</sup> Water-in-oil emulsification is based on the approach of Mackay et al.,<sup>8</sup> and is used to calculate viscosity.<sup>10</sup> The dispersion of oil into the water column is described by equations derived from Mackay et al.,<sup>8</sup> which predict the fraction of sea surface subject to dispersions per second (based on the square of the windspeed) and the fraction of oil droplets below a critical size that do not return to the slick. The latter calculation is dependent on the oil viscosity, the slick thickness, and the oil-water interfacial surface tension. The mass fraction that leaves the slick as dispersed droplets applies to each distillate cut of the oil. Dissolution of specific aromatic components is not modeled because it does not significantly affect the overall mass balance of the slick.<sup>15</sup>

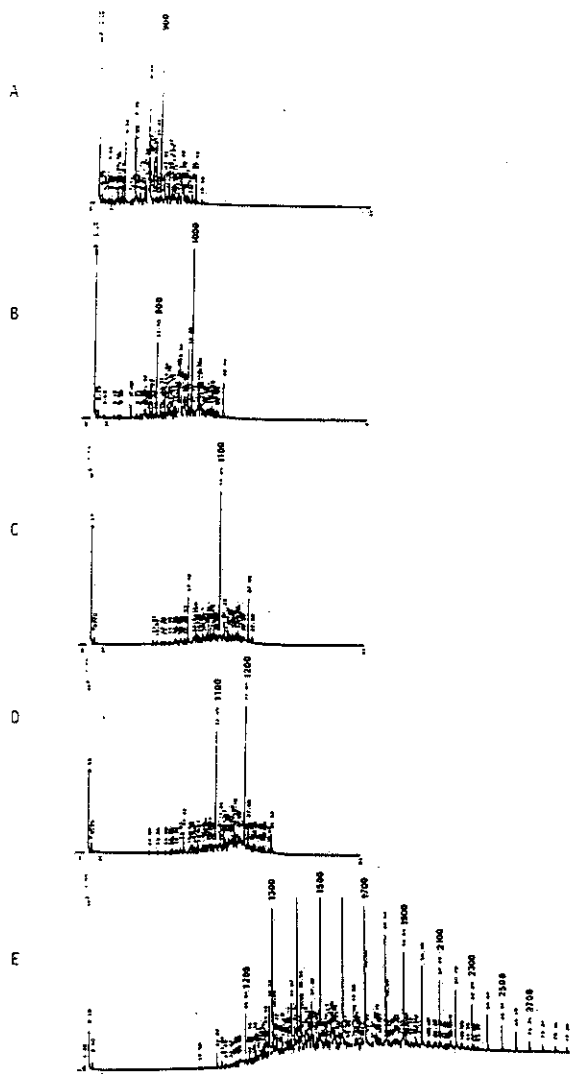


Figure 3. FID gas chromatograms of distillate cuts of fresh Prudhoe Bay crude oil: (A) cut 4 (282–304° F), (B) cut 5 (324–348° F), (C) cut 6 (369–393° F), (D) first half of cut 7 (393–414° F), and (E) pot residue (bottoms) after distillation

The mathematical equations used in the computer code were obtained from the open literature and by derivations based on the experimental observations described below. The equations are classified as either thermophysical property predictions or mass transfer (rate) equations. The thermophysical properties appear directly in the mass transfer equations along with environmental variables such as wind speed and temperature. The environmental variables are the independent variables used to predict mass transfer coefficients. A complete presentation of all equations used in the computer code is available in Payne et al.<sup>15</sup>

**Wave tank experiments.** To develop and validate the model code input parameters, to fine-tune initial spill parameters and coefficients, and to evaluate temporal changes in crude oil under ice-free subarctic marine environments, SAIC conducted a series of outdoor seawater wave tank experiments with Prudhoe Bay crude oil.<sup>13–15</sup> Replicate studies were conducted in summer and winter (water temperatures of 11–14° C and 2–4° C, respectively) in 2,800-liter wave tanks constructed at the NOAA Kasitsna Bay Laboratory near Homer, Alaska. The experiments continued for periods up to 13 months under ambient conditions to allow for processes such as natural photooxidation and bacterial degradation, as well as rain and snow, to contribute to oil weathering. Turbulence was introduced continuously into the wave tanks by paddle wheels.

Each experiment began with a spill of 16 liters of unweathered Prudhoe Bay crude oil into the tanks. Oil and water samples were taken periodically to analyze physical and chemical changes over time. The flow-through system was adjusted to a one tank-volume turnover every 3 to 4 hours, creating a dynamic equilibrium that simulated the advection of oil by wind over water unexposed to the oil. Dissolved/dispersed oil thus could be removed from the water column by advection. Ambient levels of natural nutrients, bacteria, and SPM were continuously introduced to the wave tank.

Following the tank "spill," oil spread readily into various thicknesses estimated to range from (1) no oil coverage (open water) near the paddle to (2) a colorless and silver sheen (0.05–0.2  $\mu\text{m}$ ), (3) a broken rainbow (1–4  $\mu\text{m}$ ), (4) dark brown patches (10–100  $\mu\text{m}$ ), and (5) black continuous coverage (1 mm to 1 cm) at the opposite end of the tank.<sup>11</sup>

At 8 hours the rise in oil viscosity permitted easy identification of the oil-water discontinuity at the edge of the slick. Silver and rainbow-colored sheen still emanated from the slick edge, but the oil coverage generally was thicker and more continuous. Within 24 hours, increased oil viscosity caused rising air bubbles (introduced by paddle wheel turbulence) to remain unbroken in the oil for several minutes. By 72 hours, seawater splashed by waves onto the slick was sustained in pools atop the oil for 20 to 30 seconds before being worked into it by wave stretching and compression of the slick. After 9 days, water had accumulated in the oil to form a stable, light brown emulsion, viscous enough to open and close in a mosaic pattern during wave action.

After a four-month autumn period, although oil patches formed into discrete tarballs (10–15 cm), there was no evidence of microbial degradation (see chemical discussion) nor did the tarballs slough off particles or oil flakes. By early spring, however, some surface tarball microbial degradation occurred and increased significantly during the early summer. The released weathered oil flakes (1–2 cm) contained significantly lower *n*-alkane component concentrations relative to the isoprenoid components, pristane and phytane. Analysis of the tarballs yielded more variable results: surface *n*-alkane degradation had occurred; whereas, the internal tarball composition remained identical to that observed after only 12 days of weathering.

Thirteen months after the "spill," oil remained in tarballs, but surface flaking was significant. Algal material was evident in the water, and barnacles grew throughout the tanks.

**Oil phase physical properties.** The wave tank studies also monitored bulk physical and chemical changes in the oil (Figure 4). An increase in water content, density, and viscosity occurred during the oil weathering process, while oil/water interfacial surface tension decreased.

The water content remained at less than 5 percent for the first 24 hours, increasing to 50–60 percent over the next 6 to 10 days. Density increased from 0.88 to 0.98 g/mL, owing to evaporation of lighter hydrocarbons and water incorporation; however, in the absence of significant SPM, this density increase was insufficient for the emulsified oil to sink.<sup>1, 19, 20</sup> The oil/water interfacial surface tension decreased over a 12-day period from 27 to 10–14 dynes/cm (stabilizing at that level for up to four months), with the incorporation of water and the formation of photooxidation<sup>16</sup> and possibly microbial degradation products. However, the oil/air interfacial surface tension remained essentially unchanged (~35 dynes/cm over four months).

Viscosity (at 38° C) increased from 16 to 2,800 centipoise over the first 12 days of the experiment due to both evaporative weathering and water-in-oil emulsion formation,<sup>17</sup> with the latter process being more important. For example, the viscosity data for pan evaporative weathering show an increase from 16 to only 100 centipoise over the same time frame. As noted, viscosity is temperature-dependent. The values in Figure 4 were obtained at a laboratory-controlled temperature of 38° C to provide maximum reproducibility. When measured at the ambient temperatures in the wave tanks, viscosity increases are even more apparent. During the summer experiments (Table 1), the viscosity at ambient temperatures (12–14° C) increased from approximately 68 to 2,300 centipoise after only three days. For the fall/winter ice-free experiments at 2–4° C (Table 2), the viscosity increases were more significant; initial values increased from 270 to 5,600 centipoise after only 24 hours.

**Oil phase chemical analyses.** Oil spilled on water undergoes rapid evaporation and dissolution weathering as illustrated by the chromatograms of time-series samples from the wave tank studies (Figures 5 and 6). Under the spring/summer conditions, all compounds with vapor pressures greater than *n*-C<sub>11</sub> (boiling point < 400° F) were lost within the first nine days. Between two weeks and seven months, there was

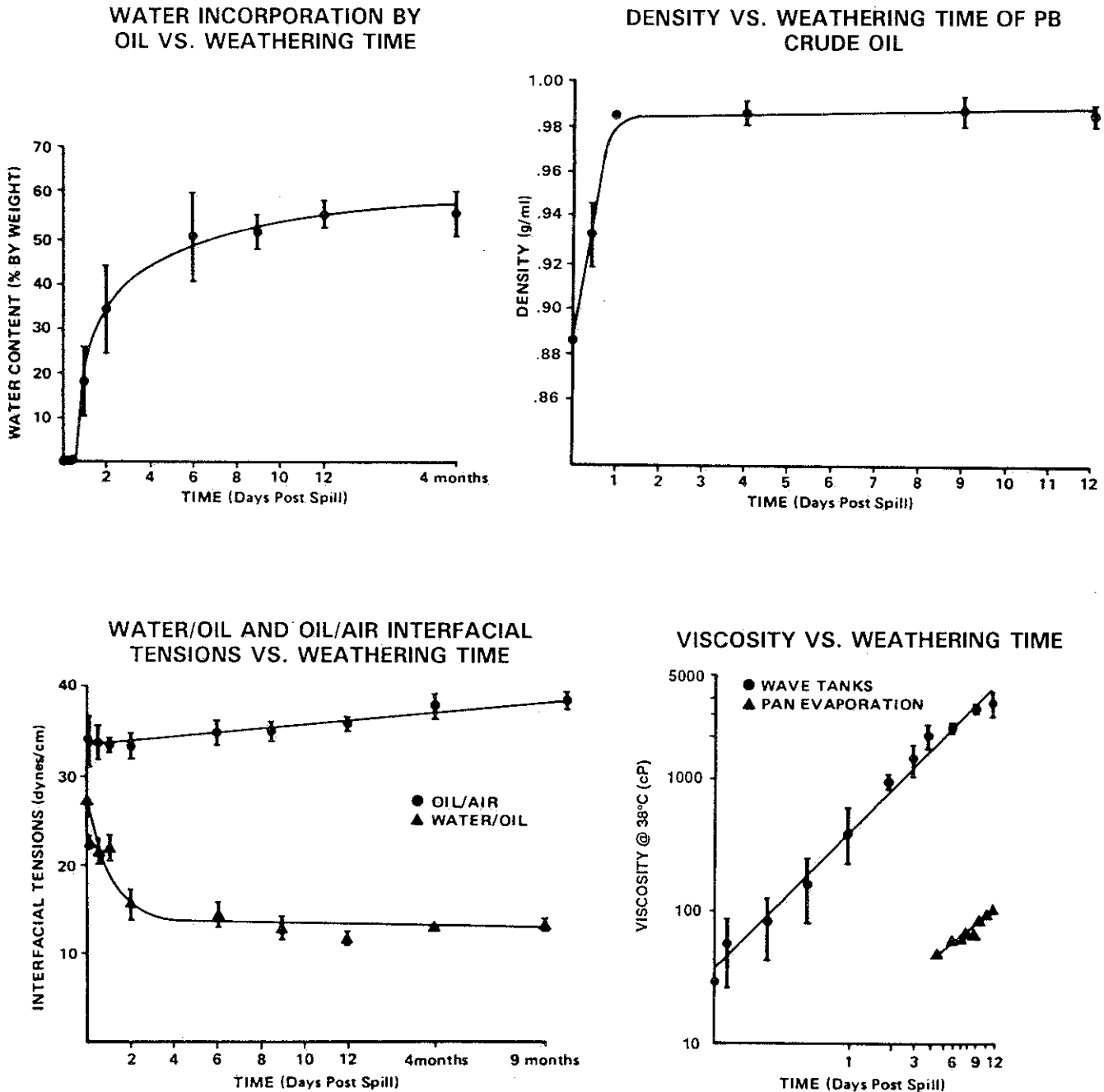


Figure 4. Rheological properties data on Prudhoe Bay crude oil weathering in the summer wave tank systems—The values given are means from the three tanks  $\pm$  one standard deviation<sup>13</sup>

additional loss of compounds between  $n$ -C<sub>11</sub> and  $n$ -C<sub>13</sub> (boiling point < 450° F). Under subarctic winter conditions, however, there was little evidence of microbial degradation. For example, ratios of  $n$ -C<sub>17</sub>/pristane and  $n$ -C<sub>18</sub>/phytane essentially were unchanged over that period. Between the late spring and the following summer/fall period, however, there was a significant change in these straight-chain/branched-chain hydrocarbon ratios due to selective bacterial degradation of the  $n$ -alkanes in preference to the isoprenoid components. With the warming conditions and increased nutrient levels commonly associated with spring phytoplankton/zooplankton blooms, bacterial degradation of outer surfaces of tarballs became the predominant weathering process. When weathered material was sloughed off the tarball surfaces, undegraded material appeared, was exposed, and slowly degraded until the tarballs were fragmented into flakes and droplets small enough to be assimilated into the water column by wave turbulence.

**Model refinements based on wave tank observations.** The equations contained in the computer program are empirical, not absolute; thus, minor user modifications are not only allowable but encouraged. Better agreement between observed and predicted oil behavior was obtained by slight adjustment of user-specified constants. Table 3 gives the suggested (default) values and the modifications that were applied to modeling of the wave tank spills.

In addition, spreading was turned "off," and the slick thickness was set at 1 cm because the oil was "corralled" within the tanks. As reported in Payne et al.<sup>13,15</sup> and shown in Tables 1 and 2, good temporal agreement was obtained between predicted and observed wave tank oil weathering behavior for viscosity, weight fraction water-in-oil, and dispersion flux (whole droplets into the water column). As illustrated below, there also is very close agreement between observed and predicted percent mass distillable (i.e., distillate cut fraction remaining).

Table 1. Observed versus model-predicted data from the summer wave tank experiments,<sup>15</sup>

Time (hours)	Viscosity (centipoise) <sub>2</sub>		Water incorporation (percent by weight)		Dispersion Flux (g/m <sup>2</sup> /hr)	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
1	68.0	160	<0.10	0.96	1.1	1.2
2	130	190	<0.10	1.9	1.1	1.1
1	4	220	240	0.15	1.0	0.99
8	340	320	<.10	7.4	0.91	0.86
12	620	410	0.22	10.0	0.80	0.79
24	690	630	18.0	19.0	0.55	0.62
48	1080	1300	34.0	33.0	0.28	0.43
72	2350	2000	49.0	44.0	0.16	0.35
144	5400	6500	50.0	58.09	0.070	0.19
216	6200	8450	51.0	60.07	0.050	0.17

1. Based on the average values from three wave tanks

2. Observed viscosity data were obtained at ambient temperature (averaging 58° F); predicted values were calculated using a temperature of 55° F.

Table 2. Observed versus model-predicted data from the fall/winter wave tank experiments,<sup>15</sup>

Time (hours)	Viscosity (centipoise) <sub>2</sub>		Dispersion flux (g/m <sup>2</sup> /hr)	
	Observed	Predicted	Observed	Predicted
1	270	730		
2	280	830	0.96	0.71
4	580	980	0.90	0.65
8	2,200	1,200	0.78	0.59
12	2,900	1,300	0.68	0.56
24	5,600	1,800	0.45	0.49
75	8,700	3,400	0.097	0.36
144	9,800	6,400	0.035	0.26
288	11,500	16,000	0.030	0.17

1. Based on a single wave tank experiment

2. Observed viscosity data were obtained at ambient temperature (averaging 30–32° F); predicted values were calculated using a temperature of 30° F.

### Exxon Valdez studies and oil weathering model validation

When 11 million gallons of North Slope crude oil were released from the *Exxon Valdez* in Prince William Sound on March 24, 1989, an unfortunate but scientifically valuable spill of opportunity was available to verify model-predicted behavior of spilled oil in open water, subarctic conditions.

**General observations.** Helicopter observations of the oil 10 days after the spill suggested that the physical state of the oil was highly variable. For example, the extent of emulsification was significantly affected by the degree of previous exposure of the oil to wave turbulence. Wind-driven oil along the southeast side of Knight Island (Figure 7) was extremely fluid and formed into silver-sheened windrows (0.05 to 0.2  $\mu\text{m}$  thick) that were 5 to 10 miles long. In other affected areas of Prince William Sound, isolated patches of more emulsified oil and mousse were trapped in eddies on the leeward sides of rocky points and other outcroppings. In numerous coves and bays, brown to black oil (estimated at 100  $\mu\text{m}$  to 5 mm thick) completely covered the water except for localized areas where the shear stress of currents and island topography disturbed the oil, revealing open water and sheens that were silver (0.05 to 0.2  $\mu\text{m}$  thick) to variegated (0.2 to 0.8  $\mu\text{m}$  thick) in color.

**Sampling operations.** Two weeks after the spill, an investigation of oil weathering was initiated from NOAA Launch 1273 at numerous locations around Knight Island in Prince William Sound. Station locations (Figure 7) included areas of heavy shoreline impact, areas in

coves and bays with a persistent 70-to-90 percent oil coverage on the water surface, open water areas between the larger islands where oil had weathered into occasional windrows of surface oil, and uncontaminated control areas in open water, bays, coves, and inlets.

Sampling activities included collection of surface oil for measurements of chemical and rheological properties, 20-liter water column and SPM samples for dissolved component and dispersed/adsorbed whole-oil droplet analyses, and near-shore surficial sediment/floc samples for analysis of sedimented oil. Analytical methods are described in Payne et al.<sup>21</sup>

Environmental contamination by oil during sampling principally appeared along shorelines and intertidal zones (as opposed to the water column). Steeper shorelines were frequently contaminated by oil for 30–40 m in the intertidal zone, owing to the significant tidal ranges in Prince William Sound. These beaches frequently consisted of cobble, with oil penetration to depths of 20–30 cm being observed. Some shoreline areas were characterized by vertical cliffs, where oil coated the rock face with a "bathtub-like" ring, or band, up to 3–5 m high. Several areas contained booms to corral oil at the heads of small inlets or bays. Even in these enclosed bays, however, little subtidal contamination by oil was noted in surficial sediments and flocculent material adjacent to heavily contaminated shorelines during the first 2 to 3 weeks after the spill.<sup>21</sup> A primary mechanism for transport of oil to subtidal areas after a spill is through oiling of sandy intertidal substrate followed by wave erosion and near-shore deposition. Fortunately, such conditions were not widespread in the areas immediately affected after the spill. Likewise, SPM loads in the water column in Prince William Sound were measured at from less than 0.01 to 4.57 mg/L.<sup>21</sup> At these levels, very little oil/SPM interaction and sedimentation would be expected to occur.<sup>1,19</sup>

**Water column analyses.** Water column measurements taken in the Knight Island coves and bays beneath continuous surface oil slicks and in oil-free open water samples collected two weeks after the spill also yielded concentrations of components consistent with those measured in the wave tank system.<sup>13–15</sup> For example, concentrations of dissolved naphthalene, methyl-naphthalene, and other alkyl-substituted aromatics in the Prince William Sound samples were 0.05 to 0.6 ppb, with concentrations of total hydrocarbon constituents being 0.3 to 1.5 ppb (Table 4). While levels of compounds were relatively low in all samples, detection of one or more compounds in samples from Herring Bay, Northwest Bay, and the passage between Naked and Eleanor Islands presumably reflects dissolution from surface oil slicks present at these locations. Paraffinic hydrocarbons in the dispersed/particulate phases of the water samples from Prince William Sound were measured at concentrations ranging from 0.4 to 2.7 ppb (Table 5).

**Comparison of wave tank and model predicted oil weathering behavior with field samples from the *Exxon Valdez*.** The physical and chemical properties of oil samples collected following the *Exxon Valdez* spill were analyzed for comparison not only to samples obtained during the outdoor wave tank studies, but also to computer model predictions. Physical properties were determined in bulk oil samples from Herring Bay (Knight Island), Northwest Bay (Eleanor Island), and Point

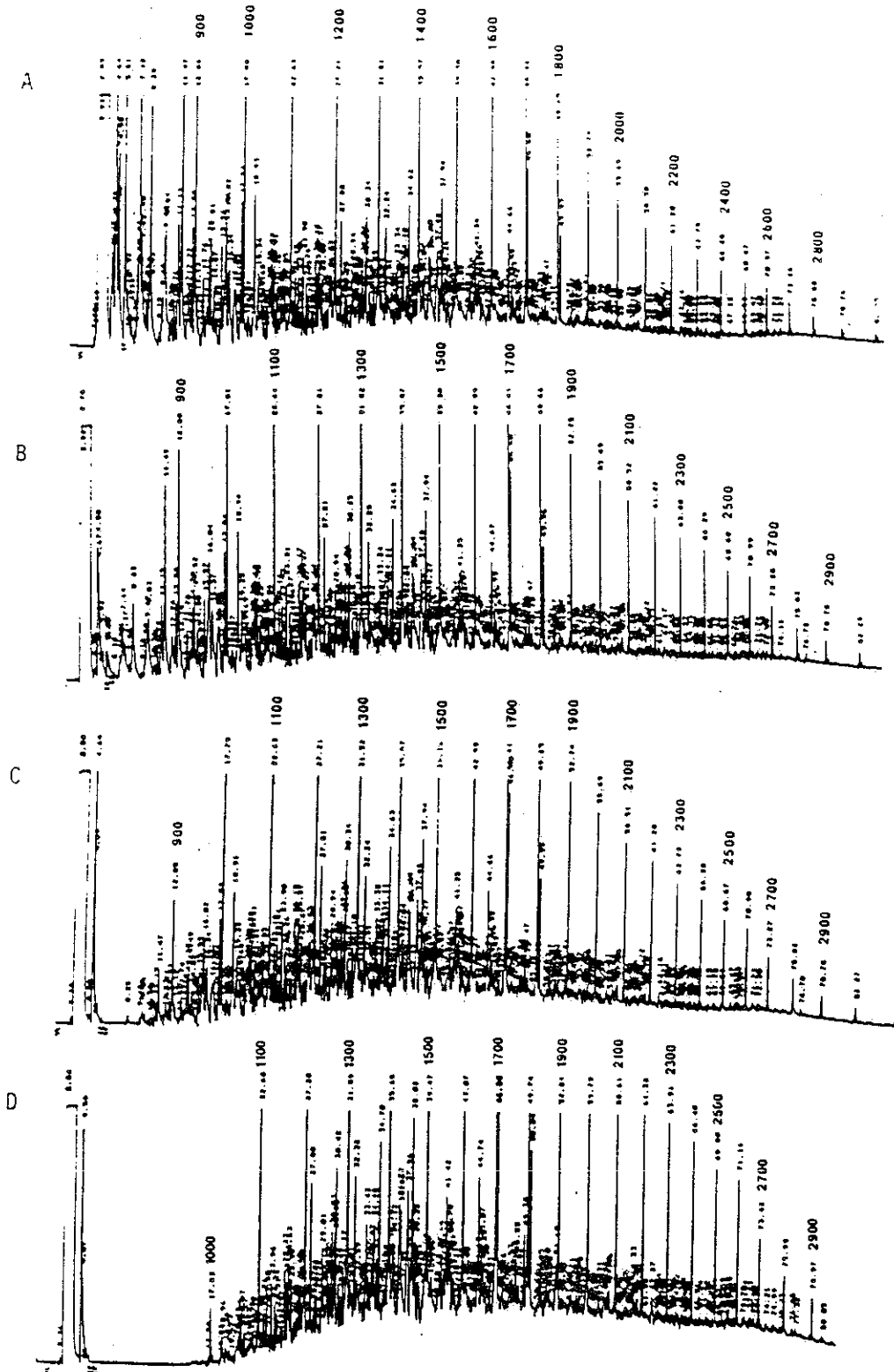


Figure 5. FID gas chromatograms of oil samples obtained from summer wave tank experiments at (A) 0 minutes, (B) 8 hours, (C) 48 hours, and (D) 9 days after a spill of 16 liters of Prudhoe Bay crude oil

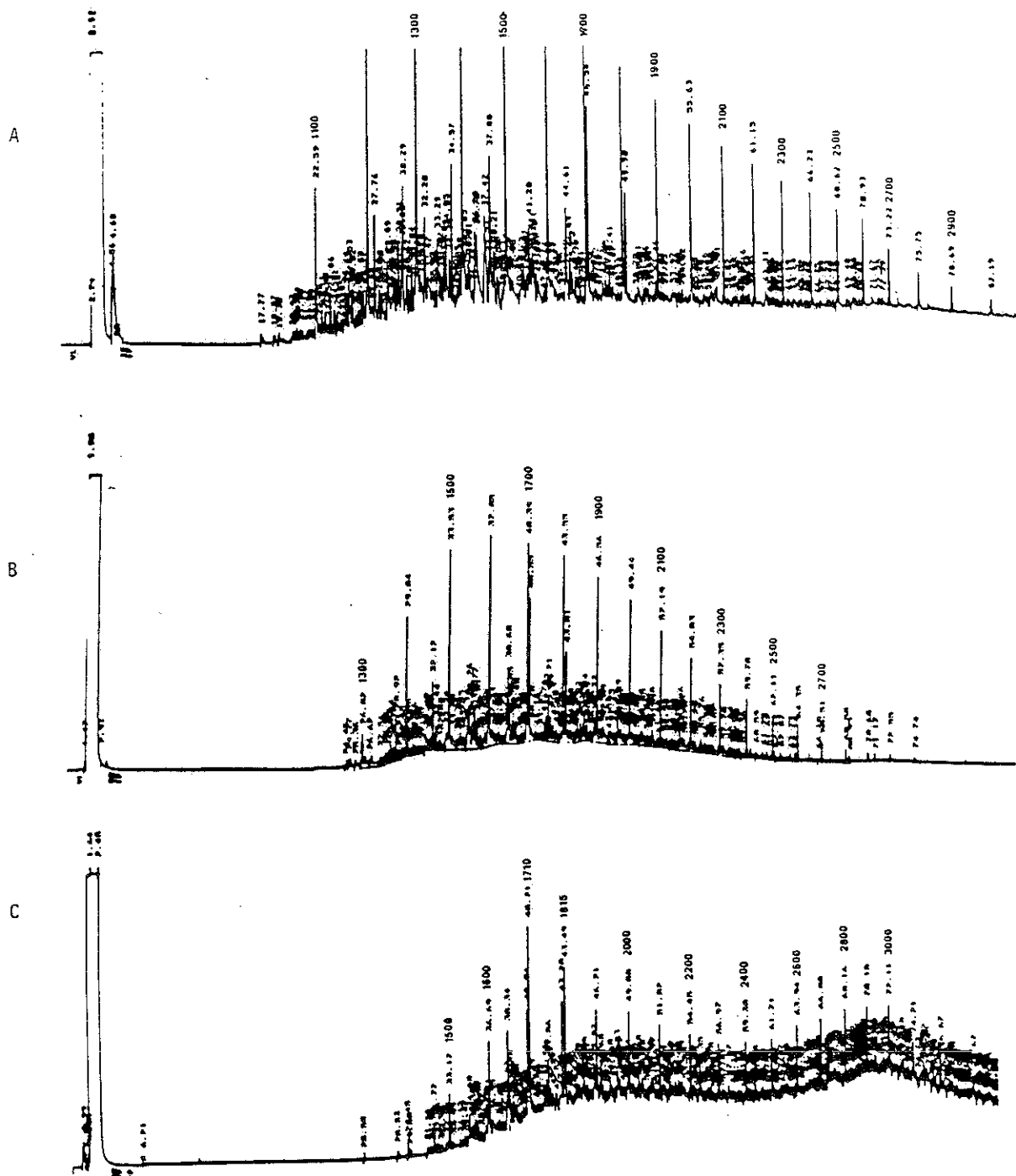


Figure 6. FID gas chromatograms of oil samples obtained from summer wave tank experiments at (A) 12 days, (B) 7 months, and (C) 12 months after a spill of 16 liters of Prudhoe Bay crude oil

Table 3. Suggested values and values used in modeling wave tank experiments

Constant	Suggested value	Value Used	
		Summer	Winter
Maximum weight fraction H <sub>2</sub> O	0.55	0.6	0.5
Mousse viscosity	0.65	0.67	0.65
Water incorporation rate	0.001	0.01	0.003
Oil/water inter-facial tension	30	27	27
Viscosity-fraction-oil-weathered	10.5	12.5	14
Wind speed constant (K <sub>w</sub> )	0.1	0.075	0.1

Adam (on the west end of the Kenai Peninsula) as well as unweathered Prudhoe Bay crude oil and a sample of the cargo crude carried by the *Exxon Valdez*. Results of the measurements are summarized in Table 6.

Figure 8 presents the oil characterization and weathering output data for the computer model simulation of North Slope crude oil weathering after the *Exxon Valdez* spill. For this particular case, an average wind speed of 8 knots and an ambient temperature of 38° F were assumed. Note that the 15 true boiling point cuts for the starting crude are characterized individually and are referred to separately in the output that follows. At each time step, the mass fraction of the remaining slick is presented along with its specific gravity, area, thickness, mean molecular weight, viscosity, weight fraction of water in the

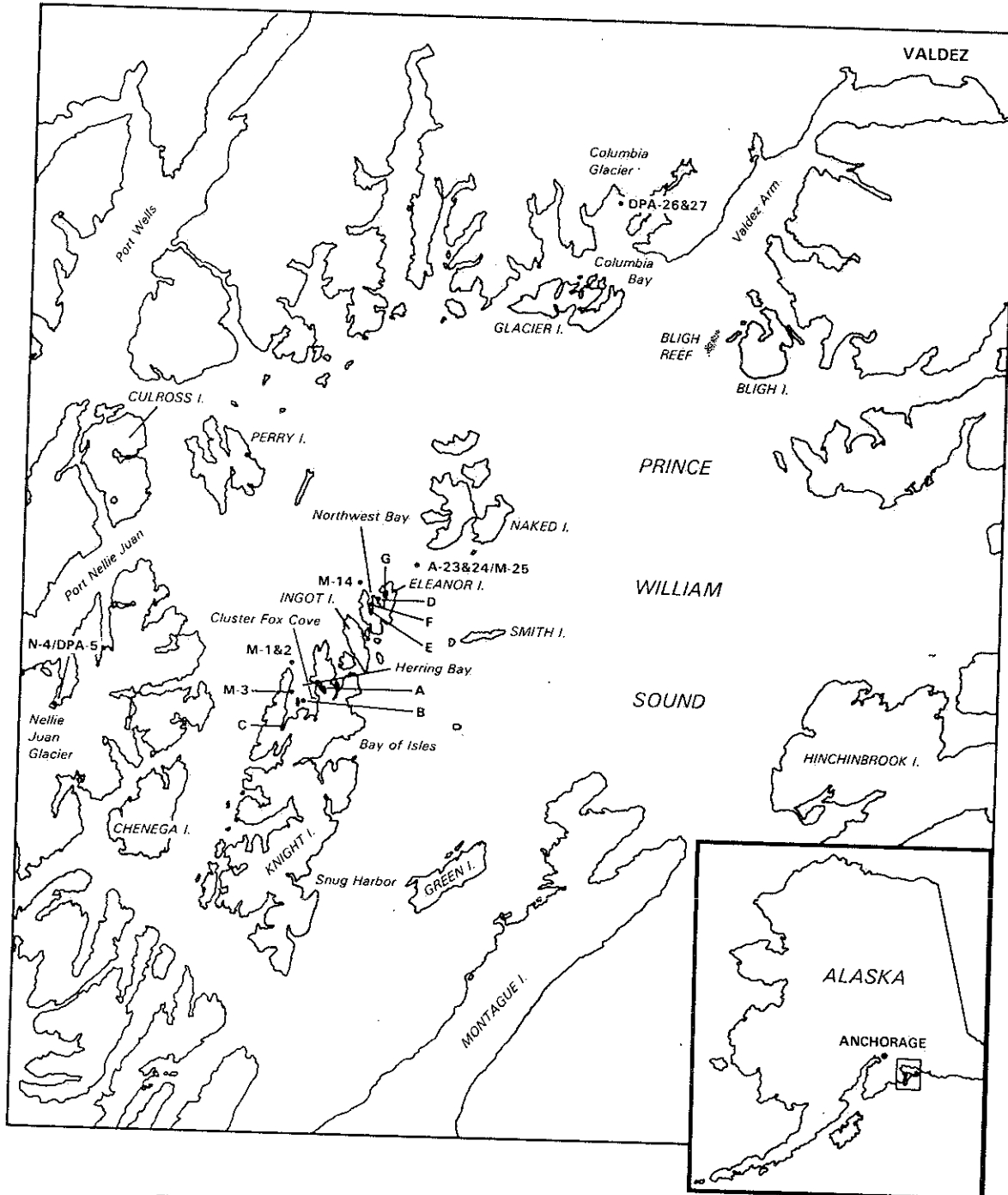


Figure 7. Station locations for NOAA Launch 1273 survey in Prince William Sound



Table 4. Dissolved aromatic hydrocarbon concentrations in filtered seawater samples from Prince William Sound three weeks after the Exxon Valdez oil spill

Sample ID	Station ID	Sampling depth (m)	PAH Concentration (µg/L)					
			Naph	2-MeNa	1-MeNa	Biphenyl	2,6-DiMeNa	Fluorene
A-5	Face of Nellie Juan Glacier	1	0.000	0.000	0.000	0.000	0.000	0.000
A-6	Cluster Fox Cove, Herring Bay	1	0.095	0.166	0.158	0.065	0.000	0.000
A-12	Sta. C, Herring Bay, Knight Is.	10	0.169	0.184	0.188	0.000	0.000	0.000
A-13	Sta. C, Herring Bay, Knight Is.	1	0.068	0.098	0.108	0.000	0.000	0.000
A-16	Sta. E, NW Bay, Eleanor Is.	1	0.234	0.575	0.547	0.155	0.154	0.066
A-18	Sta. F, NW Bay, Eleanor Is.	1	0.192	0.207	0.211	0.000	0.000	0.000
A-21	Sta. G, NW Bay, Eleanor Is.	1	0.313	0.334	0.349	0.000	0.000	0.000
A-23	Between Naked and Eleanor Is.	1	0.092	0.156	0.157	0.000	0.000	0.000
A-24	Between Naked and Eleanor Is.	30	0.047	0.067	0.086	0.000	0.000	0.000
A-26	Face of Columbia Glacier	1	0.135	0.165	0.155	0.096	0.000	0.000
A-27	Face of Columbia Glacier	5	0.107	0.112	0.102	0.000	0.000	0.000

Table 5. Dispersed and particulate-bound aliphatic hydrocarbon concentrations from filtered seawater samples collected in Prince William Sound three weeks after the Exxon Valdez oil spill

Sample ID	Station ID	Sample depth (m)	N-alkane/isoprenoid concentration (µg/L)											
			n-C <sub>12</sub>	n-C <sub>13</sub>	n-C <sub>14</sub>	n-C <sub>15</sub>	n-C <sub>16</sub>	n-C <sub>17</sub>	Pristane	n-C <sub>18</sub>	Phytane	n-C <sub>19</sub>	n-C <sub>20</sub>	n-C <sub>21</sub>
DP-5	Face of Nellie Juan Glacier	1	0.000	0.000	0.000	0.048	0.077	0.119	0.063	0.075	0.036	0.059	0.000	0.000
DP-6	Cluster Fox Cove, Herring Bay	1	0.098	0.210	0.261	0.463	0.532	0.418	0.227	0.224	0.100	0.140	0.107	0.134
DP-12	Sta. C, Herring Bay, Night Is.	10	0.182	0.276	0.239	0.361	0.430	0.362	0.196	0.180	0.074	0.090	0.000	0.000
DP-13	Sta. C, Herring Bay, Night Is.	1	0.097	0.174	0.181	0.296	0.342	0.289	0.147	0.118	0.054	0.090	0.000	0.000
DP-16	Sta. E, NW Bay Eleanor Is.	1	0.101	0.174	0.177	0.290	0.328	0.298	0.155	0.146	0.051	0.087	0.000	0.000
DP-18	Sta. F, NW Bay Eleanor Is.	1	0.272	0.383	0.288	0.361	0.421	0.367	0.196	0.164	0.064	0.090	0.000	0.000
DP-21	Sta. G, NW Bay Eleanor Is.	1	0.145	0.256	0.216	0.308	0.341	0.297	0.166	0.139	0.056	0.000	0.000	0.000
DP-26	Face of Columbia Glacier	1	0.102	0.157	0.141	0.216	0.250	0.228	0.125	0.105	0.044	0.000	0.000	0.000
DP-27	Face of Columbia Glacier	5	0.118	0.186	0.147	0.218	0.261	0.223	0.129	0.105	0.046	0.000	0.000	0.000

Table 6. Physical properties of oil samples collected in Prince William Sound three weeks after the Exxon Valdez oil spill

Sample ID	Oil type	Station ID	Viscosity at 38° C (centipoise)	Surface tension (dynes/cm)		Density (g/mL)	Water content (% by weight)
				Oil/water	Oil/air		
	Unweathered PB crude		<30	23.3	31.9	0.81	0.0148
	Exxon Valdez cargo crude		NA <sub>1</sub>	NA	NA	NA	0.119
M-1	Floating oil	Mouth of Herring Bay, Knight Is.	NA	6.8	36.5	NA	57.8
M-2	Floating oil	Mouth of Herring Bay, Knight Is.	NA	5.5	39.9	NA	45.0
M-8	Beached oil	Cluster Fox Cove, Herring Bay	750	4.5	34.9	0.92	30.9
M-11	Floating oil	Sta. C, Herring Bay, Knight Is.	2700	5.5	35.0	0.92	45.4
M-14	Floating oil	¼ mi W. of NW Bay, Eleanor Is.	900	4.3	36.4	0.93	52.9
M-15	Floating oil	Sta. D, NW Bay, Eleanor Is.	450	4.1	37.9	0.94	53.6
	Floating oil	Pt. Adam, Kenai Peninsula	850	9.0	39.7	0.95	69.4

1. NA indicates not analyzed

water-in-oil emulsion (if present), and composition. For the composition of the oil, the columns "I" and "J" identify the first distillate cut with greater than 5 percent and 50 percent remaining in the slick, respectively.

After 48 hours of weathering, the model predicts that 88 percent of the slick will remain with a specific gravity of 0.88 g/mL and a water content of 49 percent. The first distillate cut constituting at least 5 percent of the total mass is cut 4 (boiling point 302° F) and the first cut constituting more than 50 percent of the remaining oil is cut 5 (boiling point 347° F). Examination of the chromatograms of individual distillate cuts (Figures 2 and 3) reveals that cuts 4 and 5 contain components around n-C<sub>9</sub> (Kovats Index 900), indicating that the crude oil composition at 48 hours would be predicted to be made up of components ≥n-C<sub>9</sub>. Examination of Figure 5C, which shows chromatograms of time-series oil samples from the wave tank, reveals a close match to this predicted composition. After approximately 12 to 13 days (288 to 312

hours) of weathering, the model predicts that 77 percent of the slick remains, and that it has a specific gravity of 0.91 g/mL, a water content of 70 percent, and an in situ viscosity of 130,000 centipoise. At this time cut 6 (boiling point 392° F) would constitute more than 5 percent, and cut 7 (boiling point 437° F) would constitute more than 50 percent of the remaining crude. Comparison of these boiling points to the chromatograms in Figures 2 and 3 reveals the major components in weathered oil at this time would be predicted as ≥n-C<sub>11</sub>. The chromatogram for 12-day-old oil in the wave tank studies (Figure 6A) shows this composition, and compares reasonably well with chromatograms of oil obtained in the vicinity of Knight Island at 21 days after the Exxon Valdez spill (Figure 9).

As shown by the data in Tables 6 and 7, good agreement exists between measurements for physical properties in the wave tank experiments and the field samples from Prince William Sound as well as those predicted by the computer model. For example, viscosities in oil sam-

OIL WEATHERING FOR: PRUDHOE BAY										TIME	FRACTION	SPGR	AREA	THICK	MOLE WT	VIS	MOUSSE	I	J	
CODE NAME IS CUTWP2.BAS, PRINTED BY PR180A.BAS										21	0.91	0.89	6.6E+06	5.4E-01	315.0	2.3E+03	0.28	3	4	
RUN TIME IS 11:38:48 HOURS ON 10-03-1990										22	0.91	0.89	6.7E+06	5.3E-01	315.7	2.4E+03	0.29	3	4	
OIL VOLUME (SPILL), BARRELS = 2.50E+05, MEAN MOLE WEIGHT = 274										24	0.91	0.89	6.8E+06	5.2E-01	316.4	2.6E+03	0.30	3	4	
TEMPERATURE, DEGREES F = 38, WIND SPEED = 8.0 KNOTS										25	0.91	0.89	6.9E+06	5.1E-01	317.0	2.7E+03	0.31	3	4	
FOR THE OUTPUT THAT FOLLOWS, MOLES = GRAM MOLES										26	0.90	0.89	7.0E+06	5.0E-01	317.6	2.9E+03	0.32	3	4	
GMS = GRAMS, VP = VAPOR PRESSURE IN ATMOSPHERES										28	0.90	0.90	7.1E+06	4.9E-01	318.2	3.1E+03	0.35	3	4	
BP = BOILING POINT IN DEGREES F, API = GRAVITY										29	0.90	0.90	7.2E+06	4.8E-01	319.4	3.5E+03	0.36	3	4	
MW = MOLECULAR WEIGHT										31	0.90	0.90	7.4E+06	4.7E-01	319.9	3.8E+03	0.37	4	4	
CUT	MOLES	GMS	VP	BP	API	MW														
1	6.36E+06	5.66E+08	4.58E-02	1.67E+02	7.27E+01	8.90E+01														
2	7.24E+06	7.31E+08	1.35E-02	2.12E+02	6.42E+01	1.01E+02														
3	8.97E+06	1.02E+09	3.35E-03	2.57E+02	5.67E+01	1.14E+02														
4	8.52E+06	1.08E+09	7.47E-04	3.02E+02	5.16E+01	1.27E+02														
5	7.95E+06	1.14E+09	1.53E-04	3.47E+02	4.76E+01	1.43E+02														
6	6.77E+06	1.09E+09	2.75E-05	3.92E+02	4.52E+01	1.61E+02														
7	7.86E+06	1.40E+09	4.61E-06	4.37E+02	4.15E+01	1.78E+02														
8	8.12E+06	1.59E+09	6.94E-07	4.82E+02	3.78E+01	1.96E+02														
9	7.92E+06	1.69E+09	1.02E-07	5.27E+02	3.48E+01	2.13E+02														
10	4.01E+06	9.50E+08	8.58E-09	5.80E+02	3.06E+01	2.37E+02														
11	8.31E+06	2.26E+09	3.56E-10	6.38E+02	2.91E+01	2.72E+02														
12	8.05E+06	2.41E+09	2.54E-11	6.85E+02	2.62E+01	2.99E+02														
13	6.44E+06	2.16E+09	8.58E-13	7.38E+02	2.40E+01	3.35E+02														
14	7.14E+06	2.68E+09	1.78E-14	7.90E+02	2.25E+01	3.75E+02														
15	2.35E+07	1.41E+10	0.00E+00	8.50E+02	1.14E+01	6.00E+02														
BULK API GRAVITY = 27.0, SPGR = 0.893										72	0.86	0.90	1.0E+07	3.3E-01	332.0	2.2E+04	0.61	4	5	
BULK CRUDE VISCOSITY, CENTIPOISE = 3.50E+01										82	0.85	0.90	1.1E+07	3.1E-01	333.8	2.9E+04	0.64	4	5	
VISCOSITY CONSTANT FOR FRACTION-OIL-WEATHERED = 1.05E+01										92	0.85	0.90	1.1E+07	2.9E-01	335.5	3.7E+04	0.66	5	6	
VISCOSITY-TEMPERATURE SCALING CONSTANT (ANDRADA) = 9.00E+03										102	0.84	0.90	1.2E+07	2.8E-01	336.9	4.4E+04	0.68	5	6	
MAXIMUM FRACTION WATER IN OIL (MOUSSE) = 0.70										112	0.84	0.90	1.2E+07	2.7E-01	338.2	5.0E+04	0.69	5	6	
MOUSSE-VISCOSITY CONSTANT = 0.65										122	0.83	0.90	1.3E+07	2.6E-01	339.4	5.6E+04	0.69	5	6	
MOUSSE WATER INCORPORATION RATE CONSTANT = 1.00E-03										132	0.83	0.90	1.3E+07	2.5E-01	340.5	6.0E+04	0.70	5	6	
OIL/WATER SURFACE TENSION, DYNES/CM = 27.0										142	0.82	0.90	1.3E+07	2.4E-01	341.6	6.4E+04	0.70	5	6	
DISPERSION CONSTANTS ARE: AK = 1.08E-01, BK = 5.00E+01										152	0.82	0.90	1.4E+07	2.3E-01	342.5	6.8E+04	0.70	5	6	
FOR OUTPUT BELOW THE FOLLOWING NOTATION APPLIES										162	0.82	0.90	1.4E+07	2.2E-01	343.4	7.1E+04	0.70	5	6	
TIME IS HOURS										172	0.81	0.90	1.4E+07	2.2E-01	344.3	7.5E+04	0.70	5	6	
FRACTION REMAINING IS MASS FRACTION IN THE SLICK										182	0.81	0.90	1.5E+07	2.1E-01	345.1	7.9E+04	0.70	5	6	
SPGR IS THE SPECIFIC GRAVITY										192	0.80	0.90	1.5E+07	2.1E-01	345.9	8.3E+04	0.70	5	6	
AREA IS THE SLICK AREA IN M^2										202	0.80	0.90	1.5E+07	2.0E-01	346.6	8.6E+04	0.70	5	6	
THICKNESS IS THE SLICK THICKNESS IN CM										212	0.80	0.90	1.6E+07	1.9E-01	347.3	9.0E+04	0.70	5	6	
MOLE WT IS THE MEAN MOLECULAR WEIGHT OF THE SLICK										222	0.79	0.91	1.6E+07	1.9E-01	348.0	9.5E+04	0.70	5	6	
VISC IS THE VISCOSITY IN CP										232	0.79	0.91	1.6E+07	1.9E-01	348.6	9.9E+04	0.70	5	6	
MOUSSE IS THE WEIGHT FRACTION WATER IN THE WATER-OIL MIXTURE										242	0.79	0.91	1.7E+07	1.8E-01	349.2	1.0E+05	0.70	5	6	
I IS THE FIRST CUT WITH GREATER THAN 5% REMAINING										252	0.78	0.91	1.7E+07	1.8E-01	349.8	1.1E+05	0.70	5	6	
J IS THE FIRST CUT WITH GREATER THAN 50% REMAINING										262	0.78	0.91	1.7E+07	1.7E-01	350.3	1.1E+05	0.70	5	6	
TIME	FRACTION	SPGR	AREA	THICK	MOLE WT	VIS	MOUSSE	I	J											
0	1.00	0.88	4.0E+06	1.0E+00	274.3	3.7E+02	0.00	1	1											
1	0.98	0.88	4.2E+06	9.4E-01	282.9	4.6E+02	0.02	1	2											
2	0.97	0.88	4.3E+06	8.9E-01	288.5	5.4E+02	0.03	1	2											
3	0.96	0.89	4.5E+06	8.5E-01	292.4	6.1E+02	0.05	1	3											
4	0.96	0.89	4.6E+06	8.2E-01	295.4	6.8E+02	0.06	2	3											
5	0.95	0.89	4.8E+06	7.8E-01	297.8	7.5E+02	0.08	2	3											
6	0.95	0.89	4.9E+06	7.6E-01	300.0	8.3E+02	0.10	2	3											
7	0.94	0.89	5.1E+06	7.3E-01	301.8	9.0E+02	0.11	2	3											
8	0.94	0.89	5.2E+06	7.1E-01	303.4	9.8E+02	0.13	2	3											
9	0.94	0.89	5.3E+06	6.9E-01	304.7	1.1E+03	0.14	2	4											
11	0.93	0.89	5.5E+06	6.7E-01	306.1	1.1E+03	0.15	3	4											
12	0.93	0.89	5.6E+06	6.5E-01	307.3	1.2E+03	0.17	3	4											
13	0.93	0.89	5.7E+06	6.4E-01	308.3	1.3E+03	0.18	3	4											
14	0.93	0.89	5.8E+06	6.2E-01	309.3	1.4E+03	0.19	3	4											
15	0.92	0.89	5.9E+06	6.1E-01	310.2	1.5E+03	0.21	3	4											
16	0.92	0.89	6.0E+06	6.0E-01	311.1	1.6E+03	0.22	3	4											
17	0.92	0.89	6.1E+06	5.8E-01	312.0	1.7E+03	0.23	3	4											
18	0.92	0.89	6.3E+06	5.7E-01	312.8	1.8E+03	0.25	3	4											
19	0.91	0.89	6.4E+06	5.6E-01	313.6	2.0E+03	0.26	3	4											
20	0.91	0.89	6.5E+06	5.5E-01	314.3	2.1E+03	0.27	3	4											
600	0.70	0.91	2.5E+07	1.1E-01	361.9	4.0E+05	0.70	6	7											

Figure 8. Example output of oil weathering simulations for North Slope crude oil for a period of 600 hours following the Exxon Valdez spill—See Figure 1 for input oil characterization data and specification of the weathering conditions.

ples (38° C) from Prince William Sound increased from less than 30 to 450 centipoise or more (one sample had a viscosity of 2,700 centipoise); oil/water interfacial surface tensions decreased from 23.3 to 10 dynes/cm or less; densities increased from 0.81 to 0.92–0.95 g/mL; and water contents increased from approximately 0.1 percent to 30–70 percent. Viscosities predicted by the computer model (Figure 8) are at in situ temperatures in the field, whereas those measured in the laboratory are measured at 38° C. As shown by the data in Table 7, close agreement between predicted and observed values is obtained when corrections are made for temperature.

Differences between predicted and observed chemical and rheologi-

cal properties for oil from the Exxon Valdez may have been due to the variability in weathering conditions to which the oil had been exposed at different sampling locations (including sheltered coves and inlets and open water from within Prince William Sound and locations more than 300 miles from the origin of the spill). There also was significant evidence that microbial and photooxidation processes played a greater-than-predicted role during the first few weeks following the Exxon Valdez incident. For example, both photooxidation and microbial degradation could lead to lower oil/water interfacial surface tension values than those observed in the wave tanks.

Despite the variability noted in the oil samples from the Exxon

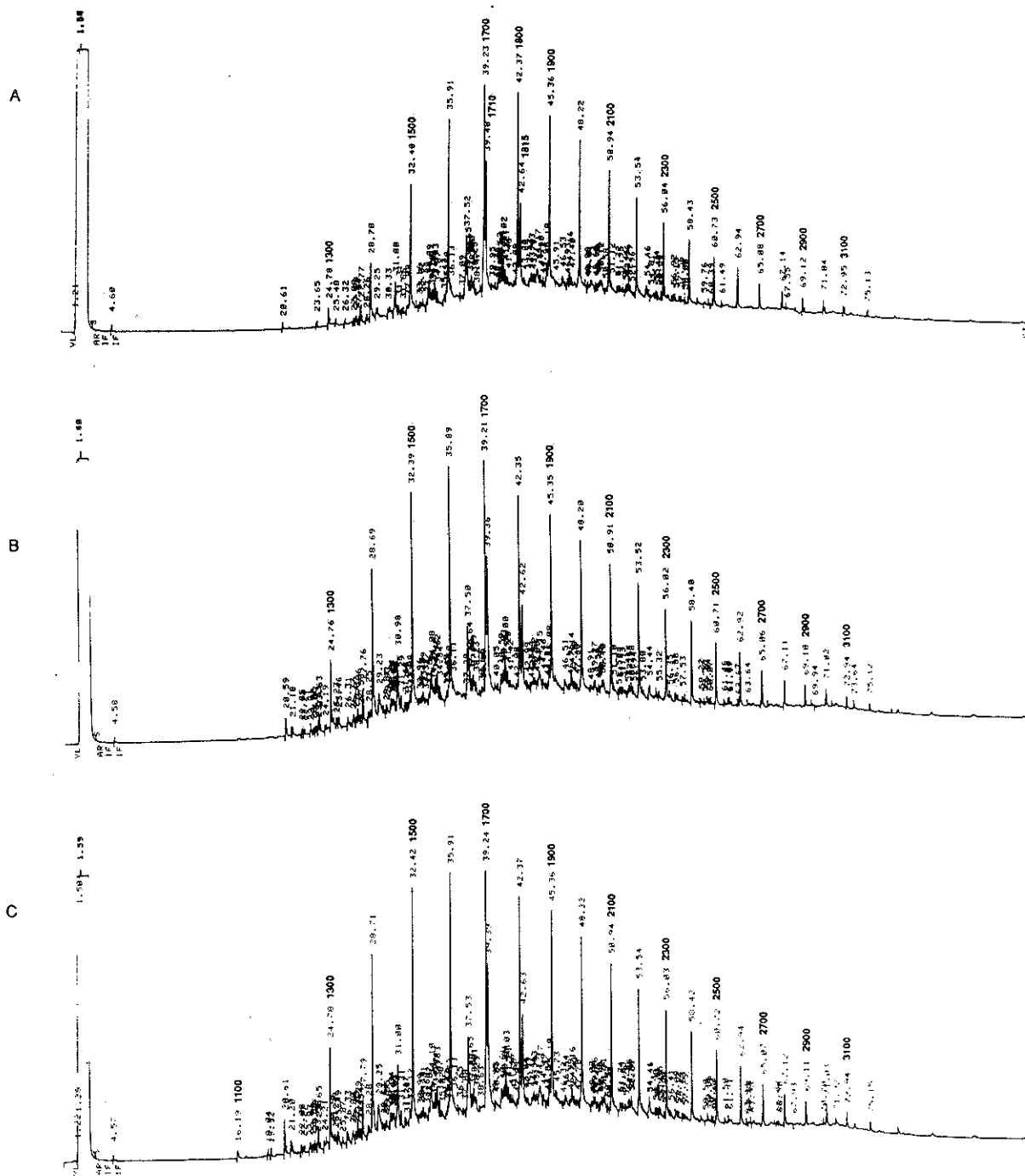


Figure 9. FID gas chromatograms of oil samples obtained from Stations M-2 (A) and M-11 (B) (Herring Bay, Knight Island), and M-15 (C) (Northwest Bay, Eleanor Island) in Prince William Sound approximately three weeks after the Exxon Valdez spill

Valdez field study, the results were similar to oil weathering behavior observed in the 10° to 14° C wave tank systems and predicted by the computer model. These results may be typical of changes in chemical and physical properties expected for similar oils spilled in ice-free environments in northern latitudes.

With regard to the model results, however, a few caveats should be noted. For the computer model predictions, an initial slick thickness of 1 cm was specified, which decreased with additional spreading and weathering. Model runs completed with thinner initial slick thicknesses (e.g., 1 mm) predicted evaporative weathering in excess of that measured in the field. Also, due to model constraints, the slick is considered to spread instantly upon initiation of the weathering pro-

cess. Further complicating accurate modeling of spreading is the fact that oil spreads in thick and thin patches. In addition to these sources of heterogeneity, the distribution of these variable patches of oil can be a weather-controlled, stochastic process. As such, it is difficult to model oil spreading behavior beyond a first approximation. Also, with thin versus thick slick formation, it is necessary to consider diffusion-controlled versus well-stirred behavior for mass transfer predictions in the oil phase. The computer model considers the slick to be well stirred, which may account for the fact that the predicted evaporation behavior greatly exceeds measured results when thinner slicks were modeled.

Likewise, spreading is not modeled to correlate with any given wind

Table 7. Comparison of oil phase physical properties data from wave tank, Prince William Sound, and computer model studies

Source	Viscosity at 38° C (centipoise)	Surface tension (dynes/cm)		Density (g/mL)	Water content (% by weight)
		Oil/water	Oil/air		
Prince William Sound <sub>1</sub>	1,100	5.7	37	0.93	51
Wave tank <sub>2</sub>	3,400	12	36	0.93	55
Computer model <sub>3</sub>	1,100 <sub>4</sub>	NA <sub>5</sub>	NA	0.91	70

1. Mean values for oil samples collected from Prince William Sound and the Kenai Peninsula in April 1989
2. Mean values for oil samples collected after 12 days of weathering in flow-through seawater wave tanks
3. Predicted values for Prudhoe Bay crude oil for a 1-cm slick (initial thickness) after 12 days of weathering (8-knot wind speed, 3° C temperature)
4. Viscosity at 38° C; viscosity at ambient field temperature (3° C) would be 130,000 centipoise
5. NA indicates not generated by computer model; user-specified input

direction or current regime, because slick trajectories generally are modeled as a stochastic process that is outside the scope of this modeling approach. If desired, results of the SAIC model predictions can be linked to larger trajectory models. Such coupling has not been neces-

sary for the purpose of predicting weathering behavior for toxicity estimates or dispersant-use decisions during responses to real spill events. It may be useful, however, for contingency planning or environmental impact statement (EIS) preparation.

```

OK
LOAD*CUTVPOD.BAS
OK
RUN

HIT THE CAPS LOCK KEY

YOU CAN READ AN EXISTING OIL CHARACTERIZATION FILE OR ENTER THE DATA YOURSELF AND THEN SAVE IT. ENTER 1 TO READ A FILE OR 2 TO ENTER DATA
? 2

ENTER THE CRUDE NAME OIL NAME? ANGOLA PALANCA (MEGA BORG - JUNE '90)

ENTER THE NUMBER OF TPB CUTS IN THIS CRUDE? 6

YOU MUST NOW ENTER THE TPB CUT DATA STARTING WITH THE MOST VOLATILE CUT AND THEN GO TO THE BOTTOM OF THE BARREL.

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 1
? 203
ENTER THE API GRAVITY FOR CUT 1
? 73
ENTER THE VOLUME % FOR CUT 1
? 10.9

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 2
? 300
ENTER THE API GRAVITY FOR CUT 2
? 64.2
ENTER THE VOLUME % FOR CUT 2
? 21.8

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 3
? 449
ENTER THE API GRAVITY FOR CUT 3
? 45.8
ENTER THE VOLUME % FOR CUT 3
? 17.4

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 4
? 648
ENTER THE API GRAVITY FOR CUT 4
? 36.6
ENTER THE VOLUME % FOR CUT 4
? 22.5

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 5
? 696
ENTER THE API GRAVITY FOR CUT 5
? 31.5
ENTER THE VOLUME % FOR CUT 5
? 4.9

ENTER THE BOILING POINT AT 1 ATM IN DEG F FOR CUT 6
? 948
ENTER THE API GRAVITY FOR CUT 6
? 25
ENTER THE VOLUME % FOR CUT 6
? 22.4

CUT # BOILING POINT API VOL %
1 203 73.0 10.9
2 300 64.2 21.8
3 449 45.8 17.4
4 648 36.6 22.5
5 696 31.5 4.9
6 948 25.0 22.4

WANT TO CHANGE ANY? N

ENTER THE BULK CRUDE API GRAVITY? 39

ENTER THE BULK CRUDE VISCOSITY, CENTIPOISE, TRY 35? 4

ENTER THE VISCOSITY TEMPERATURE SCALING CONSTANT, (ANDRADA), TRY 9000? 9000

ENTER THE VISCOSITY-FRACTION-OIL-WEATHERED CONSTANT, TRY 10.5? 10.5

1. BULK API = 39
2. BULK VISCOSITY = 4
3. VIS-TEMPERATURE CONSTANT = 9000
4. VIS-FRACTION-OIL-WEATHERED CONSTANT = 10.5

WANT TO CHANGE ANY? N

NOW ENTER THE MOUSSE FORMATION DATA

ENTER THE MAXIMUM WEIGHT FRACTION WATER IN OIL? .3

ENTER THE MOUSSE-VISCOSITY CONSTANT, TRY 0.65? .65

ENTER THE WATER INCORPORATION RATE CONSTANT, TRY 0.001? .001

1. MAXIMUM WEIGHT FRACTION WATER IN OIL = .3
2. MOUSSE-VISCOSITY CONSTANT = .65
3. MOUSSE WATER INCORPORATION RATE CONSTANT = .001

WANT TO CHANGE ANY? N

ENTER THE OIL/WATER SURFACE TENSION, DYNES/CM, TRY 30?

OIL/WATER SURFACE TENSION, DYNES/CM = 0

WANT TO CHANGE THE SURFACE TENSION? Y

ENTER THE OIL/WATER SURFACE TENSION, DYNES/CM, TRY 30? 30

OIL/WATER SURFACE TENSION, DYNES/CM = 30

WANT TO CHANGE THE SURFACE TENSION? N

CHARACTERIZING THE CUTS NOW

ENTER THE TEMPERATURE IN DEG F FOR THE VAPOR PRESSURE CALCULATION
? 86

THE CUTS HAVE BEEN CHARACTERIZED

DO YOU WANT TO WEATHER THIS CRUDE? Y

ENTER THE SPILL SIZE IN BARRELS? 105000

ENTER THE NUMBER OF HOURS FOR WEATHERING TO OCCUR? 240

ENTER THE WIND SPEED, KNOTS? 7

WANT THE SLICK TO SPREAD? Y

WANT WEATHERING WITH DISPERSION? Y

1. SPILL SIZE, BARRELS = 1.05E+05
2. DURATION OF WEATHERING, HOURS = 240.0
3. WIND SPEED, KNOTS = 7.0
4. THE SLICK SPREADS
5. DISPERSION OCCURS
6. DISPERSION RATE CONSTANT, 1/HR = .108
7. DISPERSION PROPERTY CONSTANT = 50

WANT TO CHANGE ANY? N

ENTER THE FILE NAME TO STORE OIL CHARACTERIZATION INPUT DATA? MBORGIA.ASC

ENTER THE FILE NAME FOR THE 80-COLUMN OUTPUT FILE? MBORG1B.ASC

ENTER THE DISK FILE NAME FOR THE 132-COLUMN OUTPUT FILE? MBORGIC.ASC

OK
NEW
OK
CLEAR
OK

```

Figure 10. Example of the input oil characterization parameters and environmental conditions required for initiating the oil weathering program for Angola Palanca crude oil from the *Mega Borg* spill

Conclusions

Perhaps the greatest utility of the results from the SAIC wave tank studies and computer model development is their demonstrated usefulness in responding to real spill events. The most often asked questions during the early hours of a spill are: How is this oil (or refined product) going to weather? Is it dispersible? How is its viscosity going to change with time? How toxic is it going to be after 24, 48, or 72 hours? Will it sink?

In an effort to answer these and other questions, results from the SAIC studies and model development have been used by NOAA and other response-team personnel at numerous spills, including the grounding and loss of JP-5 from the MV *Cepheus* in ice-covered waters of upper Cook Inlet, Alaska, in January 1984,<sup>18</sup> the *Exxon Valdez* spill of North Slope crude in Prince William Sound in March 1989, the *American Trader* spill of North Slope crude off Huntington Beach, California, in February 1990, and the *Mega Borg* fire and spill of light Angolan crude off Galveston, Texas, in June 1990.

The model predictions from the *Mega Borg* incident are interesting, because the spilled Angola Palanca crude was extremely volatile. The example illustrates the flexibility of the model in accepting user-entered oil characterization data. Figure 10 presents the input of actual distillate cut data on the crude as obtained by NOAA at the spill. The crude was separated into six cuts, and the boiling point, API gravity, and volume percent for each cut were entered as shown. Queries regarding the crude oil characterization and the environmental conditions at the time of the spill were completed as illustrated. In this case, an average temperature of 86° F (the water temperature) and a wind speed of 7 knots were specified.

Oil weathering results predicted by the model for the *Mega Borg* spill are presented in Figure 11. Because of the volatile nature of this crude, distillate cuts 1 and 2 were lost within the first 4 hours, and over 45 percent of the overall crude mass was lost via evaporation and dispersion within the first 24 hours. These predictions are in line with observations by the NOAA Regional Response Team and the U.S. Coast Guard at the time of the spill. The results further indicate that nearly 70 percent of the oil mass would be removed from the water surface within the first 10 days. In this case, the slick was modeled with a starting thickness of 1 mm because of its extremely low viscosity (4 centipoise) and low pour point. When thicker slicks were modeled, the percent remaining after 10 days was higher (approximately 44 percent); however, the predicted composition (all components below n-C<sub>12</sub> removed) did not match that obtained by gas chromatographic analysis as well as with the thinner slick. Note that the residuum that was left had a specific gravity of 0.85 and did form a highly viscous water-in-oil emulsion in line with observations made in the field.

The examples presented in this paper demonstrate the status of the open-ocean oil weathering code as adapted for use on personal computer systems. The results can be useful in predicting oil behavior in real spill events and in contingency planning to assess environmental impacts of oil spills from outer continental shelf oil and gas development and transportation activities. When compared to the observations from real spill events, very good agreement has been obtained between measured and predicted data.

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OIL WEATHERING FOR: ANGOLA PALANCA (MEGA BORG - JUNE '90)
CODE NAME IS CUTV2P.BAS, PRINTED BY PRTBOA.BAS
RUN TIME IS 13:15:43 HOURS ON 10-03-1990
OIL VOLUME (SPILL), BARRELS = 1.05E+05, MEAN MOLE WEIGHT = 217
TEMPERATURE, DEGREES F = 86, WIND SPEED = 7.0 KNOTS

FOR THE OUTPUT THAT FOLLOWS, MOLES = GRAM MOLES
GMS = GRAMS, VP = VAPOR PRESSURE IN ATMOSPHERES
BP = BOILING POINT IN DEGREES F, API = GRAVITY
MW = MOLECULAR WEIGHT

CUT  MOLES      GMS      VP      BP      API      MW
1  1.21E+07  1.23E+09  7.51E-02  2.03E+02  4.78E+01  1.02E+02
2  1.89E+07  2.58E+09  5.34E-03  3.30E+02  6.42E+01  1.36E+02
3  1.20E+07  2.27E+09  3.57E-05  4.49E+02  7.50E+01  1.89E+02
4  1.02E+07  3.10E+09  5.11E-09  6.48E+02  3.66E+01  3.04E+02
5  2.13E+06  6.95E+08  4.61E-10  6.96E+02  3.15E+01  3.27E+02
6  5.52E+06  3.31E+09  0.00E+00  9.48E+02  2.50E+01  6.00E+02

BULK API GRAVITY = 39.0, SPGR = 0.830
BULK CRUDE VISCOSITY, CENTIPOISE = 4.00E+00
VISCOSITY CONSTANT FOR FRACTION-OIL-WEATHERED = 1.05E+01
VISCOSITY-TEMPERATURE SCALING CONSTANT (ANDRADA) = 9.00E+03
MAXIMUM FRACTION WATER IN OIL (MOUSSE) = 0.30
MOUSSE-VISCOSITY CONSTANT = 0.65
MOUSSE WATER-INCORPORATION RATE CONSTANT = 1.00E-03
OIL/WATER SURFACE TENSION, DYNES/CM = 30.0
DISPERSION CONSTANTS ARE: AK = 1.08E-01, BK = 5.00E+01
FOR OUTPUT BELOW THE FOLLOWING NOTATION APPLIES

TIME IS HOURS
FRACTION REMAINING IS MASS FRACTION IN THE SLICK
SPGR IS THE SPECIFIC GRAVITY
AREA IS THE SLICK AREA IN MM^2
THICKNESS IS THE SLICK THICKNESS IN CM
MOLE WT IS THE MEAN MOLECULAR WEIGHT OF THE SLICK
VISC IS THE VISCOSITY IN CP
MOUSSE IS THE WEIGHT FRACTION WATER IN THE WATER+OIL MIXTURE
1 IS THE FIRST CUT WITH GREATER THAN 5% REMAINING
J IS THE FIRST CUT WITH GREATER THAN 50% REMAINING

TIME  FRACTION  SPGR  AREA  THICK  MOLE WT  VISC  MOUSSE  1  J
0  0.91  0.80  1.5E+07  1.0E-01  244.9  6.4E+00  0.00  2  2
1  0.77  0.82  1.5E+07  8.3E-02  273.4  3.2E+01  0.01  2  3
2  0.69  0.83  1.5E+07  7.4E-02  296.2  7.0E+01  0.02  2  3
3  0.66  0.83  1.5E+07  7.0E-02  308.3  1.3E+02  0.02  2  3
4  0.64  0.83  1.5E+07  6.8E-02  313.2  1.7E+02  0.03  2  3
5  0.62  0.83  1.5E+07  6.6E-02  315.6  2.3E+02  0.04  2  3
6  0.62  0.84  1.5E+07  6.5E-02  316.2  2.7E+02  0.05  2  3
7  0.62  0.84  1.5E+07  6.4E-02  316.7  3.2E+02  0.06  2  3
8  0.60  0.84  1.5E+07  6.3E-02  317.2  3.8E+02  0.07  2  3
9  0.60  0.84  1.5E+07  6.3E-02  317.2  4.4E+02  0.07  2  3
10  0.59  0.84  1.5E+07  6.2E-02  317.6  5.0E+02  0.08  2  3
11  0.59  0.84  1.5E+07  6.2E-02  318.0  5.6E+02  0.08  2  3
12  0.58  0.84  1.5E+07  6.1E-02  318.4  6.2E+02  0.09  2  3
13  0.58  0.84  1.5E+07  6.1E-02  318.9  6.8E+02  0.09  2  3
14  0.57  0.84  1.5E+07  6.0E-02  319.3  7.5E+02  0.10  2  3
15  0.57  0.84  1.5E+07  6.0E-02  319.7  8.2E+02  0.10  2  3
16  0.56  0.84  1.5E+07  5.9E-02  320.2  8.9E+02  0.11  2  3
17  0.56  0.84  1.5E+07  5.8E-02  320.6  9.6E+02  0.12  2  3
18  0.55  0.84  1.5E+07  5.8E-02  321.0  1.0E+03  0.12  2  3
19  0.55  0.84  1.5E+07  5.7E-02  321.5  1.1E+03  0.13  2  3
20  0.54  0.84  1.5E+07  5.7E-02  321.9  1.2E+03  0.13  2  3
21  0.54  0.84  1.5E+07  5.7E-02  322.4  1.3E+03  0.14  2  3
22  0.54  0.84  1.5E+07  5.6E-02  322.9  1.4E+03  0.14  2  3
23  0.53  0.84  1.5E+07  5.6E-02  323.3  1.5E+03  0.15  2  3
24  0.53  0.84  1.5E+07  5.5E-02  323.8  1.6E+03  0.15  2  3
25  0.53  0.84  1.5E+07  5.5E-02  324.2  1.7E+03  0.16  2  3
26  0.52  0.84  1.5E+07  5.5E-02  324.7  1.8E+03  0.16  2  3
27  0.52  0.84  1.5E+07  5.4E-02  325.2  1.9E+03  0.17  2  3
28  0.52  0.84  1.5E+07  5.4E-02  325.7  2.0E+03  0.17  2  3
29  0.51  0.84  1.5E+07  5.4E-02  326.1  2.1E+03  0.18  2  3
30  0.51  0.84  1.5E+07  5.3E-02  326.6  2.2E+03  0.18  2  3
31  0.51  0.84  1.5E+07  5.3E-02  327.1  2.3E+03  0.19  2  3
32  0.50  0.84  1.5E+07  5.3E-02  327.6  2.4E+03  0.19  2  3
33  0.50  0.84  1.5E+07  5.2E-02  328.1  2.5E+03  0.19  2  3
34  0.50  0.84  1.5E+07  5.2E-02  328.5  2.6E+03  0.20  2  3
35  0.50  0.84  1.5E+07  5.2E-02  329.0  2.7E+03  0.20  2  3
36  0.49  0.84  1.5E+07  5.1E-02  329.5  2.8E+03  0.20  2  3
37  0.49  0.84  1.5E+07  5.1E-02  330.0  2.9E+03  0.21  2  3
38  0.49  0.84  1.5E+07  5.1E-02  330.5  3.0E+03  0.21  2  3
39  0.49  0.84  1.5E+07  5.1E-02  331.0  3.1E+03  0.22  2  3
40  0.48  0.84  1.5E+07  5.0E-02  331.5  3.2E+03  0.22  2  3
41  0.48  0.84  1.5E+07  5.0E-02  332.0  3.3E+03  0.22  2  3
42  0.48  0.84  1.5E+07  5.0E-02  332.5  3.4E+03  0.22  2  3
43  0.48  0.84  1.5E+07  4.9E-02  333.0  3.5E+03  0.23  2  3
44  0.48  0.84  1.5E+07  4.9E-02  333.5  3.6E+03  0.23  2  3
45  0.47  0.84  1.5E+07  4.9E-02  334.0  3.7E+03  0.23  2  3
46  0.47  0.84  1.5E+07  4.9E-02  334.5  3.8E+03  0.24  2  3
47  0.47  0.84  1.5E+07  4.9E-02  335.0  3.9E+03  0.24  2  3
48  0.47  0.84  1.5E+07  4.8E-02  335.5  4.0E+03  0.24  2  3
49  0.47  0.84  1.5E+07  4.8E-02  336.0  4.1E+03  0.24  2  3
50  0.46  0.84  1.5E+07  4.8E-02  336.5  4.2E+03  0.25  2  3
51  0.46  0.84  1.5E+07  4.8E-02  337.0  4.3E+03  0.25  2  3
52  0.46  0.84  1.5E+07  4.7E-02  337.5  4.4E+03  0.25  2  3
62  0.44  0.84  1.5E+07  4.5E-02  342.6  5.1E+03  0.27  2  3
72  0.43  0.84  1.5E+07  4.4E-02  347.6  5.9E+03  0.28  2  3
82  0.41  0.84  1.5E+07  4.2E-02  352.6  6.7E+03  0.29  2  3
92  0.40  0.85  1.5E+07  4.1E-02  357.4  7.5E+03  0.29  2  3
102  0.39  0.85  1.5E+07  4.0E-02  362.0  8.3E+03  0.29  2  3
112  0.38  0.85  1.5E+07  3.9E-02  366.3  9.1E+03  0.30  2  3
122  0.38  0.85  1.5E+07  3.8E-02  370.3  1.0E+04  0.30  2  3
132  0.37  0.85  1.6E+07  3.7E-02  374.1  1.1E+04  0.30  2  3
142  0.36  0.85  1.6E+07  3.6E-02  377.4  1.2E+04  0.30  2  3
152  0.36  0.85  1.6E+07  3.6E-02  380.4  1.3E+04  0.30  2  3
162  0.35  0.85  1.6E+07  3.5E-02  383.1  1.4E+04  0.30  2  3
172  0.35  0.85  1.6E+07  3.5E-02  385.5  1.5E+04  0.30  2  3
182  0.35  0.85  1.6E+07  3.4E-02  387.5  1.6E+04  0.30  2  3
192  0.34  0.85  1.6E+07  3.4E-02  389.3  1.7E+04  0.30  2  3
202  0.34  0.85  1.6E+07  3.3E-02  390.8  1.8E+04  0.30  2  3
212  0.34  0.85  1.6E+07  3.3E-02  392.1  1.9E+04  0.30  2  3
222  0.33  0.85  1.6E+07  3.3E-02  393.2  2.0E+04  0.30  2  3
232  0.33  0.85  1.6E+07  3.2E-02  394.1  2.1E+04  0.30  2  3
240  0.33  0.85  1.6E+07  3.2E-02  394.1  2.2E+04  0.30  2  3
    
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Figure 11. Example output of oil weathering simulations for Angola Palanca crude oil for a period of 240 hours following the *Mega Borg* spill—See Figure 10 for input oil characterization data and specifications of weathering conditions.

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