Dispersed Oil Monitoring Plan (DOMP)

Monitoring Dispersed Oil and its Effects in the Sea

Appendix A:
Model Runs and Analysis of Results

Analysis Prepared for the
California Department of Fish and Game
Office of Spill Prevention and Response

by
Deborah French-McCay and Jill Rowe
Applied Science Associates, Inc.
55 Village Square Drive
South Kingstown, RI 02879
Tel: +1 401 789 6224
Fax: +1 401 789 1932
Email: dfrenchmccay@asascience.com

Mr. Robin D. Lewis and Walter Nordhausen, Ph.D., Contract Managers
California Department of Fish and Game
Office of Spill Prevention and Response (OSPR)
4949 Viewridge Avenue
San Diego, CA 92123
rlewis@ospr.dfg.ca.gov
858 467 4215

December 15, 2008

Special Studies and Evaluation Program: Projects P0475036 and P0575016

Table of Contents

Summary

Large areas off the California coastline were designated in 2003 as “Pre-approval Zones” for dispersant application in the event of oil spills. The application of dispersants may reduce impacts to wildlife (e.g., seabirds, sea otters) and shoreline habitats, but with the tradeoff that the dispersed oil may cause impacts to water column organisms. Oil-spill fate and transport modeling was used by CA OSPR to develop the time and spatial scales, and equipment needs for its Dispersed Oil Monitoring Plan (DOMP) to document hydrocarbon water column concentrations, potentially exposed organisms (fish and invertebrates, primarily zooplankton), and the impacts of oil spills with and without dispersant use.

Model estimates were made of concentrations (dissolved hydrocarbons and dispersed oil droplets) that would be expected in the water column for the largest potential volume of oil that could be dispersed at any one location and time: that amount that could be dispersed by a single sortie of a C-130 (100,000 gal of light crude oil dispersed at 80%, 45% or 20% efficiency). Runs assuming no-dispersant use were compared to those where dispersant was applied after 8 or 16 hours of weathering, for two wind conditions: 2.5 m/s (5 kts) and 7.5 m/s (15 kts).

With 5 kt winds and no dispersant, the concentration plume (dissolved aromatic concentrations >1 ppb) is relatively small and short-lived (hours). In 15 kt winds, natural dispersion is considerable and dispersant at 80% efficiency and the same wind conditions increases the volume affected by >1ppb by a factor of 2-3. Dispersant application at lower efficiencies decreases the plume volume affected roughly proportionately. Variation of other model inputs result in smaller changes in affected volume.

Potential impacts assuming a range of toxicity values characterizing 95% of species were summarized as equivalent water volumes of 100% loss. The impacted volume for a sensitive (2.5th percentile) species was negligible in 5 kts of wind with no dispersant, on the order of 1-2 million m^3 (e.g., a surface mixed layer 10-20 m deep with an area of 0.1 km^2) in 15 kts of wind for 100,000 gal (326.3 MT) of naturally-dispersed oil, 20-40 million m^3 (2 km^2 by 10-20 m deep) in 15 kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil, and 70-200 million m^3 (7-10 km^2 by 10-20 m deep) in 5 kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil. The impacted volume for a species of average sensitivity (50th percentile) is negligible in all wind conditions with no dispersant use, on the order of 0.5-0.9 million m^3 (0.05-0.045 km^2 by 10-20 m deep) in 15 kts of wind for 302.8 m^3 (80,000 gal, 261.0 MT) of chemically-dispersed oil (80% efficiency), and 6-20 million m^3 (0.6-1.0 km^2 by 10-20 m deep) in 5 kts of wind for 302.8 m^3 of chemically-dispersed oil (80% efficiency). Thus, the highest impacts were when chemical dispersant was applied under light wind conditions where dilution was relatively slow. Volumes and areas impacted would be much less if the oil were patchy or more spread out (because each patch would be a smaller volume and there would be more edge where mixing and dilution would occur), or in the cases where the efficiency of the

dispersant application is less than 80%. For example, in 5 kts of wind, the impacted volume for a species of average sensitivity (for 302.8 m^3 of chemically-dispersed oil after being weathered 16 hours, no currents, 10-m mixed depth) is 15 million m^3 (area 1.5 km^2) if efficiency is 80%, 8 million m^3 (0.8 km^2) if efficiency is 45%, and 1 million m^3 (0.1 km^2) if efficiency is 20%. For the same model scenarios except in 15 kts of wind, the impacted volume for a species of average sensitivity is 780 thousand m^3 (78 thousand m^2) if efficiency is 80%, 200 thousand m^3 (20 thousand m^2) if efficiency is 45%, and 4 thousand m^3 (400 m^2) if efficiency is 20%.

Introduction

Oil spill modeling was used to estimate the concentrations (dissolved hydrocarbons and dispersed oil droplets) that would be expected in the water column in space and time after spills in varying conditions. The results may be used to develop a sampling plan for monitoring impacts of spills with and without use of dispersants.

Aquatic organisms may be adversely impacted either directly or via the food web by the toxic effects of oil components that enter the water column, particularly the soluble compounds (i.e., monoaromatic hydrocarbons, MAHs, and polycyclic aromatic hydrocarbons, PAHs) and microscopic oil droplets mixed by waves into the water. Evaluations of bioassays and modeling have shown that while the MAHs are dissolved in higher concentrations into water, the PAHs (and particularly the alkyl-substituted homologues) are more toxic and may affect biota via dissolved concentrations or by uptake from dispersed oil droplets (see reviews in French-McCay 2002, 2003). Other soluble and semi-soluble hydrocarbons in oil may also contribute to aquatic toxicity (NRC 2005). Non-aromatic hydrocarbons are much less soluble, so are not bioavailable.

Concentrations of oil hydrocarbons in water are a complex function of environmental conditions (e.g., wind, turbulence, temperature) and dilution volume (volume of water into which the oil is dispersed). Overall, under natural conditions, adverse impacts increase the larger the spill size. However, there is great variability related to the environmental conditions after the spill: Aquatic organisms suffer much more adverse impact under windy conditions where high waves mix unweathered oil into the water than in calm weather where little or no significant natural dispersion into the water column occurs (French-McCay and Payne 2001; French-McCay 2002, 2003).

Dispersants lower the oil-water interfacial tension, which promotes increased entrainment and dissolution of oil components into the water column. Use of dispersants on fresh oil under light wind conditions could potentially increase the water column impact analogous to those under windy conditions where natural dispersion occurs, while weathering before dispersants are applied reduces the concentrations of MAHs and PAHs in the surface oil and consequently in the water column (French and Payne 2001).

Model Description

Oil Trajectory and Fates Model

The oil spill modeling was performed using the Spill Impact Model Application Package (SIMAP, described in French-McCay 2003, 2004), which uses wind data, current data, and transport and weathering algorithms to calculate the mass of oil components in various environmental compartments (water surface, shoreline, water column, atmosphere, sediments, etc.), oil pathway over time (trajectory), surface oil distribution, and concentrations of the oil components in water and sediments. Processes simulated include slick spreading, evaporation of volatiles from surface oil, transport on the water surface and in the water column, randomized (eddy) diffusion, emulsification, entrainment of oil as droplets into the water column, resurfacing of larger droplets, dissolution of soluble components, volatilization from the water column, partitioning, sedimentation, stranding on shorelines, and degradation. Oil mass is tracked separately for lower-molecular-weight aromatics (MAHs and PAHs), other volatiles, and non-volatiles. The lower molecular weight aromatics dissolve from both from the surface oil slick and whole oil droplets in the water column, and they are partitioned in the water column and sediments according to equilibrium partitioning theory.

“Whole” oil (containing non-volatiles and volatile components not yet volatilized or dissolved from the oil) is simulated as floating slicks, emulsions and/or tarballs, or as dispersed oil droplets of varying diameter (some of which may resurface). Sublots of the spilled oil are represented by Lagrangian elements (“spillets”), each characterized by mass of hydrocarbon components and water content, location, thickness, diameter, density, and viscosity. Spreading (gravitational and by transport processes), emulsification, weathering (volatilization and dissolution loss), entrainment, resurfacing, and transport processes determine the thickness, dimensions, and locations of floating oil over time. The output of the fate model includes the location, dimensions, and physical-chemical characteristics over time of each spillet representing the oil (French-McCay 2003, 2004).

Concentrations in the water column are calculated by summing mass (in the Lagrangian particles) within each grid cell of a 100 (east-west) by 100 (north-south) by 5 vertical layer grid scaled each time step to just cover the dimensions of the plume. This maximizes the resolution of the contour map at each time step and reduces error caused by averaging mass over large cell volumes. Distribution of mass around the particle center is described as Gaussian in three dimensions, with one standard deviation equal to twice the diffusive distance ($2D_xt$ in the horizontal and $2D_zt$ in the vertical, where D_x is the horizontal and D_z is the vertical diffusion coefficient, and t is particle age). The plume grid edges are set at one standard deviation out from the outer-most particle. Concentrations of particulate (oil droplet) and dissolved aromatic concentrations are calculated in each cell and time step and saved to files for later viewing and calculations. These data are used by the biological effects model to evaluate exposure, toxicity and effects.

The physical fates model has been validated with more than 20 case histories, including the *Exxon Valdez* and other large spills (French-McCay 2003, 2004; French-McCay and Rowe 2004), as well as test spills and dye studies designed to verify the model (French et al. 1997; French-McCay et al. 2007; 2008; Payne et al., 2007a,b, 2008).

Biological Effects Model

The biological exposure model estimates the area, volume or portion of a stock or population affected by surface oil, concentrations in the water, and sediment contamination. The area potentially affected by the spill is represented by a rectangular grid with each grid cell coded with habitat type, including open water, reef, wetland, and shoreline environments. Habitat types are defined by depth, proximity to shoreline(s), bottom type, dominant vegetation type, the presence of invertebrate reefs, and other biologically significant characteristics to the species concerned. A contiguous grouping of habitat grid cells with the same habitat code represents an ecosystem in the biological model.

Aquatic organisms are modeled using Lagrangian particles representing schools or groups of individuals. Pre-spill densities of fish, invertebrates and wildlife (birds, mammals, reptiles, and amphibians) are assumed evenly distributed across an ecosystem. Mobile fish, invertebrates and wildlife are assumed to move at random within each ecosystem during the simulation period. Benthic organisms either move or remain stationary on/in the bottom. Planktonic stages, such as pelagic fish eggs, larvae, and juveniles (i.e., young-of-the-year during their pelagic stage(s)), move with the currents.

Mortality of fish, invertebrates, and their eggs and larvae are computed as a function of temperature, concentration, and time of exposure. Percent mortality is estimated for each of a large number of Lagrangian particles representing organisms of a particular behavior class (i.e., planktonic, demersal, and benthic, or fish that are classed as small pelagic, large pelagic, or demersal). The percent mortalities are summed, weighed by the area represented by each Lagrangian particle to estimate a total equivalent volume for 100% mortality. In this way, mortality is estimated on a volume basis, rather than necessitating estimates of species densities to evaluate impacts. The algorithms for these calculations and their validation are described in French-McCay (2002, 2003, and 2004).

In the model, the fraction of wildlife individuals oiled is calculated from area swept by surface oil, dosage, and vulnerability. The area swept by the surface spillets in a given time step is calculated in the exposure model. A portion of the wildlife in the area swept by oil over a threshold thickness is assumed to die, based on probability of encounter with the water surface as the oil passes multiplied by the probability of mortality once oiled. The probability of encounter is related to the percentage of time an animal spends on the water or shoreline surface (as opposed to flying or swimming underwater). The probability of mortality once oiled is nearly 100% for birds and fur-covered mammals (assuming they are not rescued and successfully treated) and much lower for other wildlife. The products of the two probabilities for various wildlife behavior groups were derived from information on behavior and field observations of mortality after spills (reviewed in French et al. 1996). Area swept is calculated for the habitat(s) occupied by each behavior group of wildlife, and species or species groups are assigned to behavior groups to evaluate their loss. Wildlife mortality is directly proportional to abundance per unit area (density) and the percent mortality assumed. The wildlife mortality model was previously validated with wildlife impact data for the *Exxon Valdez* (French-McCay 2004) and the *North Cape* (French-McCay 2003) oil spills, verifying that these values are reasonable.

Oil Toxicity and Exposure Model

The following summarizes the development of a conceptual and quantitative model of oil toxicity and exposure (OilToxEx). The full development of the model, data upon which it is based, and its validation are in French-McCay (2002).

Description of Oil Toxicity Model

Oil is a mixture of thousands of hydrocarbons of varying physical, chemical, and toxicological characteristics, and therefore, varying fates and impacts on organisms. The most toxic components of oil to water-column and benthic organisms are lower-molecular-weight compounds, which are both volatile and soluble in water, especially the aromatic compounds (Anderson et al. 1987; French et al. 1996; French-McCay 2002). These include the MAHs and PAHs. It has been shown that toxicity of narcotic organic compounds, such as these lower-molecular-weight aromatics in oil (MAHs and PAHs), is related to the octanol-water partition coefficient (K_{ow}), a measure of hydrophobicity (Nirmalakhandan and Speece 1988; Hodson et al. 1988; Blum and Speece 1990; McCarty 1986; McCarty et al. 1992; Mackay et al. 1992a; McCarty and Mackay 1993; Varhaar et al. 1992; Swartz et al. 1995; French et al. 1996; French-McCay 2002, 2003). The K_{ow} is measured for the chemical by placing it in a container with octanol and water and quantifying the ratio of the concentration in the hydrophobic octanol phase divided by the concentration in the water phase. K_{ow} varies over more than six orders of magnitude, and is typically expressed as $\log(K_{ow})$. Hydrophilic (water-loving, highly soluble) compounds have $\log(K_{ow}) <2$, while hydrophobic compounds have $\log(K_{ow}) >3$. Typical values of $\log(K_{ow})$ are 2-4 for MAHs, and 3.4-6.5 for 2- to 4-ring PAHs.

Chemicals that have a narcotic mode of action impact organisms by accumulating in lipids (such as in the cell membranes) and disrupting cellular and tissue function. The more hydrophobic the compound, the more accumulation in the tissues and the more severe is the impact (i.e., more hydrophobic chemicals are more toxic). However, the more hydrophobic the compound, the less soluble it is in water, and so the less available it is to aquatic organisms. Compounds of $\log(K_{ow})>5.6$ are considered so insoluble as to be not acutely toxic (not bioavailable) to aquatic biota (DiToro et al. 2000; French-McCay 2002). Thus, impact is the result of a balance between bioavailability (dissolved-component exposure) and toxicity once exposed.

The acute toxic effects of narcotic chemicals, including lower molecular weight aromatics, are additive (Swartz et al. 1995; French et al. 1996; DiToro et al. 2000; DiToro and McGrath 2000; French-McCay 2002). The so-called Toxic Unit (TU) model is used by toxicologists to estimate the toxicity of a mixture of narcotic chemicals. A TU is defined as the exposure concentration divided by the LC50 (lethal concentration to 50% of exposed organisms). For a mixture, the toxic units are additive. When Σ TU = 1, the mixture is lethal to 50% of exposed organisms.

French-McCay (2002) demonstrated that the LC50 of the mixture ($LC50_{mix}$) is related to the LC50 of each chemical i in the mixture and the fractional concentration of chemical i in the total mixture, $F_i = C_i /(\Sigma C_i)$, where C_i is the dissolved concentration of chemical i in the water. Equation (1) is derived from the TU model.

$$(1) \qquad LC50_{mix} = 1 / \Sigma (F_i / LC50_i)$$

Ideally, the values of F_i should be measured in the field. If field samples are not available, F_i may be estimated from the source oil composition. French-McCay (2002) showed that for surface waters, where turbulent entrainment of oil has occurred, the values of F_i are nearly proportional to the source oil aromatic composition. (See discussion in next section).

The values of $LC50_i$ in equation (1) can be estimated using regression models relating LC50 to K_{ow} (French-McCay 2002). This approach has been used to develop US Environmental Protection Agency (USEPA) water and sediment quality criteria for PAHs (DiToro et al. 2000; DiToro and McGrath 2000). The 95% confidence range of the regression (from French McCay, 2002) provides LC50s for average (50^{th} percentile), sensitive (2.5^{th} percentile), and insensitive (97.5^{th} percentile) species. This oil toxicity model may be used to estimate the LC50 for the dissolved aromatic mixture originating from the spilled oil. Only compounds of $\log(K_{ow}) \leq 5.6$ should be included in this additive acute toxicity model.

Toxicity varies with time of exposure, the LC50 decreasing as exposure time increases (Sprague 1969; Kooijman 1981; McAuliffe 1987; Anderson et al.1987; French and French 1989; French 1991; McCarty et al. 1992; Mackay et al. 1992a; French et al. 1996). This is due to the accumulation of toxicant over time up to a critical body residue (tissue concentration) that causes mortality. The accumulation is slower for more hydrophobic (higher K_{ow}) compounds. The accumulation is more rapid at higher temperature, such that LC50 at a given (short) exposure time decreases with increasing temperature (French-McCay 2002).

Figure 1 shows the exponential decrease of LC50 with increasing exposure time is steeper the lower the $\log(K_{ow})$. For xylene, with $\log_{10}(K_{ow}) = 3.2$, accumulation is rapid and the LC50 decreases rapidly with duration of exposure such that after 24 hours of exposure the LC50 is approaching its minimum for infinite exposure time. However, for higher $\log(K_{ow})$ compounds accumulation takes longer, such that the LC50 takes days to decrease to its minimum for infinite exposure time. For this reason, recent toxicity tests for higher $\log(K_{ow})$ compounds have been run for 10 days or more (Swartz et al. 1995).

Figure 2 shows that the exponential decrease of LC50 with increasing exposure time is steeper the higher the temperature. The $LC50_\infty$ is reached more rapidly at warmer temperature.

The combined effect of temperature and $\log(K_{ow})$ is that LC50 decreases most rapidly at higher temperature and for low $\log(K_{ow})$ compounds, approaching the $LC50_\infty$ within 24 hours. This pattern applies to BTEX (benzene, toluene, ethylbenzene, and xylenes). The LC50 decreases most slowly at low temperature and for higher $\log(K_{ow})$ compounds, not approaching the $LC50_\infty$ for days. The later pattern is typical of PAHs. Since after an oil spill concentrations decrease rapidly on a scale of hours to days, time and temperature of exposure need to be considered in evaluating toxicity, particularly for the PAHs (French-McCay 2002).

The $LC50_\infty$ for high $\log(K_{ow})$ compounds is much lower than that for low $\log(K_{ow})$ compounds (i.e., high K_{ow} compounds are much more toxic). Bioassays are available for MAHs and PAHs, but only certain species have been tested with selected compounds. To derive a model equation to fill in the missing data, LC50s for MAHs and PAHs from the literature were corrected for time and temperature of exposure to calculate $LC50_\infty$ (French McCay, 2002). A so-called QSAR (Quantitative Structure Activity Relationship) regression for narcotic chemicals, specifically the aromatics in oil, was developed:

$$(2) \qquad \log_{10}(LC50_\infty) = \log_{10}(\phi) + \gamma \log_{10}(K_{ow})$$

For 278 bioassays on individual aromatics, the slope and intercept of the regression are: $\log_{10}(\phi) = 4.8926$ and $\gamma = -1.0878$. This QSAR ("QSAR mean" in Figure 3) describes the mean response for all species (i.e., the response of the average species). The slope of this relationship is constant for all species, as it is related to the variation in uptake behavior of hydrophobic chemicals according to their partitioning behavior ($\log(K_{ow})$, see DiToro et al., 2000 for theory). The intercept varies by species, with 95% of species falling within the range $\log_{10}(\phi) = 3.9704$ (sensitive species) and $\log_{10}(\phi) = 5.8147$ (insensitive species). Equation (2) may be used to estimate $LC50_\infty$ for any aromatic, assuming an appropriate intercept for the species of concern. The line labeled "QSAR mean – 2SD" in Figure 3 describes the LC50s for sensitive species. The line labeled "QSAR mean + 2SD" in Figure 3 describes the LC50s for insensitive species. Ninety-five percent of species fall within this described envelop (SD = standard deviation).

Combining equations (1) and (2), using F_i values for PAHs in typical oils under representative environmental conditions for a surface spill (see discussion below), $LC50_{mix}$ for the oil mixture of PAHs is 46 ppb for the average species (i.e., using the mean QSAR intercept). For sensitive species (2.5th percentile), $LC50_{mix}$ for total PAHs is

6 ppb. For insensitive species (97.5th percentile), $LC50_{mix}$ for total PAHs is 376 ppb. These LC50s apply when exposure time is long, approximated when exposure exceeds 4 days.

Observed LC50s for species that have been tested and reported in the literature are indicated in Figure 4. The most insensitive species are fathead and sheepshead minnows (*Pimephales promelas*, *Cyprinodon variegatus*), brine shrimp (*Artemia salina*) and the polychaete *Neanthes arenaceodentata*. Shrimp, mysids, and salmonids are more sensitive than average, with pink salmon (*Oncorhynchus gorbuscha*), humpy (northern) shrimp (*Pandalus goniurus*), and brown (Gulf) shrimp (*Penaeus aztecus*) being the most sensitive species. The species' degree of sensitivity is the same for all MAHs and PAHs, alone or in an oil mixture.

The $LC50_{\infty}$ for an oil mixture of MAHs and PAHs may be calculated using equation (2) and the appropriate intercept for the species of concern. The intercept may be estimated from bioassays measuring LC50s for several aromatics (exposed individually) over a range of $\log(K_{ow})$. Because of the difficulties in performing bioassays on oils (see French McCay, 2002), this approach using individual aromatics is recommended for evaluating new species. Additionally, since the slope of equation (2) applies for all species, only a few aromatics need to be tested to derive an intercept for the species of interest.

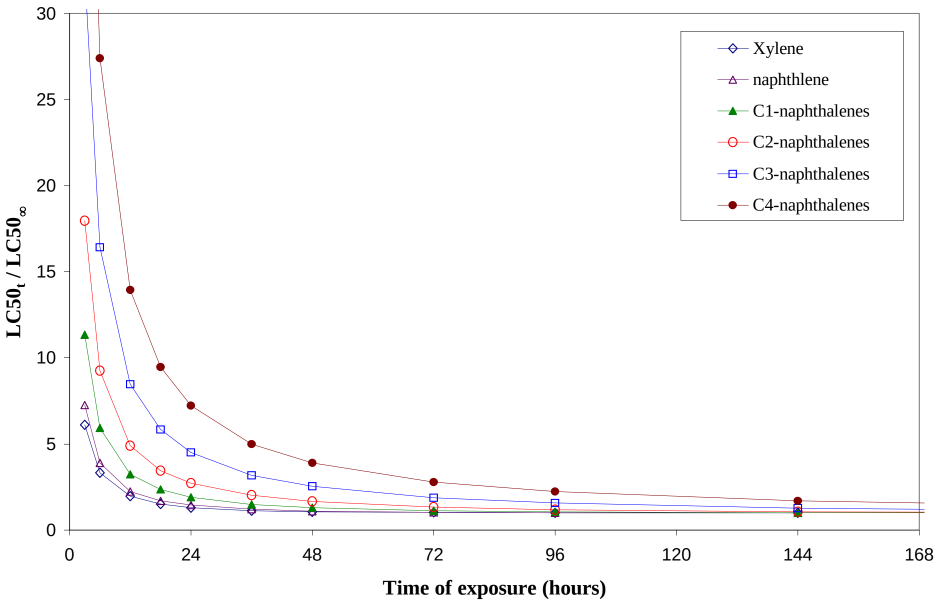

Figure 1. Time dependence of LC50 at 25°C (as fraction of incipient LC50) for various aromatics.

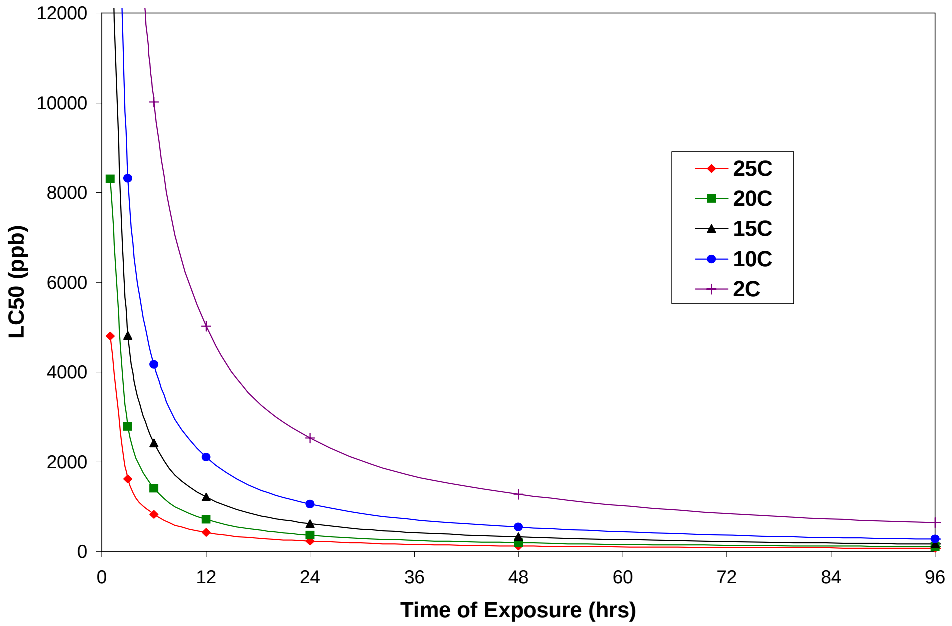

Figure 2. Effect of time of exposure and temperature on LC50:
for a chemical with log(Kow) = 5.0 and incipient LC50 = 50 ppb.

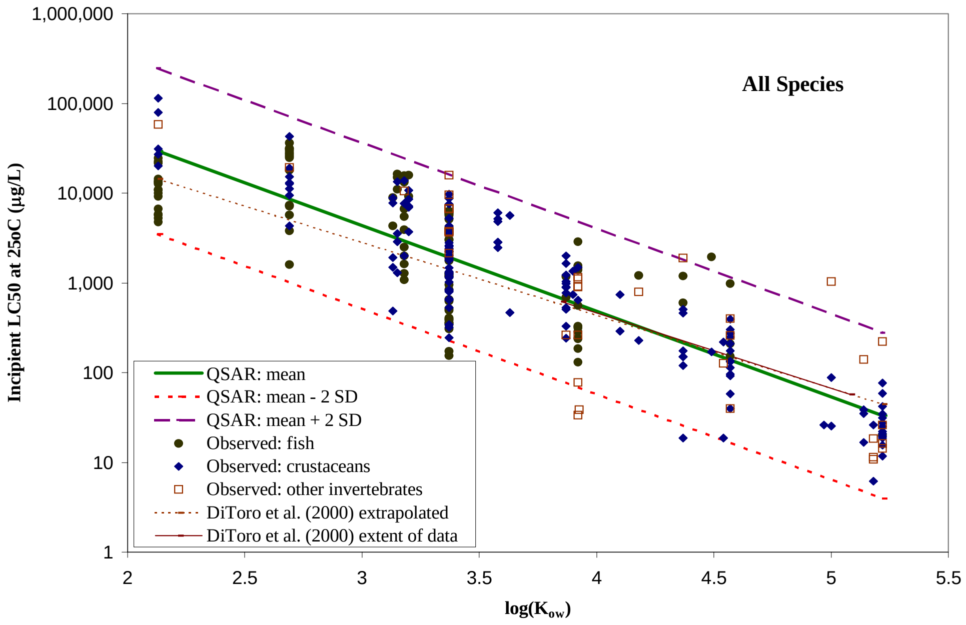

Figure 3. Bioassay data from the literature: tests for all species.

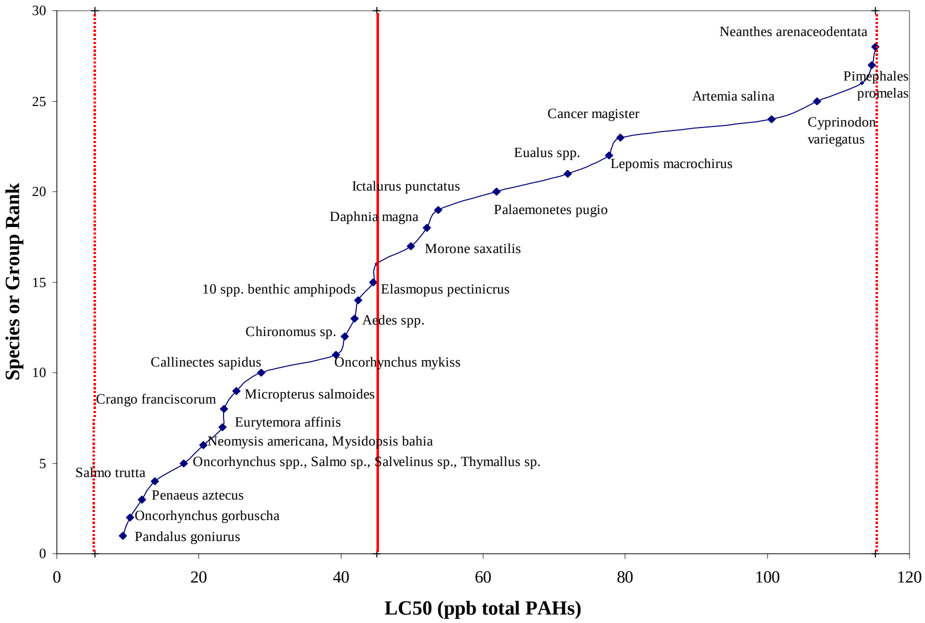

Figure 4. Species Sensitivity Ranking -- PAHs in Crudes and Fuel Oils
Vertical Red Lines are Geometric Mean and Range for 95% of Species
(based on French McCay, 2002).

Validation of the Oil Toxicity and Exposure Model

French-McCay (2002) verified the OilToxEx model using oil bioassay data from the literature. For oil bioassays, where exposure concentrations of each of the aromatics were measured, the incipient LC50 ($LC50_\infty$) was calculated from each LC50 measurement using equations (1)-(2). The LC50s from short-term bioassays were corrected for time of exposure and temperature.

The mean, minimum, and maximum of the incipient LC50s based on observed data were compared to the estimated range using the model from sensitive (mean – 2 SD) to insensitive (mean + 2 SD) species covering 95% of all species. For the model predictions, the aromatic QSAR (equation 2) and the additive model (equation 1) were used to estimate the incipient LC50s for the oil aromatic hydrocarbon mixtures in the experimental exposures. The model mean LC50 was calculated using the all-species slope and mean intercept, while the range of 95% of species was calculated using the all-species slope and the intercept ± 2 SD. The observed incipient LC50s from the bioassays were compared to the QSAR predictions for goodness of fit using Student's t (unpaired test for equal means). For all 24 data sets containing 2-91 observations on varying species, the model was not significantly different ($P < 0.01$) from the observed. The data and analysis are available in French-McCay (2002).

The algorithms for correcting incipient LC50 to LC50 at the time and temperature of exposure were also compared to available oil bioassay data. The observed data are highly variable, but agree with the model. Additional data are available from the toxicological literature for individual organic compounds that confirm that the expose time and temperature model in OilToxEx is valid (French-McCay 2002).

Estimating Relative Exposure Concentrations

In order to use the additive toxicity model (equation 1) in an oil spill situation, the relative exposure concentrations of the individual aromatics (F_i) must be known. For most aquatic organisms, it is the dissolved hydrocarbons that are bioavailable since they must be taken up by the organism for the narcotic effect to occur. Ideally, dissolved aromatic concentrations would be measured in water samples from the subsurface oil plume after a spill event. However, in the absence of such data and for predictive purposes (as OilToxEx), a model of relative composition was developed.

The relative composition of the dissolved aromatics (values of F_i) after a spill would be expected to be according to equilibrium partitioning theory *if the oil and water phases reach equilibrium* and there is no significant volatilization (or other differential loss). While equilibrium partitioning is a good model for closed or stable systems, as for chronic contamination in contact with ground water, conditions after a spill are typically not at equilibrium. The dissolution of compounds into the water phase takes hours to days, longer the higher the K_{ow}. The BTEX compounds dissolve fastest but are highly volatile, and would be rapidly lost from surface waters. Thus, the PAHs and substituted benzenes, which are more toxic and less volatile, become the primary toxicants in the mixture. For releases into deep water, BTEX would also contribute to toxicity because there would be no exposure to the atmosphere and thus no volatilization.

Initially, for example, if the oil is entrained in surface water by high turbulence, it is possible that the droplets would be so fine that the aromatics would quickly dissolve into the water phase. Dissolution rate is related to the surface area per unit volume of oil, which increases the smaller the droplets. However, the low molecular weight aromatics would rapidly be lost to the atmosphere, rather than remain at equilibrium with the oil phase. This would lead to a relative depletion of the low K_{ow} compounds and relative enrichment of the high K_{ow} PAHs in the water over time. This has in fact been observed, as shown by the data of Payne et al. (1984), Reddy and Quinn (1996), and Payne and Driskell (1999).

In cases where oil is released on the water surface and turbulence is low, volatilization (evaporation) competes with dissolution, such that little of the low molecular weight aromatics enters the water phase (French et al. 1996; French-McCay 2002). Thus, equilibrium partitioning does not apply to these situations as well.

It is difficult to predict the aromatic composition in the water phase where equilibrium partitioning does not apply. The simplest assumption is that the aromatics are in the same proportions as in the source oil, assuming the percentages of aromatics reflect the supply from the oil, and that volatilization proceeds in balance with dissolution. Since both volatility and solubility increase as K_{ow} decreases, this is a reasonable assumption. Short and Harris (1996) observed that the relative concentrations of dissolved PAHs measured in Prince William Sound after the *Exxon Valdez* oil spill matched that of the source oil. They argue that the relative composition of PAHs is not related to solubility, as these limits are never approached. Similarly, Payne et al. (1984) observed in wave-tank experiments that the relative concentrations of dissolved alkylated naphthalenes more closely paralleled their relative distributions in the oil phase than the pattern expected from solubility considerations.

Oil bioassays are conducted using two types of oil preparations. The water soluble fraction (WSF) refers to the dissolved concentrations in a so-called water accommodated fraction (WAF) prepared by slowly mixing oil in water, with the objective that the WSF comes to equilibrium concentrations. An oil-in-water dispersion (OWD) is prepared by highly turbulent shaking of oil in water. The OWD is allowed to separate before use so that the bioassay organisms are exposed to the dissolved portion (and possibly very fine oil droplets). In some cases, OWD were prepared using chemical dispersant.

The WSF (and WAF) LC50s are higher and more variable than OWD LC50s. Part of the variability is due to the length of time the WAF is mixed in preparing the WSF. Additionally, volatilization is significant in most experiments. Because of their relative solubility, in a WAF low K_{ow} aromatics enter the WSF faster than high K_{ow} compounds, making the mixture relatively less toxic initially and more toxic as equilibrium is reached. Volatilization selectively removes the less toxic low K_{ow} compounds, increasing toxicity of the mixture the longer the preparation time for the WSF. In an OWD, the small droplet size and turbulence enhance the solubilization of the high K_{ow} compounds. Thus, OWDs are more toxic mixtures than WAFs.

Thus, the WSF is a laboratory model of an equilibrium situation, while the OWD is a laboratory model for a turbulent release, such as in a storm or under high pressure as from a blowout, and for oil entrained by use of chemical dispersant. In an OWD, the relative concentrations of the dissolved compounds are nearly equivalent to that in the source oil (French-McCay 2002).

Mackay and Leinonen (1977) showed, based on theoretical calculations and modeling results, that (1) dissolution from surface slicks is insignificant, such that the main dissolution mechanism is via dispersed oil droplets, and (2) dissolution time from subsurface droplets less than 100 μm in diameter has a half life of less than 13 min. The dissolution rate is very sensitive to the droplet size (because it involves mass transfer across the surface area of the droplet), and the amount of hydrocarbon mass dissolved is a function of the mass entrained and droplet size distribution. These are in turn a function of soluble hydrocarbon content (mole fraction) in the oil, the amount of evaporation of these components before entrainment, oil viscosity (which increases as the oil weathers and emulsifies), oil surface tension (which may be reduced by surfactant dispersants), and the energy in the system (the lower the viscosity and the higher the energy, the smaller the droplets). Large droplets (greater than a few hundred microns in diameter) resurface rapidly, and so dissolution from those is also inconsequential (French-McCay 2002).

Compounds in Oil Causing Significant Toxicity

BTEX is very soluble in water, and so exposure concentrations in water can be high. However, BTEX is only moderately hydrophobic and so relatively low in toxicity. It is also very volatile. Thus, the BTEX rapidly volatilizes reducing exposure concentrations. For these reasons, the impact of BTEX after a spill is typically low and of short duration.

PAHs and many of the alkyl-substituted benzenes (substituted MAHs) are less soluble than BTEX, but do dissolve in significant quantities into the water. Thus, they are bioavailable. Because they are more hydrophobic than BTEX, they more strongly partition into the lipids in membranes and tissues. Thus, they are more toxic and can have significant impacts on aquatic organisms.

Lower-molecular-weight aliphatic hydrocarbons (e.g., alkanes and cycloalkanes with boiling points less than about 380^{o}C) may also contribute to toxicity after an oil spill. However, the aliphatics are much more volatile (have higher vapor pressure) and less soluble than aromatics of the same molecular weight (Mackay et al. 1992b, c, d) and would be more readily lost to the atmosphere from surface waters. They are also less toxic than the aromatics of similar molecular weight (French-McCay 2002).

The non-volatile and insoluble compounds (residual compounds) remain in the “whole oil” that spreads, is transported on the water surface, strands on shorelines, and disperses into the water column as oil droplets or remains on the surface as tar balls. This is the fraction that comprises black oil, mousse, and sheen. Before the whole oil droplets are weathered, they are a source of soluble and toxic compounds. Thus, exposure to partially weathered oil droplets may result in adverse effects on aquatic biota.

The volatilization rates of hydrocarbons from surface slicks are faster than the dissolution rates. Thus, dissolution from oil droplets in the water column is the main source of concentrations dissolved in the water. Experiments by Delvigne and Sweeney (1988) showed that entrainment of oil into the water column is insignificant in less than 12 knots of wind, the wind speed where breaking waves begin to form. The stronger the wind, the higher the entrainment rate and the smaller the droplet sizes. Thus, in most spills where dissolved concentrations are high enough in the water to have acute toxic effects, the mixture is analogous to an OWD, not a WSF. For subsurface releases under low turbulence, where the oil remains in the water column and is not exposed to the atmosphere, the mixture would be more analogous to the WSF.

The $LC50_{mix}$ of the aromatic mixture may be calculated using equation (1), including those aromatics that are measured in the oil and dissolved in the water (with

$\log(K_{ow}) \leq 5.6$) for long enough for exposure to aquatic organisms to be significant. Typically, for surface releases of fuel and crude oils, only the PAHs are dissolved in sufficient quantity and remain in the water long enough for their TU values to be significant. However, for a subsurface release deep in the water column or for a gasoline or other product spill where the MAHs and lower molecular weight aliphatics are significant fractions of the oil, all of these compounds may cause significant acute toxic effects.

It is important to note that the $LC50_{mix}$ is the 50% effects concentration for those compounds composing the mixture. Thus, if only PAHs have a significant effect (or if only PAHs are measured), the LC50 is for total PAHs. If MAHs are included in the mixture in significant amounts and are measured, the LC50 is for total MAHs plus PAHs. This difference in "units" means that LC50s for different mixtures will not be equivalent or applicable to another type of mixture.

Tables 1 and 2 give estimated LC50s for total PAHs and MAHs+PAHs under equilibrium (WSF) and turbulent (OWD) conditions. F_i values were calculated from concentrations of aromatics (with $\log(K_{ow} \leq 5.6)$ assuming the equilibrium partitioning model (equations in French McCay, 2002) or assuming equivalence to the source oil composition (for OWD).

Laboratory-based evidence shows that the dispersed oil water-accommodated fraction (DWAF, i.e., an OWD) is significantly more toxic than the oil-only water-accommodated fraction (WAF) or dispersant alone (Anderson et al. 1974; Middaugh and Whiting 1995; Kanga et al. 1997; Gulec and Holdway 2000; Couillard et al. 2005). Increased toxicity of DWAF is attributable to higher concentrations of low-molecular-weight hydrocarbons (LMWH) and/or a change in the relative concentrations of the individual hydrocarbons such that the more toxic and less soluble ones are in relatively higher concentrations (Couillard et al. 2005).

Note the difference in the values in Table 1 and 2 by (1) what aromatics are included in the calculation and (2) species sensitivity. Also, note that the $LC50_{\infty}$ for PAHs (Table 1) does not vary much by oil type (diesel, Bunker C, or crude oil), because the proportionate amounts of each PAH are about the same in all these oils. However, $LC50_{\infty}$ for total MAHs and PAHs are highly variable and dependent on the fuel type and conditions (Table 2). Given the higher $LC50_{\infty}$ values when both MAH and PAH are measured (Table 2), it is clear that the MAH doesn't contribute that much to the overall toxicity (higher total $LC50_{\infty}$ values are obtained). Also, note that the OWD $LC50_{\infty}$ values are similar for the No. 2 Fuel (diesel oil) in both Tables 1 and 2, since that oil doesn't contain much MAH.

Thus, to estimate oil toxicity ($LC50_{\infty}$), the following must be considered:

- the neat (source) oil composition;
- the turbulence conditions and whether equilibrium is reached; and
- the species sensitivity.

Table 1. Content (percent) of PAHs in crude oils and fuels and estimated LC50∞ (μg PAH/L) assuming equilibrium partitioning (WSF) or an oil-in-water dispersion (OWD) with equivalent percent composition to neat oil: Mean (SD).

Oil Type	n	Percent PAH	WSF: Sensitive species	WSF: Mean species	WSF: Insensitive species	OWD: Sensitive species	OWD: Mean species	OWD: Insensitive species
No. 2 Fuel	4	7.6 (7.2)	27 (4)	224 (31)	1872 (259)	5.5 (0.3)	46 (3)	383 (23)
No. 6 Fuel	4	8.3 (10.8)	27 (16)	225 (132)	1884 (1103)	5.5 (1.6)	46 (14)	387 (113)
Crude	8	1.0 (0.4)	32 (6)	271 (53)	2261 (442)	5.9 (0.6)	49 (5)	409 (44)
All	16	4.4 (6.8)	30 (9)	248 (74)	2075 (622)	5.7 (0.9)	48 (7)	400 (60)

Table 2. Content (percent) of all aromatics in crude oils and fuels and estimated LC50∞ (μg MAH+PAH/L) assuming equilibrium partitioning (WSF) or an oil-in-water dispersion (OWD) with equivalent percent composition to neat oil: Mean (SD).

Oil Type	n	Percent MAH + PAH	WSF: Sensitive species	WSF: Mean species	WSF: Insensitive species	OWD: Sensitive species	OWD: Mean species	OWD: Insensitive species
Gasoline	1	24.7	780	6,519	54,489	375	3,139	26,236
No. 2 Fuel	1	6.6	72	606	5,063	7	55	460
Crude	5	1.7 (1.1)	224 (133)	1,869 (1,110)	15,619 (9,276)	40 (45)	333 (373)	2,785 (3,116)

Modeling Approach and Methods

Matrix of Runs

The following is an outline of the inputs that were varied in the model runs performed. The objective was to estimate the *maximum* possible contamination in the water column in any one general location that could occur if dispersants were applied, and compare that to the same scenario but without dispersant application.

- One representative location off the coast of southern California: The objective is to estimate concentrations in space and time, water volumes exceeding thresholds of concern, and potential water column effects (as volume equivalents where toxicity would be expected). The results would be similar in most offshore areas of similar environmental conditions.
- One oil type: Light Arabian crude (the most common crude oil transported in California waters; does not emulsify enough to prevent dispersant use).

- One spill volume: maximum volume of oil that could be dispersed by a single sortie of a C-130 (100,000 gal of oil dispersed at 80%, 45% or 20% efficiency).
- One oil thickness: median value for dispersant application (100 μm).
- No-dispersant use as compared to 2 potential times after oil was spilled when dispersant was applied: 8 hrs and 16 hrs (weathered either 8 hrs or 16 hrs to allow volatilization of many lower-molecular-weight components, but not so weathered that dispersants would be ineffective).
- Two wind speeds with corresponding natural diffusion rates (horizontal and vertical eddy diffusion coefficients). Wind direction assumed constant from the NNW so the oil transport is southward along the coast. (Water plume dimensions and characteristics would be similar for all wind directions at the same angle relative to currents in offshore areas where dispersants might be applied, but the plume would move in different directions.)
  - Wind speed 5 kts with horizontal eddy diffusion 1 m^2/sec
  - Wind speed 15 kts with horizontal eddy diffusion 10 m^2/sec.
- Water depth in the surface mixed layer, assumed to retain all the dispersed oil (a worst-case condition)
  - 10m deep – all cases
  - 20m deep – selected cases.
- Background currents (other than surface wind drift from local winds) – constant in time and space (no tidal currents, which are not significant at sea)
  - 0 (none) – all cases
  - 0.25 kts to SSE (uniform in time and space), a typical current speed based on drifter studies during periods when the California Current prevails – selected cases
  - 0.25 kts to NNW (uniform in time and space), a typical current speed based on drifter studies during reversal periods for the California Current – selected cases.
- LC50s for acute toxic effects – range of species and life-stage sensitivities (based on French McCay, 2002)
  - 2.5th percentile sensitivity – 5 μg/L (ppb) of PAH
  - average sensitivity – 50 μg/L (ppb) of PAH
  - 97.5th percentile sensitivity – 400 μg/L (ppb) of PAH.

Oil Properties

Properties of Arabian Light crude oil were based on data in Environment Canada's Oil Property Catalogue (www.etcentre.org/spills). We had obtained data from Chevron on the properties of Arabian Light (Saudi oil). However, Environment Canada recently updated their oil database with Arabian Light crude, which has similar properties to that Chevron provided (non-significant differences). Because the Environment Canada database had additional parameters needed (e.g., C3 benzene content), and more detail on the boiling curve, as well as that fact that the Environment Canada database is published/publicly available, the Environment Canada database oil properties were used in the model runs. The key properties at the standard temperature of 25°C were: density =

0.8641 g/cm^3, viscosity = 13 cp, oil-water surface tension = 21.6 dyne/cm and maximum mousse water content =90%.

Oil Volume, Weathering Times, and Dispersant Application Assumptions

The payload volume for a typical C-130 ADDS pack is about 5,000 gal and the application rate is 100-800 gal/minute (S.L. Ross 1997; Al Allen, personal communication, September 2004). Assuming 20:1 oil:dispersant ratio and 80% efficiency (based on USCG 1999), this amounts to a maximum amount of oil that could be dispersed in one location of 80,000 gal in 6-50 minutes. The dispersed oil simulations were made starting with 100,000 gal (= 2,381 bbl = 326.3 MT) of oil released instantaneously and 80% of it (80,000 gal = 1,905 bbl = 261.1 MT) chemically dispersed immediately, with the application finishing by 0.5 hour. Model runs were previously performed to calculate the weathering that would occur by the time of the assumed dispersion, i.e., at 8hrs or 16hrs. In order to provide comparison data, parallel model runs to the dispersed oil simulations were made assuming no dispersant applied. Time “zero” in the simulations (time of dispersant application or initiation of the no-dispersant control runs) was after the 8 or 16 hrs of surface-oil weathering under the described conditions.

Oil Thickness and Initial Dimensions of the Oil Slick

The oil is assumed to be 100 μm thick at the time it is dispersed. This is half of the maximum limit for dispersant application of 0.2 mm, as described in the API 2001 guide (API et al., 2001). The oil would not emulsify enough by the time it is dispersed to inhibit the dispersion efficacy assumed. Based on the weathering model runs, the oil would not exceed dispersible viscosity limits by 24 hours after a spill.

With an initial volume of 100,000 gal (377.6 m^3), and an oil thickness of 100 μm, the initial area of the slick was 3.776 km^2. As an initial condition, it was assumed this area was circular in shape.

Spill Location and Conditions

For the spill site, we used a generic site offshore with a 10-m surface mixed layer. The oil is assumed not to diffuse below the surface mixed layer (to evaluate a worst-case condition of restricted vertical mixing). Additional runs were made assuming a 20-m surface mixed layer. Temperature is assumed 15^{o}C and salinity 33 ppt, typical for California waters.

Two wind speed conditions (constant over time) were run: (1) 5 knots, where natural entrainment is negligible, and (2) 15 knots where natural wind-driven entrainment is significant. When winds were assumed 5 kts, the horizontal eddy diffusion coefficient was 1.0 m^2/sec, a value typical of low turbulence conditions. When winds were assumed 15 kts, the horizontal eddy diffusion coefficient was assumed 10 m^2/sec. The vertical eddy diffusion coefficient was calculated from wind speed in the wave-mixed layer (based on Thorpe 1984; i.e., 1.5 times wave height, which was related to wind speed and duration) and assumed 1.0 cm^2/sec in deeper water. Using these assumptions, the dispersed oil was mixed over the surface mixed layer in a few hours (and restricted from mixing deeper by the assumption noted above).

For the base runs, the only currents included in the simulations are the wind drift in the surface mixed layer (calculated based on Youssef 1993; Youssef and Spaulding 1993, 1994). Background currents would carry the oil plume downstream at the current speed, but concentrations would remain similar to those simulated with no current unless current shear disperses (dilutes) the plume faster than the wind mixing would alone. Additional runs were made assuming typical current speeds of 0.25 kt directed either with the wind or against the wind.

Procedure for Model Runs

Weathering

Cases (with no dispersant applied) were run at each wind speed to determine weathering rates and the composition of the oil at 8 hrs and 16 hrs after release. The spill simulations with dispersants (as well as parallel no-dispersant cases) were started using oil initialized at the specified thickness of 100 μm, with the post-spreading minimum thickness set at 100 μm (so it no longer spreads), and pre-weathered as much as it would by time dispersed (8 or 16 hrs). We used the percentage of each of the volatile and semi-volatile pseudo-components left at the time dispersed (8 or 16 hrs) to determine percentage in the oil to start the with-dispersant simulation. Oil was dispersed at 0-0.5hr (so the simulation started at the time dispersed.)

The volume released in each of the non-dispersed pre-weathering cases needed to be the right amount to have 100,000 gal of floating oil remaining by time of “dispersant” application. Several non-dispersed oil runs were made to quantify the weathering by 8 or 16 hrs. We ran these using 5 kts of wind (constant). If winds were 15 kts (or higher), the oil would be naturally entrained and scattered and the dispersant application would not be as concentrated as on a contiguous area with 100,000 gal of floating oil. With different spill volumes, the percentage evaporated is slightly different. So, the spill size and percentage weathered data for each of the 8hr and 16hr dispersant application times were computed. We entered data for pre-weathered oil into the SIMAP oil database for each time one could apply dispersant.

Dispersant and Non-Dispersant Simulations

Paired runs were made, one each with and without dispersant added. The release was 100,000 gal (326.3 MT) of oil at the water surface as an instantaneous spill. Dispersant was applied within hours 0-0.5 at a rate of 10,000 gal/hr (522.2 MT/hr) to disperse 80% of the oil. Alternate runs assuming 45% (293.74 MT/hr) and 20% (130.55 MT/hr) of the oil dispersed (lower efficiencies) were made for comparison. The appropriate oil for the weathering time and thickness was used in the simulations.

Model Results

Weathering

Tables 3-5 show the composition of oil weathered for 2, 8 or 16 hrs. The results for the 8 and 16-hr weathering were used to initialize the oil properties in the dispersant simulations, as in most cases dispersant would be applied after this number of hours after release (except in the case of a continuous release). By 8 hours after release, two thirds of the MAHs have evaporated, and by 16 hours after release only 5% of the MAHs remain in the floating oil. Thus, if the oil were dispersed, most of the resulting dissolved hydrocarbon concentrations would be PAHs. These would be the components to monitor with field sampling.

Table 3. Weathering by 2 hours after a spill in 5 kts of wind (15^{o}C).

Component	Percent Left	Unweathered: Volatile Aromatics	Weathered: Volatile Aromatics	Unweathered: Total Volatiles	Weathered: Total Volatiles
MAHs	84.99	0.019571	0.016633	0.15900	0.135133
2-ring PAHs	99.31	0.001572	0.001561	0.16876	0.167588
3-ring PAHS	99.82	0.006230	0.006219	0.14004	0.139795
Total		0.027373	0.024413	0.46780	0.442515

Table 4. Weathering by 8 hours after a spill in 5 kts of wind (15^{o}C).

Component	Percent Left	Unweathered: Volatile Aromatics	Weathered: Volatile Aromatics	Unweathered: Total Volatiles	Weathered: Total Volatiles
MAHs	34.00	0.019571	0.006654	0.159	0.054060
2-ring PAHs	95.51	0.001572	0.001501	0.16876	0.161189
3-ring PAHS	98.87	0.00623	0.006159	0.14004	0.138455
Total		0.027373	0.014315	0.467800	0.353703

Table 5. Weathering by 16 hours after a spill in 5 kts of wind (15^{o}C).

Component	Percent Left	Unweathered: Volatile Aromatics	Weathered: Volatile Aromatics	Unweathered: Total Volatiles	Weathered: Total Volatiles
MAHs	5.40	0.019571	0.001058	0.159	0.008592
2-ring PAHs	88.40	0.001572	0.001390	0.16876	0.149177
3-ring PAHS	97.07	0.00623	0.006048	0.14004	0.135941
Total		0.027373	0.008495	0.467800	0.293710

Oil Fate and Plume Dimensions Over Time

Table 6 lists the model scenarios run. Appendix A.1 shows the mass balance of oil over time, indicating percentage floating, in the water, evaporated, etc. as a function of time. Note that the released mass is pre-weathered by 8 or 16 hrs, so the volatiles already evaporated are not included in the total mass. Most of the (remaining) volatilization occurs the first 24 hours after time “zero,” which is the time dispersant is applied (8 or 16 hrs after release). The cases with no dispersant show most of the mass either floating or evaporated. The cases with dispersant show about 80% in the water column initially, and most of the rest in the atmosphere or remaining floating. Mass is lost to “decay” (including photo-degradation and biodegradation) and to outside the model grid (reflected by a sharp drop of total mass at around 200 hours in some runs).

Model results are summarized as volumes, areas and dimensions of the dissolved aromatic plume > 1ppb over time. Table 7 provides a summary of the maximum dimension at any time after the oil is dispersed (or released in the no-dispersant cases). Appendix A.2 contains figures showing the change in plume dimensions over time. Figures 5 through 8 summarize the changes in plume dimensions over time for all the model simulations with 8 or 16 hours of pre-weathering, assuming no-current or a 0.25kt current, restricting vertical diffusion within a 10-m or 20-m mixed layer depth, in 5 or 15 kt winds, and with and without dispersant.

Table 6. Model scenarios run.

Scenario	Wind (kt)	Hrs of Weathering	Horiz Dispersion (m^2/sec)	Currents (dir. toward)	Surface Mixed Layer Depth (m)	Dispersed (0 = none; or 80, 45, 20%)
w8hr-5kt-h1-c0-10m-nd	5	8	1	0	10	0
w8hr-5kt-h1-c0-10m-wd	5	8	1	0	10	80
w8hr-5kt-h1-c0-20m-nd	5	8	1	0	20	0
w8hr-5kt-h1-c0-20m-wd	5	8	1	0	20	80
w8hr-15kt-h10-c0-10m-nd	15	8	10	0	10	0
w8hr-15kt-h10-c0-10m-wd	15	8	10	0	10	80
w8hr-15kt-h10-c0-20m-nd	15	8	10	0	20	0
w8hr-15kt-h10-c0-20m-wd	15	8	10	0	10	80
w16hr-5kt-h1-c0-10m-nd	5	16	1	0	10	0
w16hr-5kt-h1-c0-10m-wd	5	16	1	0	10	80
w16hr-5kt-h1-c0-20m-nd	5	16	1	0	20	0
w16hr-5kt-h1-c0-20m-wd	5	16	1	0	20	80
w16hr-5kt-h1-cnnw-10m-nd	5	16	1	NNW	10	0
w16hr-5kt-h1-cnnw-10m-wd	5	16	1	NNW	10	80
w16hr-5kt-h1-csse-10m-nd	5	16	1	SSE	10	0
w16hr-5kt-h1-csse-10m-wd	5	16	1	SSE	10	80
w16hr-15kt-h10-c0-10m-nd	15	16	10	0	10	0
w16hr-15kt-h10-c0-10m-wd	15	16	10	0	10	80
w16hr-15kt-h10-c0-20m-nd	15	16	10	0	20	0
w16hr-15kt-h10-c0-20m-wd	15	16	10	0	20	80
w16hr-15kt-h10-cnnw-10m-nd	15	16	10	NNW	10	0
w16hr-15kt-h10-cnnw-10m-wd	15	16	10	NNW	10	80
w16hr-15kt-h10-csse-10m-nd	15	16	10	SSE	10	0
w16hr-15kt-h10-csse-10m-wd	15	16	10	SSE	10	80
w16hr-5kt-h1-c0-10m-wd45	5	16	1	0	10	45
w16hr-5kt-h1-c0-10m-wd20	5	16	1	0	10	20
w16hr-15kt-h10-c0-10m-wd45	15	16	10	0	10	45
w16hr-15kt-h10-c0-10m-wd20	15	16	10	0	10	20

With the same wind speed and dispersant condition, the cases show similar patterns. With a 5 kt wind and no dispersant, the concentration plume is relatively small (Table 7, Figure 5) and short-lived (lasting a few hours, Figure 5, see also Appendix A.2). With a 5 kt wind and dispersant applied, the concentration plume is sizable and concentrations remain above 1 ppb for greater than the 10-day model run (Figure 6). In 15 kt winds, natural dispersion is considerable (as evidenced by results in Figure 7) and addition of dispersant at 80% efficiency increases the volume affected by >1ppb by a factor of 2-3 (compare Figures 7 and 8; also see Appendix A.2). In the 15-kt, no-dispersant cases, concentrations in the plume remain above 1ppb for 2-3 days. As in light-wind conditions, in the 15-kt scenarios the duration of water column exposure to concentrations >1ppb is significantly increased with dispersant use, but the plume (>1ppb concentration) is dispersed by 3-6 days (Figure 8). Dispersant application at lower efficiencies results in a proportionately smaller plume volume and shorter duration of exposure for water column biota (Figures 6 and 8). The results indicate that differences are subtle with degree of weathering over the range 8-16 hrs. The plume is generally smaller with more pre-weathering before dispersant application; however, in the high wind (15 kt) cases, the more viscous weathered oil has also spread more before entrainment, creating a larger profile (area) for the plume (see figures in Appendix A.2).

For the spills without dispersant, increasing the mixed layer depth lessens the volume affected by >1ppb because of faster dilution (Table 7, Figures 5 and 7); although in the 15-kt cases, concentrations remain >1ppb for 40-45 hours with a 20-m mixed depth as opposed to 30-32 hours with a 10-m mixed depth (Table 7, Figure 7). For the spills with dispersant applied, increasing the mixed layer depth increases the volume affected by >1ppb because it stretched (deepened) the plume without diluting it to below 1ppb (Table 7, Figures 6 and 8). The 5-kt wind, no-dispersant case after 8 hours of weathering also shows this behavior (Table 7, Figure 5). This behavior would have different patterns using other thresholds, the higher the threshold the more easily dilution overcomes the stretching phenomenon. Background currents also stretch the plume (in the horizontal) in most, but not all cases. These effects are subtle relative to other factors discussed above.

Table 7. Maximum dimensions of dissolved aromatic plume (>1ppb) after weathered for indicated amount of time.

Scenario	Maximum Volume (m^3)	Hours at Maximum Volume	Maximum Area (m^2)	Hours at Maximum Area	Maximum Length N-S (m)	Hours at Maximum Length N-S	Maximum Length E-W (m)	Hours at Maximum Length E-W	Hours Plume Dispersed to <1ppb
w8hr-5kt-h1-c0-10m-nd	59,498	3.5	59,498	3.5	2,418	5	214	1.5	2.5
w8hr-5kt-h1-c0-10m-wd	294,942,176	82	41,925,820	134	41,082	238	3,284	84	>240
w8hr-5kt-h1-c0-20m-nd	75,081	3.5	75,081	3.5	2,418	5	214	1.5	2.5
w8hr-5kt-h1-c0-20m-wd	350,729,856	206	37,186,888	76	38,671	220	4,239	154	>240
w8hr-15kt-h10-c0-10m-nd	177,345,360	11.5	40,771,568	13.5	19,510	26	5,955	15	30
w8hr-15kt-h10-c0-10m-wd	559,882,624	37	80,963,512	38	52,651	96	5,763	19	106
w8hr-15kt-h10-c0-20m-nd	103,962,744	9	49,073,864	21	23,204	35	7,331	21	40
w8hr-15kt-h10-c0-20m-wd	559,882,624	37	80,963,512	38	52,651	96	5,763	19	106
w16hr-5kt-h1-c0-10m-nd	44,323	1	44,323	1	1,173	2	198	1.5	2.5
w16hr-5kt-h1-c0-10m-wd	296,711,904	86	45,955,648	90	38,332	240	4,156	172	>240
w16hr-5kt-h1-c0-20m-nd	44,323	1	44,323	1	1,173	2	198	1.5	2.5
w16hr-5kt-h1-c0-20m-wd	413,799,328	240	38,010,796	86	42,076	238	2,981	130	>240
w16hr-5kt-h1-cnnw-10m-nd	63,761	3	63,761	3	1,674	3.5	198	1.5	2.5
w16hr-5kt-h1-cnnw-10m-wd	256,131,568	74	37,983,676	92	34,231	96	3,495	110	136
w16hr-5kt-h1-csse-10m-nd	44,390	1	44,390	1	1,174	2	198	1.5	2.5
w16hr-5kt-h1-csse-10m-wd	312,720,608	172	46,843,080	170	71,394	240	3,199	98	>240
w16hr-15kt-h10-c0-10m-nd	137,041,856	10	36,729,904	13.5	20,795	29	8,068	15.5	32
w16hr-15kt-h10-c0-10m-wd	471,411,296	23.5	68,224,832	40	46,029	100	6,390	29	110
w16hr-15kt-h10-c0-20m-nd	105,804,384	7.5	47,785,208	17	26,317	38	7,222	20	45
w16hr-15kt-h10-c0-20m-wd	539,406,976	26	108,089,064	38	51,438	112	8,024	45	126
w16hr-15kt-h10-cnnw-10m-nd	198,261,552	13	51,389,260	16	20,171	28	6,913	21.5	30
w16hr-15kt-h10-cnnw-10m-wd	550,148,864	24	81,385,376	34	55,654	80	6,246	52	82
w16hr-15kt-h10-csse-10m-nd	153,397,904	11.5	41,127,548	15.5	23,276	36	6,690	15.5	41
w16hr-15kt-h10-csse-10m-wd	491,387,776	34	84,308,312	44	42,572	134	8,185	42	90
w16hr-5kt-h1-c0-10m-wd45	177,656,320	45	26,535,880	84	38,257	220	2,981	84	>240
w16hr-5kt-h1-c0-10m-wd20	89,010,288	34	15,347,308	34	36,494	110	2,428	52	134
w16hr-15kt-h10-c0-10m-wd45	389,499,072	20	66,030,984	21	45,669	104	7,183	24	74
w16hr-15kt-h10-c0-10m-wd20	253,286,720	15	68,660,264	21	31,185	52	8,035	46	58

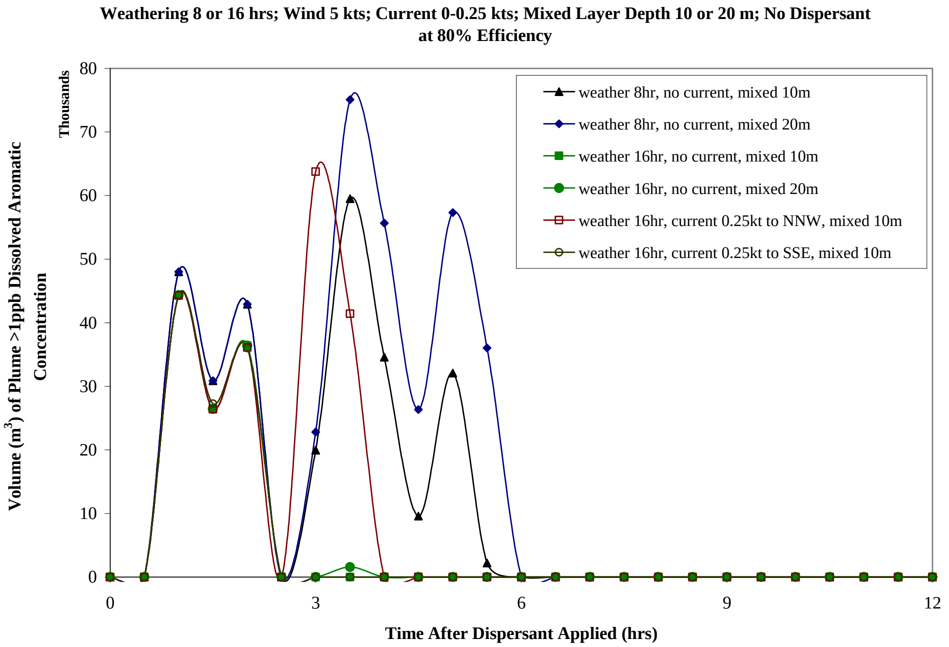

Figure 5. Volume (m^3) of the plume >1ppb over time for scenarios in 2.5m/s wind and with no dispersant.

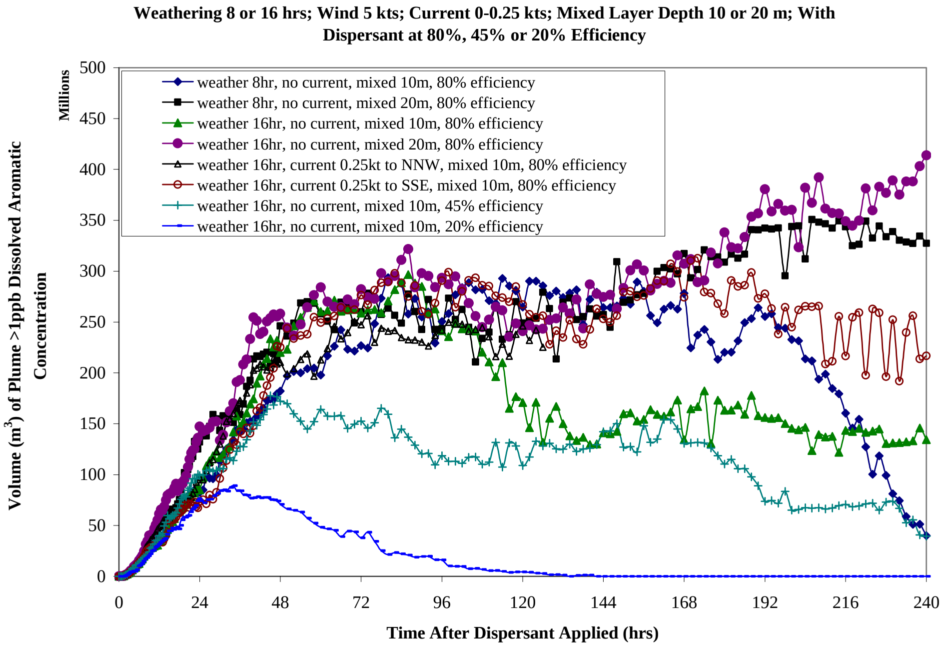

Figure 6. Volume (m^3) of the plume >1ppb over time for scenarios in 2.5m/s wind and with dispersant.

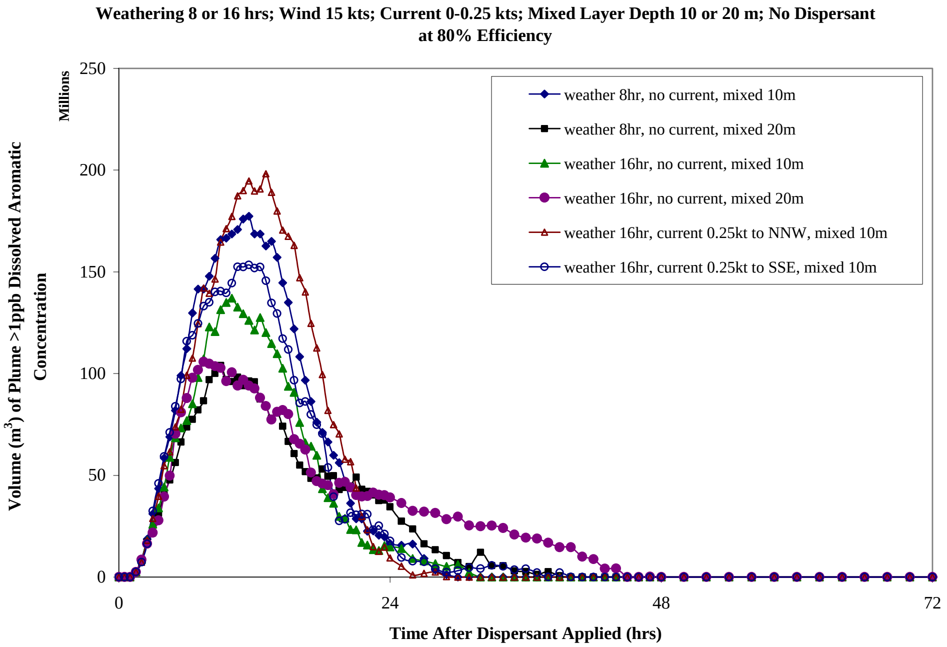

Figure 7. Volume (m^3) of the plume >1ppb over time for scenarios in 7.5m/s wind and with no dispersant.

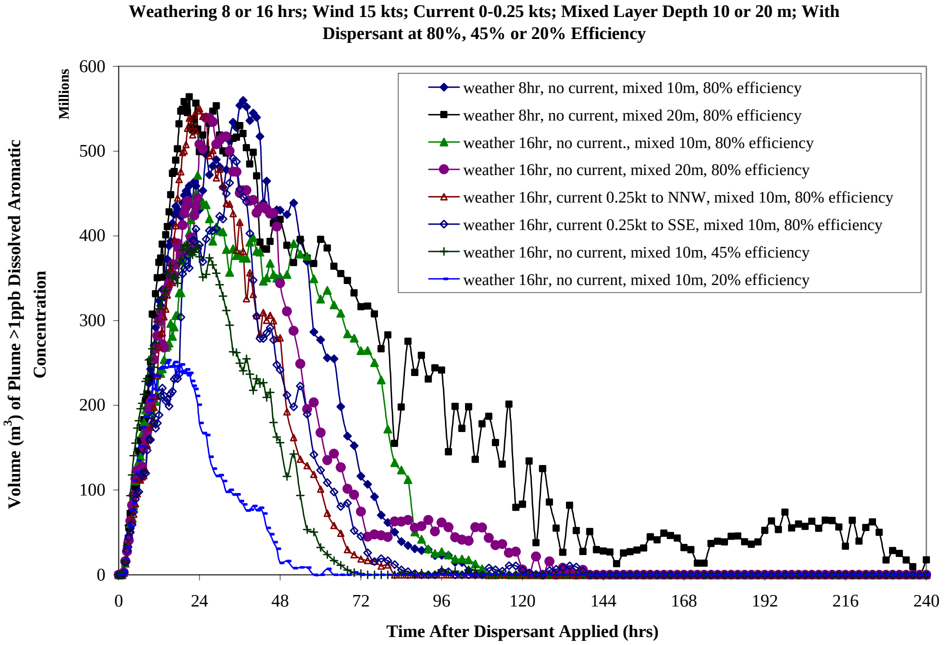

Figure 8. Volume (m^3) of the plume >1ppb over time for scenarios in 7.5m/s wind and with dispersant.

Acute Toxicity and Maximum Potential Impacts

Tables 8 and 9 summarize the equivalent areas of 100% loss, assuming a range of toxicity values (i.e., $LC50_\infty$ for the dissolved PAH mixture) characterizing 95% of species (French-McCay 2002). Percent loss in each affected volume is summed and divided by the mixed layer depth to calculate equivalent area of 100% mortality. The results in Tables 8 and 9 are the same; the cases are sorted in ascending order of impact in Table 9.

Table 8. Equivalent area (km^2) of 100% mortality of plankton.

Scenario	Sensitive: $LC50_\infty$ = 5 ppb	Average: $LC50_\infty$ = 50 ppb	Insensitive: $LC50_\infty$ = 400 ppb
w8hr-5kt-h1-c0-10m-nd	0.000	0.000	0.000
w8hr-5kt-h1-c0-10m-wd	14.650	1.753	0.105
w8hr-5kt-h1-c0-20m-nd	0.000	0.000	0.000
w8hr-5kt-h1-c0-20m-wd	7.421	0.658	0.005
w8hr-15kt-h10-c0-10m-nd	0.188	0.000	0.000
w8hr-15kt-h10-c0-10m-wd	1.428	0.060	0.000
w8hr-15kt-h10-c0-20m-nd	0.031	0.000	0.000
w8hr-15kt-h10-c0-20m-wd	2.134	0.062	0.000
w16hr-5kt-h1-c0-10m-nd	0.000	0.000	0.000
w16hr-5kt-h1-c0-10m-wd	13.583	1.541	0.092
w16hr-5kt-h1-c0-20m-nd	0.000	0.000	0.000
w16hr-5kt-h1-c0-20m-wd	7.564	0.628	0.001
w16hr-5kt-h1-cnnw-10m-nd	0.000	0.000	0.000
w16hr-5kt-h1-cnnw-10m-wd	13.751	1.061	0.027
w16hr-5kt-h1-csse-10m-nd	0.000	0.000	0.000
w16hr-5kt-h1-csse-10m-wd	18.650	2.047	0.047
w16hr-15kt-h10-c0-10m-nd	0.169	0.000	0.000
w16hr-15kt-h10-c0-10m-wd	1.687	0.078	0.000
w16hr-15kt-h10-c0-20m-nd	0.027	0.000	0.000
w16hr-15kt-h10-c0-20m-wd	2.164	0.085	0.000
w16hr-15kt-h10-cnnw-10m-nd	0.127	0.000	0.000
w16hr-15kt-h10-cnnw-10m-wd	3.356	0.054	0.000
w16hr-15kt-h10-csse-10m-nd	0.122	0.000	0.000
w16hr-15kt-h10-csse-10m-wd	3.596	0.086	0.000
w16hr-5kt-h1-c0-10m-wd45	9.368	0.779	0.010
w16hr-5kt-h1-c0-10m-wd20	1.362	0.098	0.000
w16hr-15kt-h10-c0-10m-wd45	1.128	0.020	0.000
w16hr-15kt-h10-c0-10m-wd20	0.479	0.004	0.000

Table 9. Equivalent area (km^2) of 100% mortality of plankton, sorted by area affected.

Scenario	Sensitive: $LC50_{\infty}$ = 5 ppb	Average: $LC50_{\infty}$ = 50 ppb	Insensitive: $LC50_{\infty}$ = 400 ppb
w8hr-5kt-h1-c0-10m-nd	0.000	0.000	0.000
w8hr-5kt-h1-c0-20m-nd	0.000	0.000	0.000
w16hr-5kt-h1-c0-10m-nd	0.000	0.000	0.000
w16hr-5kt-h1-c0-20m-nd	0.000	0.000	0.000
w16hr-5kt-h1-cnnw-10m-nd	0.000	0.000	0.000
w16hr-5kt-h1-csse-10m-nd	0.000	0.000	0.000
w16hr-15kt-h10-c0-20m-nd	0.027	0.000	0.000
w8hr-15kt-h10-c0-20m-nd	0.031	0.000	0.000
w16hr-15kt-h10-csse-10m-nd	0.122	0.000	0.000
w16hr-15kt-h10-cnnw-10m-nd	0.127	0.000	0.000
w16hr-15kt-h10-c0-10m-nd	0.169	0.000	0.000
w8hr-15kt-h10-c0-10m-nd	0.188	0.000	0.000
w16hr-15kt-h10-c0-10m-wd20	0.479	0.004	0.000
w16hr-15kt-h10-c0-10m-wd45	1.128	0.020	0.000
w16hr-5kt-h1-c0-10m-wd20	1.362	0.098	0.000
w8hr-15kt-h10-c0-10m-wd	1.428	0.060	0.000
w16hr-15kt-h10-c0-10m-wd	1.687	0.078	0.000
w8hr-15kt-h10-c0-20m-wd	2.134	0.062	0.000
w16hr-15kt-h10-c0-20m-wd	2.164	0.085	0.000
w16hr-15kt-h10-cnnw-10m-wd	3.356	0.054	0.000
w16hr-15kt-h10-csse-10m-wd	3.596	0.086	0.000
w8hr-5kt-h1-c0-20m-wd	7.421	0.658	0.005
w16hr-5kt-h1-c0-20m-wd	7.564	0.628	0.001
w16hr-5kt-h1-c0-10m-wd45	9.368	0.779	0.010
w16hr-5kt-h1-c0-10m-wd	13.583	1.541	0.092
w16hr-5kt-h1-cnnw-10m-wd	13.751	1.061	0.027
w8hr-5kt-h1-c0-10m-wd	14.650	1.753	0.105
w16hr-5kt-h1-csse-10m-wd	18.650	2.047	0.047

Results are highly sensitive to the toxicity value assumed, and indicate much higher impact areas for sensitive species and stages than average or insensitive species. The potential impact on sensitive species of dispersant use in these worst-case application scenarios is evident in the results. The impacted volume for a sensitive (2.5th percentile) species is negligible in 5 kts of wind with no dispersant, on the order of 1-2 million m^3 (i.e., a surface mixed layer 10-20 m deep with an area of 0.1 km^2) in 15-kts of wind for 100,000 gal (326.3 MT) of naturally-dispersed oil, 20-40 million m^3 (2 km^2 by 10-20 m deep) in 15-kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil (80%

efficiency), and 70-200 million m^3 (7-10 km^2 by 10-20 m deep) in 5-kts of wind for 80,000 gal (261.0 MT) of chemically-dispersed oil (80% efficiency). The impacted volume for a species of average sensitivity (50th percentile) is negligible in all wind conditions with no dispersant use, on the order of 0.5-0.9 million m^3 (0.05-0.045 km^2 by 10-20 m deep) in 15 kts of wind for 302.8 m^3 (80,000 gal, 261.0 MT) of chemically-dispersed oil (80% efficiency), and 6-20 million m^3 (0.6-1.0 km^2 by 10-20 m deep) in 5 kts of wind for 302.8 m^3 of chemically-dispersed oil (80% efficiency). Thus, the highest impacts are when chemical dispersant is applied under light wind conditions where dilution is relatively slow.

The design of the modeling was to evaluate worst-case scenarios. Thus, the results should not be considered typical of impacts that would occur if dispersants were applied to an oil spill. Also, it is important to note that while the volumes described above appear very impressive, the areas affected for even the most sensitive species are generally less than 4 km on a side. Volumes and areas impacted would be much less if the oil was patchy or more spread out (because each patch would be a smaller volume and there would be more edge where mixing and dilution would occur), or in the cases where the efficiency of the dispersant application is less than 80%. For example, in 5 kts of wind, the impacted volume for a species of average sensitivity (for 302.8 m^3 of chemically-dispersed oil after being weathered 16 hours, no currents, 10m mixed depth) is 15 million m^3 (area 1.5 km^2 by 10 m deep) if efficiency is 80%, 8 million m^3 (0.8 km^2) if efficiency is 45%, and 1 million m^3 (0.1 km^2) if efficiency is 20%. For the same model scenarios except in 15 kts of wind, the impacted volume for a species of average sensitivity is 780 thousand m^3 (78 thousand m^2) if efficiency is 80%, 200 thousand m^3 (20 thousand m^2) if efficiency is 45%, and 4 thousand m^3 (400 m^2) if efficiency is 20%.

Discussion

Potential Impacts of Dispersant Use on Water Column Biota

Significant water column impacts would be expected only after large crude (or light fuel) oil spills under certain conditions: surface releases under storm conditions (high turbulence), spills where dispersants are applied with high efficiency on large oil volumes, and subsurface releases (pipelines and blowouts). The larger the volume of PAH released (i.e., the combination of oil volume and PAH content) and the more turbulent the conditions, the more dissolution of the more toxic compounds into the water column. Thus, these conditions would lead to the highest exposure to the most toxic compounds.

Use of chemical dispersants on a large volume of oil concentrated in a relatively small area could lead to toxic concentrations in the surface mixed layer of the area where oil is entrained. However, in most (if not all) cases, the floating oil being dispersed will not be in a large contiguous area of the magnitude modeled here. Volumes of water where impacts would occur would be much less if the oil is patchy or more spread out, or in the cases where the efficiency of the dispersant application is less than 80%. The later conditions will be the norm when dispersants are applied in the field under less-thanperfect conditions, with imperfect knowledge of the location of the oil, and where oil has naturally broken up into patches and convergence zones.

Implications for Sampling

The modeling results show that a sampling program during monitoring of a dispersant application should include the following:

- Tracking the subsurface plume will be difficult as the plume moves with wind drift and other currents and dilutes to below 1 ppb dissolved PAH within hours to days. Wind speed and direction and currents should be measured near the oil dispersant application site with an anemometer and current meters (or instruments measuring the equivalent). Winds and currents are difficult to predict in an open ocean environment. Thus, markers such as drifters drogued at several depths within the mixed layer (and possibly dye) will be needed to allow samplers to follow the plume. Such an approach has been recently tested through seven dye and drifter studies off Point Loma (San Diego), CA in 2005 and 2006 (Payne et al. 2007a,b; 2008; French McCay et al. 2007, 2008).
- Drifters (with radio or satellite tracking of some kind) designed to move with the surface- and sub-surface mixed layers have been shown to be most effective in the above mentioned studies, and they would allow samplers to locate a dispersed oil plume from a distance and over time.
- Dyes (if used) may be readily measured using a fluorometer, most easily in a flow-through design; however, they would interfere with measurements of dispersed oil by fluorometry. Therefore, when sampling (and modeling) dispersed oil behavior, dye studies might be implemented in areas away from the dispersed oil to estimate the horizontal and vertical eddy diffusion coefficients needed to estimate the dilution rate of the plume (and potential impacts to biota). These are key data inputs to the fates and effects models. The dye measurements should be made in a grid or transect design and at multiple depths over the volume of the plume. Repeat sampling over time will allow calculation of eddy diffusion coefficients (from dilution rates) (Payne et al. 2007a; French McCay et al. 2007, 2008).
- The surface mixed layer depth is an important determinant of the dilution rate. This may be measured using a CTD (conductivity, temperature, depth) profiling instrument. A hose leading to a pump could be attached to the CTD to provide sample water for dye concentration measurements.
- Chemical sampling within the dispersed oil plume should be focused on measurement of PAHs in the water column both as part of dispersed oil droplets trapped on the glass fiber filter of the Portable Large Volume Water Sampling System (PLVWSS) and in the dissolved phase in the filtered water samples (Payne et al. 1999; Payne and Driskell 2003). Samples should be taken in a grid or transect design (as informed by the drifter movement) resampled over time (first few days after release, see Appendix A.2). Measurements of aliphatic hydrocarbons in whole water samples would document oil droplet concentrations in the water. Aliphatic concentrations in filtered samples should be very low as these compounds are only slightly soluble; however, their presence in the

particulate phase (filter) will help to quantify concentrations of dispersed oil droplets. A few samples and measurements of BTEX should be made early after dispersion to document the relatively low MAH concentrations that would be expected.

- Plankton samples should be taken to document the species and stages exposed, as well as their density in the water. Many planktonic organisms migrate on a diel cycle, so samples will be needed at different time periods of the day. As it will not be possible to synoptically sample both in and out of the plume in a design where statistical differences could be shown, the sampling should be completed near but not necessarily in the spill area to establish baseline (by number and weight for each species and life stage) and what types of organisms were exposed.
- Given the large variation in sensitivity of various species and life stages, acute toxicity bioassays may then be performed on potentially exposed organisms collected from the area. This work could be done in real time using sampled organisms from the area of the release and seawater collected from within the plume; however, it is more likely that potentially exposed organisms would be tested in a laboratory with field-collected seawater samples from the plume or (more likely) with mixtures of specific aromatics at concentrations similar to those measured in the field at the time of the spill. To simplify the task such that it would be feasible, bioassays with individual aromatic compounds of a range of solubility (e.g., toluene, naphthalene, and phenanthrene) should be done to determine the sensitivity of the species/stage to narcotic effects of soluble aromatics (the primary mode of action for acute effects). The rationale for this approach is in French-McCay (2002). Once a species/life stage's sensitivity is known, the oil toxicity model in French-McCay (2002) can be applied to estimate the LC50 for oil exposure.

References

American Petroleum Institute (API), National Oceanic and Atmospheric Administration (NOAA), U.S. Coast Guard (USCG), and U.S. Environmental Protection Agency (USEPA). 2001. Characteristics of Response Strategies: A Guide for Spill Response Planning in Marine Environments. Joint Publication of API, NOAA, USCG, and USEPA, June 2001, 80p.

Anderson, JW, Neff JM, Cox BA, Tatem HE, and G.M. Hightower. 1974. Characteristics of dispersions and water-soluble extracts of crude and refined oils and their toxicity to estuarine crustaceans and fish. Marine Biology 27: 75–88.

Anderson, J.W., Riley, R.G., S.L. Kiesser, and J. Gurtisen. 1987. Toxicity of dispersed and undispersed Prudhoe Bay crude oil fractions to shrimp and fish. Proceedings 1987 Oil Spill Conference (prevention, Behavior, Control, Cleanup), Tenth Biennial, American Petroleum Institute, Washington, DC, pp.235-240.

Blum, D.J., and R.E. Speece. 1990. Determining chemical toxicity to aquatic species, Environmental Science & Technology 24: 284-293.

Couillard, C.M., K. Lee, B. LeGare, and T.L. King. 2005. Effect of dispersant on the composition of the water accommodated fraction of crude oil and its toxicity to larval marine fish. Environmental Toxicology and Chemistry 24(6): 1496–1504.

Delvigne, G.A.L. and C.E. Sweeney.1988. Natural dispersion of oil. Oil and Chemical Pollution 4: 281-310.

DiToro, D.M., J.A. McGrath and D.J. Hansen. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. Environmental Toxicology and Chemistry 19(8): 1951-1970.

DiToro, D.M. and J.A. McGrath. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. Environmental Toxicology and Chemistry 19(8): 1971-1982.

French, D.P. 1991. Estimation of exposure and resulting mortality of aquatic biota following spills of toxic substances using a numerical model. Aquatic Toxicology and Risk Assessment Fourteenth Volume, ASTM STP 1124, M. A. Mayes and M.G. Barron, Eds., American Society for Testing and Materials, Philadelphia, 1991. pp. 35-47.

French, D.P. and F.W. French III. 1989. The biological component of the CERCLA Type A damage Assessment Model system. Oil and Chemical Pollution 5:125-163.

French, D., M. Reed, K. Jayko, S. Feng, H. Rines, S. Pavignano, T. Isaji, S. Puckett, A. Keller, F. W. French III, D. Gifford, J. McCue, G. Brown, E. MacDonald, J. Quirk, S. Natzke, R. Bishop, M. Welsh, M. Phillips and B.S. Ingram. 1996. The CERCLA type A natural resource damage assessment model for coastal and marine environments (NRDAM/CME), Technical Documentation, Vol.I - Model Description. Final Report, submitted to the Office of Environmental Policy and Compliance, U.S. Dept. of the Interior, Washington, DC, April, 1996, Contract No. 14-0001-91-C-11.

French McCay, D.P., C. Mueller, K. Jayko, B. Longval, M. Schroeder, E. Terrill, M. Carter, M. Otero, S.Y. Kim, J.R. Payne, W. Nordhausen, M. Lampinen, and C. Ohlmann. 2007. Evaluation of field-collected data measuring fluorescein dye movements and dispersion for dispersed oil transport modeling. Proceedings of the Thirtieth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, ON, Canada, pp. 713-754.

French-McCay, D.P., C. Mueller, J. Payne, E. Terrill, M. Otero, S.Y. Kim, M. Carter, W. Nordhausen, M. Lampinen, B. Longval, M. Schroeder, K. Jayko, and C. Ohlmann, 2008. Dispersed Oil Transport Modeling Calibrated by Field-Collected Data Measuring Fluorescein Dye Dispersion. Paper 393, Proceedings of the 2008 International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp 527-536.

French McCay, D.P. 2002. Development and Application of an Oil Toxicity and Exposure Model, OilToxEx. Environmental Toxicology and Chemistry 21(10): 2080-2094.

French McCay, D.P. 2003. Development and Application of Damage Assessment Modeling: Example Assessment for the *North Cape* Oil Spill. Marine Pollution Bulletin 47(9-12): 341-359.

French McCay, D.P. 2004. Oil spill impact modeling: Development and validation. Environmental Toxicology and Chemistry 23(10):2441-2456.

French McCay, D. and J.R. Payne. 2001. Model of Oil Fate and Water concentrations with and with out application of dispersants. In Proceedings of the 24th Arctic and Marine Oil spill Program (AMOP) Technical Seminar, Emergencies Science Division, Environment Canada, Ottawa, ON, Canada, pp.611-645.

French McCay, D.P., and J.J. Rowe. 2004. Evaluation of Bird Impacts in Historical Oil Spill Cases Using the SIMAP Oil Spill Model. In Proceedings of the 27th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Emergencies Science Division, Environment Canada, Ottawa, ON, Canada, pp. 421-452.

Gulec, I, and D.A. Holdway. 2000. Toxicity of crude oil and dispersed crude oil to ghost shrimp *Palaemon serenus* and larvae of Australian bass *Macquaria novemaculeata*. Environmental Toxicology 15:91–98.

Hodson, P.V., D.G. Dixon, and K.L.E. Kaiser. 1988. Estimating the acute toxicity of waterborne chemicals in trout from measurements of Median Lethal Dose and the octanol-water partition coefficient. Environmental Toxicology and Chemistry 7:443-454.

Kanga, SA, Bonner JS, Page CA, Mills MA, and R.L. Autenrieth. 1997. Solubilization of naphthalene and methyl-substituted naphthalenes from crude oil using biosurfactants. Environmental Science & Technology 31:556–561.

Kooijman, S.A.L.M.. 1981. Parametric analysis of mortality rates in bioassays. Water Research 15:107-119.

Mackay D, Leinonen, P.J. 1977. Mathematical model of the behavior of oil spills on water with natural and chemical dispersion. Prepared for Fisheries and Environment Canada. Economic and Technical Review Report EPS-3-EC-77-19.

Mackay, D., H. Puig and L.S. McCarty. 1992a. An equation describing the time course and variability in uptake and toxicity of narcotic chemicals to fish. Environ. Toxicol. Chemistry 11: 941-951.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992b. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. I, Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs. Lewis Publ., Chelsea, Michigan, 668p.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992c. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. II, Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Lewis Publ., Chelsea, Michigan, 566p.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992d. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. III, Volatile Organic Chemicals. Lewis Publ., Chelsea, Michigan, 885p.

McAuliffe, C.D.. 1987. Organism exposure to volatile/soluble hydrocarbons from crude oil spills – a field and laboratory comparison. Proceedings of the 1987 Oil Spill Conference, API, p. 275-288.

McCarty, L.S. 1986. The Relationship Between Aquatic Toxicity QSARs and Bioconcentration for Some Organic Chemicals, Journal of Environmental Toxicology Chemistry, 5:1071-1080, 1986.

McCarty, L.S., and D. Macka. 1993. Enhancing Ecotoxicological Modeling and Assessment, Environmental Science and Technology, Vol. 27, No. 9, p. 1719-1728.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn, and D.G. Dixon. 1992. Residue-based Interpretation of Toxicity and Bioconcentration QSARs from Aquatic Bioassays: Neutral Narcotic Organics, Journal of Environmental Toxicology and Chemistry 11: 917-930.

Middaugh DP, Whiting DD. 1995. Responses of embryonic and larval inland silversides, *Menidia beryllina*, to No. 2 fuel oil and oil dispersants in seawater. Arch Environ Contam Toxicol 29: 535–539.

National Research Council (NRC). 2005. Understanding oil spill dispersants: efficacy and effects. National Research Council, Ocean Studies Board, National Academies Press, Washington, DC.

Nirmalakhandan, N. and R.E. Speece. 1988. Structure-Activity Relationships, Quantitative Techniques for Predicting the Behavior of Chemicals in the Ecosystem, Environmental Science & Technology 22(6): 606-615.

Payne, J.R., B.E. Kirstein, G.D. McNabb, Jr., J.L. Lambach, R. Redding R.E. Jordan, W. Hom, C. deOliveria, G.S. Smith, D.M. Baxter, and R. Gaegel. 1984. Multivariate analysis of petroleum weathering in the marine environment – sub Arctic , Environmental Assessment of the Alaskan Continental Shelf, OCEAP, Final Report of Principal Investigators, Vol. 21 and 22, Feb. 1984, 690p.

Payne, J.R. and W.R. Driskell. 1999. Draft Preassessment Data Report: Analysis of water samples collected in support of the M/V New Carissa oil spill natural resource damage assessment. Report to NOAA, August 1999.

Payne, J.R., T.J. Reilly, and D.P. French. 1999. Fabrication of a portable large-volume water sampling system to support oil spill NRDA efforts. Proceedings of the 1999 Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp.1179-1184.

Payne, J.R. and W.B. Driskell. 2003. The importance of distinguishing dissolved- versus oil-droplet phases in assessing the fate, transport, and toxic effects of marine oil pollution. Proceedings of the 2003 Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp 771-778.

Payne, J.R., D. French-McCay, C. Mueller, K. Jayko, B. Longval, M. Schroeder, E. Terrill, M. Carter, M. Otero, S.Y. Kim, W. Middleton, A. Chen, W. Nordhausen, R. Lewis, M. Lampinen, T. Evans, and C. Ohlmann. 2007a. Evaluation of field-collected drifter and in situ fluorescence data measuring subsurface dye plume advection/dispersion and comparisons to high-frequency radar-observation system data for dispersed oil transport modeling. Final Report 06-084, Coastal Response

Research Center, NOAA/University of New Hampshire, Durham, NH, 98 p. plus 8 appendices. May 11, 2007. Available at http://www.crrc.unh.edu/.

Payne, J.R., E. Terrill, M. Carter, M. Otero, W. Middleton, A. Chen, D. French-McCay, C. Mueller, K. Jayko, W. Nordhausen, R. Lewis, M. Lampinen, T. Evans, C. Ohlmann, G.L. Via, H. Ruiz-Santana, M. Maly, B. Willoughby, C. Varela, P. Lynch, and P. Sanchez. 2007b. Evaluation of field-collected drifter and subsurface fluorescein dye concentration data and comparisons to high frequency radar surface current mapping data for dispersed oil transport modeling. Proceedings of the Thirtieth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, ON, Canada, pp. 681-712.

Payne, J.R., E. Terrill, M. Carter, M. Otero, W. Middleton, A. Chen, D. French-McCay, C. Mueller, K. Jayko, W. Nordhausen, R. Lewis, M. Lampinen, T. Evans, C. Ohlmann, G.L. Via, H. Ruiz-Santana, M. Maly, B. Willoughby, C. Varela, P. Lynch, and P. Sanchez. 2008. Field measurements of fluorescence dye dispersion to inform dispersed-oil plume sampling and provide input for oil-transport modeling. Proceedings of the 2008 International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp 515-526.

Reddy, C.M. and J.G. Quinn. 1996. North Cape oil spill, Analysis of water samples collected on the R/V Cap’n Bert Cruise II (01/25/96). Organic Geochemistry Laboratory, Graduate School of Oceanography, Univ. of RI, Narragansett, RI, October 2, 1996.

Short, J.W. and P. H. Harris. 1996. Chemical sampling and analysis of petroleum hydrocarbons in near-surface seawater of Prince William Sound after the Exxon Valdez oil spill. Proceedings of the Exxon Valdez oil spill symposium. S. D. Rice, R. B. Spies, D. A. Wolfe, and B. A. Wright (eds.), American Fisheries Society Symposium 18:17-28.

S.L. Ross Environmental Research Ltd., 1997. A review of dispersant use on spills of North Slope crude oil in Prince William Sound and the Gulf of Alaska. Ottawa, Ontario: Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska. 189p plus appendices.

Sprague, J.B.. 1970. Measurement of pollutant toxicity to fish. II. Utilizing and Applying Bioassay Results. Water Research 4: 3-32.

Swartz, R.C., D.W. Schults, R.J. Ozretich, J.O. Lamberson, F.A. Cole, T.H. DeWitt, M.S. Redmond, and S.P. Ferraro. 1995. ∑PAH: A Model to Predict the Toxicity of Polynuclear Aromatic Hydrocarbon Mixtures in Field-Collected Sediments, Journal of Environmental Toxicology and Chemistry 14(11):1977-1987.

Thorpe, S.A. 1984. On the Determination of Kv in the Near Surface Ocean from Acoustic Measurements of Bubbles. American Meteorological Society 1984: 861-863.

U. S. Coast Guard (USCG). 1999. Response Plan Equipment Caps Review: Are Changes to Current Mechanical Recovery, Dispersant, and in situ Burn Equipment Requirements Practicable? Washington, D.C.: United States Coast Guard, U. S. Department of Transportation, pp.1-177, plus appendices.

Varhaar, H.J.M, C.J. VanLeeuwen, and J.L.M. Hermens. 1992. Classifying Environmental Pollutants, 1: Structure-activity Relationships for Prediction of Aquatic Toxicity. Chemosphere 25:471-491.

Youssef, M.. 1993. The Behavior of the Near Ocean Surface Under the Combined Action of Waves and Currents in Shallow Water, PhD Dissertation, Department of Ocean Engineering, University of Rhode Island, Narragansett, RI, 212p.

Youssef, M. and M. L. Spaulding. 1993. Drift Current Under the Action of Wind Waves", in Proceedings of the Sixteenth Arctic and Marine Oilspill Program Technical Seminar, Ottawa, ON, Canada, pp. 587-615.

Youssef, M. and M.L. Spaulding. 1994. Drift Current Under the Combined Action of Wind and Waves in Shallow Water. In: Proceedings of the Seventeenth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Ottawa, ON, Canada, pp. 767-784.

Appendix A.1. Mass balance of oil over time showing percentage of the oil in each model compartment.

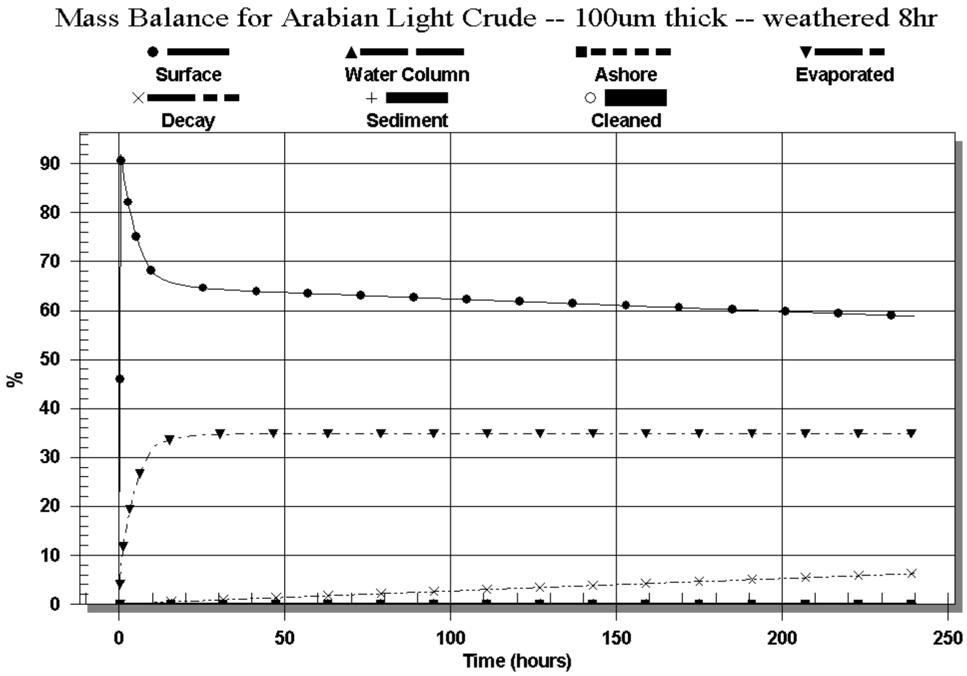

Figure A.1-1. Mass balance for scenario : W8hr-5kt-H10-C0-10m-ND (8 hour weathering, 5 kt winds, no currents, 10 m deep mixing zone and no dispersant).

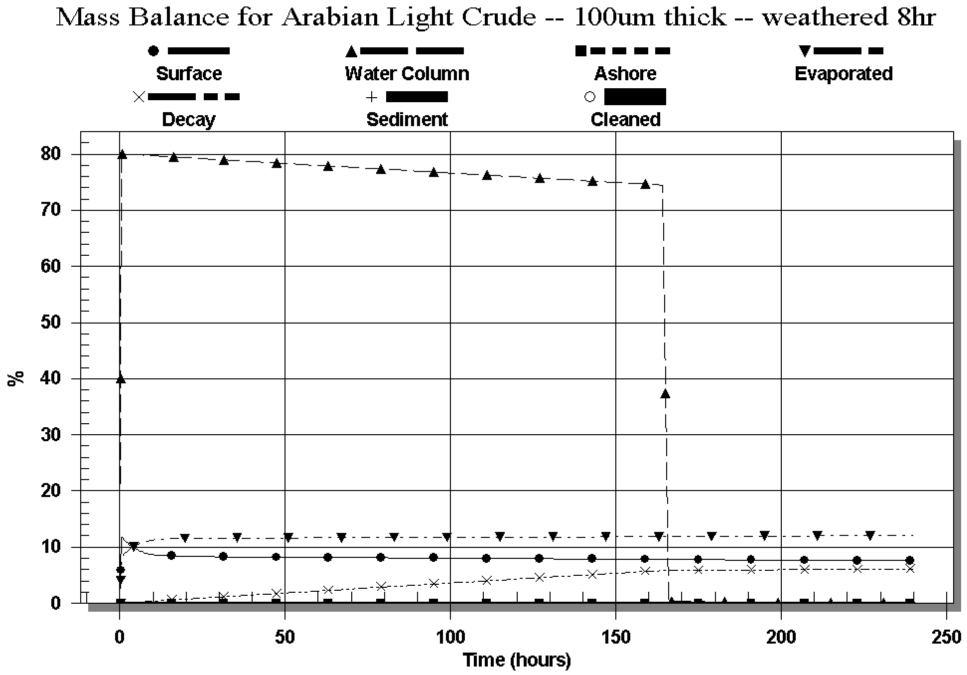

Figure A.1-2. Mass balance for scenario : W8hr-5kt-H10-C0-10m-WD (8 hour weathering, 5 kt winds, no currents, 10 m deep mixing zone with dispersant).

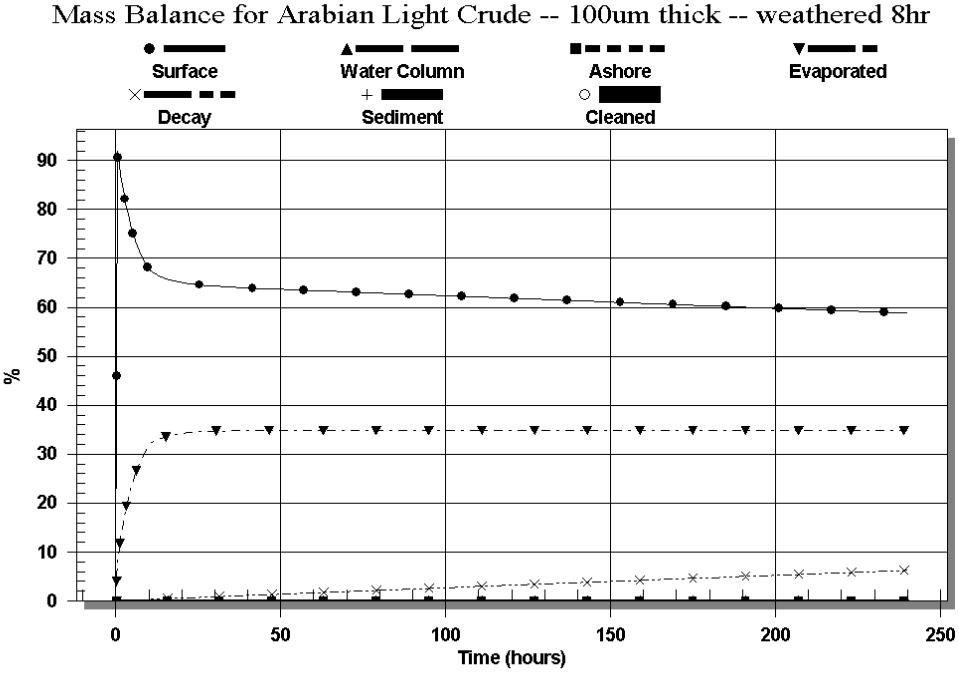

Figure A.1-3. Mass balance for scenario : W8hr-5kt-H10-C0-20m-ND (8 hour weathering, 5 kt winds, no currents, 20 m deep mixing zone and no dispersant).

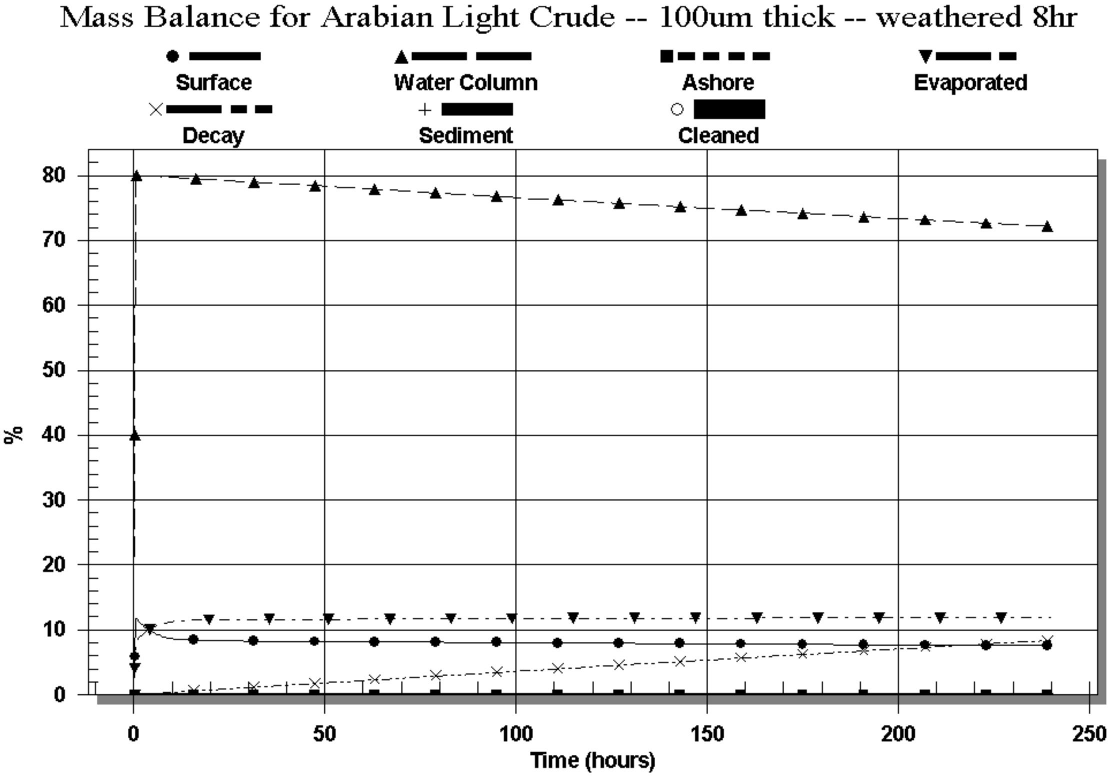

Figure A.1-4. Mass balance for scenario : W8hr-5kt-H10-C0-20m-WD (8 hour weathering, 5 kt winds, no currents, 20 m deep mixing zone with dispersant).

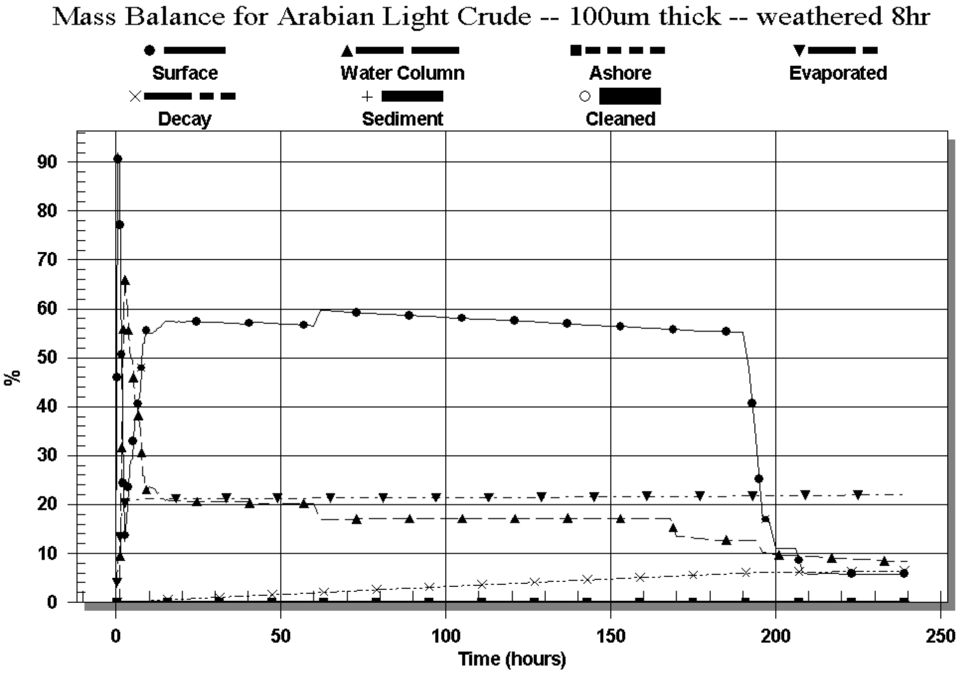

Figure A.1-5. Mass balance for scenario : W8hr-15kt-H10-C0-10m-ND (8 hour weathering, 15 kt winds, no currents, 10 m deep mixing zone and no dispersant).

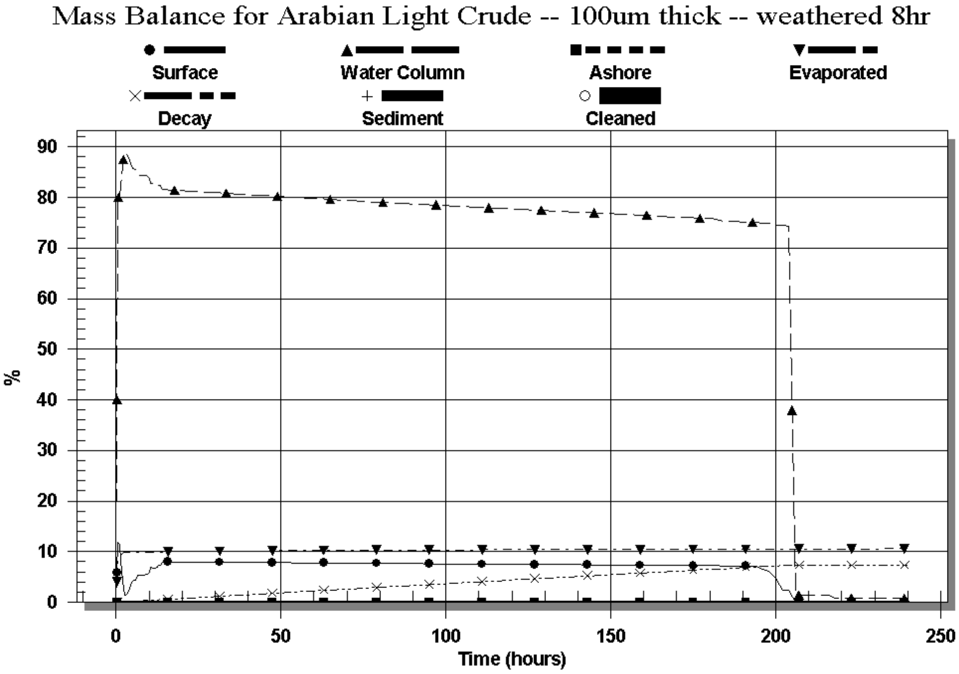

Figure A.1-6. Mass balance for scenario : W8hr-15kt-H10-C0-10m-WD (8 hour weathering, 15 kt winds, no currents, 10 m deep mixing zone with dispersant).

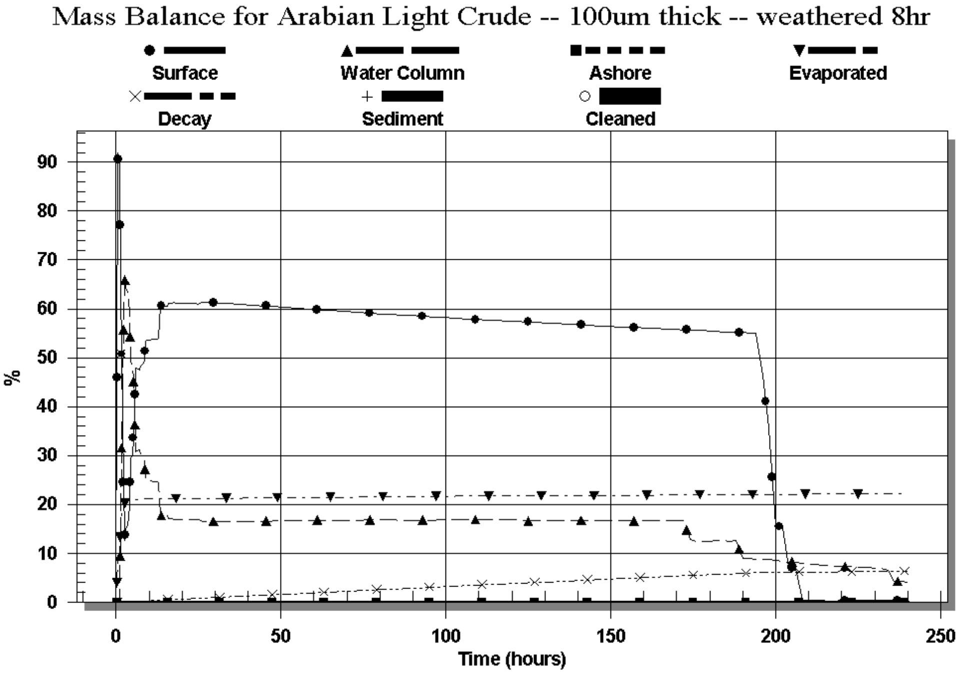

Figure A.1-7. Mass balance for scenario : W8hr-15kt-H10-C0-10m-ND (8 hour weathering, 15 kt winds, no currents, 20 m deep mixing zone, no dispersant).

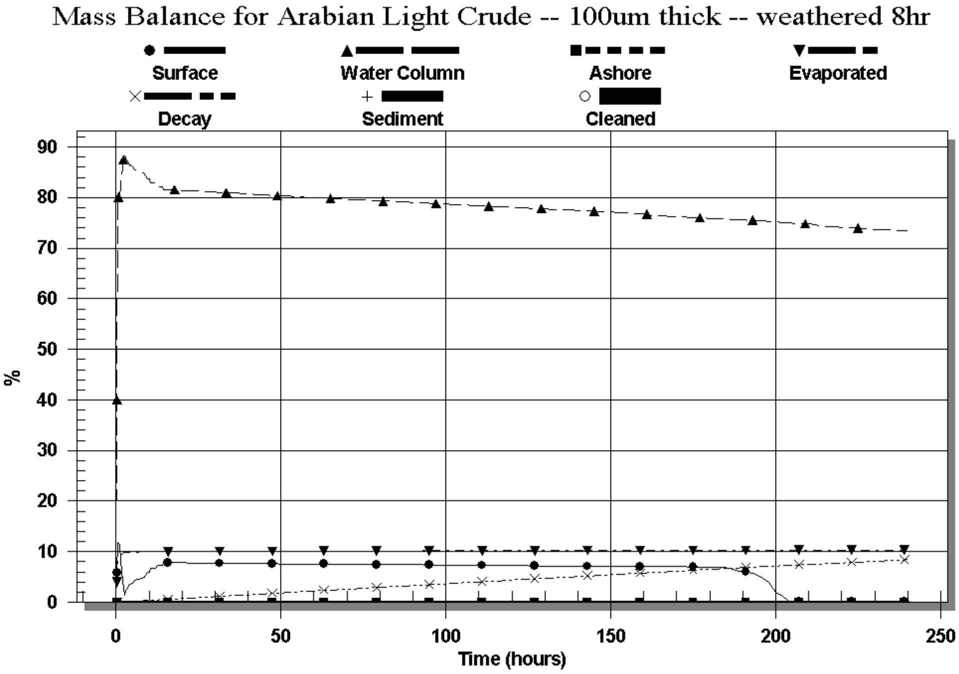

Figure A.1-8. Mass balance for scenario : W8hr-15kt-H10-C0-10m-WD (8 hour weathering, 15 kt winds, no currents, 20 m deep mixing zone with dispersant).

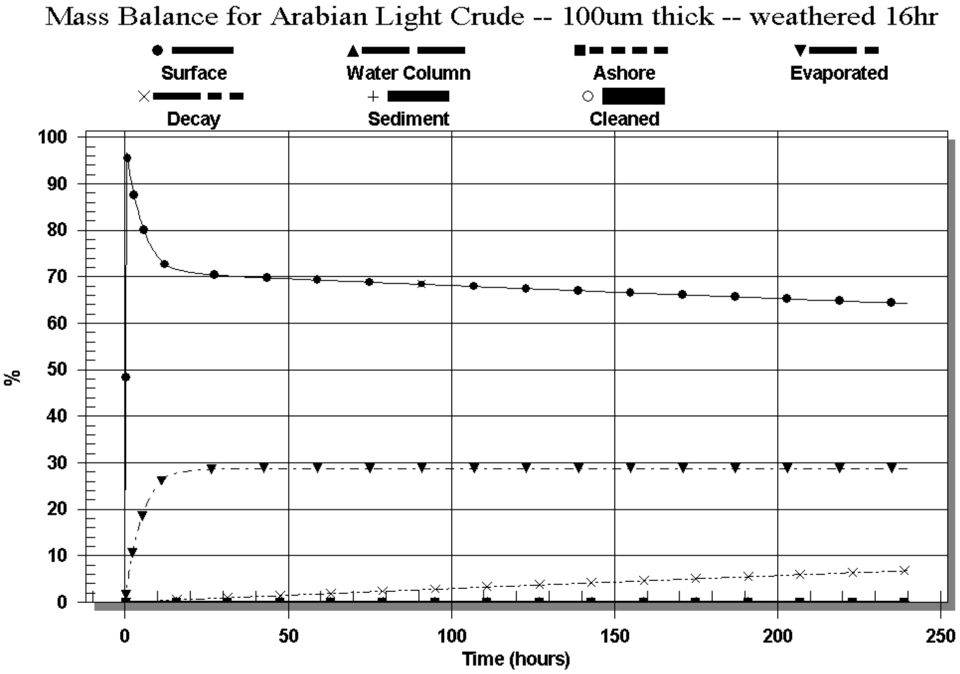

Figure A.1-9. Mass balance for scenario : W16hr-5kt-H1-C0-10m-ND (16 hour weathering, 5 kt winds, no currents, 10 m deep mixing zone, no dispersant).

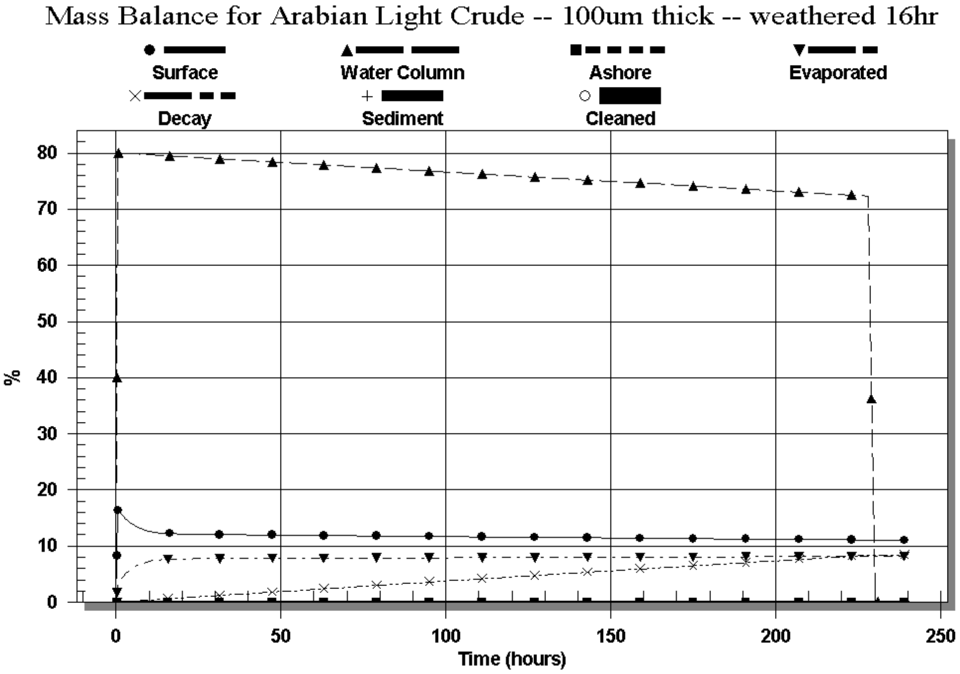

Figure A.1-10. Mass balance for scenario : W16hr-5kt-H1-C0-10m-WD (16 hour weathering, 5 kt winds, no currents, 10 m deep mixing zone with dispersant).

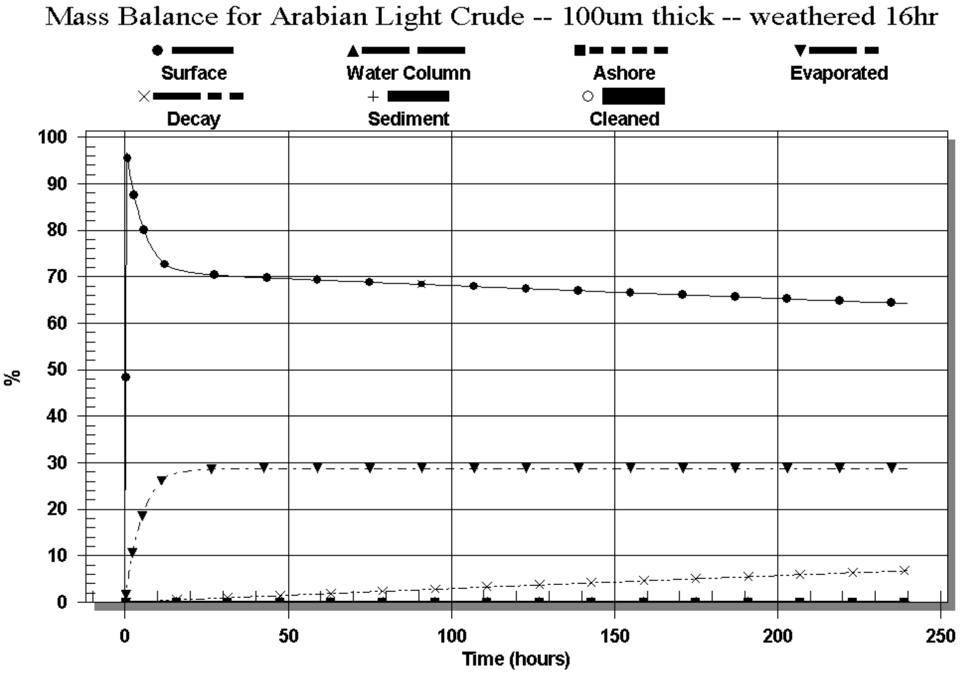

Figure A.1-11. Mass balance for scenario : W16hr-5kt-H1-C0-20m-ND (16 hour weathering, 5 kt winds, no currents, 20 m deep mixing zone, no dispersant).

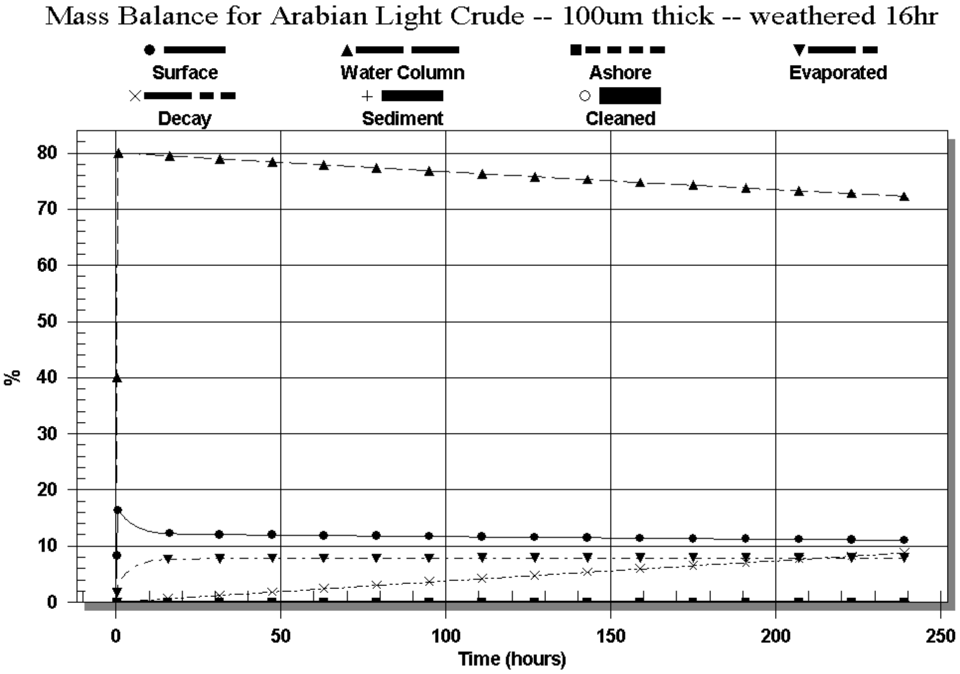

Figure A.1-12. Mass balance for scenario : W16hr-5kt-H1-C0-20m-WD (16 hour weathering, 5 kt winds, no currents, 20 m deep mixing zone with dispersant).

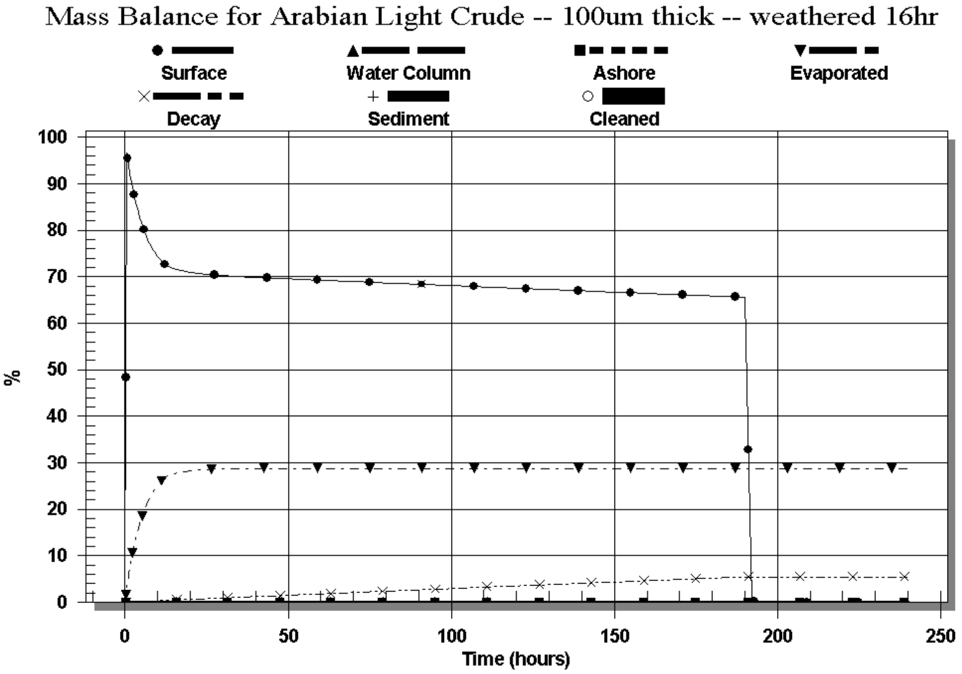

Figure A.1-13. Mass balance for scenario : W16hr-5kt-H1-CNNW-10m-ND (16 hour weathering, 5 kt winds, NNW currents, 10 m deep mixing zone, no dispersant).

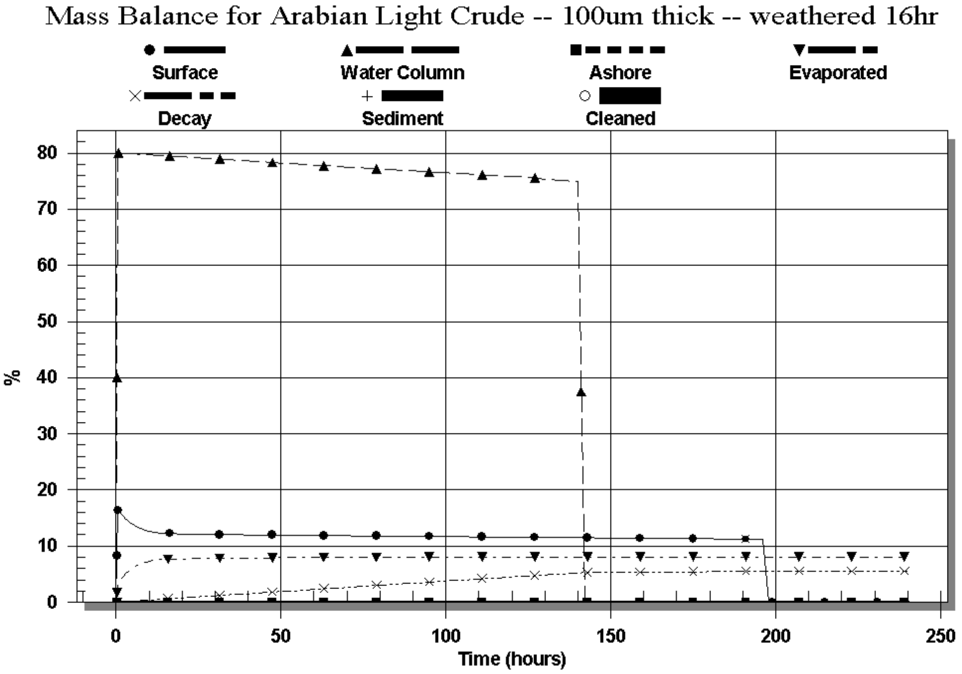

Figure A.1-14. Mass balance for scenario : W16hr-5kt-H1-CNNW-10m-WD (16 hour weathering, 5 kt winds, NNW currents, 10 m deep mixing zone with dispersant).

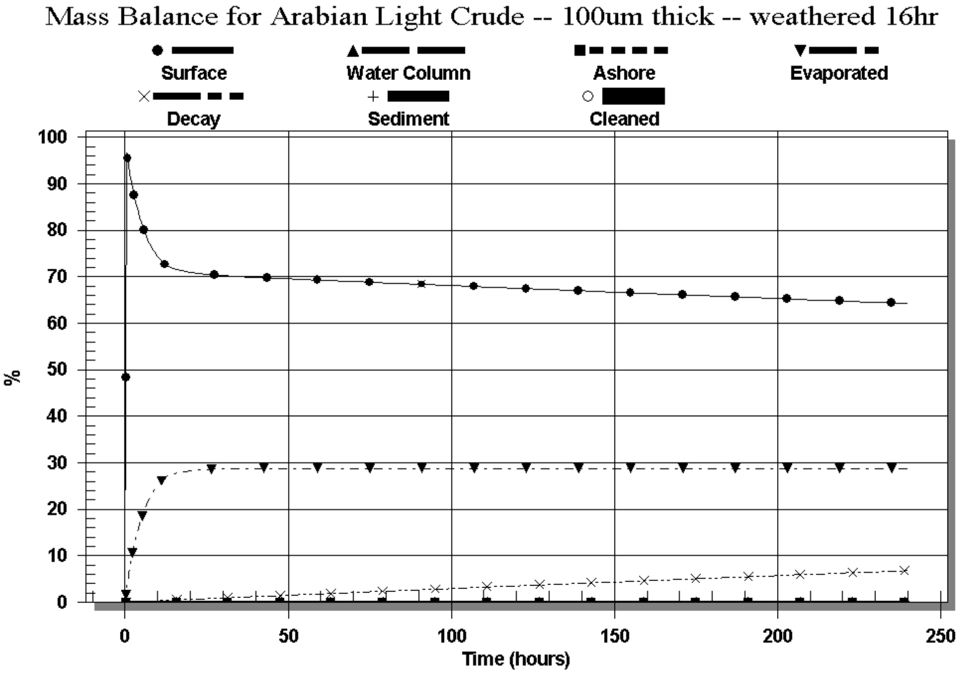

Figure A.1-15. Mass balance for scenario : W16hr-5kt-H1-CSSE-10m-ND (16 hour weathering, 5 kt winds, SSE currents, 10 m deep mixing zone, no dispersant).

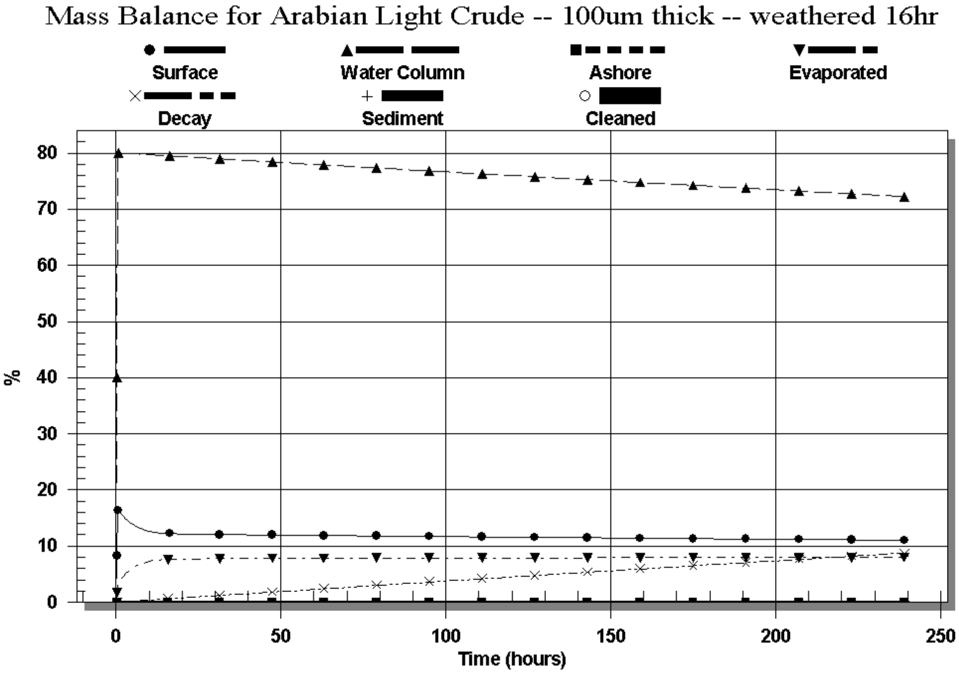

Figure A.1-16. Mass balance for scenario : W16hr-5kt-H1-CSSE -10m-WD (16 hour weathering, 5 kt winds, SSE currents, 10 m deep mixing zone with dispersant).

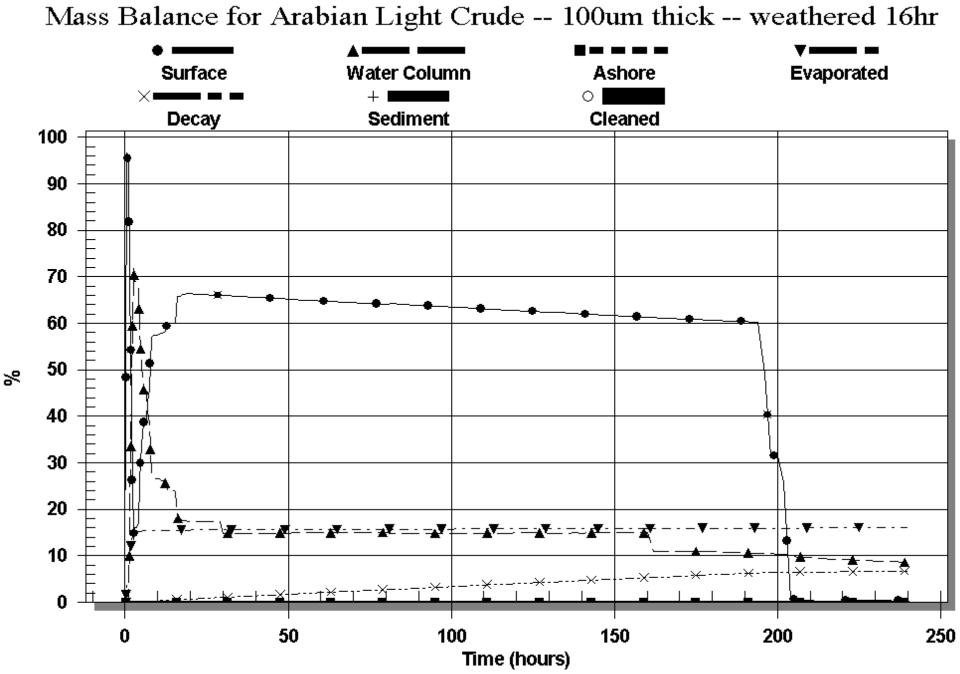

Figure A.1-17. Mass balance for scenario : W16hr-15kt-H10-C0-10m-ND (16 hour weathering, 15 kt winds, no currents, 10 m deep mixing zone, no dispersant).

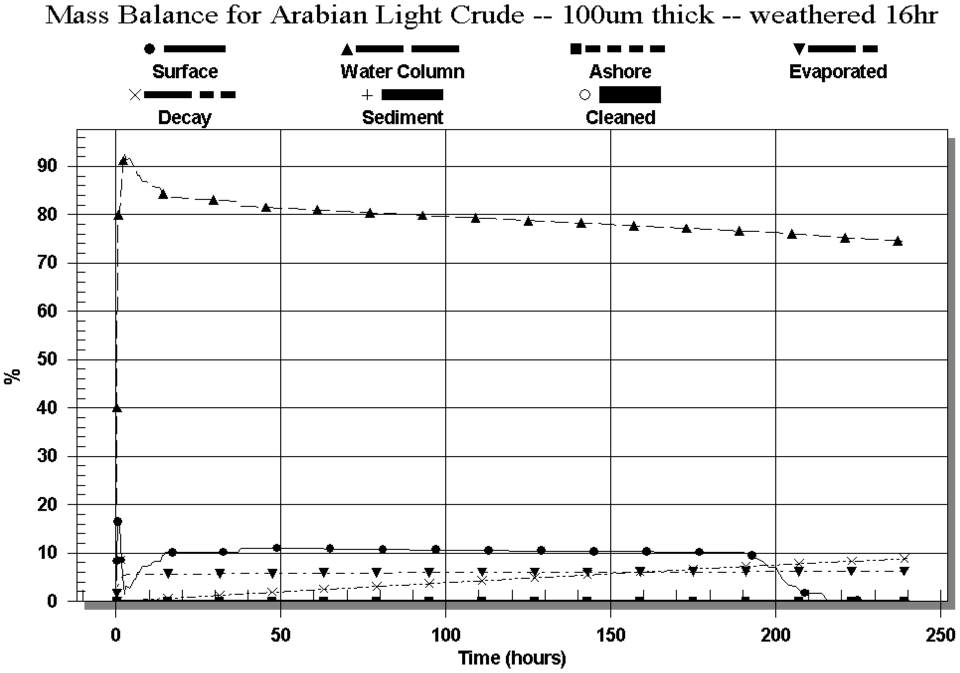

Figure A.1-18. Mass balance for scenario : W16hr-15kt-H10-C0-10m-WD (16 hour weathering, 15 kt winds, no currents, 10 m deep mixing zone with dispersant).

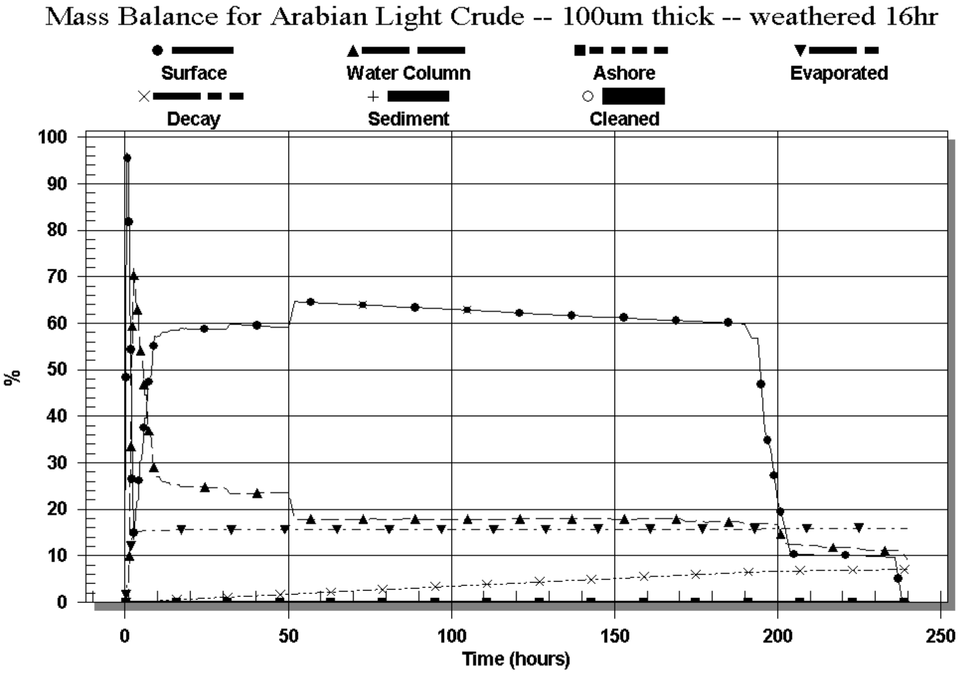

Figure A.1-19. Mass balance for scenario : W16hr-15kt-H10-C0-20m-ND (16 hour weathering, 15 kt winds, no currents, 20 m deep mixing zone, no dispersant).

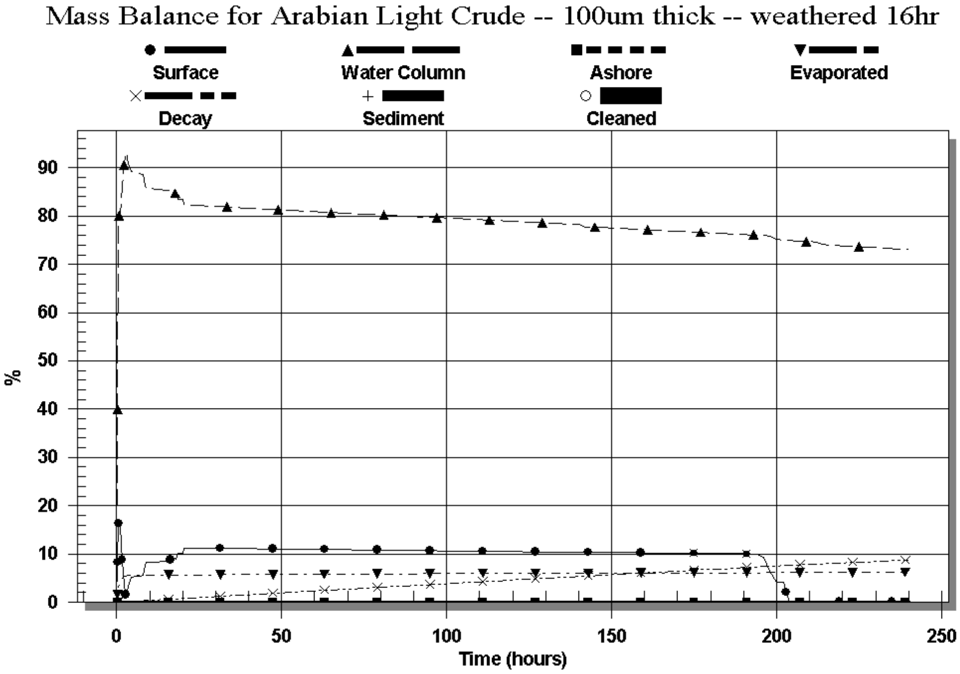

Figure A.1-20. Mass balance for scenario : W16hr-15kt-H10-C0-20m-WD (16 hour weathering, 15 kt winds, no currents, 20 m deep mixing zone with dispersant).

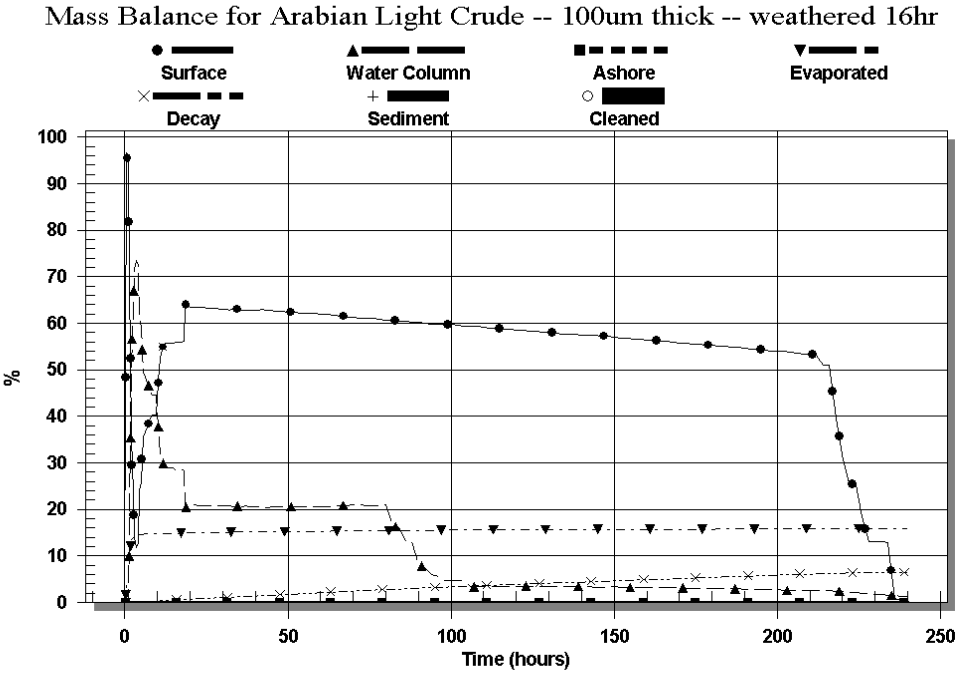

Figure A.1-21. Mass balance for scenario : W16hr-15kt-H10-CNNW-10m-ND (16 hour weathering, 15 kt winds, NNW currents, 10 m deep mixing zone, no dispersant).

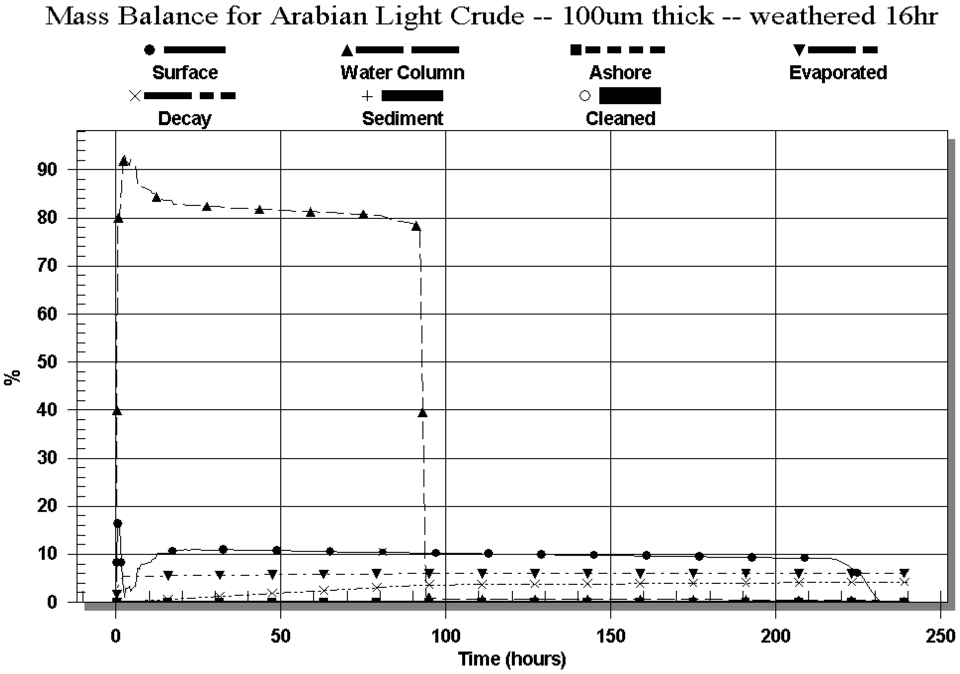

Figure A.1-22. Mass balance for scenario : W16hr-15kt-H10-CNNW-10m-WD (16 hour weathering, 15 kt winds, NNW currents, 10 m deep mixing zone with dispersant).

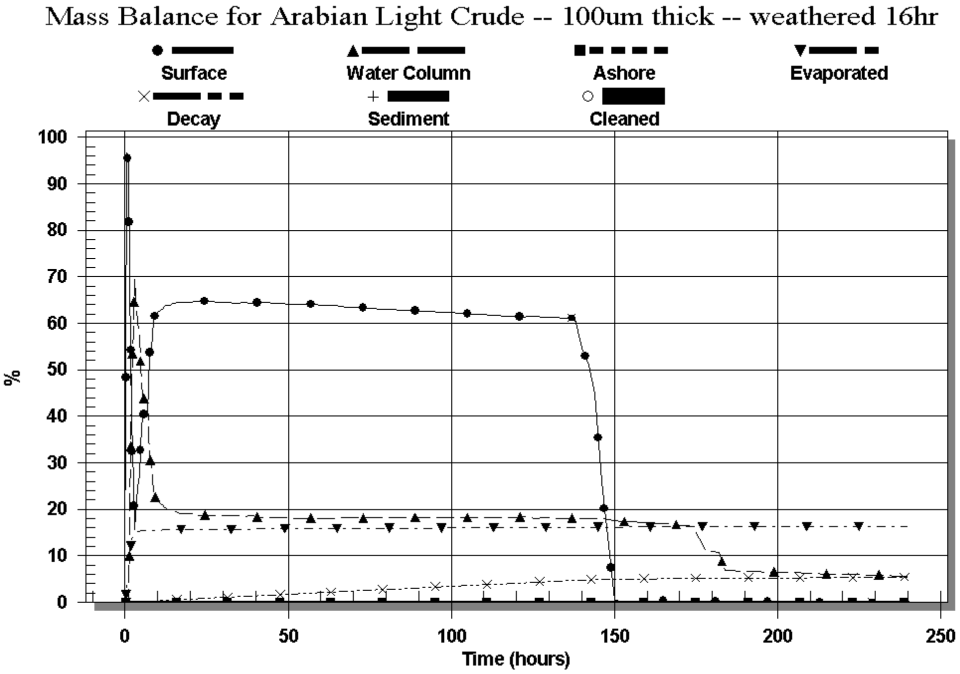

Figure A.1-23. Mass balance for scenario : W16hr-15kt-H10-CSSE -10m-ND (16 hour weathering, 15 kt winds, SSE currents, 10 m deep mixing zone, no dispersant).

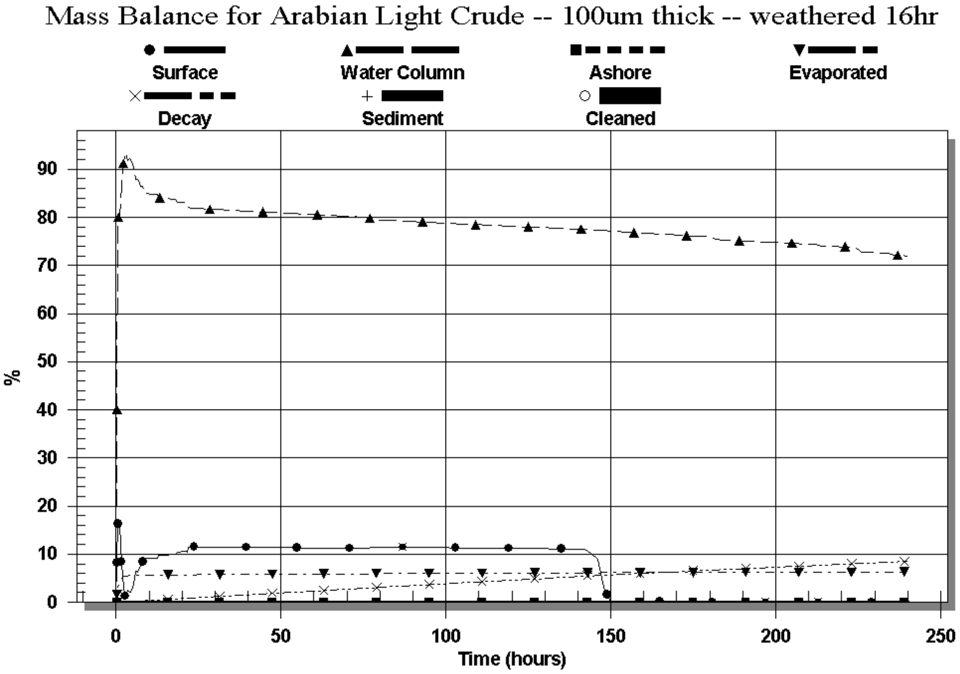

Figure A.1-24. Mass balance for scenario : W16hr-15kt-H10-CSSE-10m-WD (16 hour weathering, 15 kt winds, SSE currents, 10 m deep mixing zone with dispersant).

Appendix A.2. Dimensions of the plume over time

This appendix contains subsurface plume dimensions over time estimated by the modeling (i.e., volume, area, east-west extent and north-south extent of the volume >1ppb dissolved aromatics.)

Table B-1. Scenarios for which figures are included in this appendix.

w16hr-5kt-h1-c0-10m-nd
w16hr-5kt-h1-c0-10m-wd
w16hr-5kt-h1-c0-20m-nd
w16hr-5kt-h1-c0-20m-wd
w16hr-5kt-h1-cnnw-10m-nd
w16hr-5kt-h1-cnnw-10m-wd
w16hr-5kt-h1-csse-10m-nd
w16hr-5kt-h1-csse-10m-wd
w16hr-15kt-h10-c0-10m-nd
w16hr-15kt-h10-c0-10m-wd
w16hr-15kt-h10-c0-20m-nd
w16hr-15kt-h10-c0-20m-wd

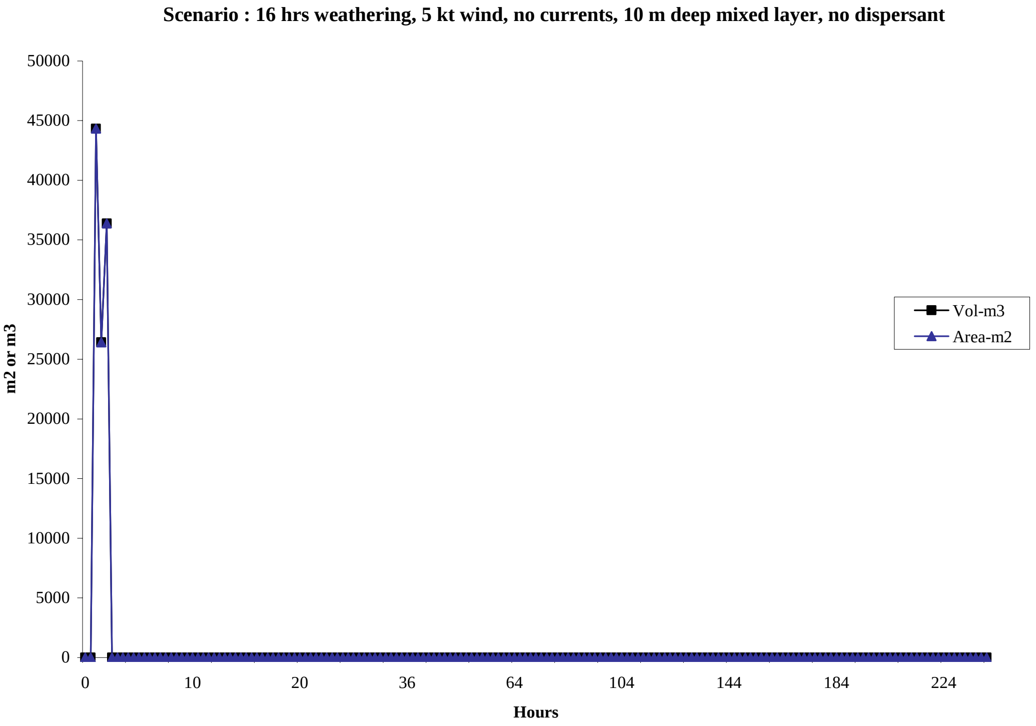

Figure A.2-1. Volume (m^3) and area (m^2) of plume >1ppb over time for "w16hr-5kt-h1-c0-10m-nd" scenario.

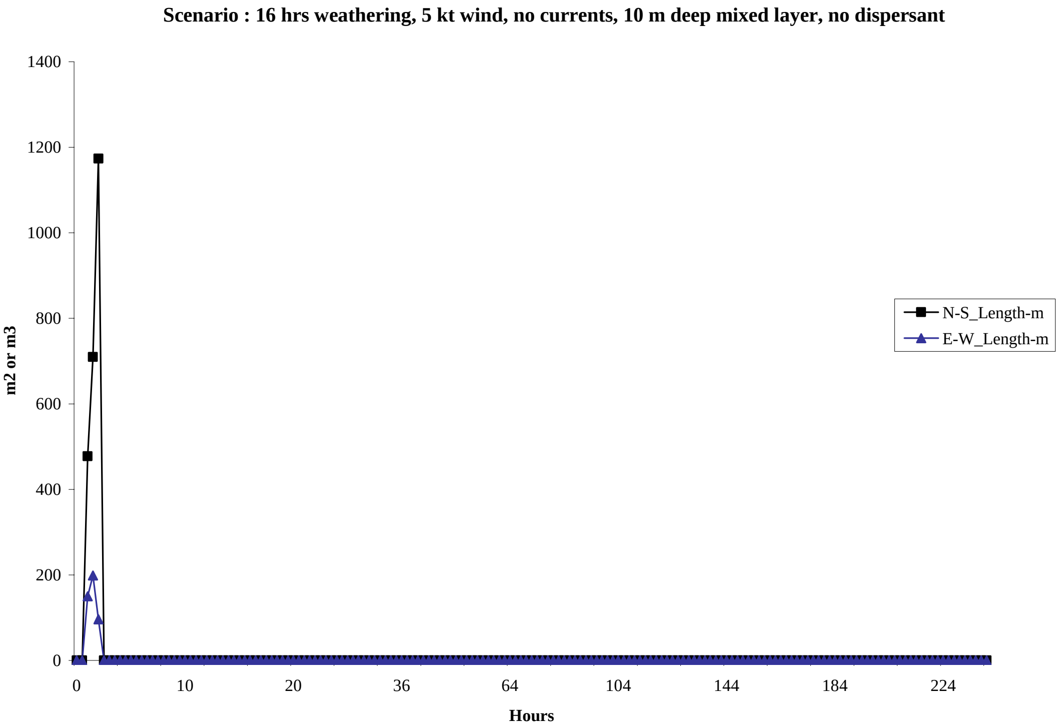

Figure A.2-2. East-west and north-south lengths (m) of plume >1ppb over time for "w16hr-5kt-h1-c0-10m-nd" scenario.

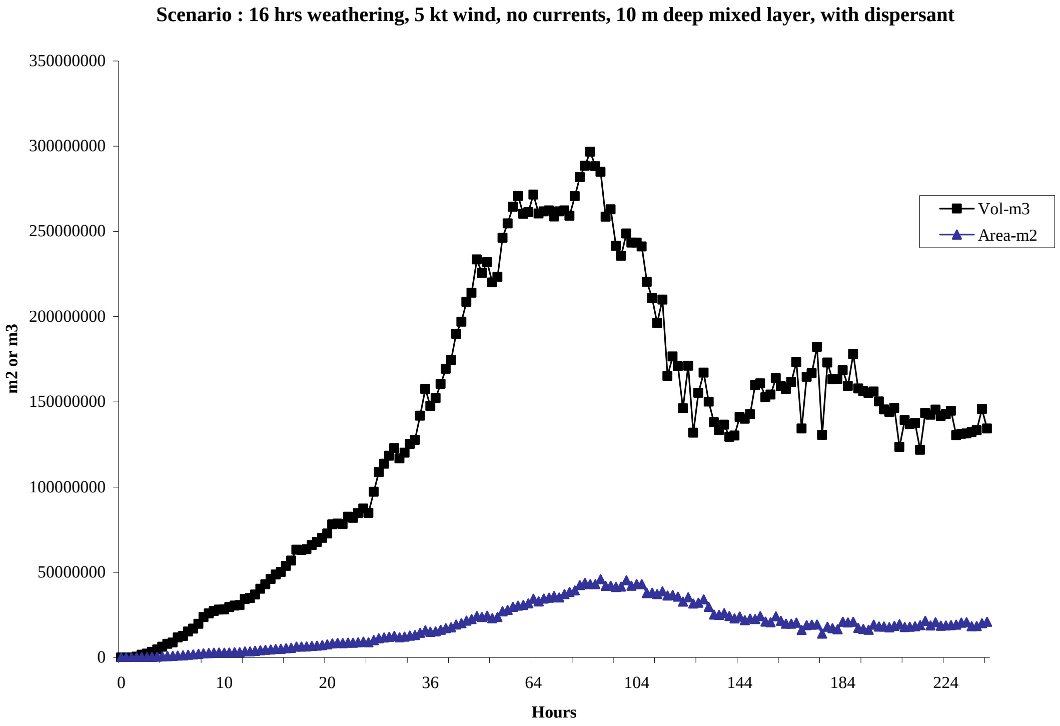

Figure A.2-3. Volume (m^3) and area (m^2) of plume >1ppb over time for “ w16hr-5kt-h1-c0-10m-wd“ scenario.

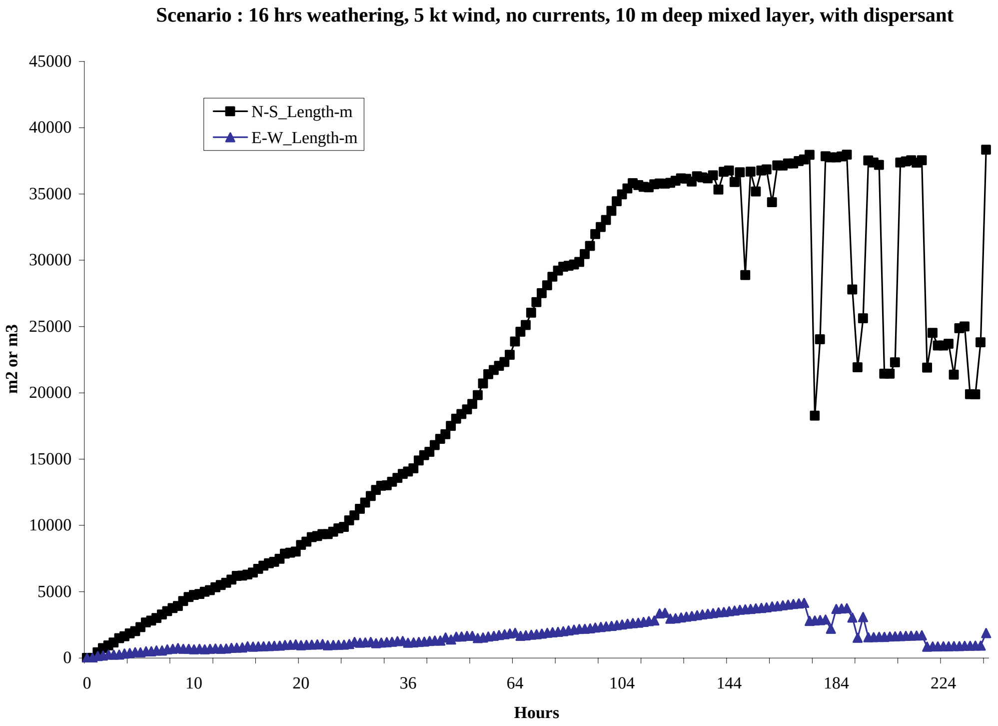

Figure A.2-4. East-west and north-south lengths (m) of plume >1ppb over time for “w16hr-5kt-h1-c0-10m-wd“ scenario.

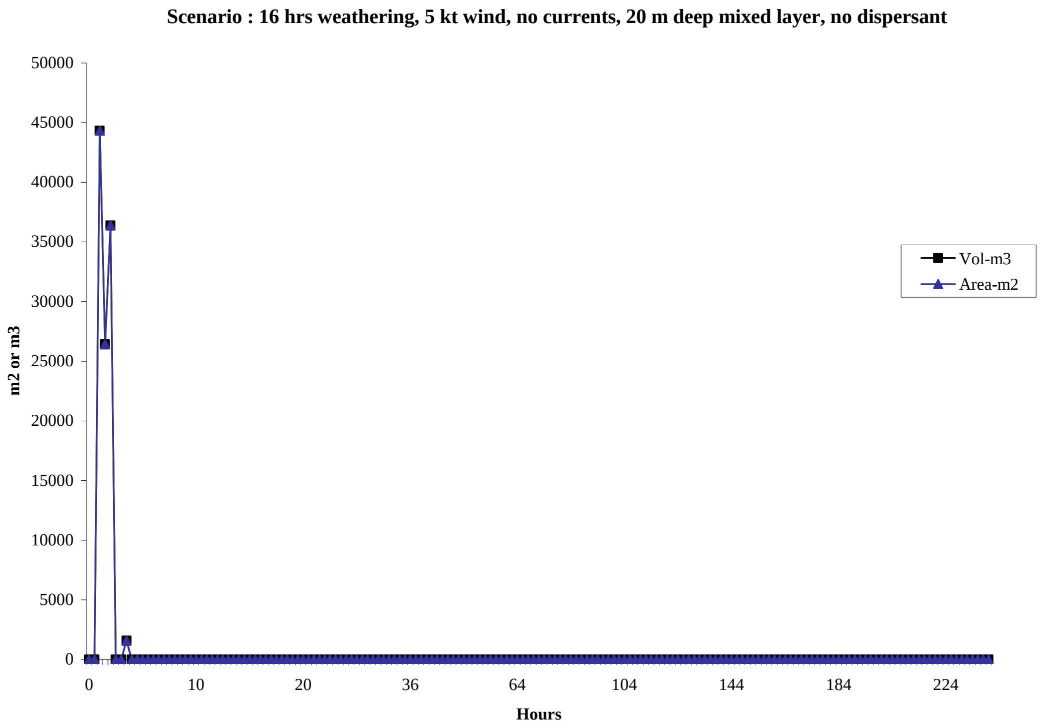

Figure A.2-5. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-5kt-h1-c0-20m-nd“ scenario.

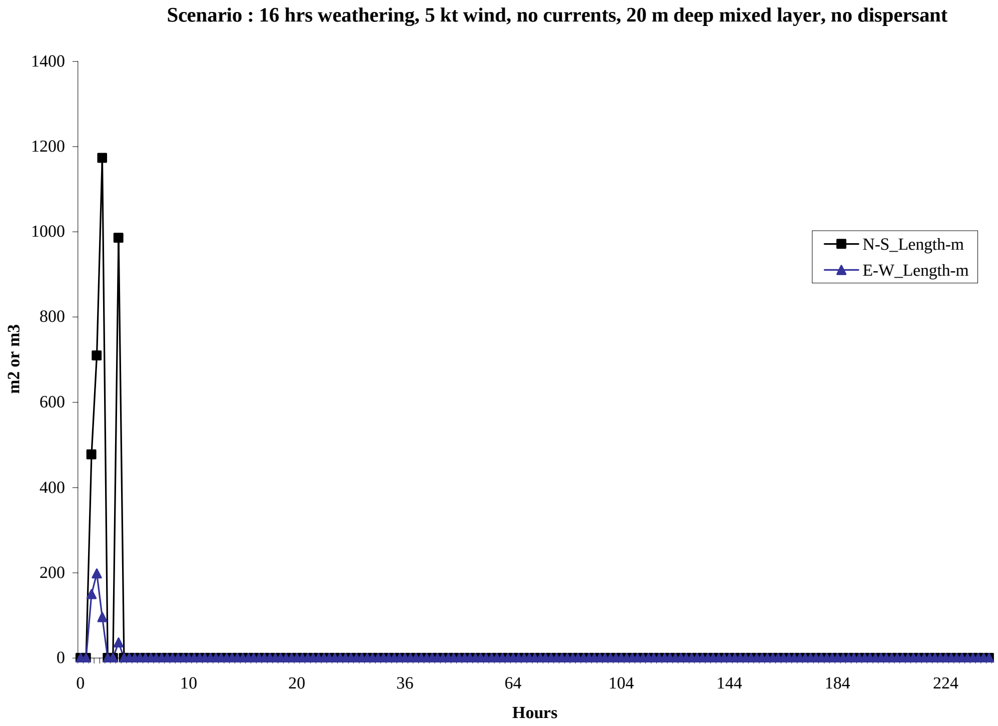

Figure A.2-6. East-west and north-south lengths (m) of plume >1ppb over time for “w16hr-5kt-h1-c0-20m-nd“ scenario.

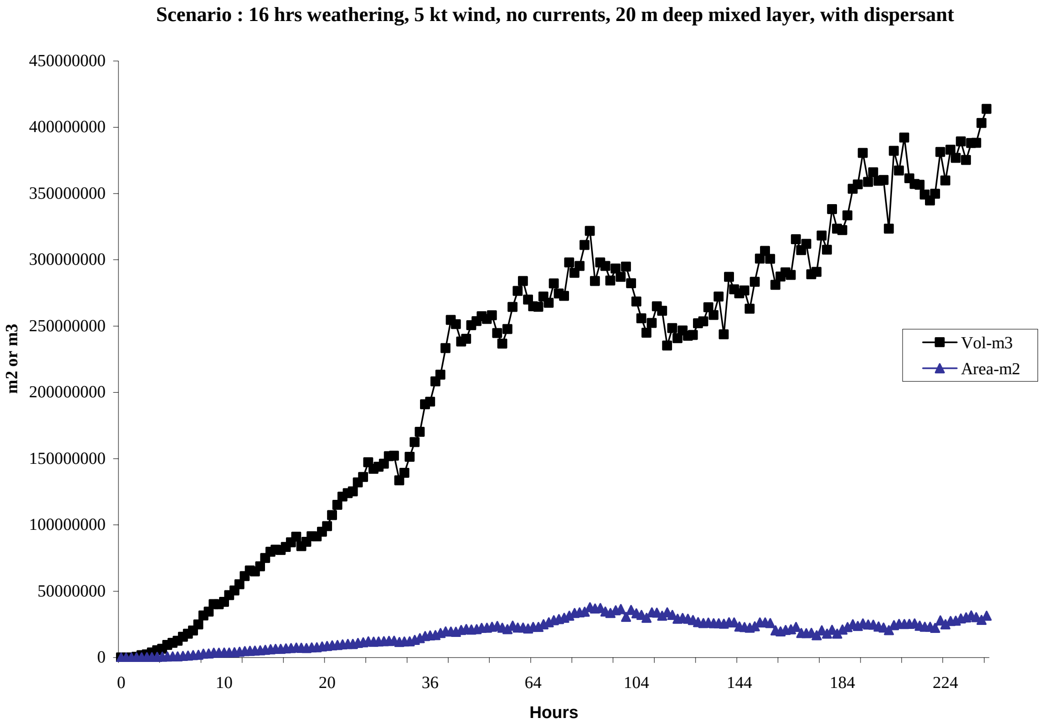

Figure A.2-7. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-5kt-h1-c0-20m-wd“ scenario.

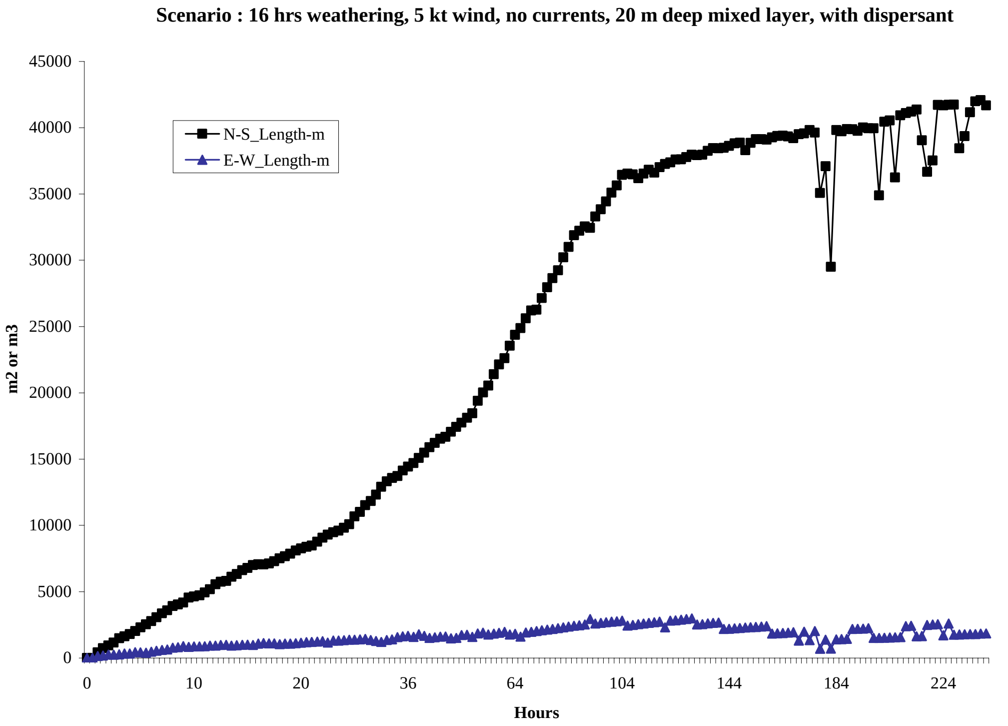

Figure A.2-8. East-west and north-south lengths (m) of plume >1ppb over time for “w16hr-5kt-h1-c0-20m-wd“ scenario.

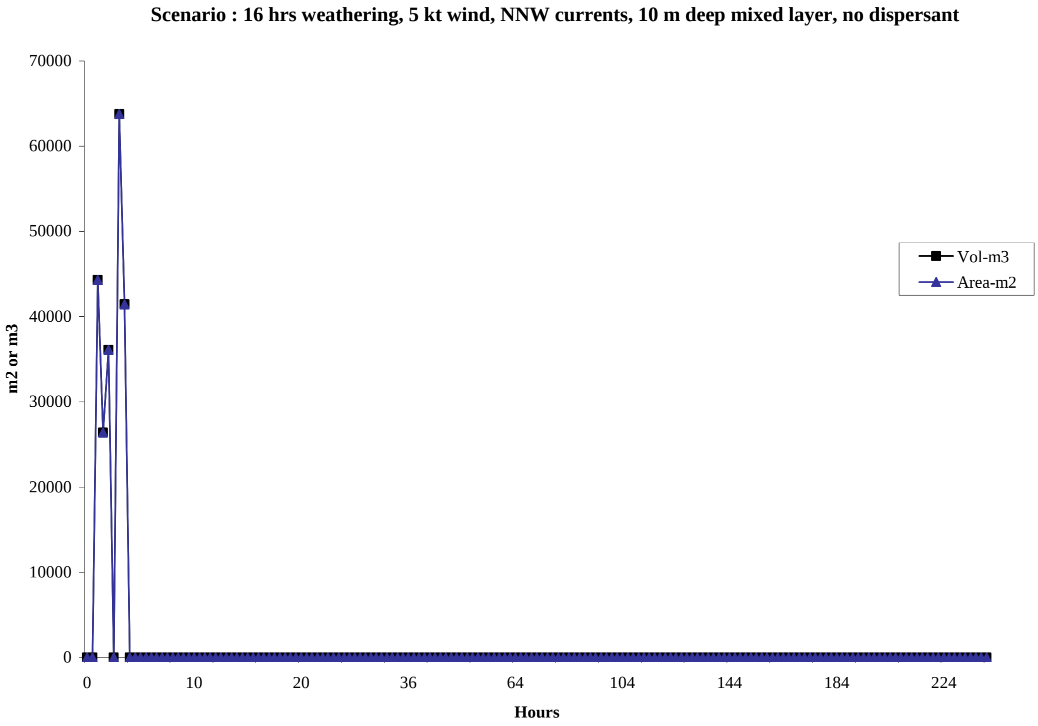

Figure A.2-9. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-5kt-h1-cnnw-10m-nd“ scenario.

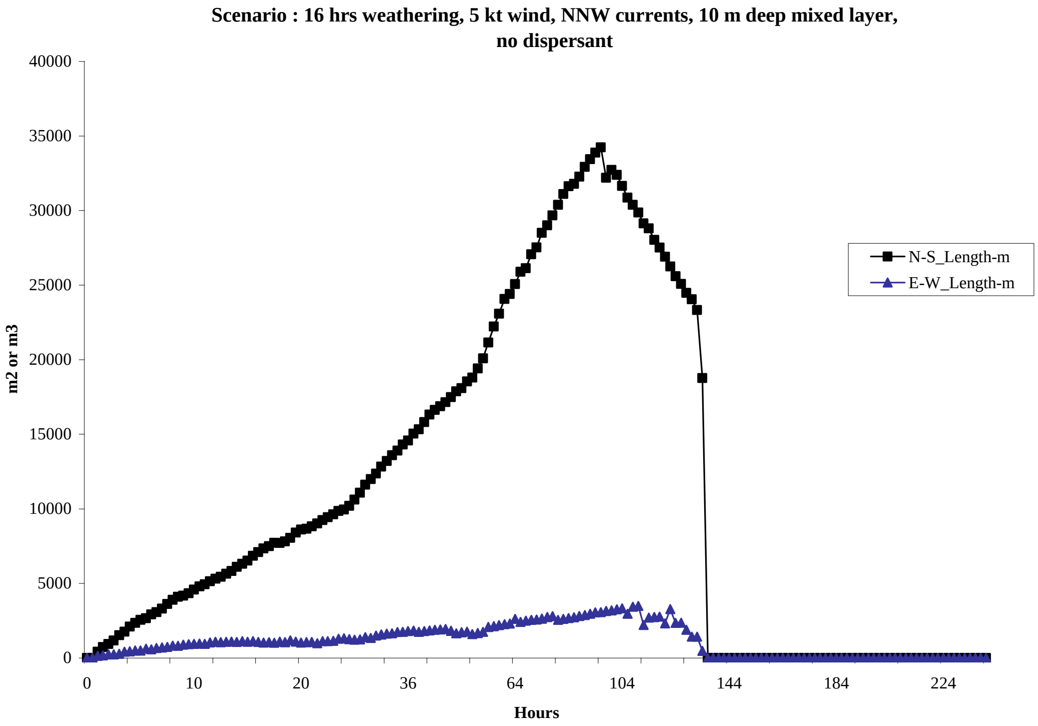

Figure A.2-10. East-west and north-south lengths (m) of plume >1ppb over time for “ w16hr-5kt-h1-cnnw-10m-nd“ scenario.

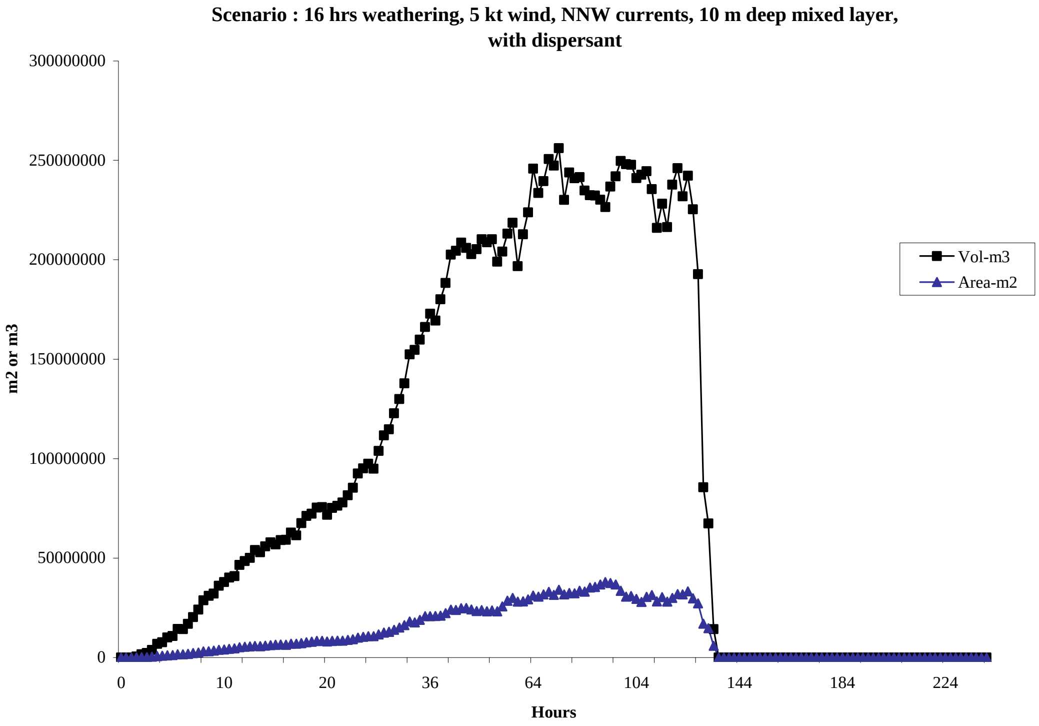

Figure A.2-11. Volume (m^3) and area (m^2) of plume >1ppb over time for "w16hr-5kt-h1-cnnw-10m-wd" scenario.

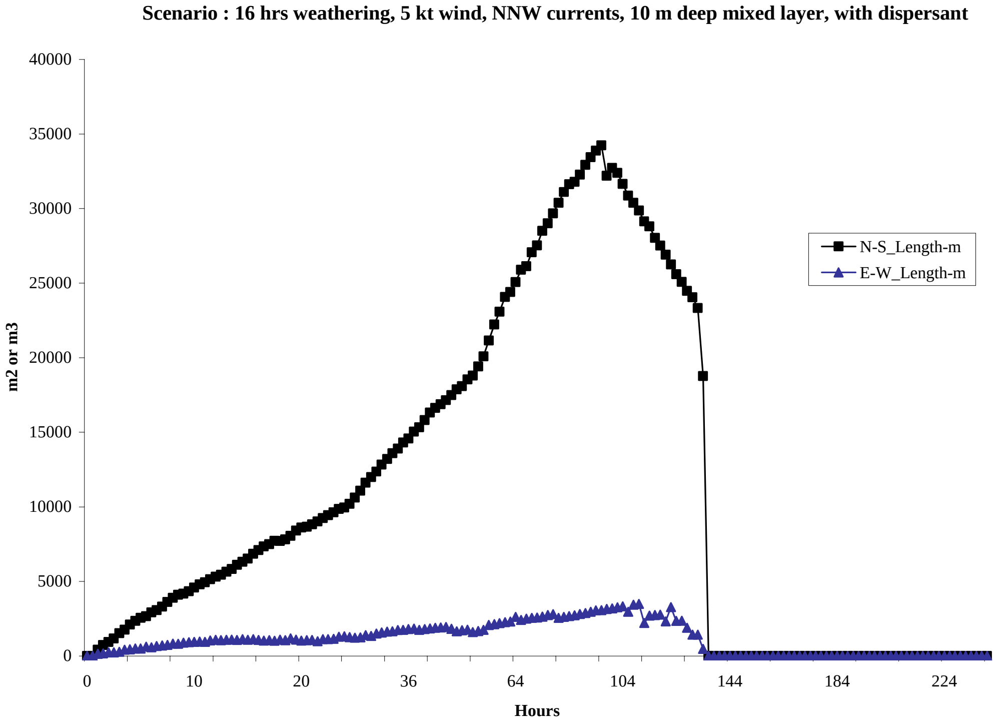

Figure A.2-12. East-west and north-south lengths (m) of plume >1ppb over time for "w16hr-5kt-h1-cnnw-10m-wd" scenario.

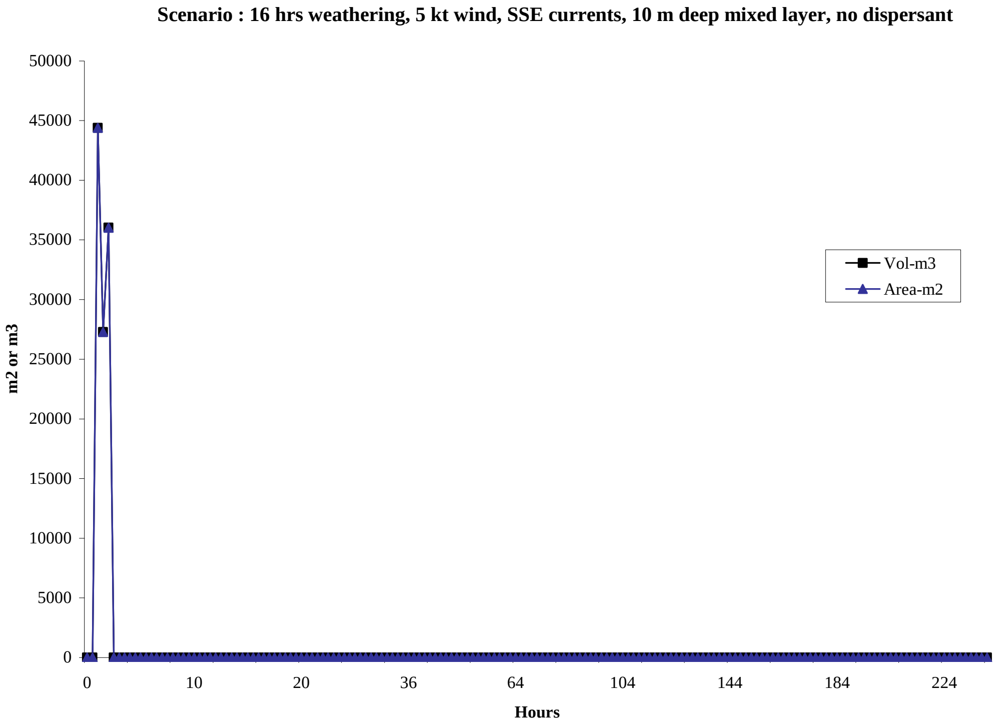

Figure A.2-13. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-5kt-h1-csse-10m-nd“ scenario.

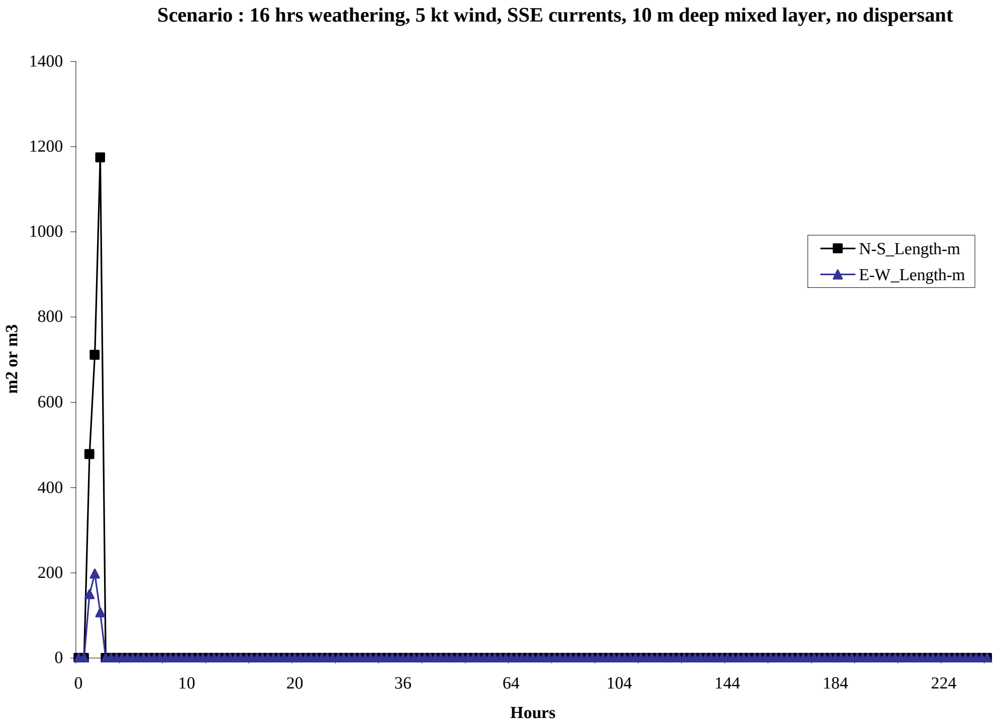

Figure A.2-14. East-west and north-south lengths (m) of plume >1ppb over time for “w16hr-5kt-h1-csse-10m-nd“ scenario.

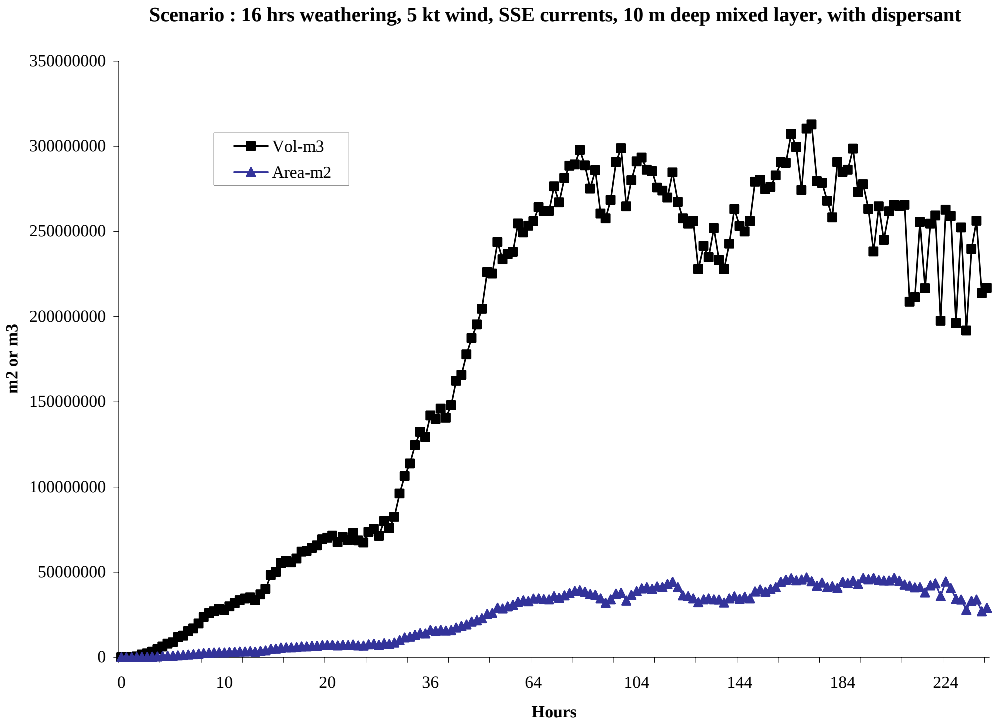

Figure A.2-15. Volume (m^3) and area (m^2) of plume >1ppb over time for "w16hr-5kt-h1-csse-10m-wd" scenario.

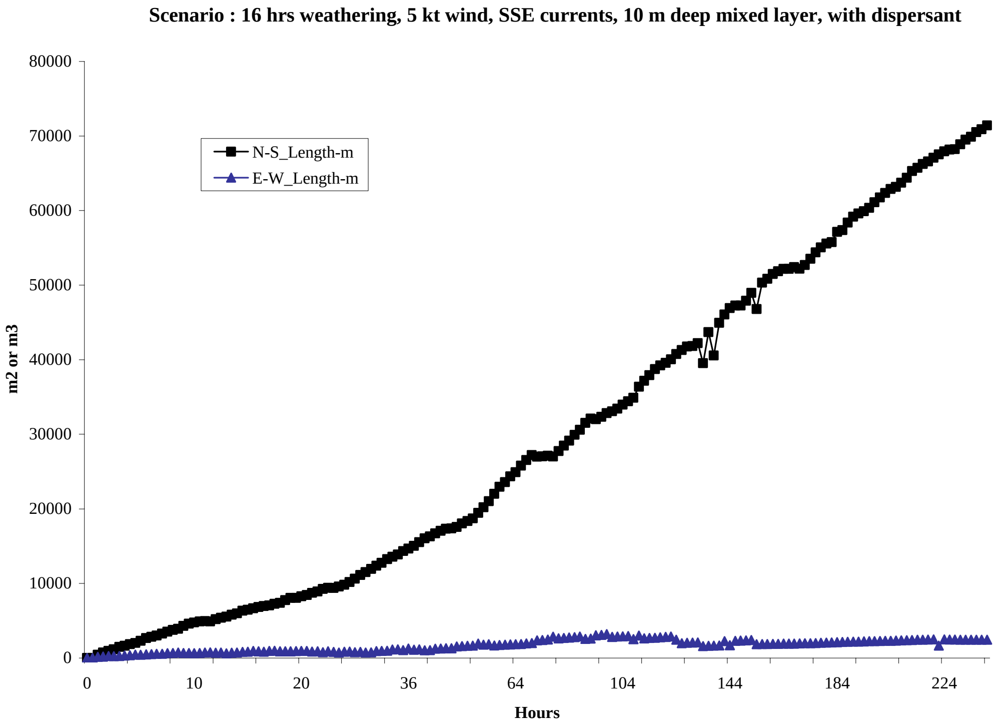

Figure A.2-16. East-west and north-south lengths (m) of plume >1ppb over time for "w16hr-5kt-h1-csse-10m-wd" scenario.

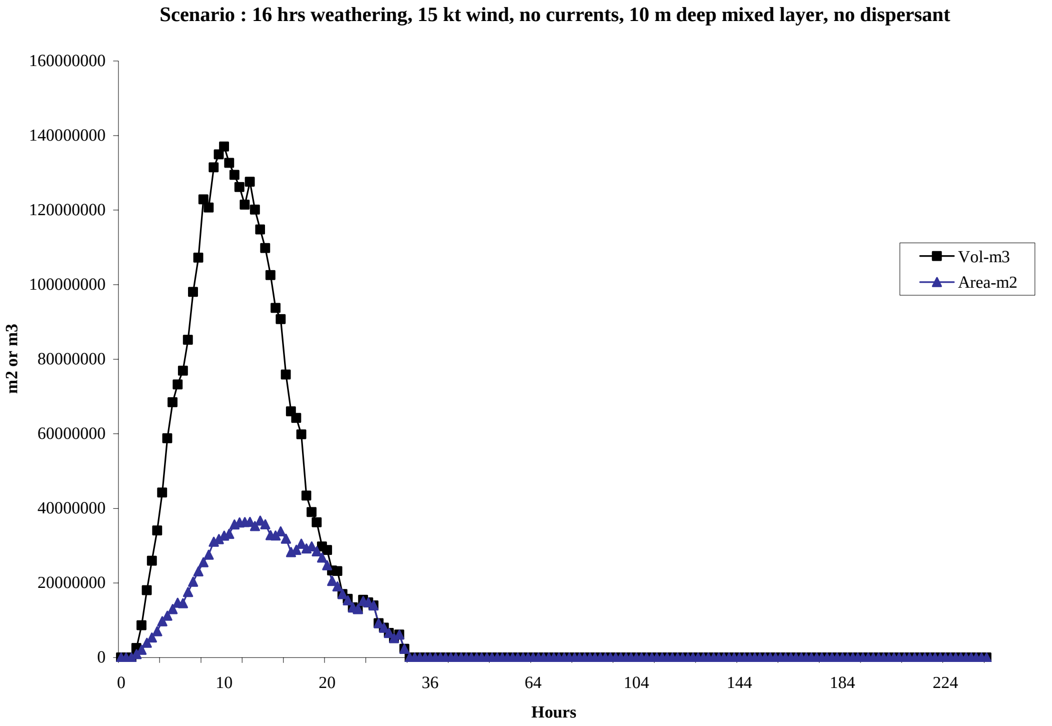

Figure A.2-17. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-15kt-h10-c0-10m-nd“ scenario.

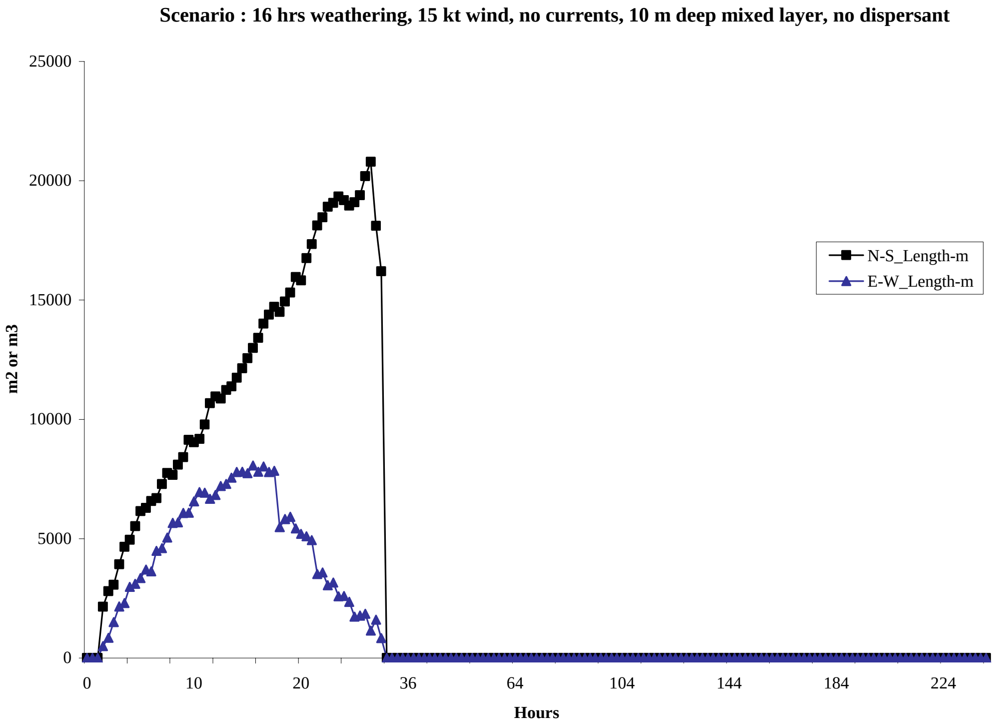

Figure A.2-18. East-west and north-south lengths (m) of plume >1ppb over time for “ w16hr-15kt-h10-c0-10m-nd“ scenario.

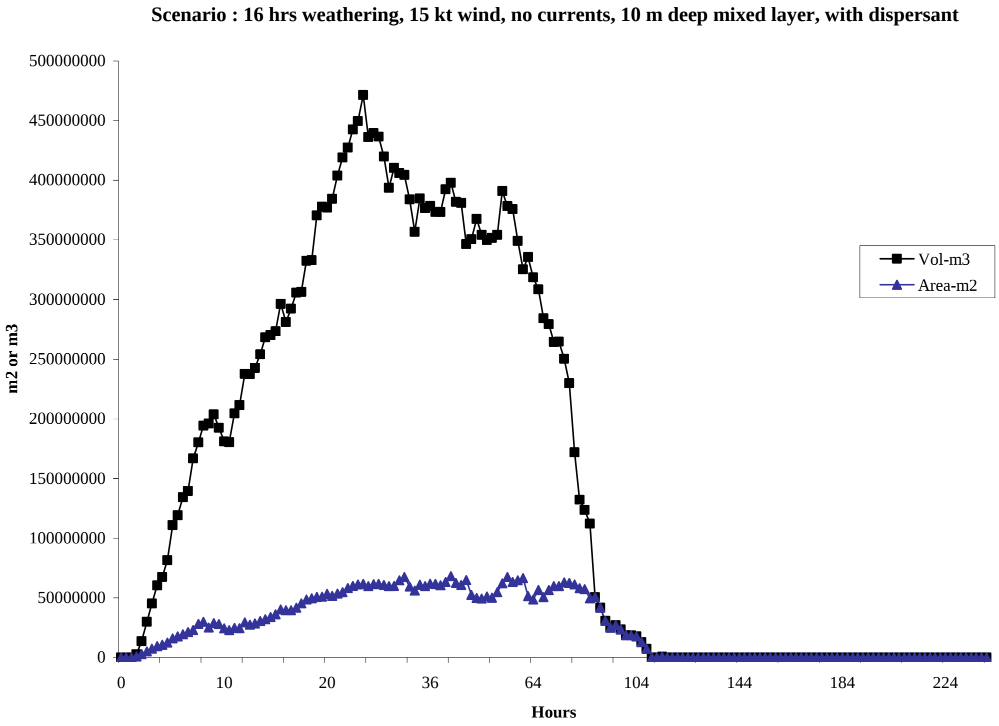

Figure A.2-19. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-15kt-h10-c0-10m-wd“ scenario.

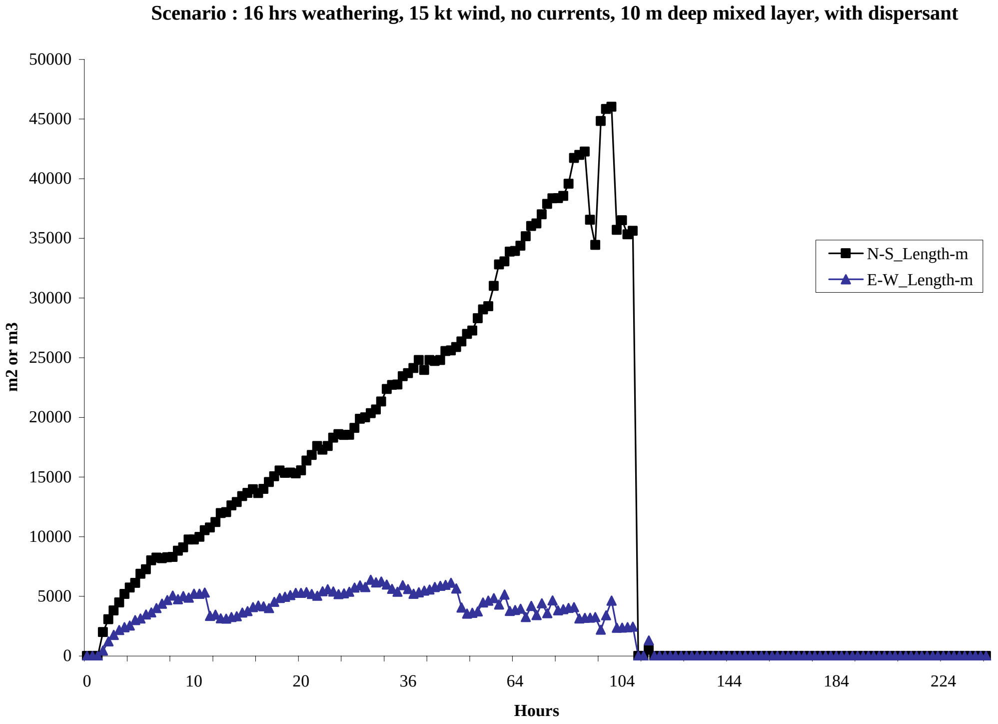

Figure A.2-20. East-west and north-south lengths (m) of plume >1ppb over time for “ w16hr-15kt-h10-c0-10m-wd“ scenario.

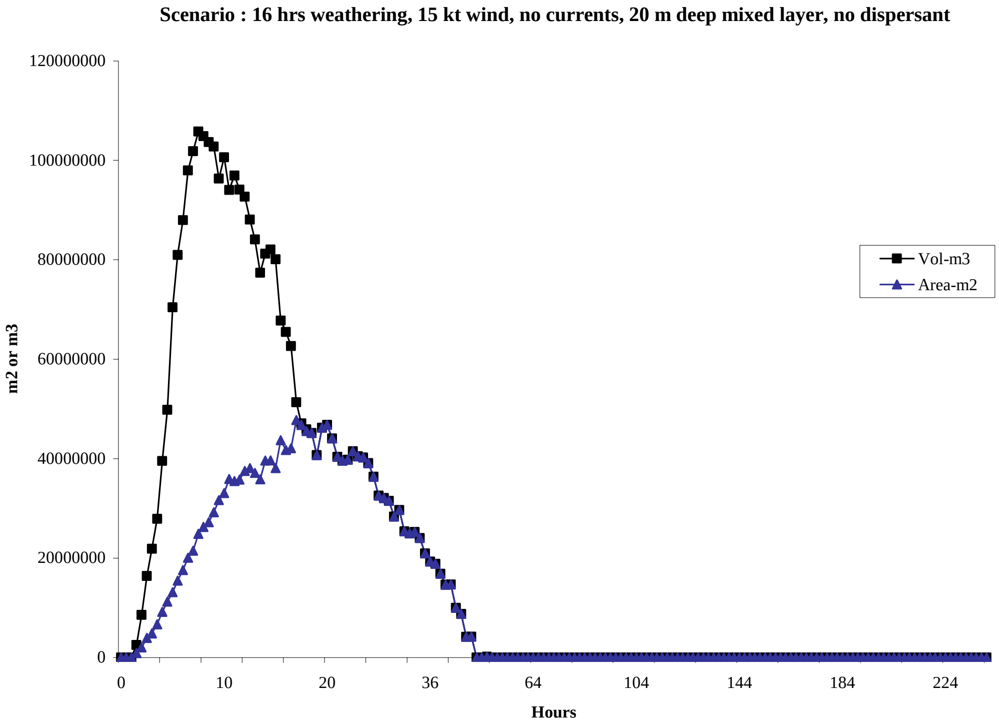

Figure A.2-21. Volume (m^3) and area (m^2) of plume >1ppb over time for "w16hr-15kt-h10-c0-20m-nd" scenario.

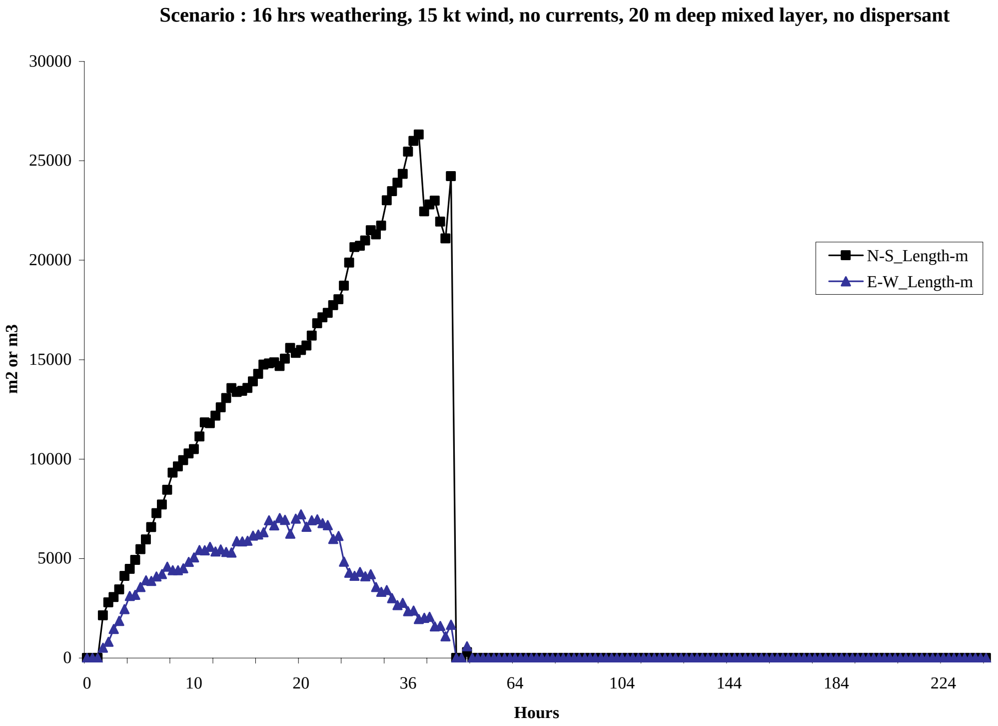

Figure A.2-22. East-west and north-south lengths (m) of plume >1ppb over time for "w16hr-15kt-h10-c0-20m-nd" scenario.

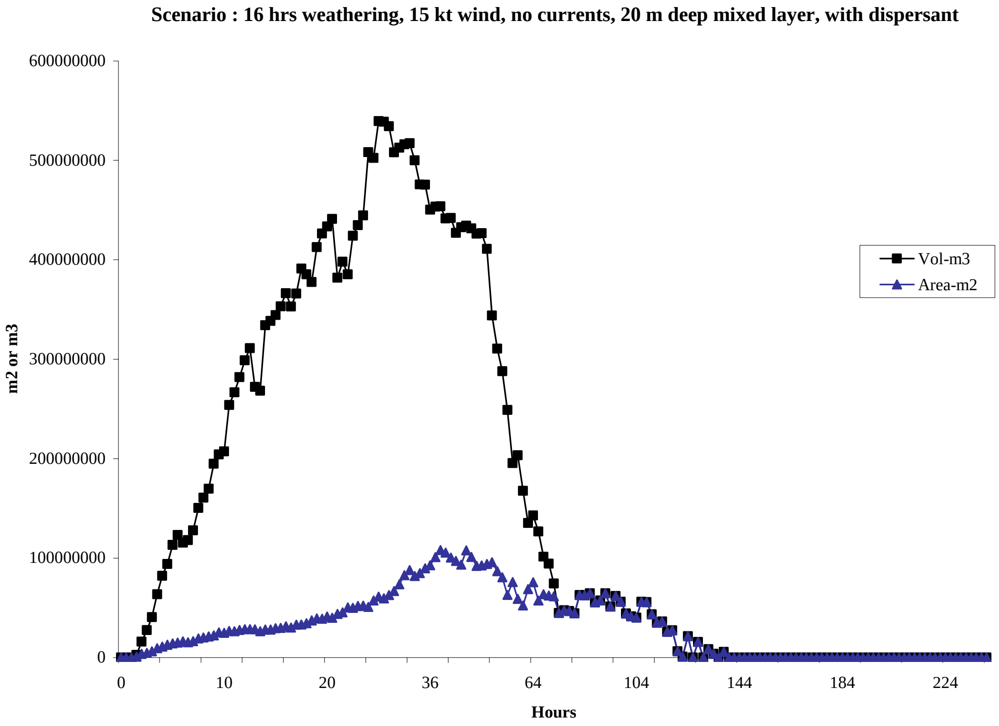

Figure A.2-23. Volume (m^3) and area (m^2) of plume >1ppb over time for “w16hr-15kt-h10-c0-20m-wd“ scenario.

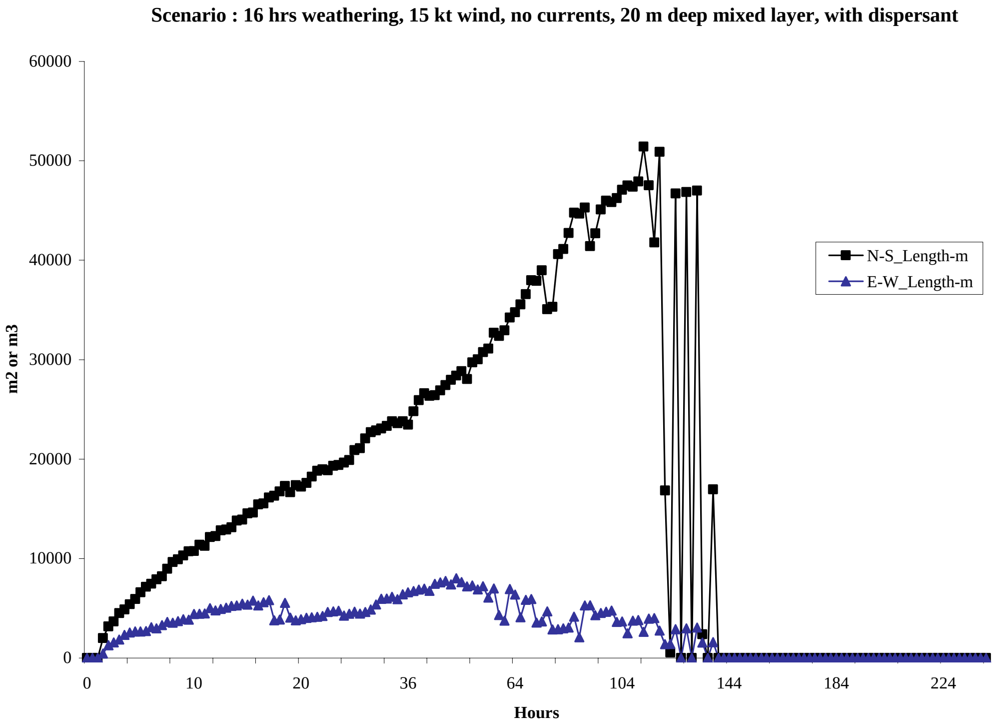

Figure A.2-24. East-west and north-south lengths (m) of plume >1ppb over time for “w16hr-15kt-h10-c0-20m-wd“ scenario.