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The effect of weathering processes on the vertical turbulent dispersion characteristics of crude oil spilled on the sea

Donald J. Boyé

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

**THE EFFECT OF WEATHERING PROCESSES
ON THE
VERTICAL TURBULENT DISPERSION CHARACTERISTICS
OF CRUDE OIL SPILLED ON THE SEA**

A thesis submitted in partial satisfaction of the requirements for the degree of

**MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING**

by

Donald J. Boyé, Jr.

1994

To: Dean Gordon R. Hopkins
College of Engineering and Design

This thesis, written by Donald J. Boyé, Jr., and entitled The Effects of Weathering Processes on the Vertical Turbulent Dispersion Characteristics of Crude Oil Spilled on the Sea, having been approved in respect to style and intellectual content, is referred to you for judgement upon its substantial merit.

We have read this thesis and recommend that it be approved

Rudolf Jaffé

Vassilios A. Tsihrintzis

Hector R. Fuentes, Major Professor

Date of examination: 29 July 1994

The thesis of Donald J. Boyé, Jr. is approved

Dean Gordon R. Hopkins
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Dean Richard L. Campbell
Division of Graduate Studies

Florida International University, 1994

Dedicated to the loving memory of my mother

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ABSTRACT OF THE THESIS

The Effect of Weathering Processes on the Vertical Turbulent Dispersion Characteristics of Crude Oil Spilled on the Sea

by

Donald J. Boyé, Jr.

Florida International University, 1994

Miami, Florida

Professor Hector R. Fuentes, Major Professor

Since the *Exxon Valdez* accident in 1987, renewed interest has come forth to better understand and predict the fate and transport of crude oil lost to marine environments. The short-term fate of an Arabian Crude oil was simulated in laboratory experiments using artificial seawater. The time-dependent changes in the rheological and chemical properties of the oil under the influence of natural weathering processes were characterized, including dispersion behavior of the oil under simulated ocean turbulence. Methodology included monitoring the changes in the chemical composition of the oil by Gas Chromatography/Mass Spectrometry (GCMS), toxicity evaluations for the oil dispersions by Microtox analysis, and quantification of dispersed soluble aromatics by fluorescence spectrometry.

Results for this oil show a sharp initial increase in viscosity, due to evaporative losses of lower molecular weight hydrocarbons, with the formation of stable water-in-oil emulsions occurring within one week. Toxicity evaluations indicate a decreased EC-50 value (higher toxicity) occurring after the oil has weathered eight hours, with maximum toxicity being observed after weathering seven days. Particle charge distributions, determined by electrophoretic techniques using a Coulter DELSA 440, reveal that an unstable oil dispersion exists within the size range of 1.5 to 2.5 μm , with recombination processes being observed between sequential laser runs of a single sample.

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I. INTRODUCTION

It is estimated that between 10 and 100 million tons of petroleum products are lost to the world's oceans annually (Sutton & Calder, 1974). These inputs stem from a wide variety of sources, which include among others, natural sources, in the form of marine sub-surface seeps and sediment erosion, municipal and industrial waste discharges, urban runoff, and accidental discharges related to the handling and transportation of crude oil and petroleum distillates. However, the marine environment has an enormous capability to assimilate and degrade these petroleum hydrocarbon compounds through effective physical, chemical, and biological weathering processes, which are initiated immediately upon release. The oftentimes competitive processes which determine the final disposition of the oil include surface spreading, drifting with prevailing winds and currents, evaporation, photo-oxidation, dissolution; dispersion of discrete oil particles into the water column under the influence of surface turbulence, spray injection into the air during severe weather, water-in-oil emulsification, adsorption onto suspended particulate matter, sinking, sedimentation, biological uptake, and microbial degradation.

For the most part these hydrocarbon discharges are unobtrusively lost to the marine environment leaving no readily apparent environmental impacts; this is evident by the fact, that the world's oceans and coastlines do not reflect the serious degradation that would be expected from the large volume of petroleum products discharged to date. However, in the case of tanker accidents at sea, which generally account for one-half the combined discharge

from both municipal and industrial sources annually (Borthwick & Joynes, 1992), an entirely different scenario develops with oftentimes catastrophic environmental consequences. When large quantities of crude oil are released in coastal waters, there is insufficient time for weathering processes to adequately degrade the oil before reaching the shore, resulting in serious and long-term environmental impacts. These may include lethal effects to many sea birds and mammals from direct smothering, and lowering of primary productivity of the affected area. Other sub-lethal effects can also include disruption of normal feeding patterns, sex attraction, host recognition in symbiotic relationships and other intricate social interactions, and growth suppression in some organisms (Winters *et al.*, 1976; Boylan & Tripp, 1971). These accidental discharges of petroleum products to the marine environment are unfortunate hazards that modern society must be prepared to accept when continuously increasing quantities of crude oil products are transported over great distances, to provide the energy needs of industrialized and developing nations.

Poignant examples exist of the severe environmental consequences of large releases of petroleum oil in sensitive coastal areas, often a result of human error in vessel handling. Among the most destructive in recent times are the super tanker *M/V Braer* running aground and breaking up off the Shetland Islands in 1993 losing the entire cargo load of light distillate oil; and, in 1987 the supertanker *Exxon Valdez* running aground in Prince William Sound spilling 242,000 barrels of crude oil, becoming the worst oil spill disaster in U.S. history.

The worst tanker accident ever on record occurred in 1978 when the supertanker *Amoco Cadiz* ran aground and broke up off the coast of Brittany losing 223,000 tons of crude oil and contaminating 320 km of shoreline.

While these tragic maritime accidents may have gained sensational coverage in the media, there are a number of additional, albeit less severe, tanker incidents which occur on a seemingly regular basis. Data compiled worldwide for the period of 1974 to 1980 indicate that 57 tanker spills of crude oil in excess of 10,000 barrels had occurred, with an additional 57 spills in the range of 1,000 to 10,000 barrels (Amstutz, 1980). Additionally, Borthwick & Joynes (1992) reported that during the year 1990, the U.K. Department of Energy recorded 791 tanker spills off the coast of the United Kingdom alone.

Since the occurrence of the *Exxon Valdez* accident in 1987, there has been a resurgence of interest by the U.S. Federal Government to push, not only for stricter regulations on the way petroleum products are transported, (i.e., requiring double hulls on newly constructed tankers), but also on furthering our understanding on the fate and transport of petroleum hydrocarbons once released in the marine environment. A more accurate prediction of the time dependent changes in the physical and chemical properties of the oil, along with the spreading characteristics of the slick for various initial conditions (e.g., wind speed, sea-state, temperature, and initial oil properties), provides crucial information for improving the forecasting of slick trajectories to define the possible extent of shoreline contamination. In

addition, it allows for the more effective selection of counter-measure technology, which if properly deployed in the right place and with the proper level of response, would mitigate or eliminate environmental impacts associated with large near-shore oil spills. Finally, it provides new insights for predicting the vertical dispersion characteristics of the crude oil, which is essential in estimating the volume of oil lost beneath the surface. The vertical turbulent dispersion of oil particles and the dissolution of soluble fractions into the water column is an important consideration in terms of the overall environmental impact of an oil spill on the marine community. The combination of these processes may be in fact the largest contributor to the overall disappearance of the oil spill in the presence of turbulent sea conditions (Lynch, 1987). These components of the combined weathering process are critical, for once the oil is lost beneath the surface of the overlying slick, it is difficult if not impossible to recover by any means.

The formation of small oil droplet dispersions in the presence of sufficient ocean surface turbulence and duration can be carried to great depths, due to the combination of two factors: significant sub-surface eddy currents in the wake of breaking waves, and the extremely small rise velocities associated with these size particles. Forrester (1971), surveying the distribution of oil particles within the water column at the site where the tanker *Arrow* ran aground in 1970, was able to positively detect oil particles as deep as 80 m; due to the advection of oil particles by sub-surface currents, he was able to detect traces of oil as far as 250 km from the spill source. Similar findings were also observed by scientists studying the

Amoco Cadiz spill. In that incident, near-bottom waters were found to generally contain more total oil than water samples taken at a 2-meter depth, even with oil still floating at the surface. Actually, the highest concentration of total oil (140 ppb) detected offshore was observed at a depth of 65 m and at a distance of 16 km northeast of the site where the *Amoco Cadiz* went aground (Wolfe, 1978). Considering that a dispersion containing 1 ppm of oil distributed within a one square kilometer section of water column to a depth of 1 meter will contain oil in excess of 1 ton (Freegarde *et al.*, 1971), these findings highlight the importance of understanding vertical dispersion dynamics. It is an extremely important issue to address in terms of better understanding and quantifying spreading dynamics, and in assessing the adverse ecological impacts that an oil spill may inflict on aquatic communities, not only at the spill site, but in areas quite distant from the accident.

A review of the modeling of oil spill trajectory and fate dependent processes is provided by Al-Rabeh *et al.* (1989); Huang (1983); Spaulding (1988); and Reed *et al.* (1989); it is a complex numerical simulation with only finite capabilities on providing information which comprehensively predicts the long-term fate of oil spilled at sea. The dependent variables driving the fate simulation of oil are so numerous that modeling would require nearly an individualistic effort (i.e., on a spill by spill basis) to completely predict fate processes with any high degree of accuracy. The fate of crude oil spilled on the sea is dependent on: (1) existing local meteorological conditions, such as prevailing wind speed and direction, air temperature, and intensity of solar radiation (dependent on percent cloud cover and localized

ozone layer thickness); (2) existing sea conditions, such as significant wave height, probability of breaking wave events within the slick area, water temperature, water depth, salinity, concentration of suspended particulate matter (SPM), and the presence of dissolved organic matter (DOM); (3) geographical conditions, including fetch distances and type of coastline, (i.e., high energy rocky shores), where dispersed oil droplet formation and the subsequent sedimentation by SPM interactions are the major concern compared to low energy estuarine backwaters, where shallow quiescent waters may promote the accumulation of toxic dissolution products, (Payne & McNabb, Jr., 1985; Owens, 1978); and most importantly, (4) the physical properties of the oil, such as chemical composition, viscosity, density, oil-water interfacial tension, slick thickness, and slick area.

According to Spaulding (1988), calibrated algorithms for photo-oxidative processes, dispersed oil-SPM interactions, and long-term biodegradation are still required, along with a more comprehensive characterization of the vertical turbulent dispersion of oil droplets into the water column. Therefore, the effort presented within this study is to characterize the effects that weathering processes have on the physical properties and chemical composition of an Arabian Crude oil (API 28), and to correlate these time dependent changes to the susceptibility of the oil to vertical turbulent dispersion under simulated surface turbulence. The oil dispersed beneath the slick under fixed turbulent energy inputs was analyzed for total oil and total aromatic hydrocarbon concentration. The toxic effects of these dispersions was then quantified by bacterial bioluminescence assay experiments using a Microtox analyzer.

Research conducted in support of this study was designed to yield important insights for those concerned with fate and effects modeling, because it provides a link between the time when the oil spill occurs and the time when the oil slick encounters sufficient turbulence to induce vertical dispersion (defined herein as the weathering period), to a characterization of the relative magnitude of oil which is vertically dispersed within the water column. The quantification of the relative toxicity of these dispersions is important when assessing their time variant potential to impose adverse environmental impacts.

II. LITERATURE REVIEW

The fate and final disposition of crude oil spilled on the sea is strongly linked to vertical dispersion dynamics acting upon the slick. The magnitude of this weathering mechanism is dependent and assisted by the contributions of a number of interactive and oftentimes competitive physical and chemical processes, which include spreading, drifting with prevailing winds and local current patterns, evaporation of lighter weight hydrocarbon compounds, dissolution of the soluble fractions and the formation of additional highly soluble hydrocarbon intermediates from photo-oxidative degradation, emulsification and formation of tar balls, sinking, sedimentation under the influences of ambient suspended particulate matter, and ingestion of oil by zooplankton with its subsequent incorporation into fecal pellets. To fully understand the vertical turbulent dispersion characteristics of crude oil spilled at sea, each of these weathering processes have been isolated in the literature herein, in order to accurately define the contribution of each process to the overall

disappearance of the surface slick, and the resultant effect of each process on the vertical turbulent dispersion process. The relative magnitude and time span of the weathering processes acting upon oil spilled on the sea are depicted in Figure 1

As an introductory overview, the vertical turbulent dispersion of oil is defined as the incorporation of oil droplets into the water column under the influences of surface turbulence. Once the oil mass is entrained in the water column, it is subsequently exposed to sub-surface advection by prevailing currents, which expands the area effected by the spill. The oil dispersions are also exposed to sedimentation, depending on oil droplet size, due to adsorptive interactions with suspended particulates, which increases the environmental impacts to benthic communities. The formation of these oil droplets initiates with the shearing of an oil mass from the underside of the coherent slick under the influences of a number of forces. The primary causal factor associated with this phenomenon is generally considered to be the large energy dissipation rates associated with breaking wave conditions, but vertical dispersion can also occur in the presence of rain or sufficient upper level water circulations patterns formed in the presence of prevailing winds.

The incorporation of large parcels of oil into the water column under breaking waves results in the formation of numerous discrete oil particles which may range in size from a few microns to a few millimeters (Mackay *et al.*, 1983).

The line length indicates the probable timespan of any process. The line width indicates the relative magnitude of the process through time and in relation to other contemporary processes.

Figure 1
Processes versus Time Elapsed Since The Spill
(Wheeler, 1978)

The particles found at the upper end of this particle size distribution will resurface and recombine with the surface slick at a rate proportional to the second-power of the droplet size and to oil-water density differences according to Stokes Law.

$$W = g d_o^2 (\rho - \rho_w) / (18 \rho_w \nu_w) \quad [1]$$

where:

- W = resurfacing rate (m/sec)
- ρ = density of the oil (kg/m³)
- ρ_w = density of water (kg/m³)
- ν_w = kinematic viscosity of water (cSt)
- d_o = diameter of the oil droplet (m)

Equation [1] says that the smaller droplets have larger residence times under the slick due to negligible buoyant forces. These droplets generally resurface as a sheen of oil trailing behind the main body of the surface slick. If these small droplets are propelled deep enough, they are generally considered permanently incorporated into the water column (Al-Rabeh *et al.*, 1989; and Mackay *et al.*, 1983), and are then subjected to sub-surface advection by deep ocean currents which may transport the oil long distances away from the original spill site and in directions counter to the prevailing direction predicted by traditional surface slick trajectory models.

The rate at which oil is incorporated into the water column is a function of a number of parameters including the prevailing sea state (i.e., wave height, wave period, frequency of breaking wave events within the slick area), and the physical and chemical characteristics of the slick during the period the oil is encountering sufficient turbulence (i.e., viscosity, density, oil-water interfacial tension, and slick thickness) (Al-Rabeh *et al.*, 1989). The point at which oil becomes susceptible to vertical dispersion and the subsequent rate at which oil is incorporated into the water column is an important consideration, for once the oil is lost beneath the surface of the slick, it is virtually impossible to recover by any available counter-measure technology, and therefore, must be quantified to determine environmental impacts of an oil spill on benthic communities.

2.1 Evaporation

The evaporation of lighter weight hydrocarbons, predominantly n-alkanes, is initiated shortly after the release of oil (Figure 1), and is considered to be the most significant factor in the overall disappearance of the slick; dependent on oil type, especially during the first 48 hours (Aravamudan & Marsh, 1981; Payne & McNabb, Jr., 1985; Davis & Gibbs, 1975; Buchanan and Hurford, 1988; and Frankenfeld, 1973). Evaporation rates generally far exceed the rates of all other processes, and may exceed the dissolution rate of aromatic hydrocarbons by a factor of 100 (Payne & McNabb, Jr., 1985); for aliphatic hydrocarbons the rate of evaporation may be 10,000 times greater than the dissolution rate (Harrison *et al.*, 1975; and McAuliffe, 1976a). This factor is crucial from an environmental standpoint because the

more toxic water soluble compounds found in the surface slick, such as benzene and toluene, are quickly removed from the spill when allowed to equilibrate with the air (Frankenfeld, 1981; and Page *et al.*, 1983).

The percentage of the original mass of the slick lost to evaporation, as stated in the literature, can vary significantly, from 20% to 40% (Spaulding, 1988; Lynch, 1987; Raj and Griffiths, 1979; and Venkatesh, 1988), under most situations, to as high as 60% in extreme environmental conditions, of solar intensity and temperature, found in the Arabian Gulf region (Al-Rabeh, 1989). The evaporation rate from a slick is influenced by the chemical characteristics of the original crude, the vapor pressure of the oil as affected by the percent of lighter hydrocarbon fractions lost to the atmosphere (Spaulding, 1988; Mackay *et al.*, 1983; and McAuliffe, 1976a), sea-state, meteorological conditions (i.e., wind speed, air and water temperatures, and local solar radiation levels which are dependent on the percentage of cloud cover and the ozone layer thickness above the slick) (Lee & Downum, 1991), and the relationship that decreasing slick thicknesses are associated with increasing surface areas, which increase the mass transfer rates of the volatile fraction (Spaulding, 1988; Berridge *et al.*, 1968; and Huang, 1983).

The evaporation of lighter hydrocarbons alters the chemical composition and physical characteristics of the oil. The loss of the volatile fraction causes a significant increase in the viscosity of the oil, and increases the relative concentrations of sulfur, metals (i.e., nickel and

vanadium), waxes, and asphaltenes. The effect of these alterations are self-limiting on the rate of evaporation, due primarily to the increase in viscosity and the tendency of the oil towards emulsification which reduces the diffusion of volatile fractions to the air-oil boundary layer (McAuliffe, 1976a).

The effect of evaporation on the vertical turbulent dispersion characteristics of crude oil is to increase the dispersion potential, due to an increase in the density of the oil as the lighter hydrocarbons are preferentially lost. Sivadier & Mikolaj (1981) and Harrison *et al.*, (1975) noted that under sea-state four conditions virtually all of the volatile hydrocarbons were lost in the first two hours, with essentially all the lighter hydrocarbons boiling up to 216 °C (C-12) lost in the first 24 hours. The loss of lighter weight hydrocarbons, combined with the incorporation of water during emulsification, increases the specific gravity of the remaining oil. For example, the residuum contained in the boiling fraction above 1000 °F for a Kuwait crude, which forms 27% of the total mass of the fresh crude, was found to have a specific gravity of 1.023 (Berridge *et al.*, 1968). The specific gravity of seawater is approximately 1.025 which makes this residue highly susceptible to sinking, especially in the presence of suspended particulate matter (SPM). The result of evaporation and the associated effects of increasing densities, makes the oil more susceptible to sinking, and therefore, subject to long range transport by deep ocean currents (Sivadier & Mikolaj, 1981; and Berridge *et al.*, 1968).

2.2 Spreading/Drift

The spreading of crude oil spilled on the sea is a physical process which is controlled by the driving forces of gravity and surface-tension, and retarded by the combined forces of viscosity and inertia. The spreading of crude oil (Figure 1) is the first process contributing to weathering which acts upon the slick; beginning immediately upon the release of oil to the sea surface, and continuing until the slick is reduced to a sub-millimeter thickness, surrounded by sheens considered to be mono-molecular (Mackay *et al.*, 1983). The process of oil spreading increases the surface area to volume ratio of the spill, which enhances the rate of evaporation and dissolution (Payne & McNabb, Jr., 1985), and enlarges the area influenced by photo-oxidative degradation. The results of these weathering mechanisms, combined with the resultant reduction of slick thickness during the spreading process, all put the oil more at risk to water-in-oil emulsification and vertical dispersion mechanisms, which expands the area affected by the related environmental impacts of the spill (Elliott *et al.*, 1986). In addition, the spreading of oil on the sea surface increases the range area of containment and the magnitude of cleanup efforts (Huang, 1983).

The spreading of oil is generally considered to occur in three distinct phases (Al-Rabeh *et al.*, 1989; and Lehr *et al.*, 1984). The first phase is defined as gravity-inertial (i.e., driven by gravity and impeded by the inertia of the coherent oil mass) and dominates only during the first few minutes after a spill, except in extremely large oil discharges. Phase II, defined as gravity-viscous, is the primary mechanism starting approximately 1 hour after the spill and

lasting roughly 7 days. This phase of the slick spreading is considered to be the most useful phase for estimating oil spill sizes in any type of fate modeling. The spreading rate during this phase has been determined to be a function of the initial oil volume lost, gravity effects, elapsed time after the spill, kinematic viscosity and density of the oil, density of water as related to salinity (Lehr *et al.*, 1984), and additionally by the chemical composition of the oil, pour point, and by wind speed and current.

Lehr *et al.* (1984) predicted that the spreading of oil resembles an ellipse, with the major axis aligned with the prevailing wind vector by the following relationships:

$$A = (\pi / 4) Q R \quad [2]$$

$$Q = 1.7 [(\rho_w - \rho_o) / \rho_o]^{1/3} V^{1/3} t^{1/4} \quad [3]$$

$$R = Q + 0.03 W^{4/3} t^{3/4} \quad [4]$$

where:

Q = length of the minor axis

R = length of the major axis

ρ_w = water density

ρ_o = oil density

V = the initial volume of the spill in barrels

W = the wind speed in knots

t = the elapsed time after the spill

Additional concerns during Phase II, are the effects of vertical dispersion on the spreading dynamics of the spill. The forces of surface turbulence will result in a size spectrum of oil particles in the water column. The larger particles being more buoyant will remain closer to the surface with smaller resultant residence times. Therefore these particles will be advected at the speed of the surface drift in the direction of the wind and waves. In contrast, smaller droplets will be less buoyant and will be mixed down by the turbulence to depths of several meters where the advective flow will be weaker. The smaller droplets will have significantly larger residence times in the water column and will trail behind the main body of the slick as submerged particles, eventually resurfacing, forming a tail of oil sheened across the water surface (Elliott *et al.*, 1986).

Phase III, defined as surface tension-viscous, is the sole mechanism acting upon the slick after the first week. The spreading characteristics at this point are driven by the surface active constituents having functional groups containing oxygen, nitrogen, and/or sulfur which act as natural dispersants. The adsorption of these surface active species at the oil-water interface aids in the reduction of the interfacial energy of the boundary, which assist in the emulsification process, and reduces the energy required by wind and waves to further disperse oil into the water column as discrete oil particles (NAS, 1973).

The drifting of oil slicks, influenced primarily by the forcing functions of wind and currents, (Beer *et al.*, 1983), has the adverse effect of bringing oil spilled offshore into coastal areas

where energy dissipation rates are significantly greater, promoting emulsification mechanisms and dispersion of oil droplets into the water column. The energy dissipation rate of the surface layer in the coastal regime is significantly higher due to the larger presence of breaking wave conditions. The vertical turbulent dispersion of oil into the water column has been found to be linearly related to this energy dissipation rate (Delvigne & Sweeney, 1987).

The speed of the drifting oil is generally considered to be approximately 3 percent of the wind velocity (Johansson *et al.*, 1980; Huang, 1983; McAuliffe, 1976a; Payne & McNabb, Jr., 1985; and Spaulding, 1988), superimposed with 100 percent of the current velocity (Lynch, 1987). However, field data collected by Lange & Huhnerfuss, (1978) has shown that 3% drift velocities may be understated; in the presence of deep water gravity waves, the drift velocity may be actually 25-30% higher due to the additional mass transport and increased vorticity exhibited in the presence of larger waves. The drifting of oil at sea, in the absence of interactions with coastal land masses and near-shore currents, has been also found to shift 20-30 degree to the right, in northern latitudes, because of the Coriolis Effect.

2.3 Dissolution

The dissolution of hydrocarbons from under a surface slick is generally not considered to play a significant role in the overall disappearance of crude oil spilled at sea. In terms of defining the resultant environmental impacts to marine ecosystems, understanding the rate of hydrocarbon dissolution and their association with adverse toxicological effects may be

of prime importance (Payne & McNabb, Jr., 1985; Huang, 1983; and Mackay & Shiu, 1976). As shown in Figure 1, the dissolution process is short-lived, acts primarily during the first few hours after a spill, and faces direct competition from the evaporative process. As stated previously, the highly soluble lighter hydrocarbon fraction is also extremely volatile, and will evaporate quickly. The dissolution of these hydrocarbon compounds can be facilitated by the vertical dispersion of oil droplets into the water column; with increased surface areas for mass transfer, larger dissolution rates can be expected.

The dissolution of hydrocarbons process is a relatively minor process compared to the evaporation rate. Experiments conducted to evaluate the relative rate of these competitive processes have allowed pairs of compounds with similar vapor pressures, but drastically different solubilities, to equilibrate with water, i.e., benzene and cyclohexane (McAuliffe, 1976a) or cumene and nonane (Harrison *et al.*, 1975). Concentrations of the two compounds were measured over time in the aqueous phase and for the remaining slick, and no appreciable difference in the aqueous phase concentration was noted. The rate of dissolution estimated to be at roughly 1% of the evaporation rate. The competitive rate dynamics for these low molecular weight hydrocarbons will partially determine if residence times are sufficiently long for these compounds to be transported to adjacent shorelines (McAuliffe, 1976b).

The compounds most susceptible to dissolution (i.e., benzene and toluene) are also rapidly depleted from the slick by evaporation. The peak concentration of dissolved hydrocarbons occurs approximately 8 to 12 hours after the initial release of the oil. The concentration of dissolved hydrocarbons is then observed to exponentially decay because of the turnover of water volume under the slick due to advection, and the evaporative loss of these volatile hydrocarbons when they return to the surface and are exposed to the air-oil mass transfer boundary (Payne & McNabb, Jr., 1985; Harrison *et al.*, 1975; and Payne *et al.*, 1983). The most profound effect of dissolution would occur in quiescent water under the cover of thick oil slicks, where toxic concentrations of aromatic compounds could be realized and maintained for extended periods of time (Owens, 1978). The water soluble aromatic and aliphatic hydrocarbons extend sub-lethal effects to marine organisms at concentrations of 10-100 ppb, lethal toxicity at 0.1-1.0 ppm for most larval stages, and lethal effects at 1-100 ppm for most adult organisms (Harrison *et al.*, 1975). A comprehensive review of the effects of oil on marine mammals can be found in Geraci & St. Aubin (1988).

The concentration of benzene and toluene, which constitute only 2% of the total mass of crude, will make up 50% of the total dissolved hydrocarbons in the water column (McAuliffe, 1973). The more persistent aromatic hydrocarbons in the water column are indanes, naphthalenes, acenaphthenes, acenaphthalenes, flourenes, and phenanthrenes (Frankenfeld, 1973). Additionally, the intermediate products of photo-oxidative reactions during weathering would increase the concentrations of two-ring oxygenated compounds

(i.e., naphthol) (Frankenfeld, 1981). Siron *et al.*, (1993) observed that benzene, naphthalene, and their branched homologs accounted for the largest proportion of the total dissolved oil compounds, and were largely responsible for inhibiting bacterial growth in toxicity evaluations. The concentrations of these compounds, considered to be the most toxic, were observed to increase in the aqueous phase during laboratory experiments conducted by Boylan & Tripp (1971) in the presence of increased surface turbulence. This has important implications from an environmental impact perspective. In the presence of sufficient turbulence at the time the oil is spilled and relatively unweathered, significant quantities of potentially toxic hydrocarbons, including the most lethal low molecular weight hydrocarbons like benzene and toluene could be carried quite deep into the water column precluding the loss of these components to evaporation.

The large quantity of small oil droplets carried deep into the water column by breaking waves and turbulent eddies would significantly increase the boundary layer across which the mass transfer of soluble hydrocarbons could occur. For example Mackay *et al.* (1981) concluded that a 1-mm thick oil slick has an area to volume ratio of $1000 \text{ m}^2/\text{m}^3$, and a 10- μm oil droplet would have a ratio of $3.01 \times 10^5 \text{ m}^2/\text{m}^3$. Drops of such small diameters would reach equilibrium with the surrounding water very rapidly and would lose much of their soluble material.

The dissolution rate of hydrocarbons is related primarily to component solubility and the individual mole fraction of each component in the slick; additional factors include diffusivity coefficients, pH, mass transfer surface area, oil temperature, volume of discharged oil, concentration of other hydrocarbon species in solution, concentration of dissolved organic and colloidal materials, and sea-state conditions at the time of the spill (Huang, 1983).

The solubilization of hydrocarbons in water is directly related to the size of the hydrocarbon molecule, with larger molecules being less soluble. Typical solubility values are generally in the range of 1-10 ppm for aromatics and 0.0001 - 0.01 ppm for n-paraffins. This phenomenon was analyzed by Bohon & Claussen (1951), who proposed that the volume occupied by the hydrocarbon in a water solution is related to the solubility of the molecule. Hermann (1972) stated that a more idealized quantity that is readily computed is the area of the cavity surface which connects the centers of all the water molecules in the first layer around the solute. The area defined in this manner was found to be linearly related to the logarithm of the hydrocarbon solubility. The salinity of the water column is also related to the hydrocarbon solubility. The solubility in seawater being approximately 70-80% of that for distilled water (Delvigne *et al.*, 1986; and Mackay *et al.*, 1983). Higher salinities reduce the solubility of hydrocarbons due to the salting out effect, which could have important implications if pollutants are transported through salinity gradients (Sutton & Calder, 1974). Dissolved salts in water decrease the solution volume, which in turn makes cavity formation energetically unfavorable (Shaw, 1976). Detailed information on solubilities for

hydrocarbons can be found in McAuliffe (1966) and Mackay *et al.* (1980); a comprehensive list of the solubility of hydrocarbons in salt water can be found in Yaws (1992).

Shaw (1976) also determined that a threshold concentration exists for soluble hydrocarbons below which the average spacing of hydrocarbon molecules is sufficiently large that their ordered region exist independently of each other. At higher concentrations there appears to be an interaction between the ordered regions of water molecules surrounding the hydrocarbon molecule, causing one solute to affect the solubility of another. For example, the aqueous solubility of phenanthrene, in the presence of saturation concentrations of biphenyl and naphthalene, was observed to fall from 1.07 ppm to 0.92 ppm.

The concentration of dissolved organic matter in the water column has also been found to effect the solubilization of certain hydrocarbons, which has important implications for dispersion and sedimentation of hydrophobic pollutants in estuarine and coastal areas (Boehm & Quinn, 1973). In natural waters, dissolved organics, generated from sediments and sewage outfalls (Delvigne *et al.*, 1986), may serve as surface active agents to solubilize oil. The reduction of dissolved organic matter in water samples analyzed from Narragansett Bay, while having no effect on aromatic hydrocarbon solubilities, resulted directly in a 50-99% reduction in the amount of n-alkanes and isoprenoid hydrocarbons solubilized (Boehm & Quinn, 1973). This relationship was suggested to be linked to the incorporation of hydrocarbons into micelle formed by surface active humic materials. A reduction in the

concentration of solubilized material in the aqueous phase reduces their potential for bioaccumulation because of their reduced bioavailability (Jaffé, 1991). The n-alkane solubility was also affected by the pH of water solutions in the presence of humic substances, and reached a maximum value with respect to ionic strength at 0.3.

2.4 Photo-Oxidation

Photo-oxidative reactions, initiated by sunlight, alter the original properties of the crude oil, which results in the formation of oxidized compounds containing polar functional groups, such as peroxides, aldehydes, ketones, carbonyl compounds, alcohols, phenols, and fatty acids (Payne & Phillips, 1985b; Hansen, 1975; Berridge *et al.*, 1968, and Larson *et al.*, 1977). These compounds have increased solubilities (Burwood & Speers, 1974; Siron *et al.*, 1993; and Spaulding, 1988), and are generally more toxic than their parent compounds, which is an important aspect in assessing the environmental impacts of oil spilled at sea (Andersson & Bobinger, 1992; Blackman & Law, 1980a; Ehrhardt & Douabul, 1989; Larson *et al.*, 1979; and Gala & Giesy, 1992). For example, the solubility of naphthalene is 35 mg/L, whereas the solubility of its oxygenated counterpart, 2-naphthol, is 1000 mg/L (Larson *et al.*, 1979).

The build up of oxygen containing polar structures leads to a decrease in the oil-water interfacial tension which reduces the energy required to force oil into the water column under the action of surface turbulence which enhances the dispersion of oil droplets (Hansen, 1975). Burns (1993) provided evidence for the importance of including hydrocarbon

oxidation products in environmental assessment studies through the analysis of 10 samples of bivalve tissue collected as part of the impact assessment of the *Exxon Valdez* spill. Results of the analysis by ultraviolet spectroscopy revealed that the ongoing effects of photo-oxidation and biodegradation processes created a complex assemblage of toxic intermediate oxidation products which are bioaccumulated in marine organisms. In another study, the toxicity of a #2 fuel oil was observed to reach a maximum during laboratory experiments in approximately 24 hours, because of the formation of reactive peroxides. The toxicity, turbidity, acidity, or the presence of photo-oxidative by-products was unaltered in control experiments kept in the dark, but a noticeable toxic effect on natural bacteria was observed after a few hours of illumination (Larson *et al.*, 1977; Pengerud *et al.*, 1984).

The effects of photo-oxidation also facilitates the formation of stable water-in-oil emulsions (Thominette & Verdu, 1984), some of which are extremely resistant to dispersion by physical or chemical means. In fact, several oils studied by Payne & McNabb, Jr. (1985) could only form stable water-in-oil emulsions after simulated photochemical or microbial oxidation. The formation of stable water-in-oil emulsions along with the increase in viscosity from photo-oxidation, alters the spreading characteristics of the surface slick for a number of crude oils. Results indicated by Payne & Phillips (1985a) show that viscous oils have different spreading characteristics than non-viscous oils, and may actually display a tendency to contract as opposed to continued spreading in the presence of photo-oxidative mechanisms. Decreases in the floating oil lense diameters of heavy crudes were observed with irradiation

in as little as two hours, and were attributed to the inability of the photo-oxidation products formed at the oil-air interface to diffuse through the viscous oil layer and disperse through the oil-water interface (Payne & Phillips, 1985a; and Klein & Pilpel, 1974)

Several mechanisms have been proposed for the photo-oxidation of petroleum, including: (a) free radical oxidation in the presence of oxygen; (b) singlet oxygen initiation of hydroperoxide formation; and ground state triplet oxygen combining with free radicals to form peroxides (Payne & McNabb, Jr., 1985). Reaction rates are directly affected by natural variations in cloud cover, atmospheric ozone, conditions affecting the transmittance of light in water, and the concentrations of humic substances (Larson et al., 1977; Payne & McNabb, 1985, and Payne & Phillips, 1985a).

The rate of oxidation is also proportional to the chemical nature of the compound, with more highly substituted molecules such as alkyl-substituted naphthenes being oxidized more readily than normal paraffins (Feldman, 1973; Berridge *et al.*, 1968; Payne & Phillips, 1985a, and Thominet & Verdu, 1984). Additionally, the oxidation of aromatic compounds such as phenanthrene or anthracene, which yield quinones that are used as photosensitizers, may actually increase the efficiency of the photo-oxidation process (Andersson and Bobinger, 1992).

Larson *et al.* (1977) determined that a Nigerian crude oil was not significantly affected by exposure to light and the photo-oxidation process was actually inhibited by the presence of a high sulfur content; he stated that these inhibition reactions are significant in the overall environmental photochemistry of some spills. Organosulfur compounds, particularly heterocyclic sulfides common in crude oils, are known to be effective inhibitors of radical reactions, even at low concentrations, and are readily converted to sulfoxides by hydrogen peroxide which effectively terminate the radical chain reaction initiated by photo-oxidation (Thominette & Verdu, 1984; and Berrideg *et al.*, 1968).

Johansson *et al.* (1980) conducted experiments and concluded by exposing oil to different types of light sources, that photo-oxidation of crude oil does not occur to any appreciable amount when exposed to wavelengths above 350 nm; no degradation products are detectable even with exposure periods as long as 6 weeks. In spite of low quantum efficiencies at longer wavelengths, the total rate of decomposition to be expected in natural sunlight may be responsible for the decomposition of a 2.5-um thick oil slick per 100 hours of sunlight (2.5 tons per square kilometer during this exposure period). The decomposition rate stated is for slicks with a thickness greater than 0.1m; thinner slicks are partially transparent to longer wavelengths and therefore have reduced destruction rates.

Petroleum hydrocarbons observed to respond in wavelengths 310 nm or longer include acenaphthene, anthracene, B-methyl anthracene, and naphthalenes, along with nitrogen, oxygen, or sulfur-containing organics (Feldman, 1973). Polymerization and disproportionation can result in the formation of smaller molecules, along with longer chain higher molecular weight compounds, were stated to occur in wavelengths longer than 320 nm; the intermediate steps of these type reactions which initiate from a polycyclic aromatic base can lead to carcinogenic by-products (Feldman, 1973).

2.5 Emulsification

The two weathering processes which determine the ultimate fate of oil spilled on the sea, and the degree of environmental impacts associated from the oil spill, are vertical dispersion into the water column under the forces of wind and wave action, or emulsification (McAuliffe, 1976a). The fate is driven primarily by oil composition, spill location, meteorological conditions, and prevailing ocean conditions (Bobra *et al.*, 1992; Exxon, 1989; and Buchanan & Hurford, 1988). The formation of water-in-oil emulsions significantly reduces the rate of natural dispersion mechanisms and results in the formation of an extremely viscous residual material that persists on the surface of the sea (Lynch, 1987). The incorporation of water into the oil increases the volume of the polluted material and impedes the effective cleanup by mechanical recovery equipment (Bobra *et al.*, 1992). The emulsion formed magnifies the clean-up effort and generally requires a labor intensive effort of removing the emulsion from the coastline by hand.

The fractions of a given oil spill that evaporates, disperses into the water column, is degraded, or is left on the surface as mousse could depend critically on the exact sequence of light and wind/wave energy acting on the spill during the first few days (Thingstad & Pengerud, 1983).

In a complex mixture such as petroleum, all these factors interact in such a way that all components of the mixture remain in the liquid oil phase (i.e., the lighter components of the mixture acting as solvents for the higher molecular weight molecules). As long as this solvency interaction continues and thermodynamic conditions remain unchanged, the oil remains stable. If the equilibrium point is changed, a point will be reached where the solvency strength of the oil is insufficient to maintain the heavy components in solution, and they subsequently precipitate out of solution (Bobra *et al.*, 1992).

Indigenous petroleum emulsifying agents are concentrated in the higher boiling fraction of the crude, specifically in the component boiling above 370 °C and particularly in the residuum. Asphaltenes, resins, and waxes are believed to be the main constituents of the interfacial films that encapsulate the water droplets contained in the mousse (Bobra *et al.*, 1992; Bridie *et al.*, 1980; Berridge *et al.*, 1968; Mackay *et al.*, 1973). There is tremendous mechanical strength associated with these films which act as effective physical barriers, preventing droplet recoalescence. The stabilizing effect of the emulsion is solely dependent

on the strength of these mechanical films and has no relation to any double layer interaction (Mackay *et al.*, 1973).

Oil which reached the shore from the *Amoco Cadiz* spill was observed to be in the form of a water in oil emulsion. The volume and weight of this material which had to be removed from the beaches was substantially greater than the amount of oil alone, as much as five times in the case of "chocolate-mousse" (Huang, 1983; and Berridge *et al.*, 1968), which is a persistent stable emulsion, highly viscous, with water content on the order of 70%. Samples of the emulsion contained between 50-80% water (Wolfe, 1978), and contained varying amounts of clay and sand.

As the water content of the emulsion increases and concurrently degrades along the coastline due to continued weathering processes the physical properties of the oil become increasingly more difficult to handle. The initially inviscous free-flowing oil eventually becomes a relatively stable, heavy, non-pumpable material that must be either removed by hand or special equipment, or simply left on the beach (Wolfe, 1978; and Payne *et al.*, 1983). As an example of the disparate physical properties between a parent oil and the final emulsion, an emulsion formed with 70% synthetic seawater and 30% Kuwait crude (fraction boiling above 200 °C) displayed thixotropic flow behavior, with viscosity measured in the range of 196,000 and 2,200,000 cP depending on the applied shear rate. The viscosity of the 200+ fraction of Kuwait crude at the same temperature was measured to be 490 cP (Bridie *et al.*, 1980). The

initial rate of viscosity increase was shown to be dependent upon the asphaltene content of the oil (Lynch, 1987), and determines the window of opportunity for any counter-measure strategy, before highly viscous fluid properties pose handling difficulties.

Large lumps of emulsified oil eventually form impervious skins which effectively protect the oil from further weathering, and maintain the oil's buoyant condition for a long period of time (Davis & Gibbs, 1975). Even in the presence of suitable populations of microorganisms in the water column, along with adequate amounts of mineral nutrients, oxygen and other components necessary to sustain microbial growth, the formation of stable emulsions precludes biological degradation, due to the sheltering of the bulk of the oil within the emulsions where conditions are unfavorable for microbial attack (Thingstad & Pengerud, 1983; Patton *et al.*, 1981).

The amount of energy required to form water-in-oil emulsions is quite small, and has been observed even in relatively gentle seas; therefore, the energy associated with breaking waves and spray induction must be many times that needed to form stable emulsions (Bridie *et al.*, 1980; and Jeffery, 1981). In tests performed with various combinations of oil, wax content, and asphaltene percentage, it was determined that crude oil that has been de-asphaltenized does not form a stable emulsion; it was observed to shed 93% of its water content after 15 minutes, regardless if the original wax content was retained or concurrently removed (Bridie *et al.*, 1980; and Berridge *et al.*, 1968). The crude oil was only observed to form a stable

emulsion when left in an unaltered configuration, or from an original oil composition with only 1/10 of the original asphaltene content.

Asphaltenes are by definition high molecular weight heterocyclic organic compounds. These asphaltene molecules contain sufficient functional groups to penetrate the water phase boundary; yet the hydrophilic portion of the molecule is so large that it forms a layer on the oil side of the interface (Bobra *et al.*, 1992). Waxes are simply high molecular weight alkanes.

The oil-water interfacial tension is an important parameter for predicting dispersion characteristics of an oil spill; this property is critical in performing an overall final mass balance for the slick. Asphaltenes, waxes, metallo-porphyrins (including vanadium complexes) (Berridge *et al.*, 1968), and possibly the products of photochemical and microbial degradation, all are important in the stabilization of water in oil droplets by lowering the oil-water interfacial tension. Nitrogen, sulfur and organic compounds in the oil can act as natural surfactants, reducing the oil-water interfacial tension similar to chemical dispersants (Exxon, 1989). These materials act as surfactants which effectively prevent the separation of the oil water phase due to water-water micelle droplet coalescence in the continuous oil phase; under these conditions stable emulsions can be formed (Payne *et al.*, 1983). The oxidative polymerization of aromatics and/or oxygenated aromatics during weathering might also

result in the production of additional asphaltenic materials (Frankenfeld, 1973; and Thingstad & Pengerud, 1983).

Betancourt & McLean (1973) observed that asphaltene content was increasing faster than could be explained by losses of volatile, non-asphaltenic materials, and therefore some asphaltenes must have been produced; they suggested that the increase in asphaltenes is due in part to atmospheric oxidation, drawing parallels to the commercial production process of asphalt.

Bobra *et al.* (1992) noted that the stability of the emulsion formed was related to the alkane/aromatic ratio of the parent oil. For example, precipitation of the asphaltenes did not occur in an oil composed of 100% alkane, and the asphaltenes maintained their original size of approximately 1 micron, which is too small to effectively stabilize water droplets. There was a strong correlation for oils tested with a 50-95% alkane percentage for the formation of stable emulsions.

The effects of emulsification are to form rigid mats of oil material which are highly resistant to break up by surface turbulence. On the other hand, if emulsion flakes break off, vertical dispersion characteristics of the oil are enhanced because of the elevated densities of the emulsion which promote sinking. The oil density increases both because of evaporation of low boiling point constituents and the incorporation of water during emulsification. Few

crude oils will weather sufficiently to sink alone; however, the density of many water-in-oil emulsions approaches that of seawater, and therefore, it requires very little uptake of particulate matter to sink it.

Temperature may also cause the floating oil to sink and resurface later (Buchanan & Hurford, 1988). The final density of the emulsion depends to a great extent on the salinity of the water in which it was formed; therefore, mousse formed in high salinity waters would be expected to sink when drifting into less saline waters (Thingstad & Pengerud, 1983).

2.6 Sinking/Sedimentation

Combined with the effects of vertical turbulent dispersion and depending on regional conditions, sedimentation of petroleum can be a significant factor which determines the ultimate fate of crude oil (Feldman, 1973). This factor can be of major importance when assessing the environmental impact of the oil spill on benthic communities. Most crude oils do not undergo weathering to the point where densities exceed that of seawater, but the sedimentation or sinking of oil can result from the increased density of water-in-oil emulsions generated as weathering proceeds; additional pathways include the incorporation into fecal pellets via zooplankton ingestion, adhesion to or flocculation of the oil with suspended particulate matter (SPM), incorporation of detrital material or sand during deposition on shore, or because of attached pelagic organisms (i.e., barnacles) (Payne & McNabb, Jr., 1985; and Huang, 1983). According to Spaulding (1988), the sinking of oil

through weathering alone is generally not encountered in colder northern waters: it has been observed however in Gulf of Mexico and Persian Gulf blowouts, depending on the bulk oil characteristics and the percentage of clay within the SPM population. The presence of microbes may also augment the tendency of the oil to sink, by increasing the density of the slick through the selective removal of lighter paraffins, or through the formation of agglomerates (possibly clathrates) with certain polynuclear aromatics. The biomass formed as organisms proliferate, provides a surface on which additional particulate matter collects, increasing the tendency of the mass to become negatively buoyant (Frankenfeld, 1973).

Oil spills in near shore waters with high suspended particulate loads experience rapid dispersal and removal of the oil due to sorption onto SPM along frontal zones (Payne & McNabb, Jr., 1985). Experiments conducted by Payne & McNabb, Jr., (1985), with simulated spills in outdoor wave tanks, revealed that at SPM concentrations from 1-10 mg/L, no appreciable transport of particle-associated oil to the sea-bed occurs. At SPM loads from 10-100 mg/L, considerable oil/SPM interactions with subsequent transport and deposition is possible in the presence of sufficient turbulent mixing, and at concentrations in excess of 100 mg/L massive oil transport may occur with the potential for significant adverse impacts to benthic communities. These results are consistent with typical SPM concentrations found in open ocean environments and estuarine areas, which generally fall within the range of 0.01 to 1.0 mg/L, and 10 to 100 mg/L, respectively (Delvigne *et al.*, 1986).

With higher energy dissipation rates found in coastal areas, it is evident that turbulence is important for oil-SPM interactions. The turbulence regime facilitates the formation of oil droplets from the coherent slick and the subsequent splitting of the oil droplets to suitable size ranges, and is the causal factor in coastal erosion and resuspension of bottom sediment. These two factors acting simultaneously in the same area increase the probability of particle-oil droplet collisions. Oil droplet dispersion and sedimentation by oil-SPM interactions are more apt to occur before any appreciable weathering can alter the viscosity of the oil, because higher viscosities result in the generation of larger droplet sizes from the coherent slick which are less prone to sedimentation by SPM interactions. Additionally, once a stable water-in-oil emulsion has formed, further input of hydrocarbons to the water column and subsequent SPM adsorption is greatly reduced (Payne & McNabb, Jr. 1985).

A comprehensive study of oil-SPM interactions is given by Payne & McNabb, Jr. (1985). The interaction between dispersed oil and suspended particulates occurs either through the molecular sorption of the dissolved fraction or from the actual physical collision between oil droplets and suspended particulate materials. The collision of two particles in solution could result in particle destabilization and an overall reduction in the electric potential between the particles, due to compression of the electric double layer, decrease in surface charge, or particle bridging by substances in solution between the particles (Payne & McNabb, Jr., 1985). It is also noteworthy to mention at this point that most suspended particles in solution, including the dispersed oil droplets carry a negative surface charge due to the

dissociation of components into solution or from the selective adsorption of ions. The molecular adsorption of dissolved hydrocarbons to SPM is strongly correlated to the saltwater solubility of the individual species. Results of Gas Chromatographic studies performed by Payne & McNabb, Jr. (1985) indicate that lower molecular weight aromatics and volatile aliphatic compounds will preferentially partition into the water column while the intermediate and higher weight aromatic and aliphatic hydrocarbons remained with the suspended particular material.

Zurcher & Thuer (1978) pointed out that the identification of the dissolved, adsorbed, and colloidally dispersed oil fractions are significant in terms of assessing ecological impacts. The water soluble fraction has been identified as the one primarily responsible for acute toxicity, while the interruption of biological communication (i.e., chemotaxis) could possibly be linked to fractions adsorbed on particulates and accumulated in sediments. Herein lies the important relationship between the extent of crude oil weathering, the magnitude of vertical turbulent dispersion and the associated sedimentation of dispersed oil. Mayo *et al.* (1978) determined that the distribution of hydrocarbons in marine sediments subsequent to a major spill is strongly dependent on the extent of physical weathering encountered by the oil during the surface transport from the spill site to the area where final sedimentation occurs. This is important because once the oil penetrates into bottom sediments, further weathering is extremely limited, especially in cold anoxic sediments.

The contribution of zooplankton to the overall sedimentation rate of crude oil was evaluated by (Freegarde *et al.*, 1971). Research conducted using the zooplankton species *Calanus finmarchicus* estimates that the maximum rate of oil consumption by this species could be about 0.3 g per m³ of seawater per day. In the presence of an oil concentration on the order of 1.5 ppm, which is typical in choppy ocean conditions, an immobilization rate of 3 tons per day was estimated. This rate is contingent on a population of 2,000 individuals per cubic meter.

2.7 Vertical Turbulent Dispersion

The weathering process which contributes the most to the overall disappearance of crude oil slicks spilled on the sea is the incorporation of discrete oil droplets into the water column under the driving forces of surface turbulence (Lynch, 1987). Vertical dispersion is defined as an entrainment process in which oil droplets are sheared from the coherent surface slick and subsequently entrained in the water column by such forcing mechanisms as breaking waves, downwelling surface currents generated by prevailing winds, or rain. Once dispersed in the water column, the final fate of the oil contained within these droplets depend on a number of processes, including: (1) potential interactions with suspended particulate materials which could transport oil to bottom sediments, imposing detrimental effects on benthic communities; (2) rapid dissolution of soluble hydrocarbons from the oil droplet due to an extremely large surface area to volume ratio associated with the droplets, which allows for toxic lower weight aromatic hydrocarbons, such as benzene and toluene, which are

normally lost to evaporation, to enter the water column; (3) ingestion of dispersed oil by marine organisms which is ultimately deposited to bottom sediments sequestered within fecal pellets; and (4) long range transport by deep ocean currents which expands the area impacted by the spill.

The susceptibility of a surface slick to vertical dispersion, and the rate at which this process occurs, is a function of oil slick thickness which is dependent on: the degree of spreading; oil water interfacial tension; the characteristics of the oil, including density, viscosity, and the degree to which the oil is effected by weathering (Exxon, 1989); sea-state conditions, such as wave height, wave period, fraction of the sea surface encountering breaking waves (Huang, 1983; and Leech & Walker, 1992); and meteorological conditions, such as wind, temperature and solar intensity.

The study of vertical dispersion mechanisms is important in assessing the potential environmental impacts to benthic communities, especially where high concentrations of suspended particulates are present, which increases the sedimentation of oil to the bottom. The quantification of vertical dispersion in the overall disappearance of the surface slick is important in assessing potential environmental impacts, especially in coastal areas rich in biodiversity, where toxic compounds can gain entry in food chains. The effects of vertical dispersion on the enhancing the spreading of oil was determined by Forrester (1971). He studied the distribution of submerged oil particles in way of the tanker *Arrow* grounding by

utilizing a modified plankton sampling gear towed through the water column. It was determined that oil concentrations relative to oil droplet sizes with effective lengths (i.e., cube root of volume) in the range of 0.1 to 1.0 mm decreases with increasing depths. This is because of particle resurfacing forces which gain an edge on downwelling forces at deeper depths, resulting in droplet size distributions progressively shifting to smaller sizes with depth; oil consuming bacteria can also exert outside influence on the distribution of oil within the water column by preferentially degrading smaller droplets; concurrent chemical alterations also occur through preferential degradation (Atlas *et al.*, 1981). With oil droplets less than 0.1 mm effective length, the total volume of oil did not show any decrease with depth. These oil droplets with negligible resurfacing forces become permanently incorporated into the water column. As an indication of the extent to which vertical dispersion affects the spreading of oil, positive traces of oil were detected at depths as large as 80 meters, which coincided with the deepest sampling undertaken.

As a general rule, droplets with diameters greater than 0.1 mm will return to the sea surface once the turbulence or surface agitation abates, while droplets with diameters below this critical diameter are considered to remain permanently incorporated in the water column (Payne & McNabb, Jr., 1985; and Huang, 1983). The physical process of oil droplet formation results in the generation of sizes believed to fall within the range of 20 to 500 μm in diameter (Leech & Walker, 1992). Studies carried out by Shaw (1976) determined the size distributions of particles and subparticles formed by hydrocarbons mixed with seawater

under controlled laboratory conditions. As determined by a Coulter counter, the greatest number of oil particles was in the size 1 - 30 μm . Field data on droplet size distributions of dispersed oil is limited and encompasses a wide range of sizes. Berridge *et al.* (1968) recorded oil droplet sizes in the range of 20 - 40 μm in the presence of vigorous wave and current action; and Forrester (1971) measured oil droplets in the surf zone adjacent to the grounded tanker *Arrow* in the range of 5 - 1000 μm . Experiments found in Delvigne *et al.* (1986) determined that mean droplet sizes were on the order of 100 μm across a wide range of breaking wave conditions in simulation conducted in a laboratory flume. These droplets are not stable and will usually recoagulate unless diffused very quickly (Berridge *et al.*, 1968). Conversely, these dispersions can be stabilized by surface active agents which can coat the oil-water interface, effectively preventing the oil from coagulating (Delvigne *et al.*, 1986).

The factors which determine droplet size distribution are oil characteristics, turbulence intensity imparted to the surface slick, and turbulence duration. Experiments by Milgram *et al.* (1978) indicated oil thickness and oil viscosity have considerable effects on the fraction of dispersed oil, and that the penetration of oil droplets (including oil coated water droplets) into the water column is significant in the wake of a breaking wave. The breaking of a wave within the surface slick results in the injection of oil particles with a wide range of droplet sizes. Raj & Griffiths (1979) studied the survival of oil slicks on the ocean as a function of sea state, to better understand the interaction between spilled oil and sea state, and to predict

the dispersion and ultimate physical fate of oil spilled on rough water. His results indicate that a sea with a significant wave height of at least 3 meters is required before any globular vertical dispersion of oil is observed. He also determined that deep ocean non-breaking swells do not usually fracture a coherent oil slick, even though the energy associated with these type waves is more than sufficient to disperse oil droplets vertically into the water column. In the event of large scale oil spills, vertical dispersion is initially restricted by the large thickness of the slick, because of the effective dampening out of ocean waves passing through it, which results in the slick riding intact atop the large swells. Breaking of waves, except the very large ones are inhibited within the slick. Eventually, the slick becomes sufficiently thin from the effects of surface spreading, and becomes vulnerable to the effects of waves and upper ocean turbulence. A point is reached where the coherent slick is fractured by surface waves resulting in a shower of oil droplets being thrown down into the water column. The size distribution of these oil droplets depends largely on the properties of the crude oil, the thickness of the slick, and the energy dissipation rate of the ocean surface. Raj & Griffiths (1979) defined the thickness where vertical dispersion of oil droplets becomes significant as being on the order of 5 mm.

Lynch (1987) conducted laboratory tests with tanks and large free floating rings at sea. The mechanism by which oil is dispersed naturally is considered to be as follows: the oil spreads out to a thin enough layer (estimated to 1 mm or less). Once thin enough the oil layer will disperse, however the initial dispersion rate is highly dependent on the rate at which the

viscosity of the oil increases as weathering proceeds, which is directly proportional to the asphaltene content carried by the parent oil. The dispersion rate is inhibited by an increase in viscosity, and will continue, albeit at a reduced rate until an emulsion is fully formed, whereby further dispersion is contingent on emulsion stability. It was also recorded from field data that total concentration of dispersed hydrocarbons was approximately ten times greater than the truly dissolved lower aromatic hydrocarbons.

In addition to the energy imparted to the slick by the bore of the breaking wave, there exists a turbulence wake that trails behind the wave that induces droplet splitting and vertical advection. As a criterion of whether the oil droplet will continue to split under the forces which are exerted upon it, Delvigne *et al.* (1986) lists the Weber Number as a means of evaluating this phenomenon. The oil droplets dispersed into the water column will continue to break up into smaller droplets until the dominant splitting forces, which are associated with the turbulent fluctuations in the water found in the wake of a passing wave, are again smaller than the dominant internal resisting force of surface tension (i.e., Weber Number >1). The tendency for droplet splitting is determined by the value of the Weber Number, and provides an indication of the minimum size of oil droplets to expect for a given set of input energy conditions and oil properties.

$$W_e = T d / (\rho_w v_d^2 d^2) = \text{surface tension} / \text{inertia force} \quad [5]$$

where:

- W_e = Weber Number (dimensionless)
 T = oil-water interfacial surface tension
 d = droplet diameter
 ρ_w = density of water
 v_d = rms velocity over distance d .

In order to accurately quantify the extent of vertical dispersion and the effects of this process may have on other weathering processes (i.e., sedimentation or dissolution), and in a effort to predict environmental fate of oil spilled at sea, a means must be available for predicting oil droplet sizes and the depths to which these droplets are forced into the water column. Raj & Griffiths (1979) predicts that the minimum diameter of submerged oil droplets, as a function of the surface turbulence in the presence of breaking waves, follows a relationship similar to:

$$d \text{ (min)} \approx 0.12 [T^{3/5} \omega^{2/5}] / [\rho_w^{3/5} g^{4/5}] \quad [6]$$

where:

- $d \text{ (min)}$ = minimum diameter of submerged oil droplets
 ω = modal wave frequency of the ocean spectrum
 (value of 2 rad/sec assumed for laboratory wave experiments)
 T = oil surface tension
 ρ_w = density of water

If the thickness of the slick is less than $d \text{ (min)}$ as calculated above, then smaller droplets can be formed and are predicted to follow the relationship:

$$d(\text{thin}) \sim 0.3 T^{2/5} \omega^{4/15} h^{1/3} / [\rho^{2/5} g^{8/15}] \quad [7]$$

where:

h = thickness of the film

A number of mathematical models were formulated by Aravamudan & Marsh (1981), utilizing previously published data from other studies, which can predict droplet formation by braking waves with special attention given to determining minimum and maximum droplet sizes expected under different conditions; along with the vertical transport (i.e., penetration depth) of the oil droplets. A relationship was presented which depicts the maximum oil droplet size as being a function of the properties of the oil itself, and not in terms of ocean conditions. The theoretical maximum droplet size is given by the following equation:

$$d_{\text{MAX}} = [(12 \sigma_i) / g (\rho_w - \rho)]^{1/2} \quad [8]$$

where:

σ_i = oil-water interfacial tension

ρ_w = water density

ρ = oil density

The factors which determine whether these oil droplets return to the surface and recombine with the coherent surface slick are primarily droplet size distributions and the density

differential between the oil droplet and the bulk solution. For constant oil density, the smaller the buoyant resurfacing forces associated with the particle, the deeper the intrusion depth of the droplet for a given turbulence energy.

The depth to which dispersed oil droplets penetrate the water column was determined in Delvigne et al. (1986) to be in the vicinity of twice the breaking wave height, with oil concentrations displaying a linear decrease with increasing depth immediately after the passage of the wave. From measurements made during small-scale and large-scale outdoor wave tanks an estimate of the intrusion depth was shown to follow the relationship:

$$z_i \text{ (m)} = [1.50 \pm 0.35] H_b \quad [9]$$

where:

H_b = height of breaking wave (m)

Modelling efforts conducted by Raj & Griffiths (1979) to predict the intrusion depth indicates a penetration depth in the region of a fraction of a meter, with depth strongly linked to oil-water density differential and oil droplet size. These calculations underestimated the depth of intrusion due to the assumption that the entire quantity of energy contained within the wave was released as a quick pulse of energy in the bore of the breaking wave. Experiments conducted by other researchers, as reported in Raj & Griffiths (1979), indicated that the maximum depth of intrusion was achieved long after the breaking wave event, and

the driving forces responsible for this dispersion was the turbulent eddy currents located in the wake of the breaker. A relationship was provided which estimates the maximum depth of intrusion for oil droplets due to the forces of breaking waves.

$$(Z)_{MAX} = 0.32 M / [\rho_w c u_t] \quad [10]$$

where:

- (Z)_{max} = maximum depth of intrusion
- M = the rate of loss of wave momentum per unit crest length
approximated by $(10^{-2.3}) \rho_w [g^3 / \omega^4]$
- c = wave phase speed
- u_t = the terminal velocity of the drop which penetrates to depth (Z)_{MAX}.

The formula implies that for a given wave energy, the depth of intrusion is greater for smaller oil droplets. The depth of intrusion was estimated to be 100 meters for a 50 μ m oil droplet formed by the passage of a 15-m long wave with a height of 2 m.

As reported in Raj & Griffiths (1979), the terminal velocity of these size oil droplets is roughly 0.15 mm/s, which requires a time of 8 days to reach the maximum depth. A residence time of this magnitude is significant from the standpoint of long-range transport of dispersed hydrocarbons and the expansion of the area impacted by the spill. The presence of significant turbulence in the wake of passing waves was also supported by laboratory flume tank experiments conducted by Milgram *et al.* (1978). With breaking waves stated to

to be essential for the formation of discrete oil droplets, another relationship was provided for estimating the intrusion depth of oil droplets:

$$\text{maximum depth of intrusion : } z_{\max} = 0.06 H^2 \omega / W \quad [11]$$

$$\text{which is attained at time } t_d = z_{\max} / W \quad [12]$$

where:

W = terminal velocity of the oil droplet

H = wave height, related to wind speed by $H=0.283(U_w)^2 / g$

ω = wave frequency, related to wind speed by $\omega= 0.13 g / U_w$

In the absence of large scale circulations, all oil droplets with a residual positive buoyancy will eventually return to the surface and recombine to form a film of oil. The duration time for recombination to occur was estimated to be on the order of twice the resurfacing time in the absence of turbulence (Delvigne *et al.*, 1986). This is purely an idealistic case, for the ocean is rarely without turbulence and sub-surface advective currents. Large Langmuir circulation patterns in the water column set up by surface wind forces will generate large downwelling currents to carry oil droplets down to significant depths. Estimates of this downwelling velocity in the Langmuir circulation pattern has been reported to be approximately 0.8 percent of the wind speed (Delvigne *et al.*, 1986).

One of the most comprehensive undertakings to examine the process of vertical dispersion of oil particles in the presence of breaking waves is presented in Minerals Management

Service, OCS Study MMS 87-111 (1987). Experiments were conducted both on a small scale utilizing a vertical grid column to simulate submerged oil and suspended particulate interactions, and in large outdoor wave tanks simulating near-full-scale wave heights. The most significant results of these experiments yielded an empirical relation for the droplet size distribution and entrainment rate (dispersed oil mass per unit time), as a function of the oil type, oil layer thickness, breaking wave energy, and temperature. An additional relationship was also developed for the intrusion depth of oil droplets as related to the wave height. A wide range of energy dissipation rates were required to properly satisfy scaling laws in order to ensure that turbulent eddy structures in the models truly simulated field conditions. Adequate scaling of large turbulent eddy structures is required for the study of the diffusion process, while small turbulent eddy structures are necessary for analyzing particle interactions.

These processes require widely different energy dissipation rates (ϵ), and therefore preclude any attempts at modelling these processes at the same time (Delvigne *et al.*, 1986). Typical values of energy dissipation rates (ϵ) in field conditions are:

deep ocean	$= 10^{-4} \text{ to } 10^{-2} \text{ J/ m}^3 \text{ sec}$
estuary	$= 10^{-1} \text{ to } 1 \text{ J/ m}^3 \text{ sec}$
surface layer	$= 1 \text{ to } 10 \text{ J/ m}^3 \text{ sec}$
breaking waves	$= 10^3 \text{ to } 10^4 \text{ J/ m}^3 \text{ sec}$

Results from the dispersion experiments for defining expected oil droplet sizes, found in the water column as a function of viscosity and various energy dissipation rates (ϵ), are summarized as follows:

$$d_{50}, d_{\max} \sim v_o^{0.34 (\pm 0.05)} \quad [13]$$

d_{50} (mean droplet size, μm) and $d_{\max}$ (μm) were dependent on the oil type, weathering state and temperature only as far as these parameters influence oil viscosity (v_o , cSt). This relationship is supported by experiments which were conducted for viscosities in the range of 8 - 220 cSt, but may be extrapolated into higher viscosities as long as the oil displays Newtonian behavior.

$$d_{50}, d_{\max} \sim \epsilon^{-0.50 (\pm 0.1)} \quad [14]$$

This relation is stated to be valid in the high turbulence regime with energy dissipation rates in excess of $100 \text{ J/m}^3\text{-sec}$, where the additional break up of oil droplets due to vertical shear on the rising buoyant droplets is negligible. Additionally, the oil droplet size distribution was found to be independent of salinity, but dependent on the duration of the turbulence. Measurements from small-scale experiments with turbulent durations from 5 to 600 seconds indicated that steady-state values of $d_{\max}$ in high turbulent conditions were obtained for times greater than 5 minutes. From large-scale wave outdoor wave tank experiments that the maximum droplet size $d_{\max}$ in the water mass was actually independent of the break up process due to turbulence, but rather dependent on resurfacing parameters like intrusion

depth z_1 , rise velocity of the oil droplets $W(d_o)$ (as per Stokes Law), and the vertical turbulent diffusion coefficient ϵ_z .

The size distribution of oil droplets in the water column was also found to be independent of the oil layer thickness over the applied range of 0.2 to 1.2 mm. As stated previously, it was determined by Raj & Griffiths (1979), that the minimum oil layer thickness for initiating globular dispersion was 5 mm, so it may be that droplet size distributions are independent of thickness below this critical value.

As for the entrainment rate of oil into the water column (Q) with the passage of breaking waves, it was determined that the following proportionality existed;

$$Q \sim D_{ba}^{0.57 (\pm 0.06)} \quad [15]$$

where:

$$D_{ba} = \text{energy dissipation per unit surface area (J/m}^2 \text{)}$$

Dissipated energy values ranged from 1 to 9 J/m², in small scale experiments, to a value of 200 to 900 J/m² for large wave flumes. The entrainment rate was determined to be independent of the surface oil layer thickness, and also independent of water salinity. The break up of the oil slick into discrete droplets in the water column was also found to be dependent on the oil-water density differential, oil-surface tension, and oil-water interfacial tension. Modeling conducted by Huang (1983) on the break up of oil slicks in way of

breaking waves, assumed that the volume of the entrained oil increases linearly with sea state and oil to water density ratio, and will decrease linearly with increasing oil-to-water interfacial tension.

Finally, dispersion of oil droplets can occur spontaneously through the formation of micelles by physical/chemical processes. As defined in Delvigne et al. (1986), a micelle is an agglomeration of surface active compounds comprised of long chain hydrocarbons molecules with polar functional groups at one end. The hydrocarbon part of the molecule will assemble in the center of the molecule, while the hydrophilic polar groups remain on the periphery of the cluster in contact with the bulk water phase. In this configuration, normally insoluble hydrophobic hydrocarbons are solubilized. The stability of the micelle in suspension is maintained by a net surface charge leading to repulsive forces. In the presence of electrolytes (i.e., salts contained within seawater), destabilization takes place resulting in coagulation. The coagulation could take place by collisions between particles due to different rising velocities across the particle size spectrum, velocity gradients in the water phase, or Brownian motion. This coagulation of particles has been found to influence particle size distributions.

III. EXPERIMENTAL OUTLINE

Three grades of crude oils were provided directly by MOBIL Oil Corporation for analysis which encompassed a wide range of API specific gravities that can be expected in worldwide trade. The oils available for analysis were the Statfjord Crude (Norway), Arabian Heavy Crude (Saudi Arabia), and the BCF-17 Crude (Venezuela). The API gravities of these crude oils are nominally 38, 28, and 17, respectively; they are listed in order of ascending oil viscosity. The Arabian Crude oil was selected for analysis, because it maintains a middle ground ranking in terms of physical and chemical properties, i.e., oil viscosity, percent aromatics, and sulfur content. A comparison of the three crude oils, along with distillation data for the Arabian Crude, can be found in Appendix A. These properties are directly linked to the vertical turbulent dispersion properties of the oil, the dissolution potential, the subsequent toxicity potential of the oil to the marine environment, and the propensity of the oil to undergo photo-oxidative alterations. The main focus of this research is first to enhance the data compiled to date, by reproducing the time variant alterations in the physical properties of the oil as a function of the weathering period (i.e., oil viscosity, oil-water interfacial tension, and oil density); and second, to relate these properties to the associated vertical dispersion characteristics of the oil, as a function of the physical properties that exist at the end of the weathering period.

The weathering of crude oil is the result of a series of a complex, interactive, and oftentimes competitive physical, chemical, and biological processes. These major weathering processes, previously identified, can be further classified into two major groups: those that alter the geometric configuration and geographic location of the slick, and those which reduce the mass of the slick and alter the chemical configuration of the oil.

The weathering of crude oil results in series of changes to the original physical properties of the oil. The oil will experience an increase in viscosity, largely dependent on the composition of the oil, because of the evaporative loss of lighter weight hydrocarbon compounds. A reduction in the oil-water interfacial surface tension will occur due to the increase in concentrations of natural surface active materials within the oil as the lighter hydrocarbons are lost, in conjunction with the formation of additional surface active materials from photo-oxidative processes, and the entrainment of water. Finally, an increase in the density of the oil will be observed, because of evaporative losses and the entrainment of water associated with emulsification. These physical characteristics have a significant effect on the vertical dispersion characteristics of crude oil, including: formation and size of oil droplets, resurfacing velocities of entrained oil droplets in the water column, subsequent recoalescence rate of the oil droplet upon returning to the surface, and the propensity of the entrained oil droplets to sink. In addition, oxidative processes, initiated by sunlight, have been linked to chemical alterations in the parent oil, which result in an increase in the toxicity of the oil due to the formation of more soluble intermediate products, which may increase

the environmental impacts in sensitive areas, especially in tropical and sub-tropical regions similar to south Florida. Therefore, the experiments conducted in conjunction with this research effort have been designed in such a way as to include the monitoring of the physical properties of the oil (i.e., viscosity, density, oil-water interfacial surface tension), as a function of the weathering period; to compare the collected data with previously published information, and to relate the resultant changes in these properties, due to weathering, to the vertical dispersion characteristics of the oil in a laboratory scale turbulence simulator.

The variation in the physical properties of the oil as a function of the weathering period were tracked by utilizing a Brookfield Digital Cone Plate Viscometer (Model LVDV-II++) equipped with a CP-40 spindle and a jacket water cooled sample cup, designed for measuring oil viscosities in the range of 0.3 through 1028 cP. A Fisher Scientific du Nouy Ring apparatus (Surface Tensiomat Model 21) was used for oil-water interfacial surface tension measurements, and a calibrated 10-mL pycnometer and analytical balance for recording density variations. The characterization of the dispersed oil samples extracted from the simulator was performed utilizing a Mettler AE 240 analytical balance for quantification of total oil concentration; a Gilford Fluoro IV Spectrofluorometer for quantification of total aromatic hydrocarbons, including compounds identified as having known toxic effects on marine organisms; and a Hewlett Packard Model 5890 Gas Chromatograph/Mass Spectrometer (GC/MS) for identifying chemical compounds and tracking chemical alterations due to weathering processes.

Associated average colloidal particle size and particle charge distributions within the water column were performed by a Coulter Doppler Electrophoretic Light Scattering Analyzer (DELSA 440). This device utilizes electrophoresis techniques and has the ability to scan for particles in the sub-micron range (0.02-30 μ m). Oil droplets in the colloidal fraction range may have important relationships to the overall toxicity of oil spill dispersion, the persistence of the oil suspensions in the water column, and are also identified as the size range most susceptible to long-range dispersion by sub-surface currents. The relative toxicity of the weathered oil samples was therefore characterized by a Microtox 500 Analyzer, in an effort to ascertain the time dependent relationship between the total aromatics present in the aqueous phase, a function of the weathering period, and the relative toxicity of the spill.

It is noteworthy to mention that the Arabian Crude oil was delivered directly from the MOBIL refinery to the Environmental Laboratory of Florida International University in a sealed 1 gallon can. The oil required for this analysis was subsequently transferred from the gallon can to ten (10) 300-mL amber glass bottles, and tightly sealed with no headspace prior to conducting experiments. The ten glass bottles were suitably stored in a cool dark place until needed. This procedure was deemed necessary in order to limit the variance in the initial conditions of the oil between experimental trials.

IV. EXPERIMENTAL PROCEDURES

4.1 Weathering Characteristics

This section was designed to track the change in the physical properties of the surface slick shown to have a strong correlation to the vertical turbulent dispersion characteristics of the oil, including evaporative loss, viscosity, oil-water interfacial surface tension, and density. Data was acquired as a function of the weathering period, which was recorded as the exposure time to weathering action, and in terms of the total solar irradiance recorded during the respective exposure period. Total solar irradiance across the spectrum range of 380-1100 nm was recorded by a LI-COR Pyranometer Sensor (LI-200SA), which was linked to a data logger, to provide an indication of the relative magnitude of solar intensity during the exposure period. The data logger was programmed to record solar intensity at 5 second intervals and to compute an hourly average intensity, which was then recorded in permanent memory for later retrieval at the end of the weathering period. The LI-200SA is a fully cosine-corrected sensor, with a typical cosine error of less than 5% up to an 80° angle of incidence. The silicon photodiode was calibrated, by the manufacturer, against a working quartz halogen lamp acceptable to the National Bureau of Standards (NBS). The selected duration of the weathering exposure for the oil samples was, 4, 8, and 24 hours; plus 4 and 7 days. Additionally, the initial physical properties and dispersion characteristics of the oil were determined from an unweathered oil sample.

Data was also acquired during this phase to quantify the concentrations of "soluble" hydrocarbons beneath the surface slick as a function of the exposure period. In addition, changes in the chemical composition of the weathered oil were identified by comparing the GCMS spectral data of weathered and unweathered oil samples.

A crude oil weathering station was constructed as shown in Figure 2 to support the weathering flask, and to house a magnetic stirring plate and electric Whisper 200 aquarium type air pump. The air pump provided sufficient air supply to allow for an unrestricted evaporation rate during the weathering period. The weathering flask consisted of a 2000-mL Pyrex® Erlenmeyer flask with a specially constructed rubber stopper configured to accept a 10-mL burette tower along with an air supply inlet and exhaust fitting. The weathering flask was filled with artificially prepared seawater to the 1200-mL marking. The seawater was prepared using Tropic Marin® Sea Salt to a specific gravity of 1.022 using regular tap water.

Prior to admitting the crude oil from one of the 300-mL amber glass sample bottles, the entire weathering flask assembly, which included the 1200-mL of seawater, a 1-1/4" magnetic stirring bar, the rubber stopper; and the 10-mL burette tower, was suitably preweighed using an analytical balance. After recording the initial weight, the entire contents of the 300-mL glass bottle was transferred to the weathering flask using a long neck plastic funnel.

Figure 2
Crude Oil Weathering Station

The rubber stopper was lifted slightly and the burette tower shifted to one side of the flask mouth to permit insertion of the funnel. Extreme caution was exercised at this point to ensure that the end of the burette remained well below the water surface, and that the oil was added slowly enough so that oil droplet formation in the water phase was minimized. Once the oil formed a coherent slick, the burette tower was back purged by placing the air supply line over the vent hole atop the burette, until one bubble had passed, to ensure no fine dispersions of oil had found entry into the bottom of the burette. At this point the entire weathering flask was reweighed to determine the initial weight of the oil added at the start of the weathering period, and the LI-COR data logger was initialized and activated.

The weathering flask was then placed atop the magnetic stirring plate and set at a very low mixing level to ensure that no oil droplets were sheared from the underside of the slick during the weathering period. The air supply line was then suitably connected atop the weathering flask and proper flow checked. A check of the system was made twice daily during extended weathering periods to ensure proper operation.

Upon completion of the weathering period, the air supply line was removed from the weathering flask and the entire assembly reweighed to ascertain the percent of crude oil weight lost due to evaporation.

It was assumed that the oil slick, with a initial thickness of approximately 1/2", adequately prevented the evaporative loss of water, and that the entire weight differential recorded was attributed solely to the loss of lighter molecular weight hydrocarbons from the oil sample.

After recording the post weathering weight, two (2) 250-mL volumes of water were withdrawn from below the slick directly into individual 250-mL separatory funnels. The burette tower was flushed with two volumes of water to remove any possible contamination prior to sample collection. The 250-mL water samples were immediately treated *in situ* with approximately 15 mL of methylene chloride to fix the aqueous phase and then were promptly transferred to the laboratory for completion of the extraction procedure. As a protocol for all extraction procedures the samples were suitably extracted with three (3) 15-mL aliquots of methylene chloride.

All extracts were transferred to a 100-mL volumetric flask and distilled with methylene chloride to volume, two (2) 11-mL capacity glass sample vials were then filled leaving no headspace, and immediately transferred to a freezer maintained at -20 °C. After collecting two aqueous phase samples, the burette tower was completely removed from the weathering flask, and a 50-mL oil sample was withdrawn from the slick by pipette for physical characterization. Utilizing a 10-mL pipette, the oil sample was extracted from the flask with special attention given to obtaining the best representative sample. This was achieved by collecting oil at a number of locations around the oil slick, and transferring the aliquots to

a 50-mL borosilicate glass vial leaving no headspace. Oil samples were tightly sealed and allowed to settle for a 24-hour period in a cool dark place prior to running any tests to allow for the sample temperature to stabilize at a relatively constant value of 25 °C, and to visually check for the presence of water.

In addition, a small aliquot (approximately 0.5 mL) of oil was removed from the slick, dissolved in methylene chloride within a glass vial, tightly sealed, and placed in a freezer for later analysis by GCMS. Finally, a 100-mL volume sample of the remaining oil was carefully removed from the weathering flask by pipette, and transferred into a 250-mL glass beaker for continuing analysis in procedures outlined in section 4.2 Vertical Turbulent Dispersion Characteristics.

The physical characterization of the oil was performed in the following fashion:

4.1.1 Oil Viscosity This parameter was determined by the use of a Brookfield Digital Cone Plate Viscometer (Model LVII++). Oil viscosity was measured using a precision torque meter checked for proper calibration using viscosity standards available from the manufacturer. Prior to conducting a viscosity measurement, the gap between the cone and the plate was mechanically adjusted to a gap clearance of 0.0005" (0.013mm); see Figure 3, as per specific instructions contained within the operators manual. The adjustment of the gap

clearance was performed after ensuring proper circulating water flow, and allowing 10 minutes for the sample cup to equalize at the set temperature of 25 °C.

In the absence of a controlled temperature water circulation unit, a cooling water circuit was configured directly from the cold tap water supply line. Water discharging from the sample cup was fed directly into a 1000-mL beaker where a thermometer recorded the output temperature. All viscosities were recorded at $25\text{ }^{\circ}\text{C} \pm 1.0\text{ }^{\circ}$.

The torque measuring system within the unit, consisted of a calibrated beryllium-copper spring connected in-line between the driving mechanism and the rotating cone. The resistance to rotation associated with the presence of fluid in the gap between the spindle and the stationary plate produces a torque that is proportional to the shear stress in the fluid, which is then converted to units of centipoise (cP) (refer to Appendix B).

The viscosity of the oil sample was measured at spindle speeds of 0.3, 0.5, 0.6, 1.0, and 1.5 rpm, in order to provide the most representative analysis. A weighted average viscosity was calculated using the viscosity data output from an individual run combined with the percent of maximum scale reading for viscosity that the unit has for each particular operating speed. In addition, data was recorded and suitably plotted for shear rate versus shear stress at each operating speed, in order to ensure that a linear relationship existed, indicative of the fluid behaving in the Newtonian range (i.e., fluid viscosity independent of spindle speed).

Figure A8

- Notes:
- a) The cup may be removed without resetting the gap.
 - b) Remove the spindle from the Viscometer when you clean it.
 - c) Reset the hit point every time the spindle is attached.

Cone	Sample Volume	Cone Angle
CP-40	0.5 ml	0.8°
CP-41	2.0 ml	3.0°
CP-42	1.0 ml	1.565°
CP-51	0.5 ml	1.565°
CP-52	0.5 ml	3.0°

Figure 3

**Brookfield Viscometer Cone Plate Gap Clearance
and
Correct Sample Volume Verification**

4.1.2 Oil-Water Interfacial Surface Tension This parameter was determined by the use of a Fisher Scientific du-Nouy Ring Apparatus (Surface Tensiomat Model 21). Interfacial tension data was collected by recording the force required to pull a platinum-iridium ring of precisely known dimensions through the fluid interface of two immiscible liquids. Prior to use, the sample container and the test ring were thoroughly cleaned of any impurities using sequential washings with OPTIMA grade methylene chloride, and analytical grade acetone, followed by a final rinsing with distilled water. To conduct a measurement, the glass container was first placed atop the adjustable table ensuring that the table was initially placed at the maximum height setting using the worm gear adjusting ring. The entire table assembly was then lowered, by freeing the clamping mechanism on the vertical tower inside the case, to provide sufficient clearance to set the ring in place. The test ring was then suspended from the counter-balanced lever-arm; without releasing the locking mechanism holding the arm, and the more dense liquid added to the sample container to a depth of approximately 1/2". Distilled water was used for the analysis to eliminate any possible error stemming from the reproducibility of laboratory prepared seawater samples, and to limit the corrosive effects of saltwater on the apparatus.

The entire table assembly was then raised until the ring immersed about 1/4" and was completely wetted by the heavier liquid. The locking mechanism holding the lever arm was then released and the unit adjusted for a zero reading. The adjustment for zero is accomplished by rotating the arm on the right side of the case, which thereby alters the

torsion in a stainless steel wire controlling the vertical position of the lever arm. The adjustment is completed when the index and its reflected image are aligned with the reference mark on the mirror, and the indicator dial set to zero.

The vertical position of the table may need to be corrected to ensure that the ring does not come in contact with the bottom of the glass container or the surface of the liquid. Once the unit is in the zero position, the crude oil sample was poured atop the surface of the distilled water to a depth of 1/2" to 5/8". The layer of the lighter liquid must be of sufficient depth to prevent the ring from coming in contact with the surface of the lighter liquid (i.e., air-oil interface) prior to rupturing the interfacial film. In accordance with procedures set forth in ASTM-D-971 the interface was allowed to stabilize or "age" for 30 seconds before conducting an actual measurement.

The sample table is slowly lowered by utilizing the worm gear adjustment and the test ring raised using the control knob on the side of the case. These alternating incremental adjustments are conducted in such fashion so as to maintain the position of the index at the reference mark. The interface between the two liquids will become distended (Figure 4) and will eventually rupture. The dial reading on the face of the unit at the breaking point of the interfacial surface is the "apparent interfacial tension" (P). The absolute value of the interfacial tension (S) is obtained by correcting the apparent value using the following formula:

Figure 4

Distention of the Interfacial Surface Between Two Immiscible Liquids

$$S = P \times F \quad [16]$$

The parameter (F) is a correction factor which is dependent on the size of the ring and the size of the wire used in the ring, the apparent surface or interfacial tension, and the densities of the two phases.

$$F = 0.7250 + [[0.01452 P / [C^2(D - d)] + 0.04534 - [1.679 r / R]]^{0.5} \quad [17]$$

where:

- F = correction factor
- R = radius of the ring (cm)
- r = radius of the wire for the ring (cm)
- P = the apparent value or dial reading (dynes/cm)
- D = the density of the lower phase (g/mL)
- d = the density of the upper phase (g/mL)
- C = the circumference of the ring (cm)

The physical constants of the platinum-iridium ring are $C = 5.985$ cm and $R/r = 53.6145350$. The calibration of the unit and of the experimental procedure was checked just prior to each weathered oil analysis by measuring the interfacial tension of hexane-water (51.1 dynes/cm).

4.1.3 Oil Density This parameter was determined by the use of a 10-mL glass pycnometer.

A precision glass pycnometer with a volumetric capacity rating of 10-mL at 25 °C was used in tandem with an analytical balance to accurately record the density of the weathered oil samples. The pycnometer was calibrated by initially measuring the density of distilled water

(density = 0.997 g/mL @ 25 °C) in order to determine the calibration constant of the pycnometer vial. The density of the oil samples were determined by filling the pycnometer vial with oil to the indicated mark. When the vial cover is placed in position, all fluid in excess of the rated volumetric capacity of the vial will be forced out through a pilot hole machined into the cover. The weight of the pycnometer filled with 10 mL of sample was then compared against the weight of the pycnometer alone in order to determine the density of the sample. This calculated density of the sample was then corrected using the calibration constant determined for the vial.

4.1.4 Molecular Characterization by Gas Chromatography/Mass Spectrometry

(GC/MS). This phase of the characterization was accomplished by the use of a Hewlett-Packard Model 5890 Gas Chromatograph/Mass Spectrometer. At the end of each weathering period, small aliquots (<1mL) of crude oil were removed from the surface slick contained in the weathering flask, and dissolved in methylene chloride. Small extraction columns were prepared using disposable 23-cm Pasteur pipettes filled with approximately 0.75 g activated Fisher Scientific Chromatographic Silica Gel (100-200 mesh). A 1-mL sample of the dissolved crude oil sample was placed into the top of the extraction column and the aliphatic and aromatic hydrocarbons were recovered by elution with OPTIMA grade methylene chloride. Approximately 5-mL of solvent was required to accomplish this objective. The collected sample was blown-down under a light steady stream of nitrogen, to a volume of

approximately 50-uL. A 1-uL sample was withdrawn from the sample vial and injected into the GC/MS for qualitative analysis.

The Hewlett-Packard GC/MS was fitted with a 30-m long by 0.25-mm internal diameter ®Durabond 5% phenyl methylpolysiloxane column for the chromatographic separation of the samples. The temperature of the column was programmed from 40 °C to 300 °C at a rate of 6°/min, one minute after injection of the sample. The abundance of selected aliphatic and aromatic compounds were recorded; formed into a ratio of the respective compounds to the n-C30 alkane, and a comparison made between different weathered oil samples, to formulate a relative loss rate for each of the selected compounds.

4.2 Vertical Turbulent Dispersion Characteristics

Vertical dispersion profiles for the weathered oil samples were characterized utilizing a specially designed and constructed vertical turbulent dispersion reactor, Figures 5-7. The reactor is constructed of 12" diameter clear acrylic plastic (1/4" wall thickness) and stands at a height of 72". The top cover plate of the reactor supports an internal 4" diameter acrylic tube, which houses the 3" diameter mechanical mixing head, designed to serve as the turbulence generator. The speed of the mechanical mixing head can be adjusted up to 2500 rpm to vary the energy input rate to the reactor. Refer to Appendix C for a listing of the energy input rates calculated for a range of operating speeds for the mixing head, and a

comparative listing of published energy dissipation rates commonly associated with various levels of surface turbulence in actual field conditions.

The internal 4" diameter tube projects 12" into the main body of the reactor and is fitted with three inlet ports which allow water to cascade in from the main body of the reactor into the turbulence generator. This configuration serves to concentrate the turbulence energy in a confined area, and to deliberately restrict the water flow on the low pressure side of the propeller to induce cavitation. The air induction associated with cavitation is intended to simulate the entrainment of air after the passage of breaking waves in actual field conditions. The configuration of the upper workings of the reactor is also intended to separate the surface of the slick into a turbulent area and a relatively quiescent area to allow for any water-in-oil emulsification to become visibly evident. Vertical baffles adjacent to the inlet ports guide the oil into the turbulence generator during operation. The design waterline of the reactor is situated at the center of the inlet ports to the turbulence generator when the mechanical mixing head is at the chosen speed setting, which results in a operating volume for the reactor of approximately 30 gallons. Within the reactor, samples of weathered crude oil were exposed to turbulent surface conditions, designed to simulate an energy dissipation rate for surface turbulence commonly found in a deep ocean environment approaching breaking wave conditions. Water samples containing dispersed crude oil were withdrawn from the reactor at specified time periods from three (3) sampling ports along the depth of the reactor.

Figure 5
Vertical Turbulent Dispersion Reactor

Figure 6
Internal 4" Turbulence Generator

Figure 7
Adding Crude Oil to the Vertical Turbulent Dispersion Reactor

Water samples were then analyzed to determine the chemical profile of "dispersed" hydrocarbons underneath the surface, as they relate to the physical properties of the weathered oil. Durations for simulating turbulent surface conditions were chosen to be 5 minutes and 3 hours. Additionally, to test the persistence of the oil within the water column, a water sample was also withdrawn from the reactor 3 hours after the mechanical mixing head was secured, i.e., 6 hours after initiating the experiment.

The procedure for operating the reactor begins at least 24 hours prior to the time designated for an experiment. The internal wall of the reactor was cleaned with mild dish soap and a long handled boat brush, completely filled and drained twice with clean tap water, and then refilled to volume and allowed to stabilize overnight. Approximately 2 hours prior to operating the reactor, 3700 g of Tropic Marin® Sea Salt was added to the reactor; the top cover plate was installed; and the mixing head set at the chosen operating speed, to allow time to achieve complete mixing and eliminate density gradients within the reactor. The specific gravity of the artificial sea water was 1.022 for the operation of the reactor. No controls were exerted on the temperature of the water within the reactor, which was allowed to equilibrate in the ambient temperature of the laboratory, and generally held fairly constant at 22 °C during the course of the experiments.

Prior to admitting oil to the reactor, the specific gravity was recorded, along with the temperature and pH of the water. The 250-mL beaker containing the 100-mL oil sample, which was transferred out of the weathering flask (see Section 4.1 Weathering Characteristics), was weighed prior to admitting the oil to the reactor. The oil was carefully transferred to the reactor through an inlet port designed into the top cover plate using a wide throat plastic funnel, minimizing contact with the sides of the funnel. The 250-mL beaker was then reweighed to determine the weight of oil admitted to the reactor. The quantity of oil added to the reactor was chosen to produce a standardized slick thickness of 1 mm.

At the predesignated times, two 250-mL water samples were withdrawn from the reactor directly into individual 250-mL separatory funnels, from each of the designated sampling ports located at depths of 3", 27", and 63" below the water line. Equal volumes of clean seawater were transferred into the top of the reactor during the sampling process to maintain the proper water line within the reactor. The water samples containing dispersed crude oil were then extracted using OPTIMA grade methylene chloride following extraction protocols previously referred to in Section 4.1 Weathering Characteristics.

The crude oil extracts from the aqueous phase were characterized in the following fashion:

4.2.1 Total Oil Concentration The total oil concentration contained within each extract was determined by the use of a Mettler AE 240 Analytical Balance. A 5-mL aliquot was withdrawn from one of the 11-mL samples obtained from the extraction procedure conducted for the 250-mL aqueous samples withdrawn from the reactor. The 5-mL aliquot was placed into a clean disposable glass sample vial, which was preweighed (including screw cap) to determine initial tare weight. The screw cap was used as a means of labelling the sample vial for later reference. After completing the transfer of all the available 5-mL aliquots, the vials were placed under a laboratory fume hood for a period of 36 hours to evaporate all the solvent; caps were removed and placed along-side each respective vial. When the samples were evaporated to dryness, the caps were returned to the vials, and then suitably reweighed. The differential weight was then recorded, and converted into a projection of total milligrams of oil estimated to be contained in a liter of water. Care was exercised to properly wipe down each glass sample vial with a lint-free Kim-Wipe prior to weighing. Accuracy of the Mettler AE 240 Analytical Balance was determined to be ± 0.00005 g.

4.2.2 Spectrofluorometric determination of Total Aromatic Hydrocarbon Concentration The total aromatic hydrocarbon concentration contained within each extract was determined by the use of a Gilford Fluoro IV Spectrofluorometer. A high performance spectrofluorometer capable of measuring in the wavelength range of 200-800 nm was used to quantify the aromatic fraction of the total hydrocarbons extracted from the reactor. The light source is from a high-pressure Xenon lamp, which emits a wide spectral wavelength

range. The light beam emitted from the source is focused through a collimating lense, and is subsequently split into two beams by the excitation monochromator. One beam, the reference beam (10% of the beam energy), passes directly to the photo-diode detector. The second beam, the sample beam (90% of the beam energy), is directed to the excitation grating where the beam is focused to the selected bandwidth and then exits the monochromator exit slit. The sample beam is then directed to the quartz cuvette, which induces the sample to emit fluorescence energy in all directions. The emission monochromator, which is mounted 90 degrees off the sample beam path, to reduce interference from light scattering off the sample and the cuvette, measures the fluorescence emitted from the sample. The emission monochromator focuses the beam energy and refines the emitted light to the selected emission wavelength and bandwidth before allowing the beam to impact the photo-diode detector. A microprocessor then converts the analog data from the photo-diode to a digital display of relative fluorescence units.

The operating parameters selected for the operation of the spectrofluorometer were as follows:

Excitation wavelength	= 310 nm
Emission wavelength	= 360 nm
Scan width	= 50 nm
Scan speed	= 100 nm/minute

A calibration curve for total aromatics was produced from 400ppb, 200ppb, 80ppb, 20ppb, 2ppb, solutions of chrysene, plus a blank solution of OPTIMA grade methylene chloride as

a control. The fluorescence output from the calibration standards were plotted to ensure that a linear relationship was produced for concentration versus relative fluorescence (i.e., in satisfaction of Beer's Law). A linear regression analysis was performed on the output data to develop the equation necessary for the calculation of aromatic hydrocarbon concentrations from relative fluorescence data. The correlation of the data, for each of the equations developed during this analysis, were all in excess of 98% (i.e., r^2 value > 0.980).

A large proportion of the original samples extracted from the reactor contained significant quantities of oil, and therefore displayed significant coloration. The coloration of the samples had an adverse effect on the performance of the instrument, as evident by an indication of zero relative fluorescence for samples which were predicted to contain significant quantities of aromatic hydrocarbons (e.g., unweathered oil, and after a 4-hour weathering period). The color either diffuses the light intensity sufficiently to limit the fluorescence response from the sample, or a compound associated with coloration was adsorbing light at or near the 310 nm excitation wavelength. A 10-fold dilution of the sample, giving a zero indication previously, would subsequently give a response well beyond the calibration range for the unit as defined by the calibration standards. The dilution factors for the samples ranged from 10 - 1000, and were accomplished sequentially using a 10 mL volumetric flask.

4.3 Dispersed Particle Profile

A Coulter Doppler Electrophoretic Light Scattering Analyzer (DELSA 440) was used to investigate the distribution of electrophoretic mobility and zeta potential for particles and colloids within the range of 0.02 - 30 microns in diameter, using laser Doppler velocimetry. Similar to the working principle of speed tracking devices used by law enforcement, the DELSA 440, analyzes particles within the sample chamber by simultaneously recording Doppler shifts in the laser light frequency experienced by 4 independent laser beams impinging on the sample from 4 different angles.

The sample cell, as shown in Figure 8, holds approximately 1 mL which is injected into the sample chamber by syringe, avoiding air bubbles within the cell. When an electric field is applied across the sample cell, the particles contained within the fluid will accelerate and reach maximum velocity (terminal velocity) in a matter of a few microseconds. At this maximum velocity the forces of viscous drag are in balance with the force of the electric field acting upon the particle, and the electrophoretic mobility of the particle can be recorded as follows:

$$U = v / E \quad [18]$$

where:

- U = electrophoretic mobility (um-cm / V-s)
- v = the terminal velocity of the particle (um / s)
- E = the electric field applied the sample cell (V / cm)

Figure 8
DELSA 440 Sample Chamber Assembly

The zeta potential of the particle (ζ) , defined as the electric potential between the bulk solution surrounding the particle and the shear plane around the particle, is related to the electrophoretic mobility by the following relationship:

$$\zeta = 4\pi\eta U / \epsilon \quad [19]$$

where:

- ζ = zeta potential of particle (mV)
- η = viscosity of the solution (poise)
- U = electrophoretic mobility of particle ($\mu\text{m-cm} / \text{V-s}$)
- ϵ = charge of the electron (4.8×10^{-10} statcoulombs)

In order to conduct an analysis using the DELSA 440, the unit must first be allowed to warm up for a period of 45 minutes. During this time the sample cell was generally disassembled and carefully cleaned to remove any deposits from inside the hemispheres machined into both halves of the gold electrode, and to remove any deposits from inside the glass insert (i.e., sample channel) which might interfere with the optical pathway of the laser beams, Figure 8. After disassembling and cleaning the sample cell, the DELSA 440 requires recalibration, which consists of adjusting the cell constant of the sample cell and realigning the target point for the laser to impact the sample, according to detailed procedures outlined in the manual.

The cell constant is adjusted by using a calibration solution of known conductivity, which is available from the manufacturer. This calibration is required because the overall conductivity of the circuit across the sample cell is a combination of the sample cell proper and the sample solution held within. In order for the unit to determine the conductivity of the solution it must have an accurate determination of the conductivity of the sample cell so that this figure can be backed out of the overall conductivity of the electric circuit. The conductivity of the solution is an important figure to obtain because it will determine the applied field strength across the cell in order to resolve the particle charges out of the information generated by the laser.

The second step of the calibration procedure is required in order to align the target point of the laser in relation to the sample cell channel width, Figure 9. The overall mobility of the particles across the channel under the influence of the applied field is a resultant combination of electrophoresis, the motion of the particles due to the field strength; and electro-osmotic effects. The electro-osmotic effects are the result of an uneven distribution of ions across the sample cell channel width due to the fact that the glass walls are at a different electric potential than the bulk solution.

This uneven distribution of charged ions sets up a parabolic flow pattern across the sample cell channel width; the flow being generated by the motion of the particles and fluid drag. In order to accurately determine the electrophoretic mobility of the particle, the laser must

Figure 9
Location of Stationary Layer

impact the sample at a position called the "stationary layer". This position is where the positive and negative flow directions cancel out and true mobility data on the particle can be acquired. Detailed procedures for aligning the laser target point, and the intersection point of the 4 laser beams are outlined in the operator's manual.

A confirmation of the correct positioning of the laser beam paths are obtained through the use of a mobility standard (i.e., a colloidal suspension of known size and particle mobility), which is provided by the manufacturer. The operating parameters chosen for the analysis were determined from personal site visits with the Applications Laboratory of Coulter Electronics, and listed as follows:

Particle sizing

Electric Field :	0 mA
Run time:	90 seconds
Frequency Range :	500 Hz

Particle Mobility

Electric Field :	10 mA
Field on time :	2.0 seconds
Field off time :	0.5 seconds
Run Time :	60 seconds
Frequency Range :	500 Hz

The protocol adopted for handling the sample is one that avoids the injection of large amounts of oil to the cell which results in fouling of the cell. A 25-mL water sample was

extracted from the reactor along with samples extracted during tasks explained in Section 4.2 Vertical Turbulent Dispersion Characteristics and was allowed to stand for a period of 90 seconds, to reduce the amount of discrete oil droplets in the aqueous phase. The syringe tip was inserted through the slick surface and a 5-mL water sample was extracted. The syringe tip was suitably cleaned and the sample injected into the sample cell.

Between trials the sample contained in the cell was purged, and the cell flushed with a steady stream of 2-propanol; followed by a rinsing with a steady stream of de-ionized water; then, purged to empty all remaining fluid contents. The incoming 5-mL sample fed to the sample cell was sufficient to flush the cell with 3 complete volumes of liquid before retaining an aliquot for analysis.

4.4 Relative Toxicity Evaluations

Bacterial bioluminescence assay experiments were performed on a Microbics Microtox Model 500 fluorometer. The unit is designed to detect the reduction in light levels emitted from living luminescent bacteria when confronted with toxic components present in the test sample. The reduction in light levels is expressed by the parameter gamma (Γ), and is defined as the ratio of the light reduction during the test to that of the light which remains at time (t). The light reduction during the test period is related to two mechanisms, the toxicity of the sample, and that which is associated with the drifting light levels from the reagent alone.

Therefore a blank sample must be run initially in order to normalize the light reduction data.

Calculations for Γ were conducted as follows:

$$\text{Blank ratio: } R_t = [I_t b] / [I_o b] \quad [20]$$

where:

- R_t = blank ratio for time [t]
- $I_t b$ = final light reading for the corresponding blank cuvette; t minutes after the transference of the toxicant
- $I_o b$ = initial light reading for the blank cuvette immediately prior to admitting the toxicants (t_o)

The reduction in light from the test cuvette is then normalized against the blank cell response by multiplying the initial light output of each cuvette by the blank ratio R_t determined for time [t]. The normalized gamma effect is then calculated for each cuvette using the following equation:

$$\Gamma_t = [R_t I_o / I_t] - 1 \quad [21]$$

where:

- I_o = the initial light reading for the test cuvette at time zero immediately prior to admitting the toxicants
- I_t = the final light reading recorded for the cuvette at time (t)
- R_t = mean blank ratio for time (t)
- Γ = the gamma effect calculated for exposure time (t)

Samples withdrawn from the reactor, during tasks described in Section 4.2 Vertical Turbulent Dispersion Characteristics, were extracted using methylene chloride and stored with zero head space in 11-mL glass vials in a freezer kept at -20 °C until analysis. A 2-mL aliquot was withdrawn from each vial and transferred to a clean 11-mL glass vial and brought to complete dryness under a steady stream of nitrogen. The extracts were then immediately redissolved in an equal volume of ethanol and returned to the freezer. Sample vials were sonicated under low power setting for 5 minutes prior to analysis to ensure that all the oil was resuspended in solution.

To ascertain the relative toxicity of dispersed oil as a function of the weathering period, the following modified 100% test procedure was adopted for each of the hydrocarbon extracts, after consulting with the technical staff at Microbics. A dehydrated bacterial sample was rehydrated using 1000 uL of reconstitution solution and allowed a 15-minute period to fully acclimate. If samples are dissolved in an organic solvent, such as ethanol, the concentration of the solvent cannot exceed 2% in any of the test cuvettes, in order to keep the toxicity associated with the solvent to an acceptable range. A 10-uL sample was injected into the first test cuvette containing 3000-uL of diluent, which satisfied the 2% concentration criteria. Suitable dilutions were then prepared from the original cuvette by sequential transference of a 1000-uL aliquots of diluent/sample solution between adjacent cuvettes, as per the manufactures instruction manual for the 100% test. The diluent solution was prepared from distilled water, and brought to 32 o/oo seawater using the Tropic Marin® sea salt mix. The

rehydrated mixture of bacteria was then injected into each cuvette and the initial bioluminescence recorded for time zero. The resultant bioluminescence recorded after a 5- and 15-minute periods was recorded to determine the EC-50 value of the sample. The EC-50 value was determined by plotting the gamma values (Γ) versus the concentration of the sample in the cuvette. The EC-50 value is actually the sample concentration which corresponds to a 50% light reduction in bacterial bioluminescence emitted from the cuvette, and is equivalent to a gamma value of 1 ($\Gamma=1$). A phenol standard was prepared, as per instructions in the operators manual, and included with each Microtox analysis to check the accuracy of the procedure

4.5 Experimental Replicability

The analysis of crude oil weathering characteristics is highly dependent on the meteorological conditions prevailing during the course of the exposure period. The analysis conducted herein simulated the weathering of crude oil samples under natural conditions, which imposes a high degree of variability between replicate runs. This variability stems mainly from differences in solar intensity, cloud cover, localized weather patterns, and ambient air temperature.

Table 1 delineates the recorded differences between two replicate 4-day weathering experiments. Run #2, with a higher recorded solar irradiance during the exposure period, yielded a correspondingly higher dynamic viscosity, because of the larger effects of evaporation. The effects of larger evaporative losses for Run #2 typically results in a higher resultant concentration of natural surface-active materials present in remaining oil samples. The higher concentration of these natural surface-active materials resulted in a corresponding lower resultant oil-water interfacial surface tension, as expected. As for the resultant total oil concentrations recorded from the reactor, two comments can be put forth. First, the data coming from the vertical turbulent dispersion reactor from these two replicate runs are following the trends developed during the course of the entire research project. The higher viscosities of the oil for Run #2 results in the formation of larger oil droplets dispersed into the water column (for a fixed level of turbulence), which is the main reason why oil concentrations are lower in the reactor, especially at the bottom of the reactor. Lower oil concentrations at the surface for Run #2 can also be attributed to the early-stage formation of water-in-oil emulsions, which further restricts the vertical dispersion process. Second, the variability of oil concentrations between samples extracted from the reactor at similar sampling sites, at virtually the same time, can be attributed to the wide scale distribution of oil droplet sizes within the reactor (i.e., from sub-micron to a few millimeters).

RUN COMPARISON

4 DAY RUN 1		4 DAY RUN 2	
SAMPLE I.D.	TOTAL OIL (PPM)	SAMPLE I.D.	TOTAL OIL (PPM)
4D5M SURFACE	1634.4	4D5M SURFACE	1209.6
4D5M BOTTOM	855.0	4D5M BOTTOM	621.6
4D5M BOTTOM	796.8	4D5M BOTTOM	591.2
4D3H SURFACE	1930	4D3H SURFACE	1061.6
4D3H SURFACE	1080	4D3H SURFACE	848
4D3H BOTTOM	943.2	4D3H BOTTOM	644.8
VISCOSITY (cP)	597.95	VISCOSITY (cP)	920.3
OIL-WATER IFST (dynes/cm)	28.26 avg.	OIL-WATER IFST (dynes/cm)	27.405 avg.

TABLE 1
Comparison of Replicate 4-day Weathering Experiments

The extraction of only two or three samples from the reactor at the designated sampling time will yield a range of oil concentrations, depending on the spectrum of oil droplet sizes extracted from the reactor during sampling. Overall, the variability in concentrations in the reactor was an expected result, and since it was not that excessive, no modifications were made to the experimental design, or number of samples extracted from the reactor during each sampling.

4.6 Quality Control

All protocols were implemented in accordance with best available standard methods, whose details and references are called for in this section. A concerted effort was made to assure best consistency in all activities associated with a complete experimental run. This effort covered specific aspects of sample collection, handling and analysis. For instance, all glassware was sequentially cleaned with analytical grade acetone and ACS grade methylene chloride between use to limit the potential for cross-contaminating samples. All solvents used for liquid-liquid extraction, sample dilution, and analysis by GC/MS and fluorescence spectrometry were OPTIMA grade methylene chloride only.

5.0 Results and Discussion

This chapter presents and analyzes all experimental results that were collected during the weathering and dispersion phases. Efforts focus on the scientific and environmental implications of this study.

5.1 Physical properties

This section describes the characteristics and values of viscosity, density, oil-water interfacial surface tension, and molecular characterization.

5.1.1 Viscosity

According to the MOBIL OIL data sheet for the Arabian Heavy Crude Oil (see Appendix A), the dynamic viscosity of the oil should be approximately 36.02 cP at 25 °C. The oil viscosity measured 10/93 was recorded at 43.2 cP. The small difference is attributed to the handling of the oil sample and the transfer of the sample between engineering buildings on campus to access the Brookfield Viscometer.

The oil was stored in the original 1 gallon can on receipt, and during the preconstruction and materials compatibility evaluation for the acrylic reactor. The oil was subsequently transferred to nine (9) 300-mL glass containers with zero headspace 01/94, after approval of a designated set of experiments. The initial viscosity of the oil (designated as NO weathering) recorded from one of the nine (9) sealed 300-mL bottles used during the thesis project was 118.1 cP. The discrepancy in the initial viscosity reflects the small evaporative losses, estimated at <5%, which occurred in the original 1-gallon can provided by MOBIL OIL during the 2-month storage period prior to experimentation.

Values of oil viscosity for the weathered samples, recorded as a function of the exposure period (hours), are listed in Figure 10 (see Appendix D for data file). The viscosity of the oil was then correlated to the recorded total solar irradiance (W/m^2) as shown in Figure 11, and to the mass percentage lost to evaporation during the exposure period, as shown in Figure 12. Figure 10 shows that the viscosity of the oil increases rapidly during the first 8-hours exposure, with a measured 150% increase. These results were consistent with information available from the literature. After the first 8-hours the rate of increase for the oil viscosity decreased, but remained fairly linear during the remaining 7 days, reaching an estimated maximum value of 1025 cP at the end of the seventh day (the longest weathering period). This value was estimated from a log-log relationship developed for oil viscosity vs. total solar irradiance incurred during the exposure period, Figure 11, because of limitations of the Brookfield LVDV-II+ viscometer in measuring viscosities in this range.

The total solar irradiance recorded during the exposure period by the LI-COR pyranometer is shown in Appendix E. When these weathered oil viscosities are compared to the original properties of the crude oil delivered from MOBIL OIL, an important insight is gained for those involved in oil spill containment and clean-up. The Arabian Crude Oil (API 28) will experience a 10-fold increase in viscosity after only 24-hour weathering, and a 23-fold increase after one week. This assumes that the extremely light fraction lost in the laboratory during storage, which caused the elevated initial viscosity, is rapidly lost in actual field conditions.

Figure 10
Dynamic Viscosity Versus Weathering Period

Figure 11
Dynamic Viscosity Versus Total Solar Irradiance

Figure 12
Dynamic Viscosity Versus Percentage of Crude Oil Mass Lost to Evaporation

The characteristics of the oil at the end of the seventh day were drastically different from the original oil properties at the beginning of the weathering period. The oil was visually observed to be thick and viscous, sticky, with a strong odor similar to asphalt, as it would be expected at this point due to the high asphaltene concentration in the oil. The oil maintained Newtonian behavior during exposure periods up to approximately 4 days, as determined from plots of shear stress versus shear rate during viscosity determinations. The Newtonian behavior of the 4 day oil could not be confirmed because the oil viscosity approached the maximum range of the viscometer, and viscosity determinations could only be conducted at one speed (0.3 rpm minimum unit speed). The 7-day weathered oil sample was more than likely non-Newtonian. This inference was based on the heavy sticky nature of the oil sample.

Changes in the physical properties of the oil during the exposure period were strongly dependent on ambient meteorological conditions, i.e., temperature, solar intensity, and wind speed. These variables influenced the micro-environment within the weathering flask, as evident by the 50% variability in the viscosity of the oil recorded at the end of two separate 4-day weathering periods (597.95 cP vs. 920.3 cP) and by the larger evaporative loss recorded from an 8-hour weathering experiment than from the 24-hour experiment.

Evaporative losses during the exposure period are depicted in Figure 13 (see Appendix F for data file). The rate of evaporation experienced during the experiments was most pronounced during the first 8 hours, with over 15% of the oil lost during this period. The evaporative

loss during the 7-day weathering period was 23.09%; less than 10% greater than that experienced in the first 8 hours. The evaporative loss experienced by the oil sample was strongly dependent on weather conditions during the experiment. The weather conditions prevailing during the 8 and 24-hour exposure periods could have not been more diametrically opposed, considering the predictability of south Florida weather patterns during the summer months. The 8-hour weathering period experienced an extreme in temperature, with 42 °C being recorded in the aqueous phase at the end of the period. The weather pattern for the 24-hour period was overcast at the start, turning to intermittent rain for the remainder of the day due to unsettled weather associated with Tropical Storm Alberto, which reached as far south as Miami. The percentage of oil lost to evaporation was 15.65% during an 8-hour period, and only 15.4% during the 24-hour exposure period.

The evaporative loss asymptotically approached 25% towards a 7-day exposure. Oil viscosity plotted against evaporative losses in Figure 12 indicates a steady rise during the early phase of the exposure; and, after experiencing about 15% mass loss, further evaporative losses result in increased rates of viscosity change. For example, the viscosity of the original oil was observed to rise from 118.1 cP to 202.2 cP after losing <5% to evaporation, but will experience a rise in viscosity from 338.97 cP to 1025.4 cP in going from 15.4% to 23% total mass lost to evaporation. It is important to note that evaporative losses in the weathering flask may in fact be less than those which may be experienced in actual field conditions.

Figure 13

Percentage of Crude Oil Mass Lost to Evaporation Versus Weathering Period

This conclusion is based on the fact that the oil in the weathering flask was obviously unable to spread out into a larger and thinner surface slick with the passage of time. The spreading of surface slicks at sea increases the mass transfer area available to other weathering processes, i.e., evaporation, dissolution, and photo-oxidation, and therefore results stated herein may be understated since evaporation rates may have been limited by molecular diffusion.

5.1.2 Density/Specific Gravity

The specific gravity of the fresh crude oil according to MOBIL OIL is 0.8894 (refer to Appendix A). The specific gravity of the oil prior to weathering was measured to be 0.88933. The small percentage of oil lost to evaporation while being stored in the original 1-gallon can, which caused the discrepancy in the initial viscosity, evidently had little effect on the density of the oil and is probably associated with the extremely light highly volatile fraction of the crude. The specific gravity of the oil, as shown in Figure 14, increases rapidly during the first 8 hours of exposure, which correlates with data obtained for the evaporative losses. The specific gravity of the oil asymptotically approached a value of 0.95 (refer to Appendix G for data file). This result is significant considering that this figure was obtained due to evaporative weathering alone. This weathered crude oil may be very susceptible to sinking if exposed to suspended particulate matter in actual field conditions prevailing along coastal environments.

Figure 14
Oil Density and Specific Gravity Versus Weathering Period

5.1.3 Oil-Water Interfacial Surface Tension

The oil water interfacial surface tension (IFST) was observed to decrease from a maximum reading of 28.4 dynes/cm, recorded for the unweathered oil, to a minimum of 18.6 dynes/cm, recorded for a 7-day weathered sample, as shown on Figure 15; see Appendix H for data file. The measurement of oil-water interfacial surface tension for the weathered oil samples was in each case preceded by a pre-test calibration with a known standard of 51.1 dynes/cm for hexane-water. The ratio of the actual value to the recorded value for hexane-water was defined as a calibration constant, and was applied as a multiplier to the oil-water interfacial surface tensions measured for each respective trial.

The oil-water IFST decreases rapidly and reached a localized minimum at 8 hours. The oil-water IFST rebounded slightly at the 24-hour period, but remained on a descending slope for the entire 7-day weathering period. The apparent anomaly of a localized minimum at the 8-hour weathering period is probably linked to the extreme weathering conditions encountered during the exposure period. This localized minimum in the oil-water IFST provides insights into the relationship of this parameter to vertical dispersion, because the magnitude of oil dispersed into the water column reflects a localized maximum for the 8-hour weathered oil (see below).

Figure 15
Crude Oil-Water Interfacial Surface Tension Versus Weathering Period

5.1.4 Oil Compositional Changes as Determined by GC/MS.

The aliphatic and aromatic fractions of the weathered oil samples were characterized for the unweathered crude, along samples after 8, 24, 96, and 168 hours weathering. The GC/MS results are presented in Appendix I. Results include the total ion chromatogram output and selected ion chromatograms for isolating specified families of compounds, including n-alkanes (ion 57), benzenes and alkylated-benzenes (ion 91, 105 and 119), naphthalene (ion 128), methyl-naphthalenes (ion 142), di-methyl-naphthalenes (ion 156), phenanthrene (ion 178), hopanes (ion 191), methyl-phenanthrenes (ion 192), and di-methyl-phenanthrenes (ion 206). Results indicate that only trace quantities of benzene, toluene, and xylene remain in the tested samples after only 24 hours of weathering. No hydrocarbon compounds below C-11 (aromatic or aliphatic) are detectable in oil samples weathered for 4 days. Plots of the relative loss rates for selected aliphatic and aromatic compounds are presented in Figures 16 and 17, respectively. Results are presented as the time dependent abundance ratio of the selected compound indicated versus the abundance of a relatively stable (i.e., non-volatile, non-photo-sensitive) n-C-30 alkane. Results show that n-C-11 is lost at a much higher rate as compared to the longer chain n-C-26. The loss rate for n-C-19 holds an intermediate position between the two as it is expected from their physical properties. Results for the aromatic compounds indicate that naphthalene, methyl naphthalene, and di-methyl naphthalene groups are lost at a much greater rate than phenanthrene and the corresponding methylated compounds. The phenanthrene groups are relatively stable during the 7-day weathering period. Naphthalene and phenanthrene, along with the methylated groups, are

are lost at a much greater rate than phenanthrene and the corresponding methylated compounds. The phenanthrene groups are relatively stable during the 7-day weathering period. Naphthalene and phenanthrene, along with the methylated groups, are all present in the sample weathered for 7 days, and may be responsible for the persistent toxicity of crude oil spilled in coastal environments. Anderson *et al.* (1974) reported that bioassays with pure aromatic compounds indicated that naphthalene and alkyl naphthalenes were 3 to 10 times more toxic than benzene and alkyl benzenes. The compound/n-C-30 ratio also indicates that the relative abundance of naphthalene is five-times greater than that for phenanthrene in the unweathered oil sample. The presence of naphthalene progressively diminishes with weathering, while phenanthrene remained fairly persistent, and after 7 days, the relative abundance of phenanthrene exceeded that of naphthalene. The relative abundance of methyl- and di-methyl- naphthalenes remained consistently greater than their phenanthrene counterparts during the seven day weathering period.

Additionally, Anderson *et al.* (1974) worked equalization experiments with crude oil in Instant Ocean seawater, testing for water-soluble fractions and observed that bacterial contamination affected the hydrocarbon concentration in the aqueous phase. This phenomenon would explain why an aromatic compound/n-C30 ratio would elevate; n-C30 would be preferentially degraded in the presence of bacteria, causing the ratio to increase. The interference from bacterial contamination was not observed in the weathering experiments performed herein.

Figure 16

Relative Abundance of Selected Aliphatic Compounds Versus Weathering Period

Figure 17
Relative Abundance of Selected Aromatic Compounds Versus Weathering Period

Finally, the relatively stable and strong abundance of the hopane series of compounds, as depicted in Figure 18, and observed in this analysis, confirms the fact that this series of compounds is well suited to "fingerprinting" of oil samples in order to track an oil spill back to a possible source.

5.2 Dispersion Characteristics

This section presents and discusses results from the dispersion of the various weathered oils in the turbulence simulator. Data includes quantification of dispersed hydrocarbons, relative toxicity evaluations, and particle charge distributions (including average particle size) of the colloidal fraction.

5.2.1 Aqueous Phase Oil Concentrations

Concentrations of aromatic hydrocarbons detected in the aqueous phase of the weathering flask are depicted in Figure 19 (see Appendix J for data list). The concentration was observed to decrease during the first 24 hours reflecting the initial surge of soluble volatile fractions through the oil-water interface, followed by the combined effects of partitioning back through the interface and evaporation, or photo-degradation of aromatics in the aqueous phase directly. The concentration of aromatic hydrocarbons was observed to increase after the localized minimum encountered after 24-hours exposure. The concentration of soluble aromatic hydrocarbons increased steadily, to the maximum concentration recorded, after 4 days of weathering. This second pronounced peak may be the result of photo-oxidation

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

Figure 18
Gas Chromatogram for Hopane Series (Ion 191)

Figure 19

Soluble Aromatic Hydrocarbons in Weathering Flask Versus Weathering Period

processes producing more soluble oxygenated intermediates. After 96 hours of exposure, the concentration of soluble aromatic hydrocarbons fell dramatically to a minimum value which was recorded after 7-day exposure. These oxygenated intermediates formed during the photo-oxidation of crude oil at sea, in addition to higher solubility (e.g., naphthalene versus naphthol), can also be more toxic to marine organisms than original parent compounds. This fact may support one possible explanation for the increased concentrations of soluble aromatic compounds observed in the aqueous phase samples extracted from the weathering flask, in association with the subsequent observation, that weathered oil samples were more toxic than the original unweathered crude, as determined by the Microtox analysis herein.

It is important to point out that the volume of oil in the weathering flask was chosen to allow for a complete physical characterization of the oil after weathering, with sufficient weathered oil remaining to produce a 1mm slick in the turbulence simulator during the dispersion study. Therefore, the slick formed in the weathering flask was generally on the order of 5/8". This may have limited the dissolution of soluble materials to the rate of molecular diffusion, especially in the extremely thick and sticky 7-day weathered oil. In actual field conditions, a surface slick acted upon by vertical dispersion mechanisms will allow for the more rapid transfer of soluble materials in the water column through the larger transfer areas associated with oil droplet formation than in quiescent laboratory conditions.

5.2.2 Total Dispersed Hydrocarbons in the Water Column

The concentration of total oil within the water column of the turbulence simulator is depicted in Figures 20 through 22 (see Appendix K for data list). Data is configured to delineate the concentration-depth profile that exists within the reactor as a function of the degree of weathering for the oil sample. The weight of oil added to the reactor was quantified at the start of each experiment and ranged from 80 g to 110.2 g (see Appendix L). Assuming a linear distribution of oil mass, the total oil concentrations and those of the aromatic hydrocarbons were normalized by multiplying recorded oil concentrations by the ratio of the average input oil weight to the actual weight input during each trial. Normalization multipliers are also listed in Appendix L. Total oil concentrations, as expected, decreased with increasing depth during each of the individual experiments due to the oil droplet size spectrum that exists in the presence of vertically dispersed oil. The probability of encountering larger oil droplets decreases with increasing depths with fixed energy dissipation rates at the surface, due to the larger buoyant forces associated with these size droplets. At deeper depths the oil droplet size spectrum shifts to the smaller end, with lower resultant oil concentrations encountered. Additionally, the oil was observed to become more resistant to vertical dispersion mechanisms with longer weathering exposures. This effect was the result of increased viscosities of the oil with weathering.

Total oil concentrations were recorded at three depths, 3", 27", and 63" below the surface, and at three distinct times after adding the oil to the reactor, 5 minutes and 3 hours. The

reactor turbulence was secured after collecting the 3-hour samples. A third suite of samples was withdrawn three hours after the reactor was shut down. The total oil concentration (profiled against depth), 5 minutes after initiating turbulence, is depicted on Figure 20. The surface oil concentration (3" depth) increased in direct relation to the weathering period, which is indicative of the larger oil viscosities encountered. Larger oil droplets with larger associated resurfacing rates and smaller entrainment depths were formed as the length of the weathering period was increased.

The sharp decrease in the oil-water IFST recorded at the 8-hour weathering period resulted in a slight localized peak in total oil concentrations at this weathering stage. The effect of the sharp reduction in the oil-water IFST after 8 hours weathering was more pronounced at the 27" depth. A large peak was observed in the total oil concentration at this depth after 8 hours of weathering. The oil concentration at the 27" depth continued to show signs of increasing slightly up to 96 hours, decreasing afterwards up through the 7-day weathering experiment. The decreasing oil concentration is a result of the shift in droplet size distributions towards larger droplets as weathering proceeds, which decreases the total oil concentration at deeper depths. The effect of this shift in droplet size distributions is more pronounced at the 63" depth than at the other sampling depths, as indicated by the declining total oil concentrations observed as weathering proceeds. Oil concentrations obtained from the bottom of the reactor were generally on the order of one-half the concentration found at the 27" depth.

Figure 20
Total Dispersed Hydrocarbons in Water Column Versus Weathering Period
[Turbulence Duration - 5 minutes]

As will be shown in the following section, the general trends observed for the total oil concentrations are confirmed by the total aromatic hydrocarbons. The trends observed with total aromatic hydrocarbon concentrations are clearly defined, probably due to the higher accuracy of the analytical method.

The total oil concentration profile after 180 minutes of turbulence is shown in Figure 21. The surface oil concentration (3" depth) increased rapidly to a peak for the 8-hour weathered sample. The combined effect of an associated sharp reduction in oil-water IFST and a turbulence duration of 180 minutes allowed for the production of an accentuated peak at all depths for this period. The larger peak for the 8-hour weathered oil at 180 minutes duration, as compared to the 5 minute duration, may also be the result of the duration length. Smaller oil droplets are formed with longer turbulence periods as large droplets are subsequently sheared into two smaller droplets. This process will continue until some sort of equilibrium is attained, and a steady-state oil droplet size distribution is formed. Oil concentrations obtained from the 3", 27" and 63" depths were more closely aligned at this sampling time, indicative of some form of pseudo-steady state distribution. At this sampling period, the total oil concentration within the reactor was observed to decrease for oil samples weathered longer than 8 hours. This effect was encountered at all depths, indicating that a reduction in available oil mass must have occurred during the period. The oil was observed to adhere to

Figure 21
Total Dispersed Hydrocarbons in Water Column Versus Weathering Period
[Turbulence Duration - 180 minutes]

the upper parts of the reactor, including inner walls of the reactor main body and internal turbulence generator, sampling ports, propeller and shaft. This situation was most pronounced for the more heavily weathered oils (i.e., 4 days and 7 days), which were highly viscous with an associated sticky consistency and were capable of forming water-in-oil emulsions. A water-in-oil emulsion was observed to form within the reactor from a 4-day weathered oil sample, but proved to be unstable. A 50-mL sample of emulsified oil separated into a water under an oil layer overnight. The emulsion formed from the 7-day weathered oil was extremely stable, showing no visible signs of separation 2 months after originally being withdrawn from the reactor.

The total oil concentration profile measured 3 hours after the reactor was secured is shown in Figure 22. Oil concentrations measured at this time ranged between 300 and 500 ppm depending on sampling depth and weathering period for the oil sample. The residual oil concentrations observed in the water column at the 27" and 63" depths at this time closely resembled the trend which was recorded for oil concentrations at 180 minutes. Oil samples from the bottom of the reactor (63" depth) were consistently higher than those obtained from the middle of the reactor (27" depth), which indicates that some of the small oil droplets may have had larger specific gravities than that which was measured for the oil originally input to the reactor. This effect may have been the result of further dissolution of soluble lighter hydrocarbons and/or water entrainment, which would retard the resurfacing rate of the oil droplets or even promote sinking.

Figure 22
Total Dispersed Hydrocarbons in Water Column Versus Weathering Period
[3 hours after turbulence generator shutdown]

The total oil concentration at the surface (3" depth) remained fairly constant after the initial minor peak at the 8-hour weathering period. A dramatic decline in the surface oil concentration was encountered for the 7-day weathered oil, which resulted from the combined effects of oil adherence to internal surfaces of the reactor, especially near the surface, and the formation of a stable water-in-oil emulsion after 3 hours of mixing. The 7-day weathered oil adhered to all parts of the upper works of the reactor, which may explain a lack of available oil at the surface sampling port. Additionally, oil droplets formed towards the end of the turbulence period, in the presence of water-in-oil emulsions at the surface, were actually large slugs of oil sheared off the surface mass which rapidly recombined with the surface slick. This skewed oil droplet distribution at the surface may have contributed to the sudden decline in residual oil at the surface. The oil droplets dispersed in the water column below the 3" sampling port may have well been close to neutrally buoyant with extremely small resurfacing rates. Residual oil in the reactor after 7 days of weathering was also observed to have a small complement of negatively buoyant particles sinking to the bottom.

5.2.3 Total Dispersed Aromatic Hydrocarbons in the Water Column

Total dispersed aromatic hydrocarbons in the water column generally ranged in concentration between 500 and 900 ppm, depending on the weathering state of the input oil sample and the sampling depth, depicted in Figures 23-25 (see Appendix M for data list). Two observations were noted from the aromatic hydrocarbon data.

Figure 23
Total Dispersed Aromatic Hydrocarbons in Water Column
Versus Weathering Period
[Turbulence duration 5 minutes]

Figure 24
Total Dispersed Aromatic Hydrocarbons in Water Column
Versus Weathering Period
[Turbulence duration 180 minutes]

Figure 25
Total Dispersed Aromatic Hydrocarbons in Water Column
Versus Weathering Period
[3 hours after turbulence generator shutdown]

The concentration of aromatic hydrocarbons nearly mirrors the concentration patterns recorded for total oil concentration in the presence of turbulence only, with the ratio of aromatics to the total oil budget generally remaining close to the value of 50%. A comparison of the unweathered oil and the 7-day oil reveals a slight increase in the percentages of aromatics as weathering proceeds, and higher aromatic percentages occurring near the surface as compared to the bottom of the reactor in both experiments. The aromatic concentrations in the water column, 3 hours after securing the turbulence, very closely resembles the aqueous phase aromatic concentrations recorded from the weathering flask, (Figure 19).

The residual aromatic concentration in the reactor achieves a maximum at all depths for the 4-hour weathered oil, possibly due to an optimum relationship between the strong presence of aromatics and the small oil droplets formed from a relatively unweathered oil; smaller droplets have longer residence times than the larger drops formed from weathered oil samples. The aromatic hydrocarbon concentration declines after this initial peak and resurges to a second peak for the 96-hour weathered oil sample, similar to the aqueous phase concentrations previously recorded from the weathering flask. The second peak from the reactor data is not as significant as that obtained from the weathering flask, and may be attenuated due to the larger water volume to oil sample ratio found in the reactor.

5.2.4 Toxicity of Dispersed Hydrocarbons as Determined by Microtox

The relative toxicity of dispersed oil droplets extracted from the bottom of the reactor, expressed as EC-50 values (ppm), are presented in Figure 26 (see Appendix N for data). These values represent the concentration of sample which will reduce the light emitted by a population of bioluminescent bacteria within the sample chamber by 50%. As illustrated in Figure 26, the toxicity of the sample during the first 8-hours of weathering rapidly decreases, which reflects the evaporative loss of the highly toxic and highly volatile aromatic compounds, such as benzene, toluene, and xylene. After the oil weathers longer than 8 hours, it experiences a progressive shift to a more toxic configuration. This increased toxicity may be the result of the larger loss rates for aliphatic compounds compared to that of aromatic compounds, which enriches the relative concentration of aromatics in the oil sample placed in the presence of the bacteria.

Additionally, the presence of low concentration level oxygenated aromatic compounds, known to be more toxic than their parent compounds, may have formed within the slick as a result of photo-oxidation. These more toxic configurations of the original compound may have also contributed to the increasing trend in toxicity after 8 hours of weathering. The toxicity of the oil samples extracted from the bottom of the reactor reflected a higher toxicity after 7 days of weathering than that observed for the unweathered crude. Experiments conducted by Siron *et al.* (1991) detected an increase in the water soluble fraction along with an enrichment of polar components after two weeks of weathering.

Figure 26

Microtox EC-50 Values at Bottom of Reactor Versus Weathering Period

Siron *et al.* (1991) demonstrated that photo-oxidation by-products from petroleum compounds initially dissolved in the test media was occurring. These polar by-products of photo-oxidation which are known to enhance toxicity (Siron *et al.*, 1991) may explain the greater toxicity observed from oils samples weathered beyond 24 hours in the course of this research.

5.2.5 Particle Charge Distributions and Average Particle Size Observed in the Reactor

The analysis of the dispersed colloidal oil fraction utilizing the DELSA 440 provided some insights, but with short-comings. The DELSA 440 is designed to investigate the charge distributions of discrete "particles" contained within a highly purified matrix. Oil droplets injected into a sample cell are not considered as discrete particles, but as one liquid medium dispersed within a larger liquid matrix. The oil injected into the sample cell resulted in a large proportion of the sample adhering to the internal surfaces of the sample cell, which progressively degraded the performance of the unit when multiple samples were being analyzed. In order to overcome this difficulty it would necessitate disassembling the sample cell and conducting a thorough cleaning, as per instructions outlined in the operator's manual. Subsequent to the disassembly of the sample cell, the DELSA 440 would require recalibration, in order to determine the conductivity of the sample cell and to reacquire the position of the stationary layer. These procedures, while necessary for the proper operation of the DELSA 440, are not consistent with the rapid sampling and analysis required when operating the vertical turbulent dispersion reactor during an experiment. To minimize the

deleterious effects of injecting oil into the sample cell, the cell was sequentially flushed with 2-propanol and deionized water between injections.

Additionally, the artificial seawater matrix proved to be a difficult matrix to use when analyzing charged particles, especially below 2.5 μm . The seawater mixture had a large conductivity, which prevented the proper confirmation of particle charge data observed by the laser unit. The seawater mixture also had a highly variable particle size in the range of 1.5 - 2.5 μm . In accordance with the operators manual, the frequency shift observed by the unit should shift linearly with angle, in accordance with Dopplers Law. The scattering vector is proportional to the angle of incidence of the laser light on particles contained within the sample cell. Therefore, if data observed by the laser is "real", then as the incoming light angle doubles, the frequency shift associated with the particle should also double (i.e., double the angle : double the shift). A minimum shift of 10 Hz should also be obtained by the 8 degree beam (smallest laser angle) in order to properly resolve the data. This requirement could not be attained, given the high conductivity of the seawater matrix, even at the highest field strength setting. In order to properly resolve the particle charges out of the sample, without burning the internals of the sample cell at high field strengths, the engineers at Coulter designed a best available method for analyzing the oil dispersions, as delineated in Section 4.0 Experimental Procedures.

Data obtained from the DELSA 440 unit is contained in Appendix O and is summarized on Table 2. Unstable dispersions were observed in the 1.5 - 2.5 μm range. Due to the highly variable nature in the droplet sizes that existed in the reactor, reproducibility in results was nearly impossible. A wide range of zeta potentials was observed to exist in this particle range. Both positive and negative charges were recorded, with recombination of oppositely charged particles being observed to occur.

Figure 27 shows the results of such recombination effects. Particle charges observed ranged from -13.19 mV to +15.46 mV, with an associated average particle size of 1294.1 nm. A second run with the same sample was run shortly after the completion of the first run, with the effects of recombination shown. The particle charge range was subsequently reduced to -5.5 mV to +3.28 mV with an associated increase in the average particle size to 1466.9 nm. This also leads to the conclusion that the highly variable nature of the sample and seawater matrix, and the time required to prepare the sample for injection into the laser after withdrawing the sample from the reactor, proved to be highly influential on the outcome of the analysis.

Figure 28 reveals that the sample cell experiences some degree of minor fouling during the analysis of crude oil colloidal suspensions. A laser analysis using a Coulter standard with known mobility and particle size was conducted immediately after completing a suite of injections.

**DELSA 440 PARTICLE CHARGE DISTRIBUTION
AND AVERAGE PARTICLE SIZE ANALYSIS**

WEATHERING PERIOD OF CRUDE OIL SAMPLE	RANGE OF OBSERVED ZETA POTENTIALS (mV)		AVERAGE PARTICLE SIZE DETECTED (nm)
	(-)	(+)	
NONE	ND	ND	2249.8
4 HOURS	.121 - 10.24	ND	1820.8
8 HOURS	3.22 - 28.25	2.89 - 11.11	1917.25
24 HOURS	ND	ND	1522.7
96 HOURS	3.58 - 36.5	2.78 - 16.25	1490.1
168 HOURS	5.19 - 15.20	.88 - 10.92	1758.05

Table 2
Observed Zeta Potentials and Average Particle Sizes

I
n
t
e
r
f
a
c
e-- 8.7°
-- 17.4°
-- 26.0°
-- 34.7°

Group ID: ZETA POTENTIAL SCAN 4 DAYS WEATHERING

Sample ID: 5 MIN TURBULENCE DEPTH = 63"

Comments: ID: 13.19 mV -10.42 mV +13.6 mV +15.46 mV Frequency Range: 500 Hz
 [PARTICLE SIZE 1294.1 nm] Frequency Shift: 250.0 Hz
 Temperature: 24.7 °C Refractive Index: 1.3330 Current: 10.000 mA
 Viscosity: 0.00890 poise Dielectric Constant: 78.360 On Time: 2.0 s
 Conductivity: 40.600 mS/cm Cell Constant: 20.8 1/cm Off Time: 0.5 s
 pH: 0.00 Cell Position: 16

Mon Jun 27 11:52:43 1994

Elapsed Time: 68 s

Filename: 4DSMS1.001

I
n
t
e
r
f
a
c
e-- 8.7°
-- 17.4°
-- 26.0°
-- 34.7°

Group ID: ZETA POTENTIAL SCAN 4 DAYS WEATHERING

Sample ID: 5 MIN TURBULENCE DEPTH = 63"

Comments: ID: -5.5 mV +3.78 mV [PARTICLE SIZE 1464.9 nm] Frequency Range: 500 Hz
 Frequency Shift: 250.0 Hz
 Temperature: 25.1 °C Refractive Index: 1.3330 Current: 10.000 mA
 Viscosity: 0.00890 poise Dielectric Constant: 78.360 On Time: 2.0 s
 Conductivity: 43.000 mS/cm Cell Constant: 20.8 1/cm Off Time: 0.5 s
 pH: 0.00 Cell Position: 16

Mon Jun 27 12:09:31 1994

Elapsed Time: 68 s

Filename: 4DSMS5.001

Figure 27

Particle Recombination Recorded by Coulter DELSA 440

Group ID POST EXPERIMENT MOBILITY CHECK W/ COULTER STANDARD

Sample ID ACCEPTED RANGE 3.7 - 4.3 um-cm/V-s

Comments

Temperature	24.9 C	Refractive Index	1.3330	Frequency Range	500 Hz
Viscosity	0.00890 poise	Dielectric Const.	78.360	Frequency Shift	250.0Hz
Conductivity	1.339 mS/cm	Cell Constant	20.8 1/cm	Current	0.700 mA
pH	0.00	Cell Position	16	On Time	2.5 s
				Off Time	0.5 s

Wed Jun 22 14 02:21 1994

Elapsed Time 64 s

Filename POSTMOB.001

COULTER(r) DELSA 440 Version 1.37

Wed Jul 20 16:54:13 1994

Group ID POST EXPERIMENTAL CHECK

Sample ID PARTICLE SIZE OFF MOBILITY STD.

Comments 24um (STD RANGE 245-305)

Temperature	25.2 C	Refractive Index	1.3330	Frequency Range	500 Hz
Viscosity	0.00890 poise	Dielectric Const.	78.360	Frequency Shift	250.0Hz
Conductivity	1.304 mS/cm	Cell Constant	20.8 1/cm	Current	0.700 mA
pH	0.00	Cell Position	16	On Time	2.5 s
				Off Time	0.5 s

Thu Jun 30 16 52:36 1994

Elapsed Time 72 s

Filename POSTPSZ.001

Figure 28

Post-Experimental Calibration Check of Coulter DELSA 440

As indicated by Figure 28, the values obtained for particle mobility and particle size are somewhat out of tolerance, indicating that the data obtained from the oil analysis may have slightly overstated the particle mobilities, (i.e., Coulter standard being overstated in post experiment trial). This would lead to the conclusion that particle charges, both positive and negative, observed during the course of this project, while slightly overstated, in fact actually exist. The recombination effects observed in sequential trials, while identifying the presence of an unstable colloidal suspension, also confirms the existence of oppositely charged particles.

6.0 Summary of Conclusions

- Arabian Crude Oil (API 28) was determined to weather quite rapidly, experiencing a 15% mass lost to evaporation in only 24 hours, with a corresponding 10-fold increase in dynamic viscosity. The dynamic viscosity of the crude oil after seven days weathering was observed to increase 23-fold, which is an important consideration in terms of elevating the level of effort required for any clean-up operations.
- Weathered oil samples in the presence of simulated turbulence (i.e., energy dissipation rate approaching breaking wave conditions) were observed to form water-in-oil emulsions; albeit unstable emulsions, after a 4-day weathering period. A very stable, highly viscous, water-in-oil emulsion was formed from a 7-day weathered oil sample. Effective containment measures should be well situated before any emulsification process can proceed to any great degree; for this Arabian Crude, that time-frame is approximately 4 days.

- Density of Arabian Crude Oil after 7 days of weathering approaches a value of 0.96 g/mL. This value was attained from mainly the evaporative loss of lighter weight hydrocarbons. Sinking could be a real possibility for this oil, when in the presence of typical SPM concentrations found in the coastal zone.
- Oil-Water Interfacial Surface Tension was observed to decrease fairly uniformly during a 7-day exposure period, with a typical range of 20-30 dynes/cm. A localized minimum value was attained around 8 hours weathering, with a resultant corresponding peak in oil dispersion observed after 8 hours.
- The concentration of aromatic hydrocarbons under the slick drops during the first 24 hours of weathering. Only trace concentrations of benzene, toluene, and xylene could be detected after 4 days of weathering. Higher soluble aromatic concentrations were detected in the aqueous phase from equalization experiments between weathered oil samples and artificial seawater, possibly due to photo-oxidation processes, which form oxygenated compounds with higher solubility. Similar trends were also observed in residual aromatic hydrocarbon concentrations recorded from the vertical turbulent dispersion reactor.
- The toxicity of the weathered oil samples were determined to be more toxic to bioluminescent bacteria than unweathered oil samples, as indicated by the EC-50 values obtained from a Microtox Analyzer. No hydrocarbon compounds below C-11 can be detected after 4 days of weathering. Naphthalene, methyl- and di-methyl-naphthalenes, phenanthrene, methyl- ,and di-methyl-phenanthrenes were all present in a 7-day weathered

oil sample. These compounds, along with any corresponding oxygenated compounds, may be responsible for the persistent toxicity observed for weathered oil samples.

- Concentration of oil was observed to decrease with depth within the vertical turbulent dispersion reactor. The probability of encountering larger droplets decreases with increasing depth, as determined from relationships between oil droplet size and resurfacing rate.
- Significant dispersed oil concentrations were still detected in the vertical turbulent dispersion reactor 3 hours after surface turbulence was abated. Concentrations generally exceeded 300 ppm, which provided some insights into the persistence of oil in the water column, especially with droplets having diameters $< 1\text{ mm}$.
- Unstable oil dispersions in the size range, believed to be 1.5 to 2.5 μm , were observed using electrophoresis techniques. A wide range of corresponding zeta potentials were recorded, with negative charges being more prevalent.

7.0 Recommendations

- Further analysis of the weathered oil samples by GC/MS should be conducted in an effort to ascertain the time dependent concentrations of the aliphatic and aromatic fractions; determined on a per unit mass basis from weighed oil samples. In this capacity, time dependent changes in the compositional changes of the crude oil, as a function of the weathering period, can be accurately quantified. It is further recommended that the characterization of the crude oil also include the OXY-PAH fraction, so that the potential products of any photo-oxidative process be quantified. The compound specific concentration

data determined from GC/MS analysis will enable better correlations to Microtox toxicity tests; identifying causal factors responsible for increased toxicity of weathered crude oil samples observed during this research effort. Toxicity evaluations, as a specific point analysis, should be conducted from the aqueous phase directly, thereby eliminating excessive sample manipulation, interference from solvent exchange and the inherent toxicity associated with the solvent directly.

- The experimental design for weathering the crude oil can be enhanced by providing a means of limiting excessive temperatures in the weathering flask; eliminating the magnetic stirring feature and immersing the weathering flask in a small pool of water may be one solution worthy of further investigation. Additionally, the inclusion of flash point to the list of crude oil physical properties analyzed, as a function of the weathering period, may be worthy of investigation; no information was found in literature, but would be of interest to those involved in emergency response to actual oil spill sites.
- The adherence of oil to the internals of the vertical turbulent dispersion simulator interfered with the collection of total oil and total aromatic hydrocarbon data after 3 hours of running the reactor; causing a drop in oil concentrations at all depths in the reactor, especially for heavily weathered oils. Once the oil is admitted to the reactor, equilibrium was rapidly attained at the level of turbulence used in this project, therefore the operational time-frame for the reactor should be drastically shortened from 3 hours used herein; approximately 30 minutes would probably be sufficient to acquire the required data.

- The analysis of oil droplets using the Coulter DELSA 440 is difficult based on the capabilities of the unit. The analysis of colloidal particles requires a highly purified matrix, with water filtered through a 0.2 μ m filter recommended by Coulter in the operators manual. Oil droplet dispersions in seawater run counter to this requirement. It was also determined that Milipore filters are unsuitable, because of the presence of surfactant wetting agents, or fibrous debris from the filter, showing up in the output of the laser run in the particle size range of 2 μ m. Similarly, de-ionized water obtained from the Drinking Water Research Center at Florida International University contained particles present in the laser output at 2-2.5 μ m, which are believed to be particles off the ion-exchange membrane. Prepared seawater, herein used, was determined to be undesirable from the stand-point of impurities, and the associated extremely high conductivity. Oil injected into the sample cell had the drawback of contaminating a perfectly calibrated sample cell in a short period of time. Additionally, oil adherence to the internals of the glass insert (i.e., sample chamber) interfered with data acquisition, which necessitated flushing the cell with 2-propanol, and re-injecting another sample. The wide distribution of dispersed oil droplet sizes contained within a typical sample also made reproducibility difficult. Particle sizing was highly variable and unpredictable. A Coulter counter capable of sizing the oil droplet distribution within the reactor as a function of the weathering period, may have provided the means of achieving the original objective (time-variant dispersed oil droplet sizing) and should be considered as a valuable acquisition for future studies.

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9.0 APPENDICES

9.1 APPENDIX A

ARABIAN CRUDE OIL (API 28) COMPOSITIONAL DATA TBP AND DISTILLATION DATA

CHARACTERISTICS OF WHOLE CRUDE

IDENTITY

CRUDE
COUNTRY OF ORIGIN
SAMPLE NO.
ARABIAN HEAVY
SAUDI ARABIA
92- 64371

PROPERTIES
BUREAU OF MINES CLASSIFICATION - INTERMEDIATE

GRAVITY, API	27.6	CARBON RESIDUE, PCT WT (CCR)	7.72
SPECIFIC GRAVITY, 60/60F	0.8894		
DISTILLATION, TBP			
IBP	C	F	
5 PCT VOL RECOVERED	<0	<-18	
10	52	126	3.00
20	105	222	0.00
30	174	346	0.40
40	242	467	0.02
50	306	583	6
60	369	697	3.6
	443	829	1700
			18.00
			61.00

FLASH POINT, TAG, C
F
POUR POINT, UPPER, C
F

CARBON, PCT WT
HYDROGEN, PCT WT
CARBON/HYDROGEN RATIO

84.48
12.35
6.84

VISCOSITY
KINEMATIC
15C (59F), CS
40C (104F), CS
60C (122F), CS

*LIGHT HYDROCARBON ANALYSIS

ETHANE + LIGHTER	PCT WT	PCT VOL
PROPANE	0.08	0.18
ISO-BUTANE	0.42	0.74
N-BUTANE	0.18	0.28
C4 + LIGHTER	0.86	1.29
ISO-PENTANE	1.53	2.49
N-PENTANE	0.57	0.81
TOTAL C5	1.01	1.42
C5 + LIGHTER	1.58	2.23
	3.11	4.72

* MAY BE INFLUENCED BY MANNER OF SAMPLING AND SAMPLE HANDLING.

YIELDS AND GRAVITIES OF NARROW FRACTIONS
FROM TBP DISTILLATION OF
ARABIAN HEAVY CRUDE

CUT NO.	TBP CUT POINT		MID TBP TEMP		YIELD PCT WT	SUM YIELD PCT WT	YIELD PCT VOL	SUM YIELD PCT VOL	MID PCT VOL	GRAVITY DEG API	SPECIFIC GRAVITY 60/60 DEG F
	DEG F	DEG C	DEG F	DEG C							
C1+C2					0.08	0.08	0.18	0.18	0.09	222.2	0.4001
C3					0.42	0.50	0.74	0.92	0.55	147.2	0.5077
IC4					0.18	0.68	0.28	1.20	1.06	119.8	0.5631
NC4					0.85	1.53	1.29	2.49	1.85	110.6	0.5845
IC5					0.57	2.10	0.81	3.30	2.90	95.0	0.6247
NC5	120	49			1.01	3.11	1.42	4.72	4.01	92.7	0.6311
3	195	91	158	70	2.57	5.68	3.36	8.08	6.40	76.6	0.6800
4	244	118	220	104	2.82	8.50	3.53	11.61	9.85	67.2	0.7121
5	286	141	265	129	2.89	11.39	3.48	15.09	13.35	60.4	0.7374
6	329	165	308	153	2.99	14.38	3.51	18.60	16.85	54.9	0.7591
7	380	193	355	179	3.67	18.05	4.19	22.79	20.70	50.2	0.7788
8	420	216	400	204	3.17	21.22	3.53	26.32	24.56	45.6	0.7990
9	465	241	443	228	3.18	24.40	3.51	29.83	28.08	44.5	0.8040
10	506	263	486	252	3.28	27.68	3.51	33.34	31.59	39.8	0.8260
11	547	286	527	275	3.37	31.03	3.56	36.90	35.12	36.2	0.8438
12	588	309	568	298	3.38	34.41	3.54	40.44	38.67	35.2	0.8488
13	628	331	608	320	3.44	37.85	3.54	43.98	42.21	32.5	0.8628
14	669	354	649	343	3.52	41.37	3.55	47.53	45.76	29.0	0.8816
15	710	377	690	366	3.62	44.99	3.61	51.14	49.34	26.8	0.8939
16	768	409	739	393	4.60	49.59	4.51	55.65	53.40	24.6	0.9065
17	809	432	789	421	3.03	52.62	2.95	58.60	57.13	23.6	0.9123
18	850	454	830	443	3.02	55.64	2.92	61.52	60.06	22.1	0.9212
19	890	477	870	466	3.06	58.70	2.92	64.44	62.98	20.2	0.9328
20	931	499	911	488	3.08	61.78	2.92	67.36	65.90	19.3	0.9383
21	976	524	954	512	3.07	64.85	2.88	70.24	68.80	18.2	0.9452
22	1000	538	988	531	1.46	66.31	1.36	71.60	70.92	16.6	0.9554
23	1160	627	1080	582	10.67	76.98	9.68	81.28	76.44	12.8	0.9806
BOTTOMS					23.04	100.02	19.26	100.54		1.5	1.0639

NOTE: FRACTIONS ARE DEFINED BY LABORATORY TRUE BOILING POINT (TBP) OF WHOLE CRUDE
AND ARE NOT NECESSARILY REPRESENTATIVE OF COMMERCIAL DISTILLATION.

CRUDE OIL SAMPLE CHARACTERISTICS					
NAME	COUNTRY	% VOLUME BOILING 80-170 °C	% VOLUME BOILING 218-340 °C	% VOLUME BOILING 400+ °C	API
STATEFJORD	NORWAY	23.01	26.23	29.00	38
ARABIAN HEAVY	SAUDI ARABIA	18.07	21.21	44.89	28
BCF-17	VENEZUELA	5.58	17.67	63.39	17

CRUDE OIL SULFUR CONTENT	
NAME	%, WEIGHT
STATEFJORD	0.28
ARABIAN HEAVY	3.0
BCF-17	2.3

9.2 APPENDIX B

REVIEW OF CONE PLATE GEOMETRY

A Quick Review Of Cone/Plate Geometry

Cone and Plate geometry, as illustrated, is the fixation of a conical vertex perpendicular to and in point contact with a flat plate. When the cone is made very obtuse (θ less than 4°) and rotated at constant speed (ω), precise viscosity measurements are obtained at absolute and uniform values of shearing rate and stress.

Viscosity (poise) is the ratio of shear stress to shear rate. Shear stress is related to the summation of torque (T) over the conical surface. Shear rate is related to the cone rotational speed (ω), and gap width (c) at any radial

distance (r) from the center of the rotating cone. The ratio of (ωr) and (c) is a constant for any value of (r). Since (c) is a maximum at cone radius (r), the shear rate is related to (ω) and sine (θ).

For the Wells-Brookfield Cone/Plate Viscometer, the mathematical relationships are:

$$\text{Shear Stress (dynes/cm}^2\text{)} = \frac{T}{\frac{2}{3} \pi r^3}$$

$$\text{Shear Rate (Sec}^{-1}\text{)} = \frac{\omega}{\text{Sine } \theta}$$

$$\text{Viscosity (Centipoise)} = \frac{\text{Shear Stress} \times 100}{\text{Shear Rate}}$$

(mPa·s)

Where:

- T = % Full Scale Torque (dyne-cm)
- r = Cone Radius (cm)
- ω = Cone Speed (rad/sec)
- θ = Cone Angle (degrees)

Cone Radius:

CP 40, CP 41, CP 42 - 2.4 cm

CP 51, CP 52 - 1.2 cm

9.3 APPENDIX C

CALCULATION OF ENERGY DISSIPATION RATE FOR VERTICAL TURBULENT DISPERSION REACTOR

Calculation of Energy Dissipation Rate for Vertical Turbulent Dispersion Reactor

<u>Stir Pak Speed Control Setting</u>	<u>*Speed (rpm)</u>
2	528
3	853
4	1203
5	1519
6	1820

* Speed determined by Tak-ette Model 1707 hand-held digital tachometer

Selected speed setting for experiments = 3.5

Rotation speed = 1028 rpm

Calculation of Reynolds Number: $N_R = D^2 n \rho / \mu$

where: D = propeller diameter (meters)
n = rotation speed (rps)
 ρ = fluid density (kg/m^3)
 μ = fluid viscosity (kg/s-m)

$$N_R = (.0762)^2 (1028/60)(997.0) / (0.89 \times 10^{-6})$$

$$= 111444069$$

turbulent conditions prevail >>> 10,000

Power equation for propeller mixing (turbulent conditions)

$$P = k \rho n^3 D^5$$

$k=0.32$ for square pitched propellers

$$P = 4.122 \text{ W} = 3.93 \text{ J/s}$$

if volume of reactor under turbulent conditions is assumed to be 0.06624 m^3
(i.e., one-half of the 35-gal volume)

then energy dissipation rate in the turbulence zone is then $3.93/0.06624 = 59.32 \text{ J / s-m}^3$

energy dissipation rate for deep sea conditions = 10^{-4} to $10^{-2} \text{ J / s-m}^3$

energy dissipation rate for breaking wave conditions = 1000 to $10,000 \text{ J / s-m}^3$

9.4 APPENDIX D

DYNAMIC VISCOSITY OF WEATHERED ARABIAN CRUDE OIL SAMPLES

OIL VISCOSITY DATA SHEET weathering period: none

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm ²)	viscosity (cP)	viscosity x % max range
1	39.1	7.5	8.99	119.9	4688.09
1.5	59.3	11.3	13.6	121.2	7187.16
2	75.9	15	17.4	115.3	8751.27
2.5	94.1	18.8	21.7	115.8	10896.78
1	41.5			126.9	5266.35
1.5	57			116.3	6629.1
2	77.7			119.3	9269.61
2.5	94.7			116.2	11004.14
SUMMATION	539.3				63692.5

WEIGHTED AVERAGE	118.1021695
	118.10 cP

OIL VISCOSITY DATA SHEET weathering period: 4 hours

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm2)	viscosity (cP)	viscosity x % max range
0.3	22.1	2.25		225.8	4990.18
0.6	37.9	4.5		194.2	7360.18
1	64.4	7.5		197.7	12731.88
1.5	97.5	11.3		199.1	19412.25
0.3	22.5			229.9	5172.75
0.6	42			214.6	9013.2
1	64			195.9	12537.6
1.5	97.2			198.4	19284.48
SUMMATION	447.6				90502.52

WEIGHTED AVERAGE	202.1950849
	202.20 cP

OIL VISCOSITY DATA SHEET weathering period: 8 hours

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm2)	viscosity (cP)	viscosity x % max range
0.3	31.2	2.25	7.17	318.8	9946.56
0.5	49.9	3.75	11.4	305.3	15234.47
0.6	56	4.5	12.9	286.1	16021.6
1	93	7.5	21.4	285.1	26514.3
0.3	30.4			310.7	9445.28
0.5	45.1			276.5	12470.15
0.6	58.3			297.9	17367.57
1	93.8			287.8	26995.64
SUMMATION	457.7				133995.57

WEIGHTED
AVERAGE 292.7585099

292.76 cP

OIL VISCOSITY DATA SHEET weathering period: 24 hours

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm ²)	viscosity (cP)	viscosity x % max range
0.3	35.3	2.25	8.12	360.7	12732.71
0.5	53.9	3.75	12.5	331.5	17867.85
0.6	66	4.5	15.2	337.2	22255.2
0.3	36.2			366.9	13281.78
0.5	53.4			327.4	17483.16
0.6	64.4			329	21187.6
SUMMATION	309.2				104808.3

**WEIGHTED
AVERAGE**

338.9660414

338.97 cP

OIL VISCOSITY DATA SHEET weathering period: 4 days

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm ²)	viscosity (cP)	viscosity x % max range
0.3	56.7	2.25		580.4	32908.68
0.5	98.7	3.75		605.8	59792.46
0.5	97.8	3.75		600.2	58699.56
SUMMATION	253.2				151400.7

WEIGHTED AVERAGE	597.9490521
	597.95 cP

OIL VISCOSITY DATA SHEET weathering period: 4 days

spindle rpm	% max range	shear rate (1 / sec)	shear stress (dynes/cm ²)	viscosity (cP)	viscosity x % max range
0.3	91	2.25		929.9	84620.9
0.3	89.1	2.25		910.5	81125.55
SUMMATION	180.1				165746.45

WEIGHTED AVERAGE	920.302332
	920.30 cP

9.5 APPENDIX E

TOTAL SOLAR IRRADIANCE RECORDED DURING WEATHERING PERIOD

TOTAL SOLAR IRRADIANCE VS. WEATHERING PERIOD

Weathering Period (hours)	Total Solar Irradiance (W / m2)
unweathered crude oil	0
4	2366.6
8	6102.1
24	8484.86*
96	27338.85
168	42973.63
96	30421.23

* Data unavailable for 24 hour period (estimated by regressional analysis)

LEAST SQUARES REGRESSION: $Y = 2348.726 + 255.6722 X$

TOTAL SOLAR IRRADIANCE MEASURED DURING EXPOSURE PERIOD (W / m²)

WEATHERING DURATION 4 HOURS
WEATHERING DURATION 8 HOURS

AVERAGED HOURLY SOLAR IRRADIANCE RECORDED (W / m²)

JULIAN DAY

Hour Ending	160	161	162	163	164	165	166	167	168
600									
700									
800									
900					289.2				
1000	562				574.9				
1100	687.8				785				
1200	600.1				788				
1300	331				828				
1400	185.7				935				
1500					990				
1600					912				
1700									
1800									
1900									
2000									
2100									
TOTAL DAY	2366.6				6102.1				

TOTAL SOLAR IRRADIANCE MEASURED DURING EXPOSURE PERIOD (W / m²)

WEATHERING DURATION 4 DAYS AVERAGED HOURLY SOLAR IRRADIANCE RECORDED (W / m²)

JULIAN DAY

HOUR ENDING	174	175	176	177	178	179	180	182	183
600		0	0	0	0				
700		5.744	5.351	4.474	3.587				
800		85.6	82.3	83.6	17.98				
900		206.8	261.8	253.9	29.04				
1000		327.8	479	461.8	190.8				
1100	669	557.5	680.1	610.8					
1200	799	706	824	779					
1300	919	792	919	875					
1400	1027	875	943	882					
1500	886	865	820	852					
1600	898	639.9	613.6	886					
1700	647.6	613	498.7	693.8					
1800	484.7	480.7	282.9	528.1					
1900	271.5	272.2	152.2	255					
2000	74.3	79.9	76.6	98.7					
2100	3.488	5.316	0.973	1.701					
TOTAL DAY	6679.588	6512.46	6639.524	7265.875	241.407				

TOTAL SOLAR IRRADIANCE MEASURED DURING EXPOSURE PERIOD (W / m²)

WEATHERING DURATION 4 DAYS AVERAGED HOURLY SOLAR IRRADIANCE RECORDED (W / m²)

JULIAN DAY

HOUR ENDING	132	133	134	135	136	137	138	139	140
600		0	0	0	0				
700		4.438	5.417	4.468	4.315				
800		80.4	56.93	45.49	43.91				
900		323.8	259	280.3	311.4				
1000		539.3	471.7	601.1	577.7				
1100		599.7	667.2	698.5	675.7				
1200	921	685.1	767	850	780				
1300	998	562.6	1037	961					
1400	1019	898	938	1083					
1500	991	929	888	954					
1600	909	836	917	900					
1700	598.1	701	542.2	742					
1800	238.6	486.9	460.8	529.1					
1900	159	228.5	212.6	265.6					
2000	21.19	44.51	48.43	66.28					
2100	0.399	0.467	0.538	0.551					
TOTAL DAY	5855.289	6919.715	7271.815	7981.389	2393.025				

TOTAL SOLAR IRRADIANCE MEASURED DURING EXPOSURE PERIOD (W / m²)

WEATHERING DURATION 7 DAYS AVERAGED HOURLY SOLAR IRRADIANCE RECORDED (W / m²)

JULIAN DAY

HOUR ENDING	166	167	168	169	170	171	172	173	174
600		0	0	0	0	0	0	0	
700		6.116	6.077	6.61	6.112	3.353	3.919	7.19	
800		76.7	93.3	94.5	82.4	38.61	44.08	56.17	
900	369	284.4	244	308.7	337.4	150.1	157.8	236.3	
1000	351	523.1	487.8	481.2	555.2	340.4	465.9		
1100	654	642.9	727	569.4	758	570.7	588.5		
1200	831	771	563.8	855	712	653.5	777		
1300	790	876	782	594	1010	929	938		
1400	383.8	1010	657.8	724	717	1018	998		
1500	512.8	942	323.9	522.7	533.6	985	916		
1600	774	760	382	582.6	286.7	417	793		
1700	679.6	749	383.2	707	92.6	562.6	526.3		
1800	514.7	568.8	472.8	125	166.9	274.6	153.5		
1900	231.4	172	212.1	32.99	146.1	113.5	54.76		
2000	36.65	35.92	56.37	70.1	80.6	67.67	20.8		
2100	2.514	2.252	1.909	1.551	4.065	2.55	1.094		
TOTAL DAY	6130.464	7420.188	5394.056	5675.351	5488.677	6126.583	6438.653	299.66	

9.6 APPENDIX F

PERCENTAGE OF CRUDE OIL MASS LOST TO EVAPORATION DURING WEATHERING PERIOD

EVAPORATIVE MASS REDUCTION VS. WEATHERING PERIOD

Weathering Period (hours)	Initial Weight (g)	Oil Input (g)	Final Weight (g)	Weight Reduction (g)	Percent Loss %
0	N/A	N/A	N/A	0	0
4	2056.5	221.7	2045.7	10.8	4.871
8	2065.5	217.9	2031.4	34.1	15.649
24	2077.7	219.5	2043.9	33.8	15.399
96	2076.2	218.9	2029.4	46.8	21.38
168	2075.7	220	2024.9	50.8	23.091

9.7 APPENDIX G

DENSITY AND SPECIFIC GRAVITY OF WEATHERED ARABIAN CRUDE OIL SAMPLES

OIL DENSITY VS. WEATHERING PERIOD

Weathering Period (hours)	Initial Weight (g)	Final Weight (g)	delta (g)	Pycnometer Volume (mL)	Oil Density (g/mL)	Pycnometer Constant	Oil Density Corrected (g/mL)	Specific Gravity
0	14.933	23.8478	8.9148	10	0.89148	0.9948	0.8868443	0.889334
4	14.933	24.1986	9.2656	10	0.92656	0.9948	0.92174189	0.92433
8	14.933	24.285	9.352	10	0.9352	0.9948	0.93033696	0.932949
24	14.933	24.2999	9.3669	10	0.93669	0.9948	0.93181921	0.934436
96	14.9328	24.3986	9.4658	10	0.94658	0.9948	0.94165778	0.944302
168	14.9328	24.4518	9.519	10	0.9519	0.9948	0.94695012	0.949609
96	14.933	24.434	9.501	10	0.9501	0.9948	0.94515948	0.947813

Oil Density vs. Weathering Period

Oil Specific Gravity vs. Weathering Period

9.8 APPENDIX H

OIL-WATER INTERFACIAL SURFACE TENSION OF WEATHERED ARABIAN CRUDE OIL SAMPLES

OIL-WATER INTERFACIAL SURFACE TENSION VS. WEATHERING PERIOD

Pre-Test Calibration with Hexane-Water

Weathering Period (hours)	Apparent Tension (dynes/cm)	Density Hexane (g/mL)	Correction Factor	Absolute Tension (dynes/cm)	Standard Value (dynes/cm)	Calibration Constant
0	46.6	0.6603	0.98971559	46.1207	51.1	1.108
4	47.5	0.6603	0.99175244	47.1082	51.1	1.085
8	49.6	0.6603	0.99644566	49.4237	51.1	1.034
24	49.8	0.6603	0.99688841	49.645	51.1	1.029
96	48.2	0.6603	0.99332597	47.8783	51.1	1.067
168	49.5	0.6603	0.99622401	49.313	51.1	1.036

Oil-Water IFST Determination

Weathering Period (hours)	Apparent Tension (dynes/cm)	Density Oil (g/mL)	Correction Factor	Absolute Tension (dynes/cm)	Calibration Constant	Interfacial Tension (dynes/cm)
0	26.8	0.8868	1.0602997	28.41603196	1.108	31.485
	28.4	0.8868	1.06894859	30.35813996	1.108	33.637
4	26.5	0.9217	1.12035009	29.68927739	1.085	32.213
	26	0.9217	1.11694031	29.04044806	1.085	31.509
8	25.8	0.9303	1.13773491	29.35356068	1.034	30.351
	22.6	0.9303	1.11353675	25.16593055	1.034	26.022
24	25.9	0.9318	1.14279826	29.59847493	1.029	30.457
	24.6	0.9318	1.13304144	27.87281942	1.029	28.681
96	23.2	0.9416	1.15297883	26.74910886	1.067	28.541
	21.6	0.9416	1.13912669	24.6051365	1.067	26.254
168	20.9	0.947	1.15253746	24.08803291	1.036	24.955
	18.6	0.947	1.13023588	21.02238737	1.036	21.779

**Oil-Water Interfacial Surface Tension versus
Weathering Period**

9.9 APPENDIX I

TOTAL ION CHROMATOGRAMS AND SELECTED ION CHROMATOGRAMS FOR WEATHERED ARABIAN CRUDE OIL SAMPLES, AS DETERMINED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

- UNWEATHERED ARABIAN CRUDE OIL SAMPLE

- WEATHERING PERIODS

- 8 HOURS**
- 24 HOURS**
- 4 DAYS**
- 7 DAYS**

INDEX TO REFERENCED COMPOUND PEAKS
(REFER TO UNWEATHERED SAMPLE OUTPUT - FILE DJBNO.D)

<u>ION NUMBER</u>	<u>PEAK NUMBER</u>	<u>COMPOUND NAME</u>
57	1	n-C11
	2	n-C19
	3	n-C30
128	1	Naphthalene
142	1	2-Methyl-Naphthalene
	2	1-methyl-Naphthalene
156	1	1+2 Et Naphthalene
	2	2,6 di-methyl Naphthalene 2,7 di-methyl Naphthalene
	3	1,3 + 1,7 di-methyl Naphthalene
	4	1,6 di-methyl Naphthalene
	5	2,3 + 1,4 di-methyl Naphthalene 1,5 di-methyl Naphthalene
	6	1,2 di-methyl Naphthalene
178	1	Phenanthrene

INDEX TO REFERENCED COMPOUND PEAKS
(REFER TO UNWEATHERED SAMPLE OUTPUT - FILE DJBNO.D)

<u>ION NUMBER</u>	<u>PEAK NUMBER</u>	<u>COMPOUND NAME</u>
191	1	C29 $\alpha\beta$ Hopane
	2	C30 $\alpha\beta$ Hopane
	3	C31 $\alpha\beta$ S Hopane - double peak C31 $\alpha\beta$ R Hopane
	4	C32 $\alpha\beta$ S Hopane - double peak C32 $\alpha\beta$ R Hopane
	5	C33 $\alpha\beta$ S Hopane - double peak C33 $\alpha\beta$ R Hopane
	6	C34 $\alpha\beta$ S Hopane - double peak C34 $\alpha\beta$ R Hopane
	7	C35 $\alpha\beta$ S Hopane - double peak C35 $\alpha\beta$ R Hopane
192	1	methyl-Phenanthrenes
206	1	di-methyl-Phenanthrenes

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.547	VV	0.073	15075979	5.458	5.612
2	5.708	VV	0.069	48386570	5.612	5.978
3	6.413	PV	0.057	97500416	6.324	6.576
4	6.978	VV	0.066	9588350	6.880	7.054
5	7.245	VV	0.054	26553756	7.184	7.324
6	7.381	VB	0.058	23563487	7.324	7.655
7	7.766	BV	0.056	7939502	7.655	7.853
8	7.964	VV	0.055	23848731	7.853	8.015
9	8.059	VV	0.051	20976960	8.015	8.166
10	8.226	VV	0.052	23800202	8.166	8.383
11	9.036	VV	0.052	118452450	8.927	9.137
12	9.487	VV	0.054	8668229	9.439	9.540
13	9.588	VV	0.044	14356037	9.540	9.656
14	9.935	VV	0.061	5379326	9.850	9.982
15	10.024	VV	0.048	6750258	9.982	10.156
16	10.513	VV	0.045	13614974	10.460	10.566
17	10.613	VV	0.045	8575962	10.566	10.672
18	10.735	VV	0.049	14439242	10.672	10.832
19	10.900	VV	0.047	17066874	10.832	11.006
20	11.727	VV	0.048	120933750	11.622	11.780
21	11.987	VV	0.047	3874964	11.929	12.032
22	12.079	VV	0.061	10441417	12.032	12.176
23	12.371	PV	0.044	5725722	12.321	12.456
24	13.090	VV	0.063	19399637	12.987	13.177
25	13.235	VV	0.042	6412792	13.177	13.297
26	13.373	VV	0.043	13350315	13.297	13.472
27	13.533	PV	0.041	14140551	13.472	13.582
28	14.339	VV	0.051	114841286	14.199	14.415
29	14.621	VV	0.041	20583392	14.561	14.673
30	15.586	VV	0.063	15378089	15.490	15.687
31	15.761	VV	0.046	6409545	15.687	15.812
32	15.900	VV	0.048	11960414	15.812	15.971
33	16.072	PV	0.066	25339623	15.971	16.175
34	16.819	VV	0.052	106686979	16.665	16.895
35	17.030	VV	0.053	5524586	16.991	17.081
36	17.169	VV	0.051	10158662	17.081	17.233
37	17.956	PV	0.055	11938886	17.778	17.997
38	18.027	VV	0.050	4523169	17.997	18.085
39	18.151	VV	0.047	6085014	18.085	18.208
40	18.293	VV	0.046	10260024	18.208	18.352
41	18.446	PV	0.047	10933279	18.352	18.493
42	18.556	VV	0.045	13313215	18.493	18.612
43	19.168	BV	0.055	91094752	18.973	19.250
44	20.216	PV	0.075	10276881	20.075	20.259
45	20.474	VV	0.069	13937987	20.349	20.514
46	20.559	VV	0.046	6921685	20.514	20.619
47	20.706	VV	0.045	8108983	20.619	20.756
48	21.383	PV	0.055	69947566	21.139	21.448
49	22.361	PV	0.075	8800797	22.143	22.403
50	22.440	VV	0.045	2870916	22.403	22.528
51	22.698	BV	0.044	5595751	22.634	22.752
52	22.844	PB	0.046	5221281	22.752	22.988
53	23.479	BV	0.063	62429098	22.988	23.538
54	24.391	VV	0.085	18453530	24.177	24.445
55	24.872	VV	0.049	4474802	24.785	24.982
56	25.467	PV	0.070	54064464	24.982	25.610

57	27.355	VV	0.059	33921607	27.173	27.401
58	27.456	VV	0.063	10004333	27.401	27.617
59	29.155	VV	0.058	22929922	28.984	29.213
60	30.872	VV	0.047	17475344	30.749	30.925
61	32.512	VV	0.048	16539060	32.178	32.566
62	34.082	VV	0.043	13096075	33.968	34.136
63	35.584	PV	0.044	11155228	35.401	35.636
64	37.029	BV	0.045	10782926	36.884	37.162
65	38.415	VV	0.049	10076752	38.219	38.593
66	39.750	BV	0.048	9890311	39.481	39.961
67	41.039	BV	0.045	7395275	40.909	41.235
68	42.281	BB	0.049	7228837	42.050	42.420
69	43.481	PB	0.048	6512714	43.212	43.631
70	44.645	BB	0.045	5505069	44.436	44.771
71	45.894	BV	0.053	4879237	45.701	45.989
72	47.313	BB	0.060	4446287	47.234	47.503

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.495	BV	0.059	25658692	5.432	5.644
2	5.714	VV	0.075	38552454	5.644	6.103
3	6.237	VV	0.054	21131820	6.103	6.543
4	7.781	BV	0.050	11043928	7.559	7.922
5	7.980	VV	0.051	2879950	7.922	8.027
6	8.063	VV	0.048	1739851	8.027	8.151
7	8.426	BB	0.045	2582526	8.364	8.585
8	8.859	BV	0.050	3049214	8.748	9.045
9	9.226	BV	0.058	1402208	9.150	9.438
10	9.563	PV	0.061	1902571	9.438	9.639
11	9.690	VB	0.045	766243	9.639	9.811
12	10.282	BV	0.045	851196	10.137	10.333
13	10.378	VV	0.045	961411	10.333	10.458
14	10.524	VV	0.064	6815075	10.458	10.693
15	10.762	VB	0.047	1283044	10.693	10.894
16	11.044	BV	0.043	1536711	10.971	11.078
17	11.117	VV	0.045	2425560	11.078	11.218
18	11.280	VV	0.052	2010984	11.218	11.364
19	11.789	BV	0.078	2266349	11.565	11.876
20	12.148	VV	0.047	684965	12.080	12.184
21	12.224	PV	0.037	513071	12.184	12.259
22	12.627	BV	0.044	801826	12.495	12.670
23	12.792	VV	0.064	2428560	12.670	12.891
24	13.043	VV	0.063	2795374	12.995	13.149
25	13.210	VV	0.045	1253784	13.149	13.230
26	13.252	VV	0.044	1411414	13.230	13.301
27	13.399	VV	0.075	2280753	13.345	13.509
28	14.210	VV	0.074	1318906	14.149	14.321
29	15.819	PV	0.044	1002756	15.658	15.885
30	18.315	PV	0.048	715469	18.214	18.364

File: C:\CHEMPC\DATA\DJBNO.D
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Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.716	VB	0.076	8379627	5.633	5.988
2	6.237	BB	0.053	3977255	6.179	6.448
3	7.007	BB	0.051	4589278	6.946	7.205
4	7.981	BV	0.049	27923151	7.904	8.026
5	8.064	VV	0.049	20846877	8.026	8.154
6	8.202	VV	0.050	8751221	8.154	8.361
7	8.429	VB	0.045	26740532	8.361	8.626
8	8.860	BB	0.049	36336030	8.776	9.131
9	9.269	BB	0.042	3334606	9.208	9.409
10	9.577	BB	0.048	13609137	9.495	9.802
11	10.285	BV	0.041	3974595	10.223	10.329
12	10.379	VV	0.045	11114646	10.329	10.459
13	10.515	VV	0.059	12164410	10.459	10.693
14	10.762	PB	0.045	18976972	10.693	10.923
15	11.044	BV	0.041	1489648	10.981	11.085
16	11.714	PV	0.089	3847221	11.460	11.881
17	12.070	VV	0.054	1939824	11.999	12.184
18	12.793	VV	0.055	1683786	12.681	12.894
19	13.084	VV	0.051	3092496	12.992	13.160
20	13.254	VV	0.049	3340789	13.160	13.328
21	13.420	VB	0.047	9383707	13.328	13.587
22	14.858	VV	0.060	2116174	14.811	14.930
23	15.613	PV	0.050	1453963	15.505	15.717
24	15.944	VV	0.047	4235260	15.859	16.059
25	17.199	PV	0.042	1515906	17.141	17.286
26	18.395	VB	0.048	3769352	18.318	18.494
27	20.737	VB	0.049	2673957	20.669	20.832
28	22.949	VV	0.053	2048063	22.859	23.043
29	25.057	VB	0.048	1527330	24.969	25.145

File: C:\CHEMPC\DATA\DJBNO.D
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Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.861	BB	0.051	4560365	8.738	9.064
2	9.554	BV	0.050	5798508	9.486	9.641
3	9.692	VB	0.044	3720925	9.641	9.850
4	10.284	BV	0.044	3804080	10.214	10.343
5	10.555	VV	0.056	13552194	10.453	10.693
6	11.043	BV	0.043	11803408	10.961	11.077
7	11.117	VV	0.044	20444244	11.077	11.216
8	11.280	VV	0.046	12016351	11.216	11.355
9	11.398	VV	0.047	1921602	11.355	11.536
10	11.792	VV	0.065	10668638	11.536	11.894
11	11.968	VV	0.039	2144751	11.894	12.013
12	12.134	VV	0.040	3052900	12.086	12.177
13	12.225	VB	0.042	7499142	12.177	12.370
14	12.627	BV	0.042	3913002	12.562	12.692
15	12.793	VV	0.050	6894519	12.692	12.831
16	12.855	VV	0.041	2696530	12.831	12.897
17	12.933	VV	0.040	1815928	12.897	12.980
18	13.041	VV	0.048	15244646	12.980	13.176
19	13.252	VV	0.048	10085709	13.176	13.324
20	13.389	VV	0.051	13275642	13.324	13.512
21	13.569	VV	0.042	1270661	13.512	13.596
22	13.640	VV	0.046	4209429	13.596	13.748
23	14.048	VV	0.050	6113374	13.924	14.147
24	15.297	VV	0.044	2440834	15.251	15.377
25	15.763	BV	0.044	2242469	15.705	15.850
26	15.934	VV	0.047	5399477	15.850	16.014
27	16.226	VV	0.052	1754394	16.154	16.328
28	16.578	PV	0.041	1381600	16.449	16.628
29	17.694	VV	0.046	1808339	17.633	17.745
30	18.310	PV	0.046	1773819	18.221	18.369
31	20.016	VV	0.046	1540369	19.955	20.056
32	20.609	VV	0.046	1632737	20.521	20.695
33	22.810	VV	0.051	1493405	22.672	22.867

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.712	VB	0.062	608035	5.644	5.844
2	6.415	BB	0.064	5661243	6.333	6.630
3	14.000	VV	0.057	5047699	13.939	14.154
4	14.217	VV	0.047	414150	14.154	14.271
5	18.176	PV	0.044	382621	18.094	18.220
6	19.684	VV	0.070	887534	19.580	19.738
7	19.794	VV	0.062	1009582	19.738	19.886
8	20.134	PV	0.033	136503	20.043	20.163
9	21.616	PV	0.071	751310	21.485	21.686
10	21.880	PV	0.044	274630	21.809	21.925

File: C:\CHEMPC\DATA\DJBNO.D
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File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.963	BV	0.068	666293	7.847	8.021
2	8.226	PB	0.047	364104	8.153	8.297
3	9.041	BB	0.056	5444664	8.930	9.141
4	16.791	PV	0.058	6340792	16.707	17.022
5	17.162	VV	0.056	8156733	17.075	17.459
6	19.692	PV	0.063	709875	19.567	19.735
7	19.789	VB	0.051	538315	19.735	19.903

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

Ion 156.00: DJBNO.D

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.730	BB	0.054	5256141	11.623	11.795
2	19.114	BV	0.067	2047379	19.011	19.270
3	19.389	VV	0.084	5852124	19.270	19.557
4	19.690	VV	0.061	8638323	19.557	19.740
5	19.790	VV	0.056	7481090	19.740	19.980
6	20.187	VV	0.085	6253198	19.980	20.355
7	20.465	VB	0.058	2215504	20.355	20.669

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	20.856	VV	0.069	280024	20.749	20.927
2	21.369	VV	0.094	338418	21.190	21.445
3	21.574	VV	0.077	271095	21.498	21.686
4	21.878	VV	0.061	263028	21.798	21.945
5	22.250	VV	0.082	243910	22.126	22.368
6	25.659	VV	0.064	86400	25.619	25.697
7	25.731	VV	0.049	118114	25.697	25.785
8	26.111	PV	0.052	70672	26.013	26.170
9	27.283	VV	0.085	855607	27.054	27.386
10	27.435	VV	0.054	112801	27.386	27.513
11	27.792	PV	0.054	148555	27.741	27.838
12	27.877	VV	0.052	166373	27.838	27.924
13	27.971	VV	0.052	165297	27.924	28.040
14	29.375	VV	0.032	49440	29.351	29.416
15	29.522	VV	0.070	259556	29.455	29.674
16	29.819	VV	0.049	89714	29.773	29.844
17	29.873	VV	0.052	120720	29.844	29.969
18	30.300	VV	0.060	220654	30.238	30.360
19	30.674	VV	0.092	320976	30.614	30.754
20	30.966	VV	0.066	156408	30.863	30.982
21	31.057	VV	0.069	402684	30.982	31.138
22	31.280	VV	0.055	176713	31.229	31.332
23	31.654	VV	0.066	168417	31.548	31.703
24	31.772	VV	0.074	224181	31.703	31.866
25	32.162	VV	0.070	226171	32.073	32.218
26	32.421	PV	0.051	62768	32.353	32.463
27	32.533	VV	0.057	109468	32.463	32.556
28	32.715	VV	0.070	189056	32.643	32.836
29	32.953	VV	0.043	45720	32.930	33.018
30	33.588	BV	0.055	83956	33.540	33.634
31	45.611	VV	0.074	683938	45.491	45.721
32	46.297	VV	0.055	90077	46.175	46.354

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.746	PV	0.052	439574	29.618	29.805
2	31.650	PV	0.056	560410	31.565	31.735
3	35.759	VV	0.044	279828	35.702	35.835
4	39.356	VV	0.053	548868	39.289	39.481
5	43.507	BV	0.056	678613	43.401	43.632
6	44.032	VV	0.051	1457513	43.963	44.107
7	44.307	VV	0.066	557561	44.216	44.369
8	45.610	VV	0.063	6422436	45.524	45.864
9	46.302	VV	0.061	431158	46.229	46.405
10	46.750	PV	0.063	4688143	46.601	46.818
11	46.845	VV	0.061	849752	46.818	46.955
12	47.366	VV	0.067	458954	47.257	47.502
13	48.266	VV	0.067	2977944	48.153	48.369
14	48.464	VV	0.080	2380720	48.369	48.614
15	48.911	VV	0.109	1185106	48.685	48.992
16	49.633	PV	0.082	1908582	49.478	49.735
17	49.935	VV	0.083	1509954	49.832	50.176
18	50.731	VV	0.078	521083	50.600	50.894
19	51.519	VV	0.084	1482401	51.357	51.701
20	52.014	PV	0.086	928180	51.902	52.152
21	53.919	VV	0.139	1581456	53.807	54.144
22	54.643	BV	0.094	683980	54.479	54.797
23	56.028	VV	0.118	1197903	55.895	56.212
24	56.815	VV	0.105	1274021	56.620	56.954
25	57.864	VV	0.115	1316052	57.735	58.074

File: C:\CHEMPC\DATA\DJBNO.D
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Date Acquired: 21 Jul 94 3:03 pm
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Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.328	VV	0.092	758529	29.103	29.394
2	29.456	VV	0.083	721210	29.394	29.554
3	29.745	VV	0.070	1469423	29.602	29.812
4	29.856	VV	0.068	629511	29.812	30.006
5	44.031	VV	0.061	405305	43.877	44.095
6	45.609	VV	0.066	1624277	45.471	45.724
7	46.751	VV	0.060	1044278	46.601	46.816
8	48.261	VV	0.068	713019	48.160	48.373
9	48.459	VV	0.068	550510	48.373	48.562
10	49.627	VV	0.075	473619	49.470	49.736
11	49.944	VV	0.079	329270	49.849	50.066
12	51.529	PV	0.076	320983	51.394	51.663

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

File: C:\CHEMPC\DATA\DJBNO.D
Operator: DON. B
Date Acquired: 21 Jul 94 3:03 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE UNWEATHERED
Misc Info: 9 X ORIGINAL
ALS vial: 1

ARABIAN CRUDE UNWEATHERED

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.136	VV	0.077	399847	30.982	31.189
2	31.239	VV	0.075	439166	31.189	31.318
3	31.369	VV	0.053	406179	31.318	31.414
4	31.651	VV	0.068	2327208	31.524	31.724
5	31.776	VV	0.060	1065349	31.724	31.836
6	31.879	VV	0.059	862282	31.836	31.964
7	32.009	VV	0.057	663452	31.964	32.236
8	45.583	VV	0.091	472303	45.497	45.739

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.693	VB	0.069	7035124	5.605	5.892
2	6.387	BV	0.057	20995865	6.323	6.553
3	7.233	VV	0.054	8277905	7.173	7.317
4	7.371	VB	0.052	7028294	7.317	7.559
5	7.759	BV	0.056	3096337	7.646	7.842
6	7.951	VV	0.055	10057375	7.842	8.003
7	8.046	VV	0.053	8650131	8.003	8.158
8	8.213	VV	0.053	10656499	8.158	8.373
9	9.011	PV	0.046	60991767	8.910	9.126
10	9.478	VV	0.054	4849581	9.428	9.530
11	9.577	VV	0.044	8560773	9.530	9.648
12	10.017	VB	0.049	4293152	9.972	10.147
13	10.504	VV	0.045	9145943	10.450	10.556
14	10.602	VV	0.044	5837024	10.556	10.660
15	10.725	VV	0.048	9959635	10.660	10.827
16	10.889	VV	0.049	11711909	10.827	10.997
17	11.709	VV	0.047	91012764	11.615	11.766
18	11.980	VV	0.048	3065433	11.919	12.024
19	12.072	VV	0.057	8166252	12.024	12.168
20	12.365	PV	0.046	4800774	12.314	12.453
21	13.081	VV	0.058	15381123	12.981	13.170
22	13.226	VV	0.043	5033875	13.170	13.291
23	13.366	VV	0.042	10899934	13.291	13.458
24	13.525	PV	0.041	12134940	13.458	13.576
25	13.824	VV	0.058	4096614	13.687	13.899
26	14.323	VV	0.050	98322412	14.190	14.406
27	14.525	VV	0.046	3008573	14.406	14.553
28	14.612	VV	0.041	18635409	14.553	14.665
29	15.580	VV	0.062	14179765	15.483	15.678
30	15.754	VV	0.048	6318057	15.678	15.816
31	15.894	VV	0.046	10978054	15.816	15.969
32	16.062	PV	0.065	23048394	15.969	16.175
33	16.808	VV	0.047	97163952	16.669	16.887
34	17.027	VV	0.051	5116747	16.985	17.075
35	17.164	VV	0.051	9804026	17.075	17.232
36	17.573	PV	0.047	2902056	17.462	17.616
37	17.951	PV	0.055	11422453	17.773	17.991
38	18.022	VV	0.046	4643487	17.991	18.082
39	18.146	VV	0.046	5822821	18.082	18.206
40	18.288	VV	0.047	10329864	18.206	18.355
41	18.441	PV	0.048	10308599	18.355	18.489
42	18.551	VV	0.043	13073351	18.489	18.610
43	19.160	BV	0.055	88903425	18.992	19.243
44	19.315	VV	0.089	6487545	19.243	19.403
45	20.214	PV	0.065	10818821	20.071	20.256
46	20.282	VV	0.045	3639874	20.256	20.329
47	20.468	VV	0.066	14285848	20.329	20.510
48	20.553	VV	0.044	7133560	20.510	20.617
49	20.701	VV	0.044	8232121	20.617	20.750
50	21.377	PV	0.052	74795875	21.141	21.446
51	21.499	VV	0.050	1689507	21.446	21.553
52	22.354	PV	0.075	11327238	22.147	22.397
53	22.438	VV	0.070	5854250	22.397	22.516
54	22.563	VV	0.049	3960388	22.516	22.617
55	22.695	VV	0.049	8420291	22.617	22.752
56	22.842	VV	0.048	6889274	22.752	22.914

57	23.476	VV	0.059	64601672	23.276	23.532
58	24.387	VV	0.081	19869995	24.171	24.441
59	24.726	VV	0.053	4767775	24.639	24.780
60	24.870	VV	0.047	5045427	24.780	24.917
61	25.466	VV	0.070	64929327	25.070	25.604
62	26.257	PV	0.060	5084242	26.139	26.304
63	26.654	PV	0.044	2753712	26.571	26.735
64	26.794	VV	0.039	2492988	26.735	26.844
65	27.357	VV	0.055	38872630	27.172	27.402
66	27.454	VV	0.063	12274406	27.402	27.618
67	28.084	VV	0.067	4167740	27.999	28.144
68	28.628	VV	0.046	2616589	28.548	28.682
69	28.933	VV	0.061	3756549	28.826	28.987
70	29.156	VV	0.045	24957228	28.987	29.211
71	30.872	BV	0.043	19297805	30.770	30.983
72	32.038	VV	0.050	3210421	31.969	32.103
73	32.513	VV	0.043	17653543	32.397	32.568
74	34.083	PV	0.046	15984975	33.893	34.138
75	35.587	PV	0.041	12794190	35.439	35.644
76	37.031	PV	0.043	12181306	36.913	37.084
77	38.419	VV	0.049	12385312	38.225	38.581
78	39.755	BV	0.046	11089453	39.635	39.904
79	41.042	PV	0.046	8921454	40.927	41.187
80	42.286	PV	0.045	8582920	42.101	42.393
81	43.487	PV	0.046	8102568	43.301	43.564
82	44.652	PV	0.047	7311396	44.398	44.732
83	45.903	PV	0.051	6368945	45.684	45.981
84	47.328	BV	0.064	6190212	47.167	47.608
85	48.980	BB	0.074	6018890	48.672	49.247

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.494	BV	0.062	2933544	5.432	5.647
2	5.709	VV	0.073	5675458	5.647	6.036
3	6.232	VV	0.060	4144450	6.169	6.477
4	7.776	BV	0.050	3625473	7.655	7.918
5	7.970	VV	0.048	1126978	7.918	8.019
6	8.054	VV	0.051	764822	8.019	8.152
7	8.193	VV	0.045	372194	8.152	8.290
8	8.422	VV	0.048	1135759	8.349	8.533
9	8.849	PV	0.052	1536692	8.761	9.032
10	9.214	PV	0.069	681563	9.156	9.365
11	9.561	BV	0.061	973875	9.495	9.635
12	9.683	VV	0.046	427914	9.635	9.766
13	10.277	PV	0.046	514518	10.185	10.329
14	10.373	VV	0.050	571273	10.329	10.449
15	10.520	VV	0.063	4382843	10.449	10.692
16	10.754	VV	0.049	837855	10.692	10.854
17	11.032	PV	0.042	1091868	10.962	11.070
18	11.107	VV	0.049	1616650	11.070	11.217
19	11.275	VV	0.053	1340466	11.217	11.354
20	11.783	VV	0.087	1690958	11.628	11.889
21	11.958	VV	0.051	311231	11.889	11.995
22	12.138	VV	0.050	737932	12.080	12.177
23	12.216	VV	0.048	777894	12.177	12.256
24	12.279	VV	0.048	362868	12.256	12.333
25	12.620	VV	0.048	708240	12.480	12.666
26	12.787	VV	0.068	2050190	12.666	12.888
27	12.931	VV	0.083	569692	12.888	12.990
28	13.035	VV	0.064	2316884	12.990	13.144
29	13.198	VV	0.038	834034	13.144	13.214
30	13.244	VV	0.054	1401168	13.214	13.294
31	13.403	VV	0.080	2001944	13.338	13.501
32	13.874	VV	0.056	361328	13.820	13.922
33	14.034	VV	0.097	1451437	13.922	14.140
34	14.207	VV	0.072	1210614	14.140	14.344
35	14.541	VV	0.090	658134	14.410	14.630
36	14.693	VV	0.042	356171	14.630	14.721
37	14.847	VV	0.067	763444	14.797	14.913
38	15.121	VV	0.053	680019	15.073	15.163
39	15.199	VV	0.044	724141	15.163	15.241
40	15.285	VV	0.058	1109191	15.241	15.391
41	15.598	VV	0.068	759433	15.501	15.654
42	15.816	VV	0.065	1536583	15.713	15.884
43	15.936	VV	0.052	952393	15.884	15.983
44	16.279	PV	0.079	821430	16.165	16.341
45	16.578	VV	0.066	657665	16.442	16.616
46	17.194	VV	0.057	480897	17.134	17.226
47	17.342	VV	0.067	623136	17.292	17.411
48	17.690	VV	0.048	629283	17.630	17.743
49	18.055	VV	0.081	605278	17.948	18.136
50	18.310	VV	0.056	1129495	18.207	18.354
51	18.387	VV	0.048	448155	18.354	18.465
52	20.015	VV	0.055	544550	19.966	20.094
53	20.667	VV	0.066	848252	20.545	20.704
54	20.733	VV	0.051	333880	20.704	20.784
55	22.247	VV	0.044	438320	22.184	22.311
56	22.896	VV	0.064	776089	22.859	23.017

57	24.361	VV	0.060	430962	24.298	24.522
58	25.010	VV	0.090	826643	24.818	25.154
59	28.917	PV	0.051	297998	28.865	29.004
60	45.621	PV	0.062	431245	45.517	45.768

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.702	BB	0.064	1179983	5.643	5.882
2	7.002	BB	0.050	1059485	6.956	7.147
3	7.971	BV	0.046	10647658	7.895	8.018
4	8.055	VV	0.051	8094407	8.018	8.145
5	8.195	VV	0.048	3908351	8.145	8.355
6	8.421	VB	0.046	11540173	8.355	8.671
7	8.850	BB	0.048	18142558	8.767	9.121
8	9.260	BB	0.043	1623405	9.198	9.409
9	9.571	BB	0.047	7791088	9.486	9.802
10	10.280	BV	0.042	2387688	10.214	10.324
11	10.371	VV	0.046	7002869	10.324	10.453
12	10.509	VV	0.060	7719063	10.453	10.687
13	10.755	VV	0.045	12534963	10.687	10.981
14	11.035	PV	0.038	782894	10.981	11.077
15	11.713	BV	0.086	2770120	11.613	11.874
16	11.929	VV	0.044	757909	11.874	11.995
17	12.066	VV	0.055	1369026	11.995	12.177
18	12.790	VV	0.058	1302353	12.677	12.890
19	13.080	VV	0.051	2376711	12.989	13.162
20	13.247	VV	0.046	2707947	13.162	13.333
21	13.412	VV	0.050	7608946	13.333	13.590
22	14.541	VV	0.051	909215	14.411	14.627
23	14.770	VV	0.062	1119983	14.627	14.804
24	14.849	VV	0.069	2239671	14.804	14.977
25	15.608	VV	0.058	1414294	15.504	15.712
26	15.804	VV	0.055	1053652	15.712	15.855
27	15.938	VV	0.053	4423403	15.855	16.165
28	17.193	VV	0.048	1659905	17.134	17.278
29	18.266	VV	0.047	800779	18.210	18.319
30	18.389	VV	0.047	3577655	18.319	18.473
31	19.454	VV	0.063	1464942	19.334	19.511
32	20.736	VV	0.046	2812152	20.659	20.857
33	21.650	VV	0.048	890574	21.571	21.703
34	22.946	VV	0.048	2375953	22.859	23.084
35	25.050	VV	0.052	1893373	24.962	25.163
36	27.047	VV	0.053	1219818	26.987	27.167
37	28.948	VV	0.046	1026681	28.845	29.000
38	30.758	VV	0.056	945031	30.715	30.816
39	32.474	PV	0.041	519511	32.420	32.527

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Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.851	BB	0.049	2250765	8.786	9.006
2	9.547	BV	0.052	3082762	9.486	9.635
3	9.686	VB	0.046	2052123	9.635	9.840
4	10.280	BV	0.043	2274152	10.214	10.343
5	10.546	PV	0.055	8569139	10.456	10.683
6	11.035	PV	0.041	7817429	10.842	11.070
7	11.108	VV	0.044	13600153	11.070	11.208
8	11.273	PV	0.044	7706465	11.208	11.348
9	11.785	BV	0.064	7672716	11.661	11.895
10	11.958	VV	0.039	1531504	11.895	12.004
11	12.126	VV	0.045	2247936	12.076	12.169
12	12.217	VB	0.044	5912477	12.169	12.361
13	12.621	BV	0.044	2989571	12.562	12.687
14	12.786	VV	0.050	5246381	12.687	12.824
15	12.849	VV	0.039	2066165	12.824	12.891
16	12.926	VV	0.043	1334422	12.891	12.973
17	13.035	VV	0.051	12315303	12.973	13.174
18	13.245	VV	0.047	8053777	13.174	13.318
19	13.383	VV	0.051	10773465	13.318	13.509
20	13.562	VV	0.042	1036977	13.509	13.591
21	13.633	VV	0.045	3427866	13.591	13.743
22	14.041	VV	0.049	4595181	13.986	14.142
23	14.604	VV	0.042	936320	14.534	14.655
24	15.290	VV	0.044	2102928	15.247	15.374
25	15.757	BV	0.044	1990924	15.705	15.849
26	15.929	VV	0.047	4645429	15.849	16.009
27	16.066	VV	0.060	1313867	16.009	16.151
28	16.222	PV	0.046	1302924	16.151	16.320
29	16.574	BV	0.055	2134501	16.453	16.711
30	17.689	VV	0.045	1613889	17.634	17.742
31	18.099	VB	0.059	1422582	18.017	18.216
32	18.305	BV	0.046	1706382	18.226	18.361
33	20.013	VV	0.055	1521831	19.957	20.051
34	20.606	VV	0.041	1531509	20.525	20.676
35	22.247	VV	0.048	1468217	22.190	22.366
36	22.810	PV	0.052	1742588	22.647	22.868

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	6.389	BB	0.060	1379940	6.333	6.582
2	13.996	VV	0.055	3981706	13.932	14.138
3	14.209	VV	0.055	375417	14.138	14.268
4	16.807	VV	0.068	546754	16.701	16.951
5	18.172	BV	0.046	310604	18.072	18.221
6	19.680	VV	0.065	1006070	19.571	19.732
7	19.792	VV	0.065	1129199	19.732	19.858
8	20.130	PV	0.085	672983	19.960	20.172
9	20.466	VV	0.065	547808	20.354	20.547
10	21.614	PV	0.078	898652	21.457	21.708
11	21.877	VV	0.057	457199	21.807	21.923
12	22.138	VV	0.074	512744	22.053	22.193
13	22.439	VV	0.058	494774	22.343	22.510

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Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	9.012	BB	0.049	2962320	8.930	9.112
2	16.785	PV	0.055	5716887	16.712	17.011
3	17.156	PV	0.054	7124162	17.076	17.306
4	19.127	BV	0.068	587808	18.992	19.240
5	19.684	PV	0.059	790073	19.570	19.739
6	19.781	VV	0.055	510338	19.739	19.931

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Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.714	BB	0.059	3980771	11.613	11.786
2	19.111	BV	0.062	1982291	19.011	19.266
3	19.392	VV	0.094	5889575	19.266	19.559
4	19.682	VV	0.059	8586680	19.559	19.734
5	19.786	VV	0.056	7691937	19.734	19.979
6	20.187	VV	0.082	6381737	19.979	20.325
7	20.462	VV	0.058	2302703	20.361	20.663

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Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	20.849	PV	0.060	238342	20.737	20.947
2	21.571	PV	0.082	247812	21.479	21.678
3	21.876	VV	0.064	353750	21.791	22.036
4	22.252	PV	0.068	220982	22.124	22.309
5	25.728	VV	0.050	168929	25.669	25.804
6	27.264	VV	0.072	1095311	27.164	27.343
7	27.776	VV	0.081	409843	27.659	27.825
8	27.882	VV	0.056	257576	27.825	27.902
9	27.956	VV	0.084	524667	27.902	28.061
10	28.236	VV	0.076	357629	28.199	28.398
11	29.517	VV	0.065	206497	29.412	29.548
12	30.275	VV	0.080	332877	30.242	30.490
13	30.665	VV	0.079	354159	30.598	30.774
14	30.962	PV	0.066	215155	30.875	31.000
15	31.051	VV	0.068	367375	31.000	31.171
16	31.765	VV	0.039	88243	31.720	31.799
17	32.702	VV	0.078	229809	32.636	32.812
18	33.573	PV	0.062	132615	33.477	33.654
19	45.622	VV	0.069	746321	45.515	45.714

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Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.736	VV	0.062	794018	29.601	29.794
2	31.645	PV	0.057	662326	31.566	31.711
3	39.361	VV	0.055	572520	39.298	39.491
4	43.514	PV	0.057	864309	43.352	43.650
5	44.037	VV	0.050	1757105	43.965	44.110
6	44.311	VV	0.057	758744	44.229	44.431
7	45.620	VV	0.061	8529813	45.434	45.783
8	46.314	VV	0.053	570499	46.215	46.384
9	46.760	VV	0.063	6093274	46.613	46.829
10	46.862	VV	0.062	1033944	46.829	46.965
11	48.283	BV	0.066	3894831	48.011	48.381
12	48.480	VV	0.076	3176491	48.381	48.608
13	48.925	VV	0.113	1574577	48.747	49.052
14	49.657	VV	0.075	2431387	49.507	49.781
15	49.963	VV	0.071	1851716	49.846	50.105
16	51.547	VV	0.084	1636659	51.419	51.653
17	52.046	VV	0.082	1173324	51.930	52.170
18	53.954	BV	0.136	2025042	53.770	54.186
19	56.031	BV	0.147	1382194	55.706	56.190
20	56.841	BV	0.112	1572103	56.655	57.034
21	57.909	PV	0.143	1863628	57.442	58.159

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.329	VV	0.079	840150	29.187	29.383
2	29.437	VV	0.068	938615	29.383	29.539
3	29.735	VV	0.065	1757802	29.609	29.796
4	29.842	VV	0.060	816603	29.796	29.940
5	44.041	PV	0.051	380762	43.954	44.104
6	45.622	VV	0.064	2072037	45.270	45.783
7	46.765	PV	0.056	1058449	46.650	46.839
8	48.283	PV	0.074	927652	48.075	48.366
9	48.474	VV	0.083	719682	48.366	48.605
10	49.654	BV	0.075	495258	49.419	49.737
11	49.954	BV	0.071	372179	49.841	50.035
12	51.551	PV	0.069	342548	51.442	51.644

File: C:\CHEMPC\DATA\DJB8H.D
Operator: BOYE
Date Acquired: 21 Jul 94 9:25 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 8 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 8 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.358	VV	0.068	556129	31.301	31.422
2	31.645	VV	0.066	2660053	31.546	31.716
3	31.771	VV	0.071	1284284	31.716	31.826
4	31.866	VV	0.058	1037096	31.826	31.942
5	32.000	VV	0.065	779205	31.942	32.131
6	45.602	PV	0.090	578647	45.504	45.719

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.705	VV	0.065	1457876	5.615	5.846
2	6.394	BB	0.053	4466350	6.226	6.568
3	7.241	PV	0.048	1660297	7.181	7.314
4	7.381	VV	0.066	1335924	7.314	7.452
5	7.954	VV	0.045	1979577	7.850	8.008
6	8.050	VV	0.046	1814719	8.008	8.162
7	8.218	PV	0.042	2036702	8.162	8.295
8	9.002	VV	0.041	13980084	8.917	9.126
9	9.580	VV	0.039	1746994	9.535	9.645
10	10.505	VV	0.037	2098558	10.454	10.559
11	10.602	VV	0.038	1306076	10.559	10.669
12	10.724	PV	0.040	2187768	10.669	10.824
13	10.886	VV	0.043	2816872	10.824	10.997
14	11.690	PV	0.037	20135557	11.618	11.763
15	12.069	VV	0.036	1034390	12.024	12.091
16	12.365	PV	0.040	1067478	12.316	12.449
17	13.076	VV	0.050	3626072	12.976	13.171
18	13.222	VV	0.039	1208494	13.171	13.279
19	13.360	VV	0.039	2595731	13.279	13.465
20	13.522	PV	0.035	2832030	13.465	13.572
21	14.301	VV	0.037	21801028	14.082	14.399
22	14.607	VV	0.037	4139809	14.553	14.663
23	15.574	VV	0.037	2068551	15.484	15.603
24	15.622	VV	0.039	1142982	15.603	15.694
25	15.749	VV	0.043	1375935	15.694	15.827
26	15.888	VV	0.037	2485914	15.827	15.965
27	16.053	PV	0.063	5526508	15.965	16.157
28	16.786	VV	0.039	20410322	16.702	16.884
29	17.161	BV	0.036	1429567	17.094	17.237
30	17.947	VV	0.040	2102771	17.897	17.985
31	18.018	VV	0.049	1077178	17.985	18.087
32	18.141	VV	0.039	1367348	18.087	18.225
33	18.280	VV	0.039	2332776	18.225	18.355
34	18.434	PV	0.037	2350516	18.355	18.490
35	18.542	VV	0.036	2954755	18.490	18.604
36	19.135	VV	0.040	19615699	19.054	19.230
37	20.207	PV	0.062	2334779	20.068	20.247
38	20.274	VV	0.043	1075848	20.247	20.354
39	20.410	VV	0.040	1032575	20.354	20.427
40	20.459	VV	0.038	2164741	20.427	20.501
41	20.547	VV	0.038	1903887	20.501	20.620
42	20.694	PV	0.038	2128671	20.620	20.753
43	21.356	PV	0.039	16260494	21.271	21.443
44	22.347	BV	0.062	2394662	22.234	22.390
45	22.427	VV	0.050	1310629	22.390	22.516
46	22.687	VV	0.041	2025808	22.628	22.769
47	22.832	PV	0.039	1697239	22.769	22.907
48	23.455	PV	0.040	14542144	23.309	23.521
49	24.377	PV	0.069	5042016	24.226	24.432
50	24.718	VV	0.043	1186413	24.668	24.777
51	24.862	VV	0.042	1599633	24.777	24.917
52	25.448	PV	0.045	14180160	25.238	25.552
53	26.255	VV	0.053	1530892	26.130	26.293
54	26.645	PV	0.044	1032522	26.567	26.736
55	26.788	PV	0.037	878444	26.736	26.839
56	27.341	BV	0.045	10841083	27.107	27.389

57	27.447	VV	0.063	4240125	27.389	27.611
58	28.085	PV	0.059	1413274	27.991	28.138
59	28.619	PV	0.038	809059	28.550	28.673
60	29.142	VV	0.039	8054195	29.071	29.204
61	30.860	PV	0.040	7046677	30.784	30.966
62	32.032	PV	0.047	1082829	31.971	32.152
63	32.502	PV	0.039	6351692	32.433	32.608
64	34.072	PV	0.041	5593166	33.995	34.129
65	35.576	PV	0.037	4424238	35.488	35.630
66	37.022	BV	0.040	3983263	36.930	37.076
67	38.407	BV	0.042	3413534	38.355	38.577
68	39.742	VV	0.043	3529389	39.618	39.923
69	41.029	PV	0.045	2684248	40.921	41.177
70	42.271	VV	0.041	2187197	42.211	42.450
71	43.467	PV	0.045	1830083	43.354	43.552
72	44.631	VV	0.048	1889411	44.571	44.747
73	45.879	VB	0.048	1565059	45.808	46.041
74	47.294	PV	0.052	1354488	47.191	47.434

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.514	BV	0.059	534564	5.400	5.663
2	5.719	VV	0.080	1161175	5.663	5.999
3	6.248	PV	0.056	839682	6.175	6.372
4	7.794	BV	0.051	859048	7.746	7.941
5	7.976	VV	0.042	274380	7.941	8.029
6	8.069	VV	0.054	211697	8.029	8.172
7	8.430	BV	0.045	282127	8.383	8.519
8	8.859	BV	0.046	398165	8.668	8.972
9	9.576	BV	0.059	282274	9.504	9.661
10	10.293	BV	0.032	114793	10.188	10.347
11	10.383	VV	0.057	163844	10.347	10.468
12	10.531	PV	0.064	1039364	10.468	10.708
13	10.761	VV	0.050	250120	10.708	10.864
14	11.045	BV	0.043	278730	10.995	11.076
15	11.117	VV	0.047	408597	11.076	11.179
16	11.284	VV	0.065	380179	11.225	11.366
17	11.729	BV	0.048	197272	11.651	11.759
18	11.794	VV	0.045	250663	11.759	11.865
19	12.138	VV	0.051	176682	12.089	12.181
20	12.224	VV	0.048	209977	12.181	12.263
21	12.631	VV	0.040	148108	12.589	12.673
22	12.795	VV	0.063	489569	12.673	12.900
23	13.044	VV	0.042	359735	12.999	13.070
24	13.086	VV	0.043	239262	13.070	13.155
25	13.253	VV	0.062	513298	13.155	13.318
26	13.395	VV	0.078	531280	13.318	13.488
27	14.002	VV	0.095	372429	13.823	14.154
28	14.215	PV	0.046	226353	14.154	14.296
29	15.131	BV	0.052	190571	15.004	15.174
30	15.291	VV	0.041	188377	15.251	15.337
31	15.822	VV	0.047	259569	15.785	15.897
32	15.943	VV	0.046	195273	15.897	15.988
33	18.318	PV	0.036	105211	18.283	18.362
34	20.666	PV	0.046	129047	20.536	20.705
35	22.902	VV	0.061	202810	22.850	22.997

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.981	BV	0.042	2354123	7.927	8.029
2	8.065	VV	0.050	1943312	8.029	8.158
3	8.204	VV	0.049	1114629	8.158	8.364
4	8.430	VV	0.049	2979188	8.364	8.734
5	8.859	BV	0.046	4394759	8.782	9.060
6	9.269	BV	0.048	439776	9.219	9.394
7	9.581	BV	0.049	1986160	9.513	9.753
8	10.291	BV	0.040	561193	10.235	10.338
9	10.384	VV	0.044	1566313	10.338	10.467
10	10.520	VV	0.060	1853958	10.467	10.701
11	10.762	VV	0.042	3019127	10.701	10.910
12	11.041	BV	0.035	195332	10.976	11.085
13	11.723	BV	0.050	409661	11.651	11.767
14	12.792	PV	0.067	393235	12.693	12.895
15	13.090	VV	0.070	655587	13.000	13.182
16	13.255	VV	0.050	672593	13.182	13.350
17	13.417	VV	0.049	1943444	13.350	13.598
18	14.858	VV	0.058	420772	14.808	14.913
19	15.946	VV	0.045	846711	15.857	16.043
20	17.192	PV	0.045	354248	17.138	17.286
21	18.395	VV	0.044	777419	18.332	18.494
22	20.736	VV	0.043	704616	20.676	20.838
23	21.645	PV	0.043	302376	21.569	21.778
24	22.947	PV	0.044	597780	22.874	23.042
25	25.049	BV	0.047	510763	24.989	25.182
26	27.050	VV	0.052	473130	26.983	27.210
27	28.950	VV	0.040	294796	28.885	28.991
28	30.755	BV	0.052	407683	30.660	30.842

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Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.859	BV	0.048	572898	8.810	8.981
2	9.553	BV	0.057	794139	9.494	9.647
3	9.694	VB	0.047	567069	9.647	9.815
4	10.291	BV	0.044	537708	10.235	10.360
5	10.553	BV	0.055	2227031	10.463	10.695
6	11.042	BV	0.038	1885520	10.986	11.077
7	11.116	VV	0.043	3485029	11.077	11.220
8	11.282	VV	0.045	2173655	11.220	11.364
9	11.740	BV	0.034	474764	11.660	11.757
10	11.793	VV	0.048	1550716	11.757	11.914
11	11.958	VV	0.040	437133	11.914	12.012
12	12.135	VV	0.039	563617	12.086	12.181
13	12.225	VB	0.043	1460699	12.181	12.411
14	12.630	PV	0.041	734363	12.512	12.696
15	12.792	VV	0.046	1222924	12.696	12.827
16	12.852	VV	0.046	555314	12.827	12.899
17	13.040	VV	0.046	3092775	12.987	13.181
18	13.250	VV	0.043	2009044	13.181	13.332
19	13.387	VV	0.047	2658366	13.332	13.512
20	13.643	VB	0.044	819275	13.599	13.798
21	14.051	VV	0.047	1057136	13.991	14.157
22	15.297	VV	0.041	508360	15.254	15.381
23	15.764	BV	0.041	486516	15.717	15.841
24	15.935	PV	0.041	972834	15.884	16.015
25	16.581	PB	0.051	512149	16.440	16.701
26	18.311	PV	0.041	360205	18.213	18.366
27	20.607	PV	0.046	437345	20.538	20.685
28	22.807	VV	0.042	395072	22.753	22.856

File: C:\CHEMPC\DATA\DJB24H.D
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Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	6.392	BB	0.051	333424	6.340	6.502
2	14.039	PV	0.075	622443	13.934	14.153
3	14.200	VV	0.054	108664	14.153	14.269
4	16.013	VV	0.045	79188	15.971	16.067
5	16.795	VB	0.074	191566	16.716	16.889
6	18.170	PV	0.044	144595	18.097	18.222
7	18.545	VV	0.058	138789	18.480	18.588
8	18.965	PV	0.058	118172	18.892	19.013
9	19.144	VV	0.053	150641	19.081	19.188
10	19.694	VV	0.068	281577	19.593	19.737
11	19.793	VV	0.073	319102	19.737	19.872
12	20.126	VV	0.048	125824	20.086	20.170
13	21.357	VV	0.085	250589	21.234	21.475
14	21.622	VV	0.089	290380	21.475	21.709
15	21.884	PV	0.057	197733	21.807	21.978
16	22.006	VV	0.049	109448	21.978	22.078
17	22.165	VV	0.053	141006	22.078	22.222
18	22.443	VV	0.050	138998	22.379	22.525
19	22.863	VV	0.061	127984	22.841	23.019
20	23.325	VV	0.048	120703	23.274	23.387
21	25.443	VV	0.044	81593	25.406	25.486

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	9.005	BB	0.042	906209	8.943	9.095
2	16.828	BV	0.076	1073078	16.743	17.019
3	17.176	PV	0.059	1548111	17.114	17.382
4	19.696	PV	0.058	147253	19.584	19.755

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 24 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.692	BB	0.038	1233748	11.613	11.755
2	19.147	BB	0.062	463159	19.080	19.317
3	19.439	BV	0.089	1209774	19.355	19.628
4	19.691	VV	0.055	1809720	19.628	19.748
5	19.796	VV	0.058	1988298	19.748	20.012
6	20.135	VV	0.039	305129	20.076	20.153
7	20.199	VV	0.060	1167148	20.153	20.391
8	20.489	VV	0.059	485242	20.391	20.636

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	20.868	BB	0.050	49168	20.771	20.904
2	21.406	VV	0.046	52304	21.358	21.433
3	21.577	PV	0.078	85700	21.433	21.673
4	21.877	BB	0.055	88125	21.825	21.949
5	22.262	BB	0.048	59009	22.148	22.310
6	25.279	BV	0.035	25356	25.226	25.312
7	25.752	VV	0.064	99067	25.701	25.818
8	25.871	VV	0.073	106298	25.818	25.929
9	26.933	VV	0.036	36155	26.897	26.956
10	27.334	VV	0.087	325499	27.239	27.417
11	27.436	VV	0.041	61927	27.417	27.465
12	27.893	VV	0.067	143744	27.840	27.938
13	27.974	VV	0.064	167480	27.938	28.032
14	28.821	VV	0.044	52684	28.781	28.848
15	29.094	VV	0.084	147502	28.958	29.121
16	29.544	VV	0.078	156491	29.449	29.571
17	30.310	VV	0.083	206547	30.262	30.405
18	30.673	VV	0.068	158582	30.610	30.714
19	30.733	VV	0.053	112946	30.714	30.808
20	30.984	VV	0.076	129074	30.914	31.010
21	31.064	VV	0.084	268654	31.010	31.166
22	32.729	VV	0.069	126143	32.673	32.761
23	34.316	VV	0.069	89047	34.249	34.337
24	37.595	VV	0.066	67182	37.511	37.629
25	37.829	PV	0.065	65019	37.767	37.854
26	41.100	PV	0.019	14882	41.077	41.122
27	41.665	PV	0.045	49467	41.637	41.715
28	45.584	VV	0.084	359945	45.498	45.717
29	46.866	VV	0.043	49335	46.821	46.886
30	50.344	PV	0.055	22411	50.281	50.361

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.667	PV	0.048	226364	31.584	31.726
2	44.022	VV	0.073	477146	43.895	44.113
3	45.592	PV	0.055	1945395	45.501	45.711
4	46.734	PV	0.058	1165504	46.621	46.803
5	48.239	BV	0.070	863691	48.159	48.356
6	48.443	VV	0.068	779706	48.356	48.557
7	49.613	PV	0.080	554394	49.514	49.720
8	49.906	VV	0.091	475333	49.820	50.107

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 24 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.359	VV	0.063	154634	29.280	29.419
2	29.488	VV	0.077	233116	29.419	29.559
3	29.763	VV	0.059	474799	29.680	29.829
4	29.874	VV	0.085	335665	29.829	30.116
5	44.020	PV	0.058	136876	43.953	44.088
6	45.594	PV	0.067	475118	45.497	45.697
7	46.731	PV	0.057	247644	46.664	46.792
8	48.242	VV	0.063	224262	48.176	48.351
9	48.431	PV	0.069	196369	48.351	48.562
10	49.619	PV	0.076	154522	49.497	49.715
11	49.909	VV	0.060	122927	49.838	50.094

File: C:\CHEMPC\DATA\DJB24H.D
Operator: BOYE
Date Acquired: 21 Jul 94 11:20 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 24 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.665	VV	0.064	749906	31.597	31.734
2	31.793	VV	0.064	387742	31.734	31.847
3	31.894	VV	0.077	377583	31.847	31.969
4	32.023	VV	0.073	312183	31.969	32.171

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

ARABIAN CRUDE 96 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.681	BV	0.037	2928331	11.501	11.774
2	13.077	BV	0.052	876736	13.029	13.176
3	13.359	VV	0.040	713410	13.277	13.463
4	13.521	PV	0.034	754924	13.463	13.571
5	14.291	BV	0.036	7495738	14.208	14.444
6	14.604	VV	0.036	1465976	14.553	14.663
7	15.574	VV	0.044	869179	15.519	15.604
8	15.886	VV	0.042	1097419	15.794	15.968
9	16.058	PV	0.058	2201435	15.968	16.115
10	16.775	VV	0.037	10362197	16.702	16.875
11	17.159	VV	0.044	961557	17.110	17.237
12	17.945	VV	0.036	1151058	17.886	17.982
13	18.141	VV	0.036	692089	18.090	18.216
14	18.277	VV	0.037	1226373	18.216	18.335
15	18.433	PV	0.037	1301992	18.335	18.486
16	18.540	VB	0.036	1710197	18.486	18.602
17	19.125	VV	0.039	11206931	19.058	19.235
18	20.206	VV	0.048	1210972	20.138	20.240
19	20.408	VV	0.033	524641	20.355	20.422
20	20.456	VV	0.039	1318309	20.422	20.501
21	20.544	VV	0.039	1112041	20.501	20.639
22	20.692	PV	0.035	1102527	20.639	20.756
23	21.346	PV	0.038	10268157	21.270	21.452
24	22.347	VV	0.054	1530493	22.235	22.385
25	22.425	VV	0.058	992219	22.385	22.514
26	22.681	VB	0.039	1260449	22.629	22.740
27	22.831	BV	0.039	1036811	22.774	22.893
28	23.448	PV	0.038	9295194	23.283	23.526
29	24.374	PV	0.065	3360263	24.206	24.429
30	24.716	VV	0.044	852557	24.665	24.774
31	24.858	VV	0.039	962740	24.774	24.908
32	25.440	PV	0.044	9627379	25.359	25.587
33	26.250	PV	0.059	1052491	26.121	26.290
34	26.642	VV	0.040	715447	26.581	26.696
35	26.782	PV	0.040	589464	26.696	26.836
36	27.332	BV	0.041	7270250	27.103	27.383
37	27.435	VV	0.064	3027849	27.383	27.614
38	29.133	PV	0.038	5549979	29.022	29.195
39	30.852	PV	0.039	4780069	30.790	30.946
40	32.027	PV	0.043	725376	31.971	32.097
41	32.493	PV	0.038	4147903	32.430	32.594
42	34.064	PV	0.040	3667123	33.831	34.124
43	35.568	PV	0.037	2934020	35.500	35.624
44	37.014	PV	0.039	2481931	36.824	37.068
45	38.399	VV	0.043	2320386	38.075	38.530
46	39.733	BV	0.041	1969888	39.640	39.868
47	41.023	VB	0.045	1541760	40.950	41.178
48	42.262	BV	0.046	1335463	42.027	42.379
49	43.458	PV	0.040	1003595	43.365	43.537
50	44.620	PV	0.046	951773	44.499	44.705

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	10.798	VV	0.057	209457	10.742	10.879
2	13.443	PV	0.054	393736	13.343	13.560
3	14.852	VV	0.063	219936	14.820	14.990
4	15.957	VV	0.057	439591	15.867	16.057
5	17.198	PV	0.038	127060	17.143	17.239
6	18.403	VV	0.049	444463	18.342	18.483
7	19.405	PV	0.039	86929	19.323	19.421
8	19.447	VV	0.046	133208	19.421	19.514
9	20.633	PV	0.045	111494	20.584	20.681
10	20.741	VV	0.049	381240	20.681	20.850
11	21.652	PV	0.045	162037	21.570	21.714
12	22.953	VV	0.042	300307	22.884	23.045
13	23.780	BV	0.054	138365	23.698	23.852
14	25.056	PV	0.049	316850	24.970	25.172
15	27.051	VV	0.048	266719	26.997	27.125
16	28.948	PV	0.049	230750	28.874	29.010
17	30.762	VV	0.053	335005	30.659	30.868
18	32.479	VV	0.051	198317	32.366	32.526
19	34.127	PV	0.043	136129	34.070	34.180
20	35.696	VV	0.037	114998	35.651	35.745

File: C:\CHEMPC\DATA\DJB96H.D
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Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.074	BV	0.044	130448	10.982	11.105
2	11.144	VV	0.064	337528	11.105	11.265
3	11.314	VV	0.068	215990	11.265	11.396
4	11.814	VV	0.067	193620	11.780	11.920
5	12.248	VV	0.059	278272	12.198	12.404
6	12.658	BV	0.049	109420	12.557	12.717
7	12.806	VV	0.043	177355	12.770	12.841
8	13.062	VV	0.060	646783	13.008	13.160
9	13.262	VV	0.048	446895	13.214	13.350
10	13.404	VV	0.052	637199	13.350	13.529
11	13.655	VV	0.060	286462	13.617	13.834
12	14.062	VV	0.070	323070	13.998	14.176
13	15.307	VV	0.052	232887	15.269	15.396
14	15.778	BV	0.059	246725	15.689	15.902
15	15.948	VV	0.050	428864	15.902	16.034
16	16.075	VV	0.060	222098	16.034	16.185
17	16.245	PB	0.059	130754	16.185	16.329
18	16.589	VV	0.060	200343	16.512	16.631
19	17.263	VV	0.058	174389	17.225	17.379
20	17.572	VV	0.055	151197	17.537	17.634
21	17.701	VV	0.056	229462	17.634	17.758
22	18.115	VV	0.053	195560	18.066	18.231
23	18.320	VV	0.051	242092	18.231	18.390
24	20.023	VV	0.045	258578	19.954	20.055
25	20.082	VV	0.046	134878	20.055	20.147
26	20.399	VV	0.046	125982	20.357	20.437
27	20.613	PV	0.049	219991	20.563	20.698
28	22.249	VV	0.046	200054	22.204	22.371
29	22.577	VV	0.047	170872	22.528	22.649
30	22.806	PV	0.054	250370	22.751	22.906
31	24.365	PV	0.045	149902	24.301	24.421
32	24.886	BV	0.043	151411	24.773	24.974
33	26.379	VV	0.049	149871	26.319	26.464
34	26.869	VV	0.042	137176	26.826	26.923
35	28.295	VV	0.052	188005	28.226	28.400
36	28.790	VV	0.078	285540	28.714	28.856
37	30.124	VV	0.052	121362	30.063	30.206
38	30.557	VV	0.041	112434	30.490	30.604
39	31.646	VV	0.045	131744	31.592	31.710
40	32.272	VV	0.039	97972	32.233	32.387

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File: C:\CHEMPC\DATA\DJB96H.D
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Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 96 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	16.933	BV	0.117	321261	16.802	17.098
2	17.220	VV	0.077	633972	17.168	17.379
3	19.130	BV	0.034	41423	19.019	19.153
4	19.725	BV	0.047	69106	19.670	19.769
5	23.450	PV	0.028	38440	23.415	23.481

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Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

ARABIAN CRUDE 96 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.686	BB	0.041	147081	11.642	11.746
2	19.482	PV	0.086	407573	19.379	19.579
3	19.723	VV	0.062	718847	19.637	19.786
4	19.829	VV	0.065	755588	19.786	19.985
5	20.155	BV	0.041	146804	20.094	20.185
6	20.226	VV	0.065	474427	20.185	20.435
7	20.537	VV	0.075	194343	20.468	20.648

File: C:\CHEMPC\DATA\DJB96H.D
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Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.708	PV	0.062	155021	31.550	31.786
2	42.925	VV	0.078	242383	42.858	43.013
3	44.033	PV	0.060	198235	43.943	44.099
4	45.584	VV	0.057	768259	45.523	45.703
5	46.724	PV	0.065	516520	46.605	46.782
6	48.243	PV	0.093	397277	48.132	48.393
7	48.434	VV	0.054	256254	48.393	48.536
8	49.607	VV	0.076	194373	49.541	49.763

File: C:\CHEMPC\DATA\DJB96H.D
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Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.421	BV	0.060	95076	29.358	29.462
2	29.521	VV	0.109	191196	29.462	29.650
3	29.815	PV	0.068	273944	29.737	29.883
4	29.940	VV	0.100	254035	29.883	30.103
5	42.929	VV	0.094	135446	42.802	42.976
6	43.015	VV	0.052	62723	42.976	43.039
7	43.906	VV	0.063	75924	43.817	43.942
8	44.021	VV	0.087	144386	43.942	44.114
9	44.282	VV	0.053	70908	44.243	44.345
10	45.586	VV	0.077	362964	45.509	45.776
11	46.245	VV	0.035	34449	46.213	46.263
12	46.724	VV	0.062	187058	46.664	46.776
13	48.233	VV	0.062	135768	48.193	48.306
14	48.436	VV	0.059	95560	48.391	48.488
15	49.383	VV	0.063	50151	49.350	49.450
16	49.594	VV	0.062	98632	49.508	49.622
17	49.811	PV	0.062	20070	49.728	49.845
18	50.203	PV	0.083	49098	50.088	50.254
19	51.494	VV	0.064	79269	51.453	51.575
20	55.841	PV	0.019	16705	55.820	55.852
21	57.941	PV	0.061	60220	57.892	58.005
22	62.028	VV	0.027	22149	62.008	62.055

File: C:\CHEMPC\DATA\DJB96H.D
Operator: BOYE
Date Acquired: 23 Jul 94 1:32 pm
Method File: JAFFE.M
Sample Name: ARABIAN CRUDE 96 HRS WEATHERING
Misc Info:
ALS vial: 1

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ARABIAN CRUDE 96 HRS WEATHERING

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.703	PV	0.062	319817	31.629	31.775
2	31.839	VV	0.042	43715	31.775	31.861

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
Date Acquired: 13 Aug 94 12:39 pm
Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
Date Acquired: 13 Aug 94 12:39 pm
Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.271	BB	0.037	4296015	11.100	11.349
2	12.072	PV	0.047	4296882	11.988	12.131
3	12.659	VV	0.055	1770197	12.613	12.755
4	12.940	VV	0.043	1413713	12.858	13.032
5	13.101	PV	0.037	1573086	13.032	13.154
6	13.877	VV	0.040	16016418	13.748	13.930
7	14.183	VV	0.041	3778517	14.126	14.242
8	14.389	VV	0.054	1544800	14.335	14.450
9	14.586	PV	0.053	1520146	14.450	14.619
10	15.146	VV	0.041	2339275	15.043	15.176
11	15.322	VV	0.042	1602747	15.242	15.374
12	15.459	VV	0.039	2732694	15.374	15.495
13	15.545	VV	0.042	7317932	15.495	15.584
14	15.624	VV	0.063	5997911	15.584	15.691
15	16.362	VV	0.044	26825501	16.229	16.450
16	16.590	VV	0.050	1532168	16.551	16.637
17	16.726	VV	0.049	2866902	16.637	16.787
18	16.970	VV	0.048	1327608	16.899	17.013
19	17.514	VV	0.042	4138366	17.454	17.553
20	17.583	VV	0.042	1537744	17.553	17.616
21	17.649	VV	0.038	1389684	17.616	17.675
22	17.706	VV	0.041	2130480	17.675	17.782
23	17.846	VV	0.046	3519323	17.782	17.908
24	17.997	VV	0.042	3729784	17.908	18.052
25	18.107	VV	0.041	4800140	18.052	18.164
26	18.318	VV	0.042	8845712	18.254	18.391
27	18.710	VV	0.047	32258297	18.549	18.796
28	19.770	PV	0.061	5886510	19.625	19.810
29	19.842	VV	0.055	2660591	19.810	19.918
30	20.022	VV	0.053	6662693	19.918	20.064
31	20.105	VV	0.043	3303843	20.064	20.177
32	20.251	VV	0.044	4012537	20.177	20.327
33	20.726	VV	0.041	8807412	20.655	20.773
34	20.926	VV	0.050	31909441	20.773	20.997
35	21.898	VV	0.071	5060543	21.805	21.944
36	21.984	VV	0.050	2798401	21.944	22.061
37	22.113	VV	0.045	2479937	22.061	22.170
38	22.242	VV	0.049	4327158	22.170	22.316
39	22.383	VV	0.039	2890708	22.316	22.457
40	22.918	PV	0.043	9130377	22.808	22.951
41	23.019	VV	0.047	24818421	22.951	23.076
42	23.931	PV	0.088	12368846	23.712	23.981
43	24.013	VV	0.038	1177562	23.981	24.046
44	24.264	VV	0.056	3090295	24.174	24.313
45	24.405	VV	0.041	2303161	24.372	24.455
46	25.005	VV	0.071	40021594	24.756	25.146
47	25.793	VV	0.069	4356975	25.670	25.840
48	25.861	VV	0.045	1690398	25.840	25.891
49	26.183	VV	0.053	2781934	26.113	26.240
50	26.324	VV	0.057	3271339	26.240	26.425
51	26.888	VV	0.063	28409131	26.648	26.931
52	26.983	VV	0.065	10565421	26.931	27.159
53	27.618	VV	0.069	3553117	27.511	27.668
54	27.691	VV	0.045	1492804	27.668	27.736
55	28.012	VV	0.048	2101899	27.954	28.077
56	28.152	VV	0.047	2612160	28.077	28.219

57	28.452	VV	0.114	2965925	28.340	28.562
58	28.686	VV	0.048	21755074	28.562	28.739
59	29.357	VV	0.070	2639270	29.288	29.419
60	29.447	VV	0.040	1369386	29.419	29.491
61	29.756	PV	0.046	1733742	29.702	29.837
62	29.896	VV	0.044	1903203	29.837	29.944
63	30.402	PV	0.044	17896061	30.305	30.492
64	31.022	BV	0.060	2159044	30.818	31.057
65	31.421	VV	0.043	1391436	31.365	31.495
66	31.558	PV	0.050	3003241	31.495	31.630
67	32.040	PV	0.042	15704535	31.953	32.119
68	32.613	BV	0.069	2095199	32.503	32.692
69	33.017	PV	0.046	1442854	32.965	33.090
70	33.157	VV	0.056	2359541	33.090	33.270
71	33.606	PV	0.044	14207162	33.520	33.659
72	34.140	VV	0.066	2045277	34.092	34.232
73	34.540	PV	0.044	1453737	34.490	34.625
74	34.674	PV	0.040	1146374	34.625	34.726
75	35.107	PV	0.043	11992525	35.019	35.157
76	35.603	BV	0.064	2111263	35.415	35.693
77	36.548	PV	0.043	10913035	36.439	36.598
78	37.931	PV	0.039	8399762	37.859	37.979
79	39.266	BV	0.048	9540343	39.022	39.458
80	40.549	PV	0.046	7022370	40.429	40.667
81	41.789	VV	0.047	6726675	41.657	42.010
82	42.986	PV	0.045	4840428	42.748	43.050
83	44.144	PV	0.045	4818135	43.957	44.259
84	45.319	BV	0.052	4329478	45.074	45.483
85	46.644	VV	0.058	3465216	46.539	46.854
86	48.170	BB	0.066	2622461	47.996	48.415
87	49.969	PV	0.080	2221501	49.720	50.175

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
Date Acquired: 13 Aug 94 12:39 pm
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Sample Name:
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ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	13.537	BV	0.050	617437	13.422	13.688
2	16.348	PV	0.067	189157	16.294	16.456
3	17.704	VV	0.045	137820	17.635	17.757
4	18.111	VV	0.060	150919	18.066	18.237
5	18.717	VV	0.068	253381	18.643	18.799
6	18.881	VV	0.058	230495	18.799	18.911
7	19.191	VV	0.054	323019	19.105	19.245
8	19.300	VV	0.055	455738	19.245	19.416
9	19.654	VV	0.108	378869	19.542	19.806
10	20.830	VV	0.071	197948	20.768	20.879
11	21.123	VV	0.079	415673	20.997	21.192
12	21.273	VV	0.058	155238	21.192	21.323
13	21.379	VV	0.044	176449	21.323	21.414
14	21.452	VV	0.045	110845	21.414	21.471
15	21.655	VV	0.051	189143	21.588	21.694
16	21.741	VV	0.048	147809	21.694	21.808
17	21.943	VV	0.045	166345	21.897	22.018
18	22.809	PV	0.040	105072	22.761	22.853
19	23.014	VV	0.054	229598	22.964	23.098
20	26.886	VV	0.051	149419	26.828	26.934
21	28.691	BV	0.049	126921	28.572	28.751
22	30.408	PV	0.048	118811	30.333	30.490
23	32.039	VV	0.064	196476	31.940	32.077
24	33.601	PV	0.052	115401	33.514	33.665

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Sample Name:
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ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	15.244	BV	0.061	522345	15.192	15.411
2	15.702	BB	0.054	571220	15.639	15.830
3	16.309	BV	0.045	1872258	16.239	16.443
4	16.675	PV	0.046	2108711	16.443	16.823
5	19.192	PV	0.044	202485	19.118	19.243

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
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Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	11.273	BB	0.035	232331	11.224	11.319
2	18.398	BV	0.092	544147	18.351	18.559
3	18.622	PV	0.053	754206	18.559	18.685
4	18.734	VV	0.047	798331	18.685	18.799
5	18.887	VV	0.056	1887580	18.799	18.917
6	18.931	VB	0.039	952105	18.917	19.047
7	19.193	BV	0.049	2994638	19.075	19.244
8	19.293	VB	0.047	3091667	19.244	19.503
9	19.643	BV	0.058	967234	19.541	19.662
10	19.694	VV	0.047	1266480	19.662	19.807
11	19.967	PV	0.047	806206	19.880	20.092

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Operator: boye
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Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	20.874	VB	0.079	202925	20.746	20.988
2	21.378	PV	0.051	154232	21.267	21.425
3	25.198	PV	0.083	210632	24.930	25.272
4	26.702	VV	0.071	890468	26.588	26.829
5	27.413	VV	0.111	391402	27.302	27.545
6	29.751	PV	0.074	199936	29.656	29.797
7	30.115	VV	0.065	181737	30.028	30.173
8	30.511	PV	0.102	381603	30.338	30.563
9	31.968	PV	0.049	119262	31.913	32.089
10	32.172	VV	0.062	152060	32.089	32.271
11	44.983	VV	0.064	522778	44.901	45.166

File: C:\CHEMPC\DATA\DJB7DARB.D
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Sample Name:
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	29.172	PV	0.052	417570	29.101	29.229
2	31.083	BV	0.048	400729	30.961	31.163
3	38.805	BV	0.060	390784	38.660	38.926
4	42.944	PV	0.053	509787	42.759	43.020
5	43.467	VV	0.048	1035378	43.391	43.536
6	43.739	BV	0.044	371609	43.666	43.813
7	44.989	VV	0.056	4817800	44.815	45.109
8	46.057	VV	0.058	3256172	45.940	46.120
9	46.151	VB	0.054	565074	46.120	46.273
10	47.470	BV	0.061	1882856	47.358	47.554
11	47.651	VV	0.075	1465038	47.554	47.777
12	48.744	PV	0.081	1297724	48.471	48.852
13	49.025	VV	0.070	984739	48.902	49.148
14	50.498	VB	0.071	783332	50.365	50.642

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
Date Acquired: 13 Aug 94 12:39 pm
Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	28.766	VV	0.058	415814	28.685	28.811
2	28.873	VV	0.060	552639	28.811	28.965
3	29.174	VV	0.060	1039437	29.044	29.224
4	29.281	VV	0.061	639308	29.224	29.448
5	42.947	PV	0.052	146754	42.873	43.032
6	43.463	VV	0.052	276052	43.394	43.542
7	44.989	PV	0.049	1107513	44.863	45.087
8	46.054	PV	0.051	604067	45.942	46.115
9	47.471	PV	0.058	463639	47.346	47.565
10	47.661	VV	0.075	364256	47.565	47.747
11	48.732	PV	0.067	330344	48.629	48.903
12	49.041	VV	0.094	237977	48.903	49.164

File: C:\CHEMPC\DATA\DJB7DARB.D
Operator: boye
Date Acquired: 13 Aug 94 12:39 pm
Method File: JAFFE.M
Sample Name:
Misc Info:
ALS vial: 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	31.084	VV	0.060	1591054	30.972	31.155
2	31.216	VV	0.065	838184	31.155	31.260
3	31.302	VV	0.058	662015	31.260	31.373
4	31.448	VV	0.064	510133	31.373	31.603
5	44.964	VV	0.077	435266	44.793	45.169

9.10 APPENDIX J

**SOLUBLE AROMATIC HYDROCARBONS DETECTED IN WEATHERING
FLASK BELOW CRUDE OIL SLICK, AS DETERMINED BY FLUORESCENCE
SPECTROMETRY**

Total Aromatics Measured in Aqueous Phase vs. Weathering Period

Weathering Period (hours)	Recorded Concentration (ppm)
unweathered crude	N/A
4	* 0.449
4	0.181
8	0.146
8	0.151
24	0.129
24	0.156
96	0.174
96	0.228
168	0.066
168	0.049

* data point excluded from data plot: considered an outlier; possible contamination

9.11 APPENDIX K

**TOTAL OIL CONCENTRATION PROFILE RECORDED WITHIN VERTICAL
TURBULENT DISPERSION REACTOR FOR WEATHERED ARABIAN CRUDE
OIL SAMPLES UNDER SIMULATED TURBULENCE**

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

unweathered

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1051.2	901.6	758.4
	1053.6	951.2	708.8
180	865.6	754.4	720.8
	843.2	764.8	813.6
180 post-shutdown	344	337.6	352
	314	306.4	N/A

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1058.5584	907.9112	763.7088
	1060.9752	957.8584	713.7616
180	871.6592	759.6808	725.8456
	849.1024	770.1536	819.2952
180 post-shutdown	346.408	339.9632	354.464
	316.198	308.5448	

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

4 hours

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1063.2	984.8	591.2
	1128	912	672.8
180	861.6	887.2	765.6
	848	922.6	841.6
180 post-shutdown	320	274.4	432
	366.4	353.6	379.2

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1174.836	1088.204	653.276
	1246.44	1007.76	743.444
180	952.068	980.356	845.988
	937.04	1019.473	929.968
180 post-shutdown	353.6	303.212	477.36
	404.872	390.728	419.016

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

8 hours

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1066.4	1259.2	620.8
	1150.4	1272.8	658.4
180	1072.8	943.2	846.4
	969.6	985.6	863.2
180 post-shutdown	422.4	352	398.4
	242.4	304.8	N/A

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1170.9072	1382.6016	681.6384
	1263.1392	1397.5344	722.9232
180	1177.9344	1035.6336	929.3472
	1064.6208	1082.1888	947.7936
180 post-shutdown	463.7952	386.496	437.4432
	266.1552	334.6704	

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

1 day

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1062.4	948.8	729.6
	1063.2	1059.2	626.4
180	917.6	902.4	789.6
	1027.2	816.8	N/A
180 post-shutdown	372.8	276	447.2
	313.6	310.4	336.8

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1131.456	1010.472	777.024
	1132.308	1128.048	667.116
180	977.244	961.056	840.924
	1093.968	869.892	
180 post-shutdown	397.032	293.94	476.268
	333.984	330.576	358.692

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

4 days

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1209.6	1243.2	605.6
	1297.6	1086.4	621.6
180	808.8	956.8	549.6
	1061.6	966.4	644.8
180 post-shutdown	400.8	270.4	326.4
	337.6	309.6	359.2

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1201.1328	1234.4976	601.3608
	1288.5168	1078.7952	617.2488
180	803.1384	950.1024	545.7528
	1054.1688	959.6352	640.2864
180 post-shutdown	397.9944	268.5072	324.1152
	335.2368	307.4328	356.6856

Total Hydrocarbons Dispersed within Water Column vs. Turbulence Duration

Weathering Period

7 days

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1931.2	1128.8	581.6
	1750.4	1259.2	628.8
180	948	893.6	617.6
	984.8	828	572.8
180 post-shutdown	283.2	361.6	396.8
	296	243.2	376.8

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1548.8224	905.2976	466.4432
	1403.8208	1009.8784	504.2976
180	760.296	716.6672	495.3152
	789.8096	664.056	459.3856
180 post-shutdown	227.1264	290.0032	318.2336
	237.392	195.0464	302.1936

9.12 APPENDIX L

**NORMALIZATION METHODOLOGY FOR TOTAL OIL AND TOTAL
AROMATIC HYDROCARBON CONCENTRATIONS RECORDED FROM
VERTICAL TURBULENT DISPERSION REACTOR**

NORMALIZATION OF MASS LOADINGS TO VERTICAL DISPERSION REACTOR

Weathering Period (hours)	Weighted Volume (mL)	Initial Weight (g)	Final Weight (g)	Input Oil Weight to Reactor (g)	Normalization Multiplier
0	100			87.78*	1.007
4	100	190	110	80	1.105
8	100	194.8	114.3	80.5	1.098
24	100	198.4	115.4	83	1.065
96	100	185.8	96.8	89	0.993
168	100			110.2**	0.802
			Average=	88.413	

* determined by measured oil density alone

** entire contents of weathering flask (less water) added to reactor
loading determined by mass balance

9.13 APPENDIX M

**TOTAL AROMATIC HYDROCARBON CONCENTRATION PROFILE,
RECORDED WITHIN VERTICAL TURBULENT DISPERSION REACTOR FOR
WEATHERED ARABIAN CRUDE OIL SAMPLES UNDER SIMULATED
TURBULENCE**

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

unweathered

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	592.21	501.83	362.69
	529.58	438.36	313.52
180	448.87	383.29	332.85
	450.55	439.2	325.71
180 post-shutdown	12.23	12.02	2.97
	16.68	11.59	3.87

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	596.35547	505.34281	365.22883
	533.28706	441.42852	315.71464
180	452.01209	385.97303	335.17995
	453.70385	442.2744	327.98997
180 post-shutdown	12.31561	12.10414	2.99079
	16.79676	11.67113	3.89709

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

4 hours

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	690.99	526.22	345.04
	596.84	472.41	305.95
180	485.86	431.64	308.47
	432.47	421.97	363.96
180 post-shutdown	51.95	15	7.38
	34.29	26.5	13.53

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	763.54395	581.4731	381.2692
	659.5082	522.01305	338.07475
180	536.8753	476.9622	340.85935
	477.87935	466.27685	402.1758
180 post-shutdown	57.40475	16.575	8.1549
	37.89045	29.2825	14.95065

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

8 hours

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	609.87	605.24	310.15
	559.84	640.55	323.6
180	476.19	458.12	407.68
	515.28	474.93	336.21
180 post-shutdown	9.75	10.36	4.27
	7.01	13.02	4.03

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	669.63726	664.55352	340.5447
	614.70432	703.3239	355.3128
180	522.85662	503.01576	447.63264
	565.77744	521.47314	369.15858
180 post-shutdown	10.7055	11.37528	4.68846
	7.69698	14.29596	4.42494

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

1 day

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	515.29	456.86	305.11
	473.67	486.7	280.31
180	497.21	400.53	329.91
	465.26	439.62	294.6
180 post-shutdown	11.64	6.55	5.08
	11.26	5.12	5.41

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	548.78385	486.5559	324.94215
	504.45855	518.3355	298.53015
180	529.52865	426.56445	351.35415
	495.5019	468.1953	313.749
180 post-shutdown	12.3966	6.97575	5.4102
	11.9919	5.4528	5.76165

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

4 days

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	698.98	577.5	250.46
	644.76	540.51	252.98
180	522.85	430.37	208.01
	564.47	493.43	204.22
180 post-shutdown	21.6	7.18	5.82
	36.39	8.95	5.54

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	694.08714	573.4575	248.70678
	640.24668	536.72643	251.20914
180	519.19005	427.35741	206.55393
	560.51871	489.97599	202.79046
180 post-shutdown	21.4488	7.12974	5.77926
	36.13527	8.88735	5.50122

Total Aromatics Dispersed within Water Column vs. Turbulence Duration

Weathering Period

7 days

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	1117.46	577.5	213.89
	1205.73	641.39	204.22
180	466.11	418.6	198.34
	471.57	416.92	186.14
180 post-shutdown	5.46	4.03	2.31
	7.98	4.74	4.32

Normalized Data Set

Turbulence Duration (minutes)	Surface Concentration depth = 3" (ppm)	Mid-level Concentration depth = 27" (ppm)	Bottom Concentraion depth = 63" (ppm)
5	896.20292	463.155	171.53978
	966.99546	514.39478	163.78444
180	373.82022	335.7172	159.06868
	378.19914	334.36984	149.28428
180 post-shutdown	4.37892	3.23206	1.85262
	6.39996	3.80148	3.46464

9.14 APPENDIX N

OBSERVED PARTICLE CHARGE DISTRIBUTIONS AND AVERAGE PARTICLE SIZE DETERMINATIONS; MEASURED BY DELSA 440

DELSA 440 PARTICLE CHARGE DISTRIBUTION AND AVERAGE PARTICLE SIZE ANALYSIS

Weathering Period (hours)	File	Depth (inches)	Observed particle Charges		Average Particle Size (nm)
			(-)	(+)	
			mV	mV	
0	NO5MB2	63			2240
	NO5MS1	3			2244
	NO5MS2	3	0	0	
	NO3HB1	63			2259.8
	NO3HS3	3	0	0	
	NO3HS2	3	0	0	
	NO3HS1	3			2255.2
	NO3HB2	63	0	0	
	4H3HB1	63			1521.6
	4H3HB2	63			1980.3
	4H3HB4	63	3.03		
			0.121		
	4H3HS1	3	0.018		
			0.812		
	4H3HS2	3	3.06		
			0.15		
	4H3HS3	3	0.231		
			0.402		
	4H3HS4	3	0.38		
			0.258		
	4H3HB5	63	10.09		
	4H3HS5	3			2214.7
	4H5MB1	63	7.304		
			5.23		
			3.014		
	4H5MS1	3			2056.7
	4H5MS2	3	0	0	
	4H5MS3	3	1.216		
			1.061		
			0.792		
	4H5MS4	3			2194.5
	4H5MS5	3	0.014		
			10.33		
			2.977		
	4H5MS6	3			1586.8
	4HP3S1	3			1192.4
	4HP3S2	3	10.24		
			4.891		
			2.862		
	1D3HB1	63			719.3*
	1D3HB2	63	1424.6		
	1D3HB3	63	0	0	
	1D3HB4	63			1393.3

1D3HB5	63	0	0	
1D3HS1	3			1769.3
1D3HS2	3	0	0	
1D3HS3	3			1507.8
1D3HS4	3	0	0	
1D3HS5	3			1561.3
1D5MB1	63	0	0	
1D5MB2	63			1691.5
1D5MB3	63			737
1D5MB4	63			1126.1
1D5MB5	63	0	0	
1D5MS1	3			1549
1D5MS2	3	0	0	
1D5MS3	3			909
1D5MS4	3	0	0	
1DP3B1	63			2189.6
1DP3B2	63	0	0	
1DP3B4	63			910.6
1DP3B5	63			1262.8
1DP3S1	3			868.5
1DP3S2	3	0	0	
1DP3S3	3			1274.6
1DP3S4	3	0	0	
4D3HB1	63	0	0	
4D3HB1	63	0	0	
4D3HB2	63			1454.8
4D3HB3	63		5.744	
4D3HB1	63			1305
4D3HS1	3	3.58	2.55	
			5.389	
4D3HS1	3	0	0	
4D3HS1	3			655.4
4D5MB2	63	29.48	9.9	
4D5MB3	63	36.5	10.7	
		21.9		
4D5MB5	63	0	0	
4D5MB6	63			2357.1
4D5MS1	3	13.19	15.46	
		10.42	13.6	
4D5MS4	3			1294.1
4D5MS5	3	5.487	3.28	
4D5MS6	3	0	0	
4D5MS7	3			1466.9
4DP3B1	63	32.77	16.25	
		6.643	8	
4DP3B2	63			851.5
4DP3B3	63	0.21	2.78	
4DP3B4	63			1303.1
4DP3S1	3			1579.8
4DP3S2	3			853.5
4DP3S3	3	16.58	2.78	
4DP3S4	3	0	0	

4DP3S5	3			1159.9
7D3HB1	63	15.198	3.22	
7D3HB3	63	10.553	3.057	
			5.438	
7D3HS1	3	10.911	3.426	
		0.158		
7D3HS2	3			717.4*
7D3HS3	3	18.26	10.92	
		15.75		
7D5MB1	63	10.37	0.39	
		7.309		
7D5MB2	63			1463.2
7D5MB3	63			701*
7D5MB4	63	5.22	0.88	
7D5MS1	3	14.379	3.096	
		10.8		
7D5MS3	3	0	0	
7D5MS4	3			2052.9
7DP3B2	63	0.114		
		5.194		
7DP3B3	63	10.567		
7DP3B4	63			650*
7DP3S1	3	7.457		
7DP3S2	3			695*
8H3HB1	63			1933.4
8H3HB2	63	10.9		
		7.68		
8H3HB3	63			498*
8H3HB4	63	21.73		
		10.75		
8H3HS1	3			2069.6
8H3HS2	3	0	0	
8H3HS3	3	11.19	2.89	
8H3HS4	3			837.7
8H5MB1	63			986.5
8H5MB3	63	16.484	4.472	
8H5MB4	63	11.273	0.15	
8H5MS1	3			2063
8H5MS1A	3			2050.3
8H5MS2	3	13.928	5.346	
8H5MS2A	3	11.288	2.893	
8H5MS3	3	28.247	11.11	
8HP3B1	63			2183
8HP3B1A	63	0	0	
8HP3B2	63			503
8HP3B3	63			2114.5
8HP3B4	63	3.219		
		5.551		
		0.11		
8HP3S1	3			1007
8HP3S2	3			978
8HP3S3	3	11.245		

9.15 APPENDIX O

RELATIVE TOXICITY DATA EXPRESSED AS EC-50 VALUES FOR WEATHERED OIL SAMPLES

MICROTOX ANALYSIS				
SAMPLE I.D	AROMATIC HYDROCARBON CONCENTRATION (PPM) [NORMALIZED DATA]	EC-50 VALUE (PPM)	NORMALIZATION MULTIPLIER	ADJUSTED EC-50 VALUE (PPM)
NO3HMTB1	335.18	0.2422	1.007	0.2438954
NO3HMTB2	327.99	0.1638	1.007	0.1649466
4H3HMTB1	340.86	0.2077	1.105	0.2295085
4H3HMTB2	402.18	0.3283	1.105	0.3627715
8H3HMTB1	447.63	0.4529	1.098	0.4972842
8H3HMTB2	369.16	0.3293	1.098	0.3615714
1D3HMTB1	351.35	0.2862	1.065	0.304803
1D3HMTB2	313.75	0.2732	1.065	0.290958
4D3HMTB1	206.55	0.2501	0.993	0.2483493
4D3HMTB2	202.79	0.1894	0.993	0.1880742
7D3HMTB1	159.07	0.1349	0.802	0.1081898
7D3HMTB2	149.28	0.0549	0.802	0.0440298