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PREDICTING THE BEHAVIOR OF ORIMULSION SPILLED ON WATER

VOLUME I

FINAL REPORT
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NOTICE

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16. Abstract (MAXIMUM 200 WORDS)

Orimulsion is a fuel that is a bitumen-in-water emulsion made of approximately ~70% natural bitumen and ~30% fresh water. Orimulsion is of great interest to electric power utilities because of its competitive cost and pricing structure. Previous work on Orimulsion has determined it may largely float, remain suspended, or settle depending on the spill conditions. In this study, the mechanisms at work and the relative importance of different spill conditions (e.g., salinity, temperature, energy, Orimulsion concentration, particulate load, and particulate type) are investigated by (1) forty-seven benchtop scale (3L) experiments conducted and evaluated using design of experiment principles and (2) five flume scale (4000L) experiments. The insight gained from these laboratory experiments is interpreted in light of the limitations inherent in laboratory spills into confined vessels (e.g., vessel wall effects and absence of dilution) in order to predict the gross behavior that might be anticipated if Orimulsion were spilled in a 'real world,' open water setting. The most important environmental parameters identified, probably listed in order of their descending importance, were determined to be the receiving water salinity, receiving water energy, and presence/absence of suspended mineral matter. Interactions between these parameters determine whether most bitumen will ultimately float on or near the surface, remain suspended within the water column, or settle through the water column. The gross behavior of Orimulsion under different combinations of these parameters is predicted. These predictions provide the best available guidance to contingency planners and spill responders.

Appendices I through VI are included in Volume II of this report, and are available from the USCG Research and Development Center upon request.

17. Key Words
Orimulsion, oil spill, bitumen, PAH, petroleum, hydrocarbons, emulsion, design of experiment, flume test

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EXECUTIVE SUMMARY

Orimulsion, an alternative fuel for power generation, is currently being used in Canada, Italy, Denmark, Japan and China and has been tested in the United States (U.S.) in Florida and Illinois. Orimulsion is being shipped to these locations in ocean-going, double-hull tankers; nevertheless, prudent due diligence requires that the possibility for its accidental release must be evaluated. In order to assess the required countermeasures in case of a spill, a thorough understanding of its behavior when released in water is required. Studies performed to date have demonstrated the importance of the spill conditions on Orimulsion's behavior. For example, these previous studies have shown that receiving water salinity will markedly affect Orimulsion's behavior; i.e., Orimulsion tends to float in salt water. However, the impact and interactions of potentially important independent variables other than salinity are less predictable.

As a result, the need existed to evaluate the behavior of Orimulsion under a wide range and combination of environmental conditions. Better understanding of Orimulsion's behavior under these conditions will provide valuable information useful in developing response actions, assessing mechanical recovery systems' effectiveness, and in developing computer models to predict the fate of Orimulsion following a spill.

This study consists of two principal phases; (1) a benchtop study phase, and (2) a flume tank study phase in which the influence(s) of a number of environmental variables on Orimulsion's behavior were investigated. The benchtop phase utilized design of experiment (DOE) principles in order to reduce the number of experiments necessary to achieve a statistically valid interpretation. Experiments (24) were conducted in which the water salinity, water/air temperature, initial Orimulsion concentration, particulate (mineral matter) loading, particulate type, and water energy were carefully controlled. Other experiments showed the relative <u>un</u>importance of temperature and particulate type on the gross behavior of Orimulsion. The subsequent response surface design phase (31 additional experiments) provided fundamental information on the mechanisms and processes which different spill conditions have on Orimulsion's behavior. Growth of suspended bitumen particles was most strongly influenced by the combined effects of salinity and energy (bitumen particle coalescence was greatest under brackish salinities (~17.5 $^{0}/_{00}$) and low or high-energy conditions). The "Orimulsion budget" is the proportion of Orimulsion that floats, settles or remains suspended. A preliminary "Orimulsion budget" (for the bitumen component only) was developed based upon results of the benchtop study.

Caution was necessary in projecting the "Orimulsion budget" from the benchtop to the 'real world.' Benchtop mimicking of 'real world' conditions (e.g., water turbulence profiles, unconfined water volumes, continual dilution of bitumen, the absence of container walls) in a small (4L) laboratory vessel is a challenge. Nonetheless, the benchtop experiments statistical and observational results indicated that (1) water salinity, (2) energy level, and (3) presence/absence of mineral matter in the water were the most important factors in determining the fate of spilled bitumen.

The results of the benchtop experiments were used in developing the second testing phase of the study in which five Orimulsion 'spills' were conducted in a 4000L flume tank. The flume tests (5) were conducted under a limited set of spill conditions intended to provide data and confirmation surrounding the predicted behavior of spilled Orimulsion. Results of these tests, combined with knowledge from previous flume tank testing of Orimulsion, yielded greater insight into the phenomenon of bitumen particle growth and the "Orimulsion budget."

Flume testing confirmed that the most important environmental parameters in determining the fate of spill Orimulsion, probably listed in order of their descending importance, are:

(1) receiving water salinity,
(2) receiving water energy, and
(3) presence/absence of suspended mineral matter.

The "Orimulsion Budget" was refined and extrapolated to the 'real world' after considering the effects inherent in laboratory tests (e.g., set water volume which precludes dispersion and promotes particle collisions). The predictions of what the bulk of the bitumen component of spilled Orimulsion does under the various combinations of these parameters is presented in the table below. This table is divided into two sections, one in which the salinity is such that the surfactant component in Orimulsion remains mostly effective (top) and one in which the salinity is such that the surfactant component remains mostly ineffective (bottom). The actual salinity which 'divides' these two sections is unknown, but based on our experiments we can only state that the division lies somewhere between 0 and 17.5 $^{o}/_{oo}$.

	WATER ENERGY LEVEL			
	NO	LOW	HIGH	
LOW SALINITY		SUSPENDED - DILUTE (minor settled)	SUSPENDED HIGHLY DILUTE	MINERAL MATTER
	SETTLED TOWARD BOTTOM	SUSPENDED - DILUTE (minor settled)	SUSPENDED HIGHLY DILUTE	NO MINERAL MATTER

	WATER ENERGY LEVEL			
	NO	LOW	HIGH	
HIGH SALINITY		FLOATING - DILUTE (some suspended > some sink)	FLOATING HIGHLY DILUTE (some suspended > some sink)	MINERAL MATTER
	FLOATING NEAR SURFACE (some suspended)	FLOATING - DILUTE (some suspended > some sink)	FLOATING HIGHLY DILUTE	NO MINERAL MATTER

This study was conceived and designed through the efforts of Battelle Memorial Institute, Bitor America Corp. Bitúmenes Orinoco, S.A., Intevep S.A., the United States Coast Guard, and National Oceanographic and Atmospheric Administration. The research was equally funded by Bitor America Corp. and the United States Coast Guard Research and Development Center.

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1. INTRODUCTION

In the event of an oil spill at sea, most oils will float and rapidly begin to undergo fairly predictable modifications to their physical and chemical properties collectively known as "weathering." Most oil spill contingency measures currently available have been developed for floating oils and their respective emulsions. Recently, however, there is increased interest in predicting the behavior of a relatively new, natural, petroleum bitumen-derived fuel known as Orimulsion.

Orimulsion is a fuel that is a bitumen-in-water emulsion made of approximately ~70% natural bitumen and ~30% fresh water that is of great interest to electric power utilities because of its competitive cost and pricing structure. Orimulsion is in commercial use in Denmark, Canada, Japan, Italy, China, Lithuania, and Barbados. It is currently not in use in the United States. However, due to the increasing commercial interest in Orimulsion among U.S. electricity providers, the transport of Orimulsion in U.S. water is imminent. Thus, the need exists to better understand the behavior of Orimulsion if it were to be accidentally spilled.

Orimulsion is classified as a Group V product along with other heavy oils called low API oils (LAPIO). Various benchtop scale experiments on Orimulsion and other LAPIO fuels, in particular fuel oil #6, have been performed to date (e.g., Brown et al., 1995; Febres et al., 1995; Potter, 1995). A small number of meso-scale (i.e., flume tank) experiments (Ostazeski et al., 1997; Ostazeski et al., 1998) and open water spills (Gunter and Sommerville, 1991) of Orimulsion have also been performed. During the meso-scale studies, 14.2 L of Orimulsion was released into a 4000 L flume tank (~3542 mg Orimulsion or ~2479 mg bitumen/L water) containing, on separate occasions, freshwater (0 $^{0}/_{00}$) and salt water (32 $^{0}/_{00}$). It was determined that the behavior of Orimulsion when spilled in water was very different from other common Group V products and as a result, it presents a variety of very challenging response scenarios.

The benchtop, flume, and open water experiments had determined that the receiving water salinity was a critical factor affecting Orimulsion's behavior. For example, in the fresh water flume tests conducted on Orimulsion 100 (Ostazeski et al., 1997) and Orimulsion 400 (Ostazeski et al., 1998)[1], the Orimulsion was observed to disperse in a black cloud of fine bitumen particles that remained in suspension throughout the 120 hour experiment. In the sea water flume test, Orimulsion initially dispersed throughout the water column but within 15 minutes, a heavy viscous 'slick' of coalesced bitumen particles began to float on the surface. The surface slick continued to 'grow' by coalescence throughout the 120-hour experiment. The interaction of bitumen particle density and buoyancy, water turbulence, and reduced effectiveness and concentration of Orimulsion's surfactant component in sea water was believed to allow the bitumen particles to either (1) coalesce and rise to the surface forming the viscous surface slick, (2) rise to the surface and then coalesce, or (3) a combination of these processes.

At the initiation of this project, the behavior of Orimulsion in salinities representative of brackish estuaries was uncertain. Similarly, the effect that other potentially important variables, e.g., water temperature, Orimulsion concentration, particulate load, particulate type, and turbulence of the water (i.e., energetics), had on Orimulsion's behavior were not well studied or understood. Therefore in the event of an accidental spill or release, Orimulsion could be found to predominantly float, settle, or remain suspended within the water column. The need to better predict the fate of Orimulsion under a variety of environmental conditions was determined to be of critical importance for containment, recovery and response planning, and spill modeling.

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[1] Orimulsion 100 and Orimulsion 400 are different formulations of Orimulsion. Detailed comparison of their chemical and physical properties are reported in Ostazeski et al. (1998).

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2. STRUCTURE OF THIS REPORT

This report summarizes the research performed on Orimulsion 400 by Battelle in 1998. This research was aimed at gaining an understanding of the important parameters that affect the behavior of Orimulsion when it is spilled on water. The objective of the study was to investigate the weathering characteristics of Orimulsion in water, particularly as it relates to the ultimate fate of spilled Orimulsion. The project consisted of three phases, namely:

- ☐ **Phase I** – Development of a *Workplan* for Behavior Characterization Experiments
- ☐ **Phase II** – Evaluation of Factors Affecting Orimulsion's Fate in Water
  - Phase IIA – design and conduct an appropriate number of benchtop experiments to evaluate the numerous independent variables effecting Orimulsion's fate based on design of experiment (DOE) principles
  - Phase IIB – evaluate bench-top data using DOE principles to identify the most significant factors affecting the fate of Orimulsion.
  - Phase IIC – further investigate and quantify flume tank energetics so that Phase III can be conducted under more representative wave and wind conditions (than previous flume experiments).
- ☐ **Phase III** – Perform meso-scale flume experiments that focus on conditions which have the greatest effect on Orimulsion's fate in water (as based on the results of Phase II).

This report is a compilation of the deliverables for each of the three phases of the study. The Phase I deliverable provides the literature review, background information, working hypotheses, and detailed *Workplan* developed for this study. It was approved on April 15, 1998 and appears as Appendix I of this report. The reader should refer to the *Workplan* for more background information and experimental details.

The Phase II interim report was approved on September 3, 1998. It provided the results and interpretation surrounding the benchtop experiments and the flume energetics studies. This report had included the recommendations and justifications for Phase III's experiments. These results are re-presented in Section 3 through 9 of this report.

The Phase III deliverable provides the results of the five meso-scale flume experiments performed in the Fall of 1998. These results have not been previously presented and are found in Section 10 of this report.

Finally, a synthesis of the entire study's results is provided in Section 11 of this report.

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3. CHEMICAL CHARACTERIZATION OF FRESH ORIMULSION

3.1 Orimulsion Sample

A fresh supply of Orimulsion was provided by Bitor America Corporation. The present formulation contains a surfactant known as Intan 400 and thus, was termed Orimulsion 400. The Orimulsion 400 (or OR400) was received at Battelle's Duxbury, Massachusetts laboratory on March 9, 1998. The 55-gallon shipment originated from Lagoven S.A. on February 9, 1998. Upon arrival the 55-gallon drum was stored at room temperature and was inverted twice/week for three weeks. The drum was then opened and gently stirred for approximately six hours using a compressed air-driven mixer with three sets of propeller blades. The purpose of the mixing was to assure that thoroughly mixed samples were used in these experiments. Following mixing 45 one gallon aliquots of the mixed OR400 were prepared and sealed in pre-cleaned, metal paint cans for use throughout these benchtop and flume experiments. Fresh cans were used at the different stages of these experiments so that only fresh material was used throughout.

3.2 Bulk Physical and Chemical Analysis

A freshly stirred aliquot of OR400 was analyzed for bulk physical (bitumen particle size, density, viscosity) and chemical parameters (compound class) in order to establish the baseline characteristics of the material prior to testing. The methods used in each of these analyses are described in Appendix I.

The results of these analyses are presented in Table 3-1. To assess the variability associated with the measurement techniques, replicate analyses (n) were performed for all measurements allowing for the mean and standard deviation for each set of measurements to be presented.

Table 3-1. Bulk physical and chemical properties of the Orimulsion used in these studies.

Physical Parameters	**n**	**Mean**	σ
Particle Diameter (μm) - D[4,3]	9	22.3*	1.0*
Density (g/mL) at 15°C	5	1.0104	0.0003
Viscosity (cP) at 15°C ($D^{-1} = 100$)	4	370	32

Chemical Parameters	**n**	**Mean**	σ
Aliphatic Hydrocarbons (%)	2	9.3	0.21
Aromatic Hydrocarbons (%)	2	53.7	0.92
Resins (%)	2	19.5	0.21
Asphaltenes (%)	2	17.5	0.92

*See text below

The average bitumen particle diameter in fresh Orimulsion was 22.3 μm. However, reporting an average value and standard deviation misrepresents the bi-modal distribution of the bitumen particles, which exist (Fig 3-1). Maxima are observed at around 7 and 25 μm suggesting the presence of two populations of bitumen particles. The smallest and largest particles observed in the fresh OR400 were approximately 1.3 and 85.0 μm in diameter, respectively.

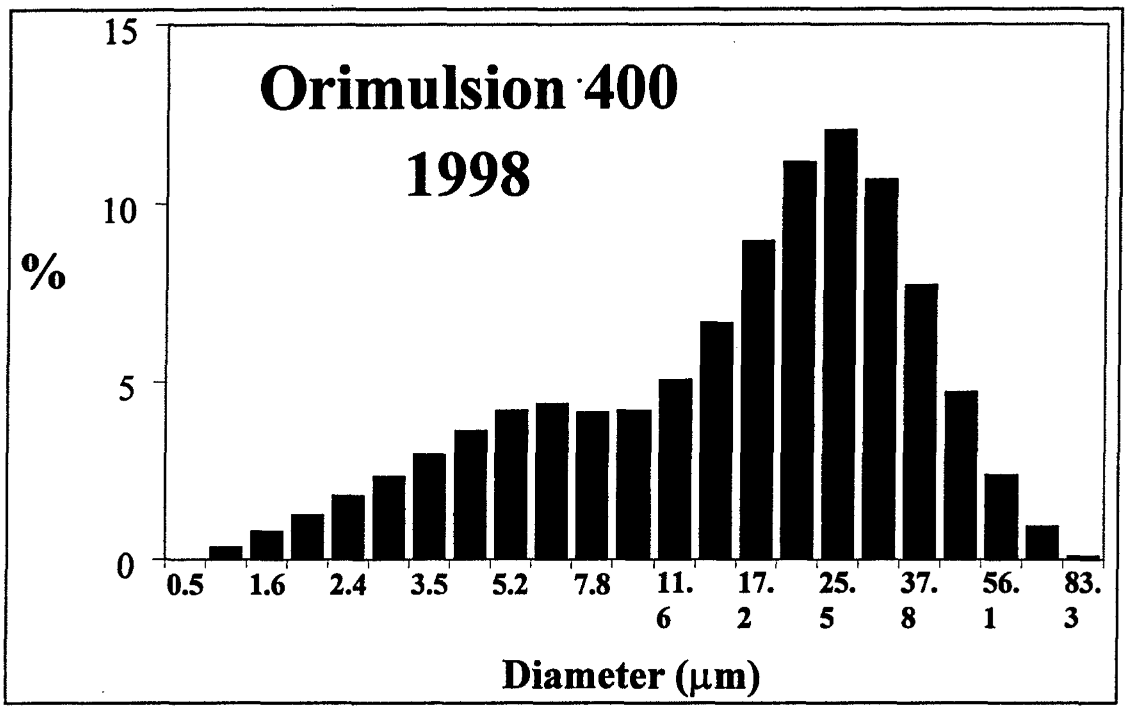

Figure 3-1. Histogram showing the distribution of particles in fresh OR-400 used in this study.

3.3 Molecular Analysis

The fresh Orimulsion was also analyzed using gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GCMS). The former was performed according to modifications of EPA Method 8015 and the latter was performed using methods modified from EPA Method 8270 (Appendix I). Using GCMS the concentration of 43 polycyclic aromatic hydrocarbons (PAH) and alkyl-PAH were quantified.

The GC-FID for the solvent-soluble organic fraction of fresh Orimulsion is shown in Fig. 3-2. There were no detectable *n*-alkanes observed. This is not surprising, given previous results (Ostazeski et al., 1998) and the highly weathered state of the Orinoco Basin (Venezuela) petroleum feedstock. Chromatographically, the most notable feature of Orimulsion is an unresolved mass of complex (UCM) of hydrocarbons, which is typical of highly-weathered, heavy petroleum (Cassini and Eglinton, 1991). (The prominent peaks in the chromatogram are internal standards.)

The concentration of PAH present in the Orimulsion studied herein is shown in Table 3-2. In duplicate analyses performed at the beginning and end of the study, the total concentration of PAH in the fresh Orimulsion 400 was 2472 mg/kg and 2997 mg/kg. Table 3-2 also shows the concentration of PAH observed in Orimulsion 100, the earlier formulation of Orimulsion characterized by Ostazeski et al., (1998). It is notable that the concentration of total PAH is significantly lower in the Orimulsion 400 from this study. However, the overall distribution of PAH is very comparable among the Orimulsion samples studied. For example, in each case the group of PAH highest in concentration are the C_0-C_4-dibenzothiophenes, i.e., the sulfur-containing PAH. The homologous series of most other PAH are dominated by the C_3- or C_4-alkyl homologues, i.e., the most resistant compounds to weathering. These characteristics are both typical of highly weathered bitumen (e.g., Cassinni and Eglinton, 1991).

It is also notable that thin layer chromatographic, compound class analysis (Appendix I) revealed Orimulsion 400 to contain more than 50% by weight aromatic hydrocarbons (Table 3-1). However, the PAH comprise only 0.25% (2472 mg/kg) of the Orimulsion indicating that a large percentage of aromatic hydrocarbons exist which are <u>not</u> among the target PAH.

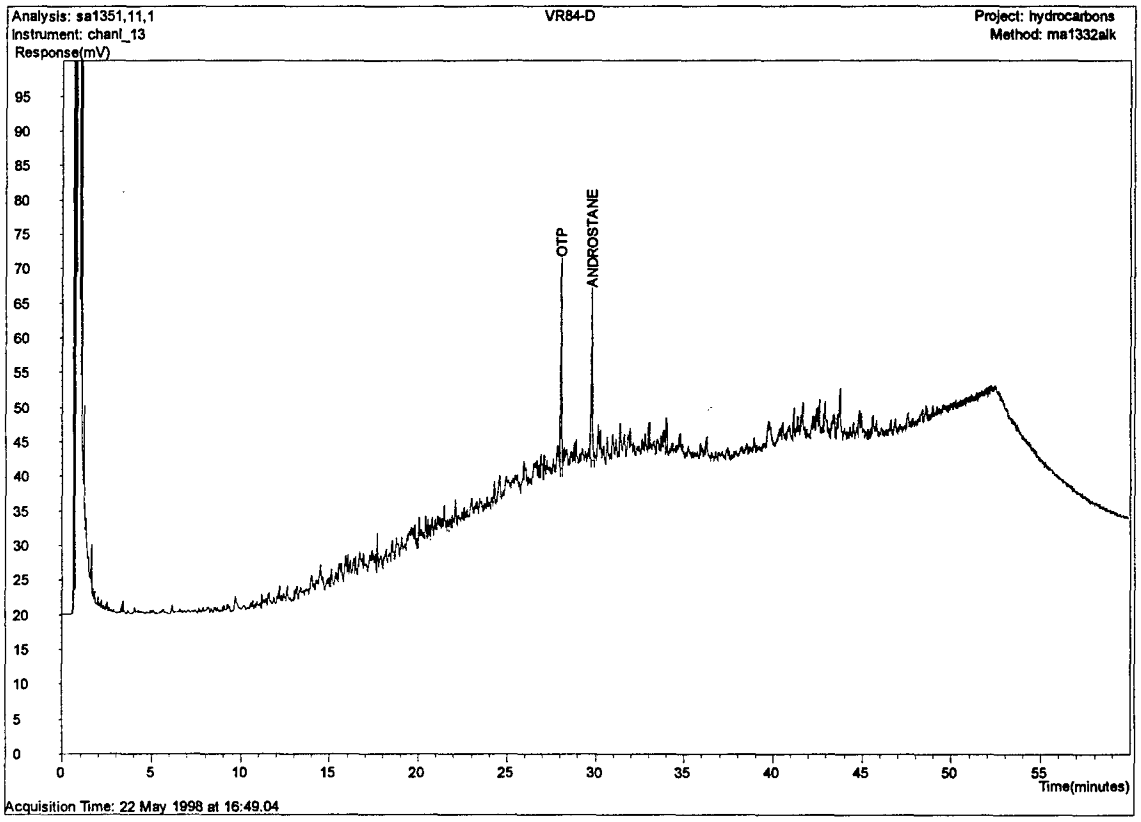

Figure 3-2. GC-FID trace of the fresh Orimulsion 400 used in these studies.
(Labeled peaks are internal standards.)

Table 3-2. PAH concentrations in the previous and current formulations of Orimulsion. All concentrations in mg PAH/kg Orimulsion.

Target Analyte PAH	Orimulsion 100 (1998)	Commercial Orimulsion 400 (1998)	Commercial Orimulsion 400 (1999)
Naphthalene	16	8	8
C1-naphthalenes	40	23	23
C2-naphthalenes	144	71	67
C4-naphthalenes	324	163	202
Biphenyl	4	2	2
Acenaphthylene	ND	ND	ND
Acenaphthene	8	6	6
Dibenzofuran	3	2	3
Fluorene	10	7	5
C1-fluorenes	50	25	27
C2-fluorenes	172	75	98
C3-fluorenes	261	122	188
Anthracene	ND	ND	ND
Phenanthrene	53	32	30
C1-phenanthrenes/anthracenes	111	66	66
C2-phenanthrenes/anthracenes	339	173	199
C3-phenanthrenes/anthracenes	451	181	265
C4-phenanthrenes/anthracenes	229	147	187
Dibenzothiophene	22	13	14
C1-dibenzothiophenes	104	59	82
C2-dibenzothiophenes	325	225	224
C3-dibenzothiophenes	680	421	478
C4-dibenzothiophenes	579	329	396
Fluoranthene	3	2	ND
Pyrene	4	7	8
C1-fluoranthrenes/pyrenes	52	31	30
C2-fluoranthenes/pyrenes	83	40	61
C3-fluoranthenes/pyrenes	123	61	68
Benz(a)anthracene	2	2	2
Chrysene	10	7	8
C1-chrysenes	28	15	21
C2-chrysenes	68	22	42
C3-chrysenes	69	17	47
C4-chrysenes	45	8	28
Benzo(b)fluoranthene	ND	ND	1
Benzo(k)fluoranthene	ND	ND	ND
Benzo(e)pyrene	5	1	2
Benzo(a)pyrene	2	2	3
Perylene	6	3	4
Indeno(1,2,3-c,d)pyrene	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND
Benzo(g,h,i)perylene	ND	1	1
TOTAL PAH	**4641**	**2472**	**2997**

ND < 1 mg/kg

4. DESIGN OF EXPERIMENT

Design of experiment (DOE) is a discipline that incorporates statistics into the process of experimentation. DOE principles can be used to systematically vary a number of independent variables in order to evaluate their effect on dependent variables (Hicks, 1982). In the case of Orimulsion's behavior in water, DOE was used to establish the minimum number of benchtop experiments that could be used to evaluate the independent variables of interest in a statistically valid manner. This approach is described in greater detail in the *Workplan* (Appendix I). Additional references on DOE principles are Box et al. (1978), Hicks (1982), Box and Draper (1987).

In this study the DOE progressed in two phases:

(1) a Plackett-Burman (PB) Screening Phase and
(2) a Response Surface Design Phase.

The results of these phases are described in the Sections 5 and 6, respectively.

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5. PLACKETT-BURMAN SCREENING EXPERIMENTS

5.1 Plackett-Burman Design

Table 5-1 summarizes the independent variables that were evaluated in Plackett-Burman (PB) benchtop screening experiments. All but one of the variables included were continuous variables, i.e., they can have any value over some numerical range. Only particulate type was considered to be a discrete variable. For more discussion surrounding the selection of these variables see the *Workplan* (Appendix I).

Table 5-1. Summary of independent variables evaluated in the PB screening experiments.

		EXPERIMENTAL RANGE			
INDEPENDENT VARIABLES	**FACTOR TYPE**	**LOW**	**HIGH**	**CENTER**	**UNITS**
Water Salinity	continuous	0	35	17.5	‰
Water temperature	continuous	4	30	14.5	°C
Initial Orimulsion concentration	continuous	1000	17000	9000	mg/L
Particulate loading	continuous	0	270	135	mg/L
Particulate Type	discrete	kaolinite	calcite	----	----
Water energetics	continuous	9	90	49.5	rpm

The twelve PB screening experiments shown in Table 5-2 were supplemented with four additional 'high Orimulsion concentration' experiments shown in Table 5-3. The objective of the 12-run PB design was to evaluate and rank the six independent variables in terms of their importance of selected dependent variables. The dependent variables measured in the course of these experiments included:

(1) Average size of particles in suspension after 1, 3, 8 and 24 hours,

(2) total petroleum hydrocarbons (TPH) in suspension after 1, 8 and 24 hours[2],

(3) dissolved TPH after 24 hours (reported as % of bitumen dissolved after 24 hr),

(4) dissolved PAH after 24 hours,

(5) TPH in sediment after 24 hours (reported as % of bitumen that sunk after 24 hr),

(6) weight of any floating material after 24 hours (reported as % of bitumen floating after 24 hr), and

(7) weight of bitumen adhering to vessel walls after 24 hours (reported as % of bitumen stuck to walls after 24 hr).

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[2] The 24 hr sample is also reported as % bitumen in suspension after 24 hr after subtraction of the dissolved TPH total.

5.2 Method of Interpreting Plackett-Burman Results

The interpretation of PB designs is conventionally achieved by a calculation of the "factor effect" for each independent variable and unassigned variable in the design (Hicks, 1982). The factor effect is determined by summing the dependent variable result for each '+' and '-' in the PB design and calculating their difference. The difference is divided by the number of '+' signs in the column above the difference to obtain the factor effect. The factor effects calculated for the unassigned variables provide a measure of the standard error of a factor effect (S_{FE}) which, in turn, is used to calculate 95% upper and lower confidence limits (CL) of the effect. PB design theory determines that those independent variables whose (1) factor effects are significantly larger than the control runs' factor effects or (2) range of effects +/- CL do not span zero are significant. In the latter's instance, if they do span zero by a broad margin (e.g., –40to +50) then that variable is considered unimportant in determining the dependent variable being assessed. If the CL range span zero only slightly (e.g., -10 to +50) then that variable is marginally important in affecting the dependent variable being assessed. Finally, if the CL range does not span zero at all (e.g., +5 to +50) then that variable is considered important. The tables in which the calculations of the factor effects and CL's were calculated for each independent variable are provided in Appendix II.

Table 5-2. Twelve-Run PB design used to evaluate the importance of six independent variables.

Trial	Salinity (°/$_{oo}$)	Temp. (°C)	OR400 concen. (mg/L)	Part. Load (mg/L)	Part. Type	Energetics (rpm)	X7	X8	X9	X10	X11
1	35	30	1000	270	kaol[1]	100	-	-	-	+	-
2	35	4	17000	270	kaol	10	-	-	+	-	+
3	0	30	17000	270	calcite	10	-	+	-	+	+
4	35	30	17000	0	neither	10	+	-	+	+	-
5	35	30	1000	0	neither	100	-	+	+	-	+
6	35	4	1000	0	neither	10	+	+	-	+	+
7	0	4	1000	270	calcite	100	+	-	+	+	+
8	0	4	17000	0	neither	100	-	+	+	+	-
9	0	30	1000	270	kaol	10	+	+	+	-	-
10	35	4	17000	270	calcite	100	+	+	-	-	-
11	0	30	17000	0	neither	100	+	-	-	-	+
12	0	4	1000	0	neither	10	-	-	-	-	-

[1] kaolinite

Table 5-3. Additional "very high concentration" experiments conducted for qualitative purposes.

Trial	Salinity (°/$_{oo}$)	Temp. (°C)	OR400 concen. (mg/L)	Part. Load (mg/L)	Part. Type	Energetics (rpm)
13	35	4	50,000	0	neither	10
14	0	4	50,000	0	neither	100
15	35	25	50,000	0	neither	100
16	0	25	50,000	0	neither	10

The interpretation of the PB design studies are typically made on the basis of measuring a single result (dependent variable) rather than multiple dependent variable results. Thus, as is discussed in the following sections, our measurement of numerous dependent variables in each experiment has complicated the otherwise straightforward calculations and interpretations of factor effects, etc. A further complication in our approach resulted from incomplete sets of our dependent variable measurements. For example, it was not always possible to obtain a particle size measurement due to an absence of particles in the water. In such an instance, reporting a result of 'zero' is inappropriate, therefore, the value must be eliminated from the CL calculations. Nonetheless, important clues were obtained by these screening experiments, and these are described below.

5.3 Results of PB Screening Experiments

5.3.1 Effects on Particle Size

5.3.1.1 General Overview

In this section the effect of the six independent variables on particle size is discussed. Recall, that in those experiments in which mineral matter was added, the particles in suspension include both bitumen and minerals. Table 5-4 contains the mean particle diameter data for the 16 screening experiments. As can be seen, in several saltwater experiments the concentration of suspended particles (i.e., obscuration) was too low to obtain reliable particle size measurements. These results are therefore reported as "NA", not available.

Table 5-4. Summary of mean particle diameter after 1, 3, 8 and 24 hours – PB screening experiments. Values reported are D[4,3] in μm. See text above discussing limitations below.

Trial	1 Hr	3 Hr	8 Hr	24 Hr
1	NA	NA	NA	NA
2	46.4	54.2	293.8	365.2
3	20.4	17.9	11.1	7.9
4	NA	NA	NA	NA
5	20.4	18.4	NA	NA
6	NA	NA	NA	NA
7	48.3	15.8	5.1	2.0
8	23.2	17.0	20.3	15.6
9	22.8	17.4	13.3	9.2
10	98.3	58.3	9.1	4.7
11	19.8	22.9	18.0	12.6
12	16.6	11.9	7.1	7.8
13	18.3	20.3	13.6	9.0
14	14.3	16.5	14.6	16.8
15	101.5	54.7	16.5	6.9
16	21.9	19.0	11.5	6.0

NA – not available due to lack of particles in suspension.

The reader is reminded that reporting a single "mean particle diameter" does not necessarily capture the entire distribution of particles. The reader is further reminded of the limitation in measuring any particles larger than 600 microns by the laser diffraction method employed (Appendix I). Thus, the particle size data presented in Table 5-4 and discussed in the following sections is intended to demonstrate growth trends (e.g., increases or decreases) rather than absolute rates of growth.

5.3.1.2 Plackett-Burman Design Interpretations

The "factor effect" calculation results of the PB screening study on particle size of suspended material after 1, 3, 8 and 24 hours are given in Appendix II. These tables reveal that none of the independent variables were completely irrelevant in determining the size of particles in suspension at any given time. Some general observations from the calculated effect confidence limit ranges are:

(1) After 1 hour the particle size of suspended material was virtually unaffected by salinity, mildly affected by energetics and Orimulsion concentration, moderately affected by particulate type and temperature, and strongly effected by particulate loading.

(2) After 3 hours the particle size of suspended material was, virtually unaffected by salinity, energetics, and particulate type, mildly affected by particulate loading and temperature, and moderately affected by Orimulsion concentration.

(3) After 8 and 24 hours the particle size of suspended material was seemingly unaffected by all independent variables.

The limited interpretation provided after 8 and 24 hours is probably due to the very wide range of particle sizes observed after 8 and 24 hours, driven primarily by the large particles (>250 microns) formed in Trial 2 (Table 5-4). This result precludes any interpretation regarding the effect on particle growth in the 'long term' (after the first 3 hours). However, the overall results of the PB design suggest that Orimulsion concentration and particulate loading are the most important variables in determining particle size/growth in the 'short term' (within 3 hours of a release).

5.3.1.3 Observations from Freshwater Experiments

Further insight to particle growth can be gained by looking at the results of each trial separately. Figure 5-1 shows the particle size trends observed during the eight freshwater experiments. In all but one instance, Trial 7, the suspended particles show a fairly stable although slightly decreasing mean particle size over 24 hours. In most trials the initial particle size was close to that of fresh Orimulsion (~21 μm; Fig. 3-1) but decreased slightly over the course of 24 hours. In summary, these results indicate that particle growth under most freshwater conditions does not occur.

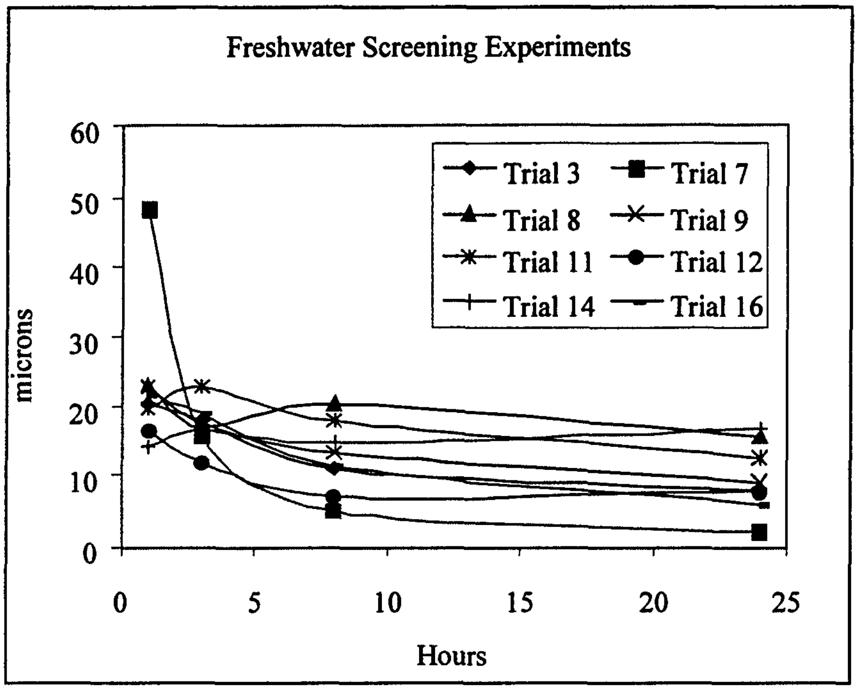

Figure 5.1. Changes in mean particle diameter during freshwater screening experiments.

Trial 7 exhibited the most interesting result. This result could be due to the fact that it was the only freshwater experiment in which both mineral matter (in this case limestone) and high-energy conditions were present.

5.3.1.4 Observations from Saltwater Experiments

Under saltwater conditions three of the eight trials yielded no mean particle size data. Two of these (Trials 1 and 6) contained only 1000 mg/L Orimulsion which led to too low of a concentration of particles in suspension to measure (most particles having floated to near the surface within the first hour). The third 'no data' trial, Trial 4, was atypical in that the Orimulsion remained on the surface of the water during the entire experiment. This probably was due to the fact that the Orimulsion was spilled on the water too slowly and therefore didn't penetrate the water surface and the low energetics of Trial 4 (10 rpm) prevented further mixing.

Figure 5-2 shows that most seawater conditions led to little to no growth among those particles which remained suspended in the water column over 24 hours. (That is not to say that particle growth among 'floating' particles at or near the surface did not occur, but these were not measured.) Only Trial 2 showed a marked increase in mean particle size among particles which remained suspended in the water column. The other saltwater trials show either (1) initial increases to around 100 microns followed by gradual decreases (Trials 10 and 15) or (2) steady conditions initially followed by gradual decreases to around 10 microns after 24 hours (Trials 5 and 13).

One can hypothesize that in the two 50,000 mg/L OR400 trials (13 and 15) the concentration of surfactant in the water was sufficient to prevent extensive particle growth. However, under the more energetic conditions of Trial 15 (100 rpm) some early collisions were inevitable and led to the initial increase in particle size to ~100 microns. However, in the mild conditions of Trial 13 (10 rpm) no early collisions occurred and particle size remained near that of fresh Orimulsion (~21 µm). Under both conditions the greater buoyancy of the larger particles gradually removed them from suspension thereby slowly lowering the average particle size of suspended particles to less than 10 µm after 24 hours.

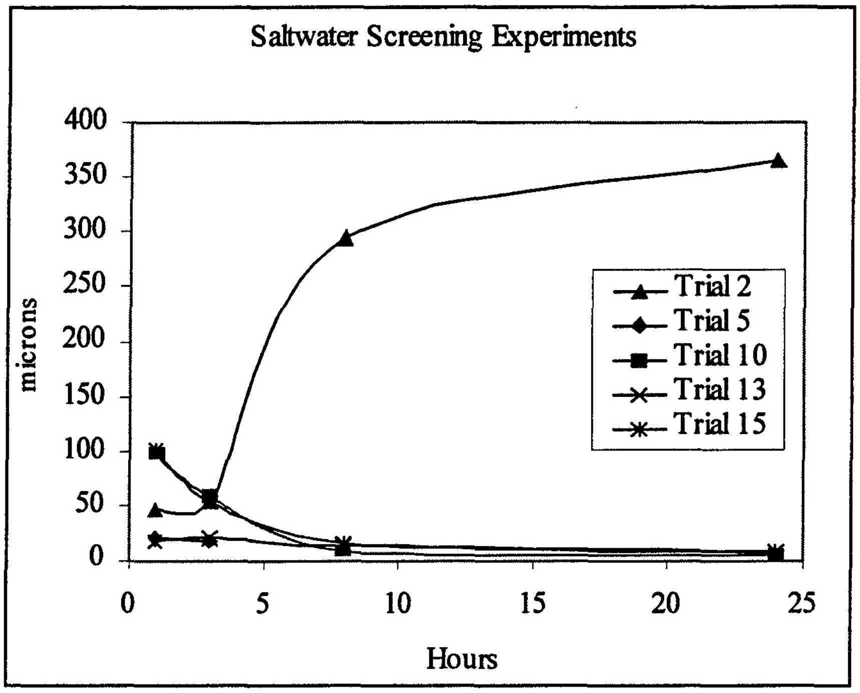

Figure 5-2. Changes in mean particle diameter during saltwater screening experiments. Particle size is D[4,3].

The two 17,000 mg/L experiments (Trials 2 and 10) showed very different results. Perhaps the collisions and particle growth were initial enhanced in Trial 10 (100 rpm) but were more limited in Trial 2 (10 rpm). Visual observations indicated that the low energy conditions in Trial 2 allowed more bitumen to remain in suspension where it formed a three-dimensional "network" of bitumen particles.

5.3.1.5 Summary of the Effects on Particle Growth

The independent variables identified as playing the greatest role in particle growth over the first 3 hours using the PB 'statistical' approach were Orimulsion concentration and particulate loading. From an observational point of view, salinity, Orimulsion concentration, particulate load and energetics all appear to play a role (Figs. 5-1 and 5-2). Water temperature and particulate type seem to have a limited effect on particle size over the course of these experiments.

5.3.2 Effects on Total Petroleum Hydrocarbons in Water

5.3.2.1 General Overview

Measurements of the total petroleum hydrocarbons (TPH) suspended in the water recovered through the sampling nipple after 1, 8 and 24 hours were made using a modified EPA 8015 method (Appendix I). The 24-hour samples were split and one-half was filtered through 0.45 µm filters prior to analysis. The unfiltered water split contained suspended and dissolved, i.e., TPH_{total} while the filtered split contained only $TPH_{dissolved}$. The difference between TPH_{total} and $TPH_{dissolved}$ yielded the $TPH_{suspended}$. Table 5-5 contains the results of these TPH measurements for each trial.

Table 5-5. Summary of total petroleum hydrocarbon (TPH) analysis on water samples from the PB screening benchtop experiments.

Trial	TPH_{total} (mg/L) 1 hr	TPH_{total} (mg/L) 8 hr	TPH_{total} (mg/L) 24 hr	$TPH_{dissolved}$ (mg/L) 24 hr
1	204.8	2.0	0.6	0.6
2	1,227.3	737.5	2,159.7	2.7
3	2,045.5	452.4	629.6	19.8
4	1.0	1.1	NA	NA
5	290.0	23.8	0.9	0.6
6	0.9	2.7	18.1	0.5
7	243.9	48.6	6.4	0.5
8	8,625.0	10,581.4	1,765.0	2.0
9	1,850.0*	245.0	77.2	0.8
10	1,350.0	305.0	26.8	3.3
11	6,232.6	6,047.6	647.8	5.4
12	168.9	79.5	12.3	0.4
13	3,690.5	1,363.6	3,609.3	5.9
14	22,439.0	15,250.0	7,427.5	6.2
15	13,589.7	3,050.0	253.5	3.8
16	14,976.7	3,170.7	149.8	6.4

NA-not available
*Erroneously high due to sample in-homogeneity

5.3.2.2 Plackett-Burman Design Interpretations

The results of the PB screening statistical evaluation of the total petroleum hydrocarbons (TPH) in water after 1, 8 and 24 hours are given in Appendix II. Recall, that the results from the very high concentration trials (13-16) are not included in the PB design and therefore, have not contributed to the PB statistical results. As was the case with the particle size calculation, these tables reveal that none of the independent variables were completely irrelevant in determining the concentration of total petroleum hydrocarbons (TPH_{total})[3] at any given time.

Generally, after 1 hour the TPH_{total} in water was virtually unaffected by temperature, mildly affected by particulate loading, moderately effected by energetics, and most strongly affected by salinity, Orimulsion concentration, and particulate type. After 8 hours the TPH_{total} in water was virtually unaffected by temperature, mildly effected by energetics and particulate loading, moderately effected by salinity and particulate type, and most strongly effected by Orimulsion concentration. After 24 hours the TPH_{total} in water was virtually unaffected by temperature, salinity, particulate type, particulate load, and energetics, mildly effected by Orimulsion concentration.

The overall results of the PB design suggest that the initial Orimulsion concentration is the most important variable in determining the amount of bitumen (as measured by TPH_{total}) that occurs in the water column during the first 24 hours in these experiments. In each time interval, the higher the

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[3] $TPH_{total} = TPH_{dissolved} + TPH_{suspended}$.

concentration of Orimulsion spilled, the higher the resulting $\text{TPH}_{\text{total}}$ concentration in the water. It is interesting that after 24 hours the remaining five variables had virtually no influence on the $\text{TPH}_{\text{total}}$ concentration. In fact, after 24 hours the effect of the initial Orimulsion concentration was also reduced. Both these facts indicate that the 24-hour experiments were sufficiently long to observe the effects of each variable under these conditions. It is notable that after only one hour; however, all of the variables except water temperature exhibited some influence on the $\text{TPH}_{\text{total}}$ concentration.

Because of the strong overall influence that the initial Orimulsion concentration had on the TPH results, the following sections contain observations of the TPH measurements made at each of the three Orimulsion concentrations examined (1000, 17,000 and 50,000 mg/L).

5.3.2.3 Observations from Low OR400 Concentration Experiments

The $\text{TPH}_{\text{total}}$ trends observed in the course of the 1000 mg/L Orimulsion experiments are depicted in Fig. 5-3. Trials 1, 5 and 6 were performed in saltwater and Trials 7, 9 and 12 were performed in freshwater. Some general observations can be made from these trends. First, all but one trial exhibited a maximum after 1 hour, which decreased markedly after 8 hours, and further decreased after 24 hours. Only Trial 6 exhibited a slight increase over the course of 24 hours. Second, regardless of the conditions after 24 hours a comparably low concentration of hydrocarbons were observed to be present in the water column (<77 mg/L; avg. ~19 mg/L). The low average TPH concentration indicates that < 3% of the bitumen introduced remained in suspension after 24 hours (i.e., assuming 30% water content, 1000 mg/L Orimulsion corresponds to 700 mg/L bitumen). This conclusion is consistent with the visual observations of these low OR400 concentration experiments.

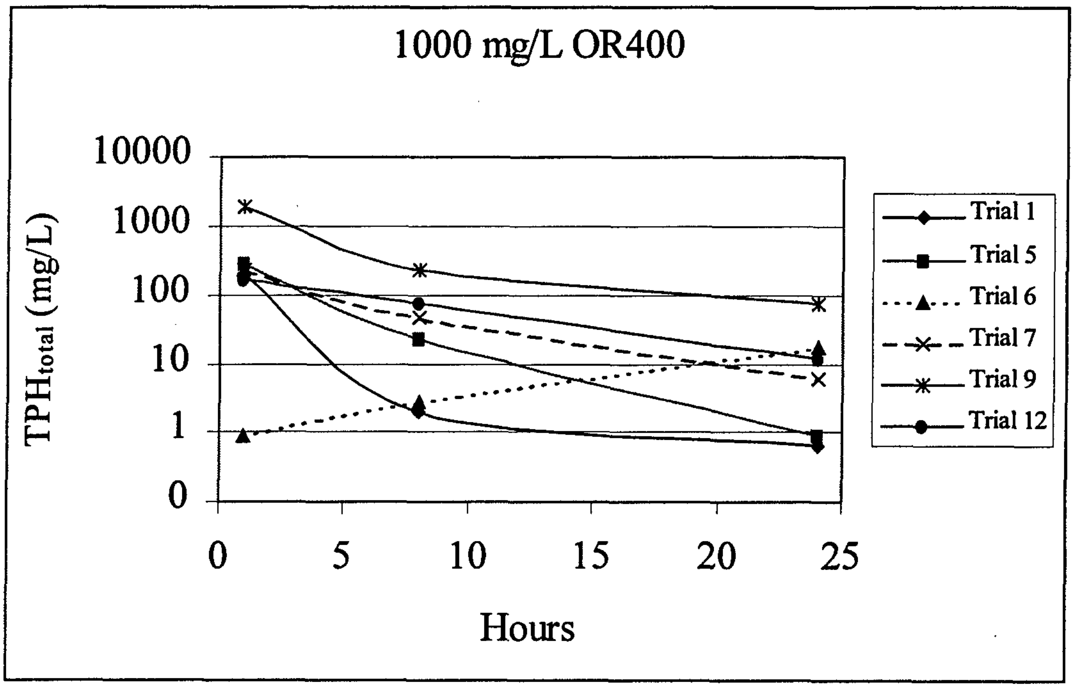

Figure 5-3. Changes in total petroleum hydrocarbons (TPH) during the low concentration screening experiments.

The most interesting trend observed in Fig. 5-3 is that of Trial 9 (freshwater, 25°C, 270 mg/L kaolinite, and 10 rpm). This trial is interesting because of its high TPH_{total} concentration after 1 hour (which, in turn, probably results in the slightly higher concentrations observed after 8 and 24 hours). The cause for this high initial TPH_{total} concentration is unknown.

5.3.2.4 Observations from High OR400 Concentration Experiments

The TPH_{total} trends observed in the course of the 17,000 mg/L Orimulsion experiments were variable (Fig. 5-4). Three general trends are observed. Trials 8 and 11 (Trend 1) were both freshwater experiments performed at high energetic levels. Intuitively speaking, it is reasonable that after 1 to 8 hours bitumen was still highly dispersed in the water and only after 24 hours had it begun to decrease (e.g., sticking to vessel walls, floating or settling toward the bottom). Trials 2 and 3 (Trend 2) were salt and freshwater (respectively) but were both performed under mild energetic conditions. One can envision that after 1 hour of only minimal agitation less bitumen would remain in suspension than did in Trials 8 and 11. The subsequent increase after 24 hours is difficult to explain. Trial 10 was the only saltwater experiment performed at high energy at this Orimulsion concentration. The decreasing TPH_{total} trend (Trend 3) indicates a loss of bitumen from the water column occurred. Visual observations indicated that this was due to adherence of bitumen to the vessel walls.

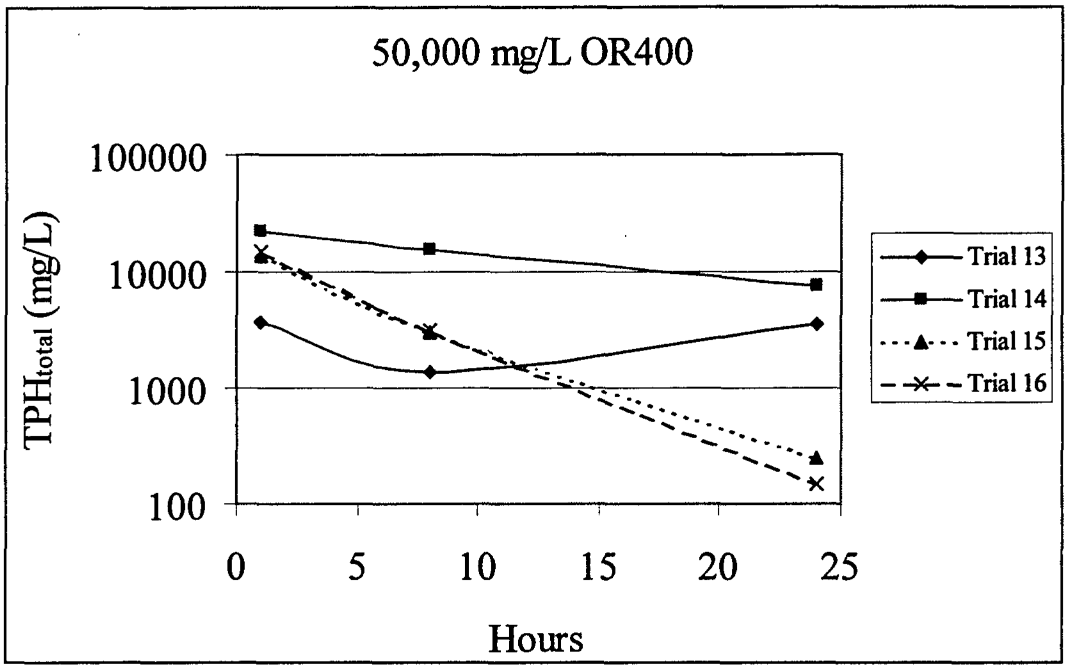

Figure 5-4. Changes in total petroleum hydrocarbons (TPH) during the high concentration screening experiments.

All told, the 17,000 mg/L Orimulsion experiments reveal that after 24 hours the TPH_{total} in the water column (avg. ~1300 mg/L), on average represented about 10% of the bitumen originally introduced (i.e.,. 17,000 mg Orimulsion contains about 11,900 mg of bitumen). Only under high energy, saltwater conditions (Trial 10) did bitumen levels in the water column significantly reduce over the course of these experiments to < 1% of the introduced.

5.3.2.5 Observations from Very High OR400 Concentration Experiments

Four trials conducted at Orimulsion concentrations of 50,000 mg/L were intended to reveal insight to the processes that might occur near the source of a large spill. The TPH_{total} trends observed in the course of the 50,000 mg/L Orimulsion experiments are depicted in Fig. 5-5. Three distinct trends are apparent.

Within 1 hour of the spill three of the four trials had water which contained TPH_{total} concentrations > 13,000 mg/L. The exception, Trial 13, a low energetics, saltwater trial, contained only 3690 mg/L. This lower value was due to the early formation of a floating bitumen patty. The other saltwater experiment (Trial 15) was performed at high energetics and patty formation did not occur.

Throughout the remaining course of the experiments Trials 13 and 14 exhibit generally consistent concentrations of TPH_{total} in the water column. Slight losses in Trial 14 are probably due to formation of a 'bathtub ring.' It is notable that after 24 hours, Trial 13 still contains the same concentration of TPH_{total} in the water column as it had after only 1 hour (~3600 mg/L). This suggests that under low energy, saline conditions most bitumen quickly (within 1 hour) moves toward the surface.

Trial 16 was a freshwater, low energy experiment in which most bitumen sank, thus the continual decrease in TPH in the water column throughout could be expected. However, the same decreasing trend in the saltwater, high-energy experiment (Trial 15) was unexpected. During this experiment no surface patty was formed (presumably due to the high energy). Instead most of the bitumen in Trial 15 was observed to settle toward the bottom of the vessel. The reason for this 'settling' in saltwater is unknown although it may be related to the physical settling of large bitumen particles formed early in the experiment (Table 5-4) under the low energetic conditions.

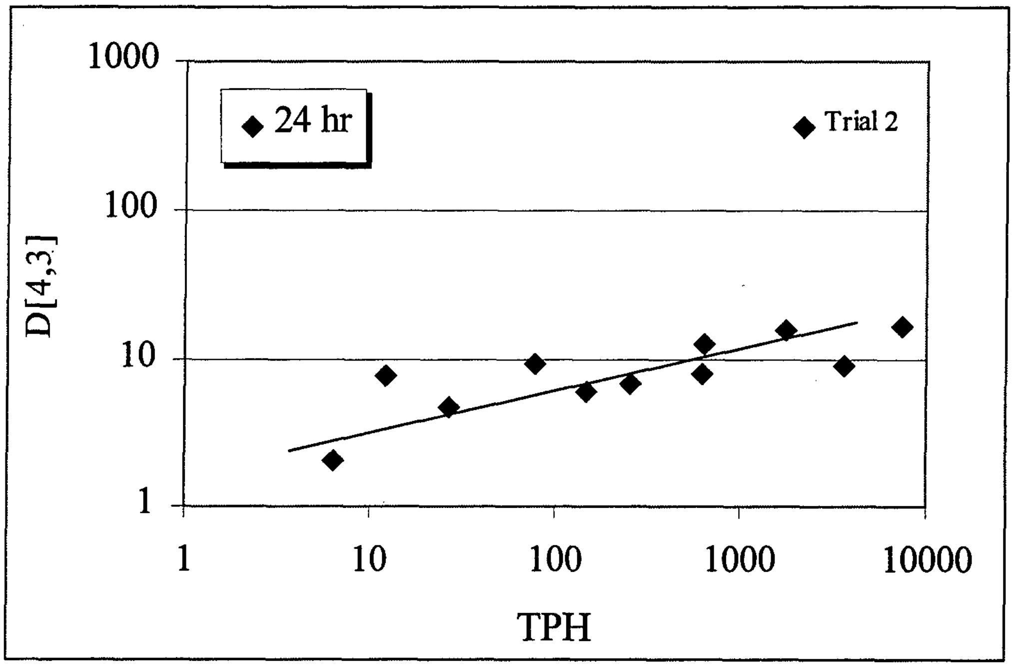

Figure 5-5. Relationship between total petroleum hydrocarbons (TPH in mg/L) and mean particle size after 24 hours following the PB screening experiments.

This last statement raises the question of whether there is any correlation between particle size and TPH. Investigation of this revealed that there was no correlation after 1 or 8 hours. However, after 24 hours a weak correlation exists between mean particle size and TPH_{total} in the water column (Fig. 5-6). Only Trial 2, in which a "network" of particles remained suspended in the water column, falls off of the general trend. This weak correlation may be indicating that when more bitumen remains in suspension the chance of collisions and coalescence is increased.

5.3.3 Effects on the Gross Behavior of Orimulsion in Water

5.3.3.1 General Overview

In this section, the gross behavior of the bitumen component of Orimulsion in the PB screening experiments is evaluated. The amount of bitumen, which occurred in one of five "compartments" after 24 hours, was measured. The mass (weight) of bitumen which was recovered from (1) the surface of the water (float fraction), (2) from the bottom of the glass vessel (settled fraction), (3) suspended in the water column, (4) dissolved in the water column, and (5) from the walls of the glass vessel were determined after 24 hours.

The results of this mass balance are contained in Table 5-6, which shows the weight (in grams) of air-dried bitumen that was recovered from these five "compartments" after 24 hours. Determination of the weight of the floating bitumen and bathtub ring bitumen was straightforward. The assumptions that went into deriving the weights of the other compartments are given beneath the table.

To the right in Table 5-6 are the totals and a calculated percentage of original bitumen accounted for in the mass balance. About one-half of the recoveries lie between 75% and 125%, a reasonable range for these experiments given the assumptions. Not surprisingly, over-recovery was common among the low concentration (1000 mg/L) trials while under-recovery was common in the high concentration (17,000 mg/L) trials. Excessively low (<75%) and high (>125%) recoveries indicate that less or more of the bitumen could not be accounted for after 24 hours. In one instance (Trial 14) this was due to loss of Orimulsion over the sides of the swirling vessel shortly after the spill. Contributing to low recoveries was the removal of bitumen during sampling for both particle size and TPH after 1, 3 and 8 hours. Contributing to high recoveries is the presence of some entrapped water within the bitumen. (It was impossible to dry the bitumen completely at room temperature.) In any case, this 'bulk' data provides important practical information regarding the gross fate of the bitumen component of Orimulsion 400 when spilled under the experimental conditions.

The data in Table 5-6 are converted to percentages in Table 5-7. Included in this table is the total percentage of bitumen that was not stuck to the sides of the vessel after 24 hours, i.e., the "bathtub ring" compartment. As can be seen, between 5.3 and 100% of the recovered bitumen occurred in one or more of the other four compartments and, on average, 67.5% was not stuck to the sides. This is an important consideration given that the presence of vessel walls is an unavoidable consequence of laboratory benchtop experiments of any kind which contributes to the disparity between what is observed in the lab and what happens in open water.

Table 5-6. Masses of air-dried bitumen recovered from "five compartments" in the PB screening experiments after 24 hours.

Trial	Floating (g)	Sunk[1] (g)	Bathtub Ring (g)	Suspended Particulate[2] (g)	Dissolved[3] (g)	Total Weight Bitumen Recovered (g)	Initial Weight Bitumen[4] (g)	% Recovery of Bitumen
1	0.00	0.59	1.80	0.0000	0.0018	2.39	2.19	109
2	7.40	1.26	3.80	5.9534	0.0073	18.42	37.25	49
3	4.50	10.48	0.20	1.6831	0.0546	16.92	37.25	45
4	NA	NA	NA	NA	NA	NA	NA	NA
5	0.00	0.58	2.40	0.0008	0.0016	2.98	2.19	136
6	2.12	0.65	0.40	0.0487	0.0013	3.22	2.19	147
7	0.00	1.63	1.10	0.0163	0.0013	2.75	2.19	125
8	0.00	1.25	20.20	4.8658	0.0055	26.32	37.25	71
9	0.00	2.48	0.00	0.2110	0.0021	2.69	2.19	123
10	0.00	2.13	39.60	0.0649	0.0090	41.80	37.25	112
11	4.92	5.90	11.10	1.7730	0.0149	23.71	37.25	64
12	0.00	1.71	0.00	0.0328	0.0011	1.74	2.19	80
13	78.17	0.00	0.40	9.9453	0.0162	88.53	109.53	81
14[5]	1.65	10.04	11.50	20.4827	0.0172	43.69	109.53	40
15	0.00	98.26	13.40	0.6892	0.0105	112.36	109.53	103
16	0.00	91.93	0.20	0.3958	0.0177	92.54	109.53	84

NA-not available due to experimental error.

[1] Dried weight of all material recovered from bottom of vessel minus the weight of the mineral matter added to that particular trial.

[2] Equals (TPH_{total} measured in water after 24 hrs x 2.76 L)-($TPH_{dissolved}$ measure after 24 hrs x 2.76 L).

[3] Equals measured $TPH_{dissolved}$ after 24 hrs x 2.76 L (Assumes that 240 ml of the original 3 L of water was removed in course of sampling at 1, 3, and 8 hr intervals).

[4] Equals mass of OR400 originally added x 0.73 (i.e., the bitumen content of OR400). Does not accommodate for losses due to sampling throughout the experiment.

[5] Some OR400 spilled over edge of vessel early in experiment.

5.3.3.2 Plackett-Burman Design Interpretations

The results of the PB screening statistical evaluation of the bitumen mass balance percentages after 24 hours are given in Appendix II. Recall, that the results from the very high concentration trials (13-16) are not included in the PB statistical evaluation and therefore, have not contributed to the PB results. As was the case with the particle size and TPH_{total}, the PB tables reveal that none of the independent variables were completely irrelevant in determining the percentage of Orimulsion's bitumen reporting to any given compartment.

Table 5-7. Normalized percentages of the recovered bitumen occurring in different compartments.

Trial	Floating	Sunk	Bathtub Ring	Suspended	Dissolved	% not stuck to sides
1	0.0	24.7	75.3	0.0	0.07	24.7
2	40.2	6.8	20.6	32.3	0.04	79.4
3	26.6	61.9	1.2	9.9	0.32	98.8
4	NA	NA	NA	NA	NA	NA
5	0.0	19.4	80.5	0.0	0.05	19.5
6	65.8	20.2	12.4	1.5	0.04	87.6
7	0.0	59.3	40.0	0.6	0.05	60.0
8	0.0	4.7	76.7	18.5	0.02	23.3
9	0.0	92.1	0.0	7.8	0.08	100.0
10	0.0	5.1	94.7	0.2	0.02	5.3
11	20.8	24.9	46.8	7.5	0.06	53.2
12	0.0	98.1	0.0	1.9	0.06	100.0
13	88.3	0.0	0.5	11.2	0.02	99.5
14	3.8	23.0	26.3	46.9	0.04	73.7
15	0.0	87.5	11.9	0.6	0.01	88.1
16	0.0	99.3	0.2	0.4	0.02	99.8

NA-not available due to experimental error.

Some general observations are that after 24 hours the % bitumen stuck to the vessel walls was virtually unaffected by temperature, Orimulsion concentration, and particulate load, mildly effected by salinity, moderately affected by particulate type, and most strongly effected by energetics. After 24 hours the % bitumen found floating was virtually unaffected by salinity, temperature, particulate type, particulate load, and Orimulsion concentration and only mildly effected by energetics. After 24 hours the % bitumen found at the bottom of the vessels was virtually unaffected by temperature, mildly effected by particulate load and particulate type, moderately effected by Orimulsion concentration and energetics, and most strongly effected by salinity. After 24 hours the % bitumen found suspended in the water column was virtually unaffected by salinity, temperature, particulate type, particulate load, and energetics and only mildly effected by Orimulsion concentration. After 24 hours the % bitumen found dissolved in the water column was virtually unaffected by all six independent variables.

Collectively speaking, the overall results of the PB design suggest that the water temperature played little role in the gross behavior of the bitumen. The other five variables played varying roles with water salinity, energetics, and Orimulsion concentration having the greatest overall effect. It is notable that energy's role was limited except for the % bitumen found stuck to the vessel walls. This might be expected considering there is likely to be centrifugal forces that increase collisions of bitumen particles with the vessel walls which would promote some sticking to the walls.

5.3.3.3 Chemical Nature of Hydrocarbons Dissolved into the Water Column

The last dependent variable to consider is the concentration/nature of the dissolved hydrocarbons resulting from an Orimulsion spill. The PB screening experiments have determined that up to 19.74

mg/L of dissolved hydrocarbons occurred in water after 24 hours (Table 5-5). The nature of these dissolved hydrocarbons is important to determine since it is the dissolved components that have the greatest bioavailability and therefore, the greatest potential to impact organisms.

Figure 5-6 shows the GC-FID fingerprints of the total and dissolved hydrocarbons recovered from the Trial 3 experiment after 24 hours. This trial was selected since it contained the greatest concentration of dissolved hydrocarbons (Table 5-5) and is representative of the nature of dissolved components in the other trials. As can be seen the TPH_{total} fingerprint (total = suspended + dissolved) is consistent with the bitumen fraction of fresh Orimulsion 400 (Fig. 3-2). This appears as a broad 'hump' of mostly unresolved compounds. The $TPH_{dissolved}$ fingerprint contains an equally broad range of hydrocarbons, however, it is enriched in some of the more water soluble, lower boiling components. As a result its 'hump' is somewhat skewed toward lower boiling components (left). This is not unexpected. Polycyclic aromatic hydrocarbons (PAH) occur in fresh Orimulsion 400 at a concentration of 2473 mg PAH/kg Orimulsion (Table 3-2). The fate of these compounds is particularly important to determine given their potential toxicity to aquatic organisms. Table 5-8 contains the concentrations of dissolved PAH in the water after 24 hours during these screening experiments. This shows that the concentration of total dissolved PAH after 24 hours ranged from 316 ng/L (Trial 1) up to 86,000 ng/L (Trial 3). (The former concentration is essentially background and can be ignored.) The distribution of PAH dissolved is very similar to the distribution in fresh Orimulsion with the exception that the more soluble components are slightly enriched in the water samples. This is demonstrated in Section 6.2.4.4 and is to be expected given solubility considerations.

The PB design statistics indicate that the concentration of PAH dissolved in the water after 24 hours was virtually unaffected by any of the independent variables. Inspection of the results, however, suggests that among the parameters salinity had the most measurable impact. The potential impact of salinity on the dissolved concentration of PAH after 24 hours is depicted in Fig. 5-7 which shows that several freshwater trials contained higher concentrations of total dissolved PAH as compared to the saltwater trials. Curiously, Orimulsion concentration had less of a role than salinity. The reason for the generally greater concentration of PAH in freshwater than in saltwater is, at least in part, due to the reduced solubility of organic chemicals in saltwater. Comparison of the measured concentrations of individual PAH *versus* their aqueous solubilities (e.g., Table 30 in Neff, 1979) indicates that none of the water samples contained PAH at concentrations approaching their solubility limits. Theoretically, this means that more PAH could have dissolved into the water, perhaps if given additional time to equilibrate.

The results of Trial 3 are atypical for these experiments raising the question of whether there may have been some problem with the filtering process. No record of any problem exists. The normalized distribution of PAH is very comparable to that of fresh OR400, i.e., there is no enrichment of the more soluble PAH in the water sample. This suggests that there may have been a small amount of bitumen that passed through the 0.45 micron filter giving rise to the high concentration observed. Most of the other Trials exhibited PAH distributions that are enriched in the more soluble PAH components than the OR400 (Table 5-8).

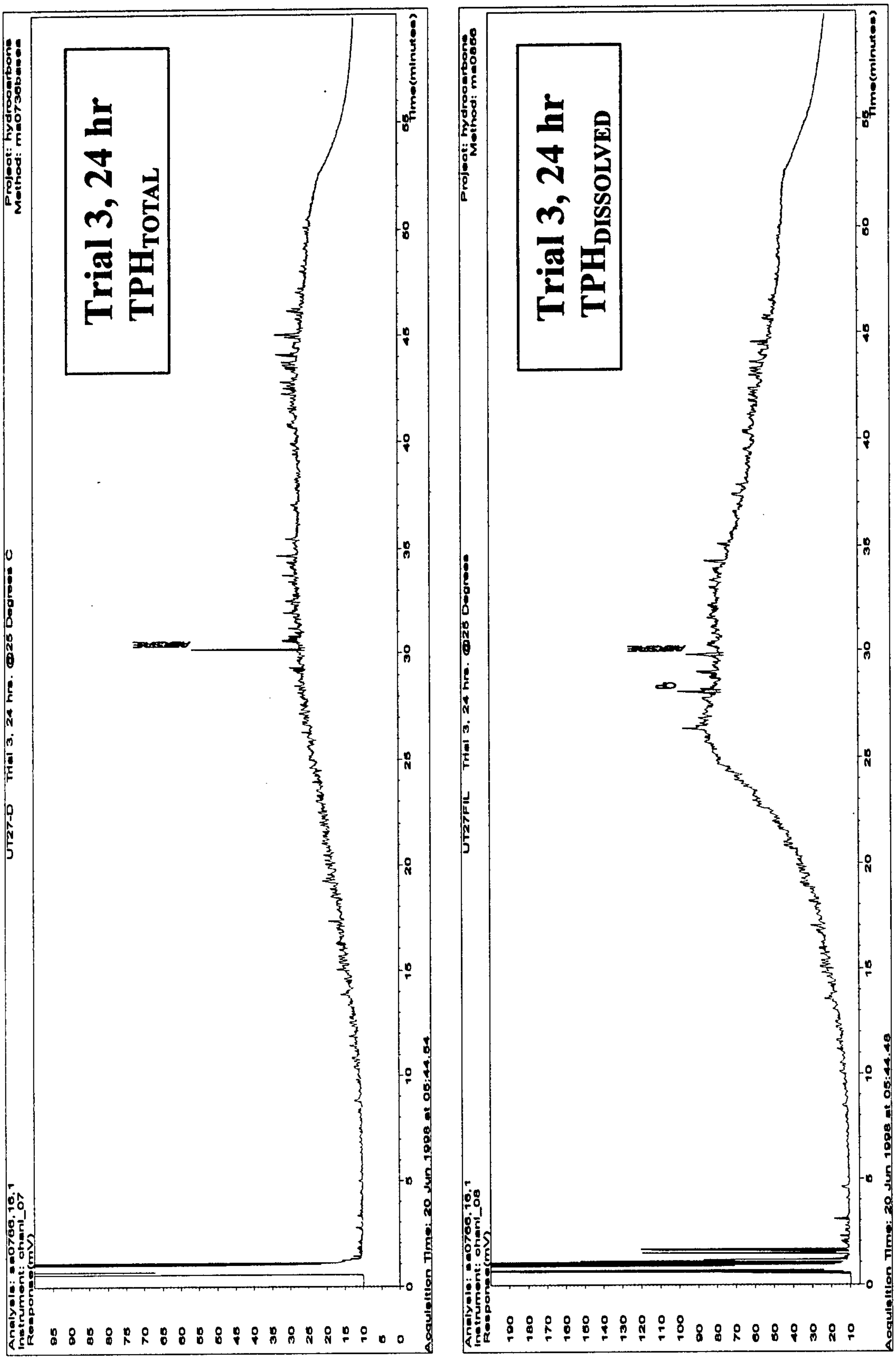

Figure 5-6. GC-FID fingerprints of representative total and dissolved petroleum hydrocarbons recovered from the water column after 24 hours. (Example shown is from Trial 3). Dissolved fraction contains a greater abundance of lower boiling, more highly soluble hydrocarbons.

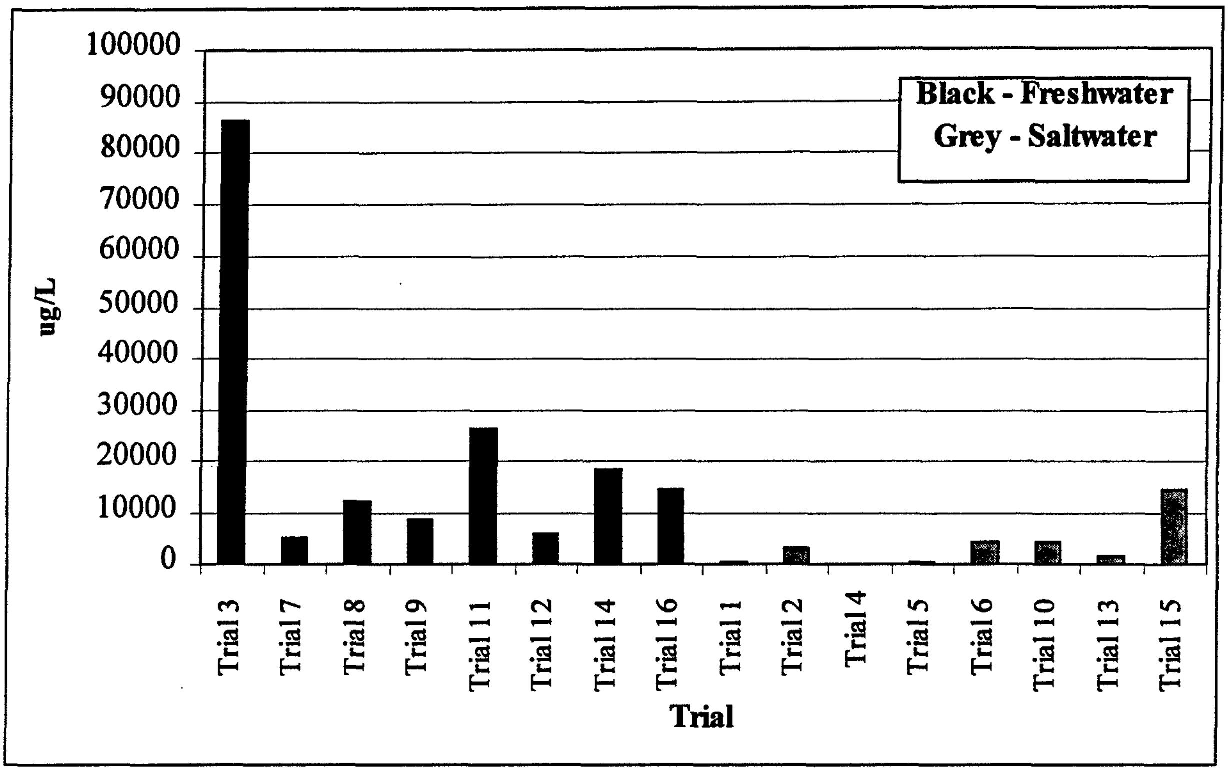

Figure 5-7. Concentration of PAH dissolved after 24 hours.

5.4 Summary of PB Screening Experiments

The 12 screening experiments and four 'very high' concentration experiments yielded a tremendous amount of data presented in Section 5. The PB screening 'factor effect' calculations (Appendix II) and our observations/interpretations surrounding these data provide some clear indications of the importance of the six independent variables under consideration. These indications can be qualitatively summarized in Table 5-9. Recall that the objective of these screening experiments was to provide insight as to the independent variables of greatest concern. Only these variables would be 'carried forward' into the response surface design experiments.

Collectively, the PB screening results indicate that four independent variables are worthy of additional study in the response surface phase benchtop experiments. These variables are:

(1) water salinity,
(2) OR400 concentration,
(3) particulate loading and
(4) water energetics.

Table 5-8. PAH$_{dissolved}$ concentrations in water from PB screening experiments after 24 hours. All concentrations are surrogate corrected in ng/L.

PAH Analyte/Trial #	Trial 1	Trial 2	Trial 3	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12	Trial 13	Trial 14	Trial 15	Trial 16
Naphthalene	13.55	1188.3	92.3	18.1	854.2	675.7	2469.5	1266.5	879.8	2604.5	750.4	309.7	2723.0	1830.2	2220.0
C1-naphthalenes	17.5	1017.7	65.5	13.3	1128.3	1172.1	2498.4	1675.6	1013.5	2660.7	1210.4	434.1	2687.9	1867.6	2225.2
C2-naphthalenes	23.6	548.1	924.9	27.6	724.0	936.4	1555.0	1452.8	986.0	2265.8	961.1	372.5	1938.6	1528.1	1864.8
C3-naphthalenes	17.9	ND	4285.0	ND	349.3	470.0	810.9	719. 9	434.3	1432.2	516.3	213.8	1266.1	860.8	1220.9
C4-naphthalenes	ND	ND	7309.2	ND	215.2	350.9	710.9	548.6	165.0	1158.8	353.3	ND	918.7	566.0	667.6
Biphenyl	ND	18.5	154.8	ND	49.0	67.3	116.3	96.3	71.6	148.1	56.9	10.4	140.4	84.6	120.1
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	149.6	620.21	ND	132.8	198.6	290.5	267. 6	228.8	361.0	164.1	122.1	335.6	292.5	332.1
Dibenzofuran	ND	ND	223.09	ND	45.3	71.0	108.3	99.2	72.6	145.2	62.2	27.7	141.4	87.2	124.8
Fluorene	ND	75.7	530.3	3.1	84.5	132.3	198.8	185.9	147.3	265.7	126.2	53.1	253.7	184.9	223.2
C1-fluorenes	ND	ND	1174.3	ND	114.6	154.6	250.8	244.5	90.4	420.1	158.7	ND	339.7	249.2	339.0
C2-fluorenes	ND	ND	2760.7	ND	81.8	138.5	316.1	278.1	ND	745.05	178.0	ND	518.1	375.6	516.9
C3-fluorenes	ND	ND	4684.7	ND	ND	ND	141.4	121.8	ND	777.31	67.7	ND	358.6	341.1	194.6
Anthracene	ND	ND	69.06	4.2	ND	ND	24.1	10.2	ND	53.2	6.0	ND	31.9	28.6	32.0
Phenanthrene	3.03	ND	980.0	4.5	149.0	244.0	372.7	375.4	149.3	637.7	255.4	ND	551.3	334.6	513.3
C1-phenanthrenes/ anthracenes	ND	ND	2011.7	ND	51.83	99.63	257.21	169.68	ND	673.7	108.9	ND	478.1	249.8	423.5
C2-phenanthrenes/ anthracenes	ND	ND	6499.6	ND	ND	50.03	336.19	121.24	ND	1386.4	74.3	ND	808.4	545.00	564.9
C3-phenanthrenes/ anthracenes	ND	ND	7111.3	ND	ND	ND	222.25	87.70	ND	1212.0	36.4	ND	659.9	665.9	403.6
C4-phenanthrenes/ anthracenes	ND	ND	4761.8	ND	ND	ND	ND	ND	ND	491.9	19.8	ND	264.4	277.8	ND
Dibenzothiophene	62.58	ND	619.04	47.6	65.9	110.2	171.0	175.7	69.3	292.4	116.2	ND	290.6	157.5	296.2
C1-dibenzothiophenes	16.28	ND	2522.3	29.5	78.9	140.7	324.1	187.9	82.2	726.7	179.9	ND	641.0	343.8	394.5
C2-dibenzothiophenes	43.51	ND	6563.3	41.7	24.7	86.6	438.4	234.2	ND	1595.9	128.5	ND	935.5	709.00	692.1
C3-dibenzothiophenes	117.84	ND	13130	98.0	ND	ND	377.2	293.9	ND	3023.5	127.4	ND	1029.8	1466.4	656.4
C4-dibenzothiophenes	ND	ND	11486	ND	ND	ND	ND	57.5	ND	1802.2	60.9	ND	717.7	1005.6	412.4
Fluoranthene	ND	ND	80.2	ND	ND	3.5	7.6	9.6	ND	13.1	1.9	ND	13.2	33.3	ND
Pyrene	ND	ND	212.5	ND	ND	2.08	10.8	32.9	ND	47.0	1.8	ND	32.5	102.2	ND
C1-fluoranthrenes/pyrenes	ND	ND	692.1	ND	ND	ND	ND	ND	ND	162.0	ND	ND	115.8	65.1	ND
C2-fluoranthenes/pyrenes	ND	ND	1405.1	ND	ND	ND	ND	ND	ND	280.5	ND	ND	151.2	100.9	ND

Table 5-8 (continued)

PAH Analyte/Trial #	Trial 1	Trial 2	Trial 3	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12	Trial 13	Trial 14	Trial 15	Trial 16
C3-fluoranthenes/pyrenes	ND	ND	2078.4	ND	ND	ND	ND	ND	ND	322.0	ND	ND	96.2	ND	ND
Benz(a)anthracene	ND	ND	105.0	ND	ND	ND	ND	ND	ND	17.1	ND	ND	8.4	13.3	ND
Chrysene	ND	ND	263.0	ND	ND	ND	ND	ND	ND	58.9	ND	ND	31.1	23.4	ND
C1-chrysenes	ND	ND	711.2	ND	ND	ND	ND	ND	ND	116.9	ND	ND	56.0	45.9	ND
C2-chrysenes	ND	ND	1615.3	ND	ND	ND	ND	ND	ND	189.0	ND	ND	ND	ND	ND
C3-chrysenes	ND	ND	677.2	ND	ND	ND	ND	ND	ND	106.1	ND	ND	ND	ND	ND
C4-chrysenes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(e)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(g,h,I)perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total PAH's	**316**	**2998**	**86,418**	**288**	**4149**	**5104**	**12,009**	**8712**	**4390**	**26,193**	**5723**	**1544**	**18,535**	**14,436**	**14,438**

ND < 1 ng/L

Table 5-9. Summary of PB ‘factor effect’ calculations for the variables of interest.

VARIABLES	Water Salinity	Water Temp.	OR400 Conc.	Part. Load	Part. Type	Energetics
Particle Size 1 hr	unaffected	moderately affected	mildly affected	strongly affected	moderately affected	mildly affected
Particle Size 3 hr	unaffected	mildly affected	moderately affected	mildly affected	unaffected	unaffected
Particle Size 8 hr	unaffected	unaffected	unaffected	unaffected	unaffected	unaffected
Particle Size 24 hr	unaffected	unaffected	unaffected	unaffected	unaffected	unaffected
TPH 1 hr	strongly affected	unaffected	strongly affected	mildly affected	strongly affected	moderately affected
TPH 8 hr	moderately affected	unaffected	strongly affected	mildly affected	moderately affected	mildly affected
TPH 24 hr	unaffected	unaffected	mildly affected	unaffected	unaffected	unaffected
% Floating	unaffected	unaffected	unaffected	unaffected	unaffected	mildly affected
% Sunk	strongly affected	unaffected	moderately affected	mildly affected	moderately affected	moderately affected
% Bathtub Ring	moderately affected	unaffected	unaffected	unaffected	moderately affected	strongly affected
% Suspended	unaffected	unaffected	mildly affected	unaffected	unaffected	unaffected
% Dissolved	unaffected	unaffected	unaffected	unaffected	unaffected	unaffected
PAH dissolved 24 hr	mildly affected	unaffected	unaffected	unaffected	unaffected	unaffected

In considering one dependent variable or another each of these four independent variables demonstrated either a statistical 'factor effect' significance or an observational significance. Water temperature exhibited virtually no influence on any of the dependent variables. Therefore, it can be confidently eliminated from additional studies. Particulate type was of some significance, however, particulate type is a discrete variable that by definition cannot be included in a response surface design (Hicks, 1982). The reason for this is because in order to recognize any non-linear effects there can be no discrete variables among the independent variables being evaluated in a response surface design. This is because if curvature effects are to be estimated, each independent variable must have at least three levels. There is no realistic intermediate level in the case of particulate type (i.e., 50:50 kaolinite:calcite is not a real world situation). It is for these reasons that only kaolinite is used in the response surface design experiments.

6. RESPONSE SURFACE DESIGN EXPERIMENTS

6.1 Response Surface Design

A response surface design was used to evaluate the four independent variables recognized as having the greatest influence on Orimulsion's gross behavior (Section 5). By considering intermediate values for the four independent variables, a three-level response surface design should be better able to describe the effects throughout the entire experimental ranges. In other words, rather than project the effect of salinity between 0 and 35 $^{o}/_{oo}$, inclusion of a mid-point (17.5 $^{o}/_{oo}$) would permit greater description of salinity effects (and not necessitate a linear projection from 0 to 35 $^{o}/_{oo}$).

6.1.1 Types of Three-level Response Surface Designs

There are two types of three-level response surface designs, namely a central composite, face-centered cube design or a Box-Behnken spherical design (Hicks, 1982). The former considers a cubical experimental region and the latter considers a spherical experimental region. These are described in greater detail in the *Workplan* (Appendix I) and can be referred to as the Box-Behnken spherical design and the central composite, face-centered cube design, respectively.

The central composite, face-centered cube design is considered more 'bold' than the Box-Behnken design and we consider it to be more appropriate for the problem at hand since it includes the entire range for each independent variable. That is to say that it seems prudent to not ignore the 'extreme' conditions given that they may occur in the "real world". For example, it is possible that a situation exists were Orimulsion is released into 35 $^{o}/_{oo}$ seawater, with no kaolinite particulates, and 'extreme' energetics. Therefore, we propose to use a central composite, face-centered cube design.

6.1.2 Central Composite, Face-Centered Cube Response Surface Design Employed

The JMP statistical software package (Version 3.2.1) was employed to design a four-factor response surface design that incorporated salinity, Orimulsion concentration, kaolinite loading, and energetics. The range of interest for these variables remained the same as in the PB screening, namely 0-35 $^{o}/_{oo}$, 1000-17,000 mg/L OR400, 0-270 mg/L kaolinite, and 10-100 rpm, respectively. The design used in these experiments is shown in Table 6-1.

As can be seen 31 experiments were designed which included 16 fractional factorial (FF) experiments in which various combinations of maximum or minimum variable values are used, 8 axial experiments in which various combinations of three mid-range variables and one maximum or minimum variables are used, and 7 center axis experiments in which the mid-range variables of each variable are used. The purpose of these center axis experiments is to test the reproducibility of the dependent variable measurements and allow for some analysis of the experimental error built into the design.

These 31 experiments were conducted in 7 batches of 4 to 5 experiments each over the course of three weeks (July 9-Aug. 3, 1998). No blocking was used but some randomization was employed in the sense that experiments of the same energy levels were selected to be run simultaneously. All of the experiments were conducted at 18°C (room temp.) using the same benchtop apparatus as was used in the PB screening experiments. (See Appendix I for a description of the benchtop apparatus.)

Table 6-1. Response surface design showing 31 benchtop experiments conducted.

Trial	Pattern	Point Type	Salinity (‰)	OR400 (mg/L)	Energetics (rpm)	Part. Load (mg/L)	Start Date
1’	----	FF	0.0	1000	10	0	30-Jul
2’	---+	FF	0.0	1000	10	270	30-Jul
3’	--+-	FF	0.0	1000	100	0	14-Jul
4’	--++	FF	0.0	1000	100	270	14-Jul
5’	-+--	FF	0.0	17000	10	0	30-Jul
6’	-+-+	FF	0.0	17000	10	270	30-Jul
7’	-++-	FF	0.0	17000	100	0	14-Jul
8’	-+++	FF	0.0	17000	100	270	14-Jul
9’	+---	FF	35.0	1000	10	0	3-Aug
10’	+--+	FF	35.0	1000	10	270	3-Aug
11’	+-+-	FF	35.0	1000	100	0	15-Jul
12’	+-++	FF	35.0	1000	100	270	15-Jul
13’	++--	FF	35.0	17000	10	0	3-Aug
14’	++-+	FF	35.0	17000	10	270	3-Aug
15’	+++-	FF	35.0	17000	100	0	15-Jul
16’	++++	FF	35.0	17000	100	270	15-Jul
17’	-000	Axial	0.0	9000	55	135	9-Jul
18’	+000	Axial	35.0	9000	55	135	9-Jul
19’	0-00	Axial	17.5	1000	55	135	9-Jul
20’	0+00	Axial	17.5	17000	55	135	9-Jul
21’	00-0	Axial	17.5	9000	10	135	3-Aug
22’	00+0	Axial	17.5	9000	100	135	15-Jul
23’	000-	Axial	17.5	9000	55	0	21-Jul
24’	000+	Axial	17.5	9000	55	270	21-Jul
25’	0	Center-Ax	17.5	9000	55	135	21-Jul
26’	0	Center-Ax	17.5	9000	55	135	21-Jul
27’	0	Center-Ax	17.5	9000	55	135	27-Jul
28’	0	Center-Ax	17.5	9000	55	135	27-Jul
29’	0	Center-Ax	17.5	9000	55	135	27-Jul
30’	0	Center-Ax	17.5	9000	55	135	27-Jul
31’	0	Center-Ax	17.5	9000	55	135	27-Jul

6.2 Results of the Response Surface Experiments

6.2.1 Interpretation of Response Surface Design Results

A large volume of literature exists on the use and interpretation of response surface experiments (Hicks, 1982 and ref. therein). It is not our intention to review these methods, however, in the sections that follow some general guidelines are presented that can help the reader in evaluating the statistical results.

For each of the dependent variables measured an analysis of the response surface was performed using the JMP (Version 3.2.1) statistical software. A one-page printout summarizing the results of these analyses are presented in Appendix II for each of the dependent variables measured. The collective contents of those sheets are summarized later in Section 6. Some of the key parameters contained on these sheets are described in Sections 6.2.1.1 and 6.2.1.2.

6.2.1.1 Regression Analysis

The primary analysis procedure in a response surface design is a regression analysis, the purpose of which is to use the collected dependent variable data (Y) to estimate the coefficients of the quadratic response surface model (i.e., b-coefficients) for each independent variable and their interactions. The solution yields a quadratic formula that best describes the dependent variable data. That is to say that for each dependent variable measured (e.g., particle size after 1 hr, TPH after 3 hr, etc.) the best solution to the 15-term (1 constant term, 4 linear terms, 6 two-factor interaction terms, and 4 quadratic terms) equation:

$$\begin{aligned} Y = \quad & b_0 + \\ & b_1X1 + b_2X2 + b_3X3 + b_4X4 + \\ & b_{12}X1X2 + b_{13}X1X3 + b_{14}X1X4 + b_{23}X2X3 + b_{24}X2X4 + b_{34}X3X4 + \\ & b_{11}X1^2 + b_{22}X2^2 + b_{33}X3^2 + b_{44}X4^2 \end{aligned}$$

was determined where;

b_0 = constant
$b_\#$ = b-coefficients for each term
X1 = salinity between 0 and 35 $^{0}/_{00}$
X2 = Orimulsion concentration between 1000 and 17,000 mg/L
X3 = energy between 10 and 100 rpm
X4 = particulate loading between 0 and 270 mg/L
X#X# = two-factor interaction between these variables
$X\#^2$ = curvature effects for this variable

The solution to this equation will give the best prediction of the dependent variable of interest (Y) under any set of dependent variables (X1 through X4) within the range of interest. The calculated b-coefficients for each dependent variable are labeled as the "*Estimates*" in the "*Parameter Estimates*" portions of each page in Appendix III.

An evaluation of the most important terms in the regression solution is achieved by the t Ratio (calculated as b-coefficient/standard error) and the probability (Prob>|t|) calculated for each term in the solution. Generally, t Ratios > 2 indicate that this term has a significant effect on the measured result (Y). Similarly, Prob>|t| values < 0.01 indicates an important term. Thus, t Ratio and Prob>|t|

can be used to 'rank' the most important terms in a solution and thereby recognize the independent variables, the interaction[4] between these variables, or the curvature[5] effect for a given variable which have the greatest impact on Y. The t Ratios and Prob>t values are also given in the "*Parameter Estimates*" portions of each page found in Appendix III.

6.2.1.2 Evaluating Fit and Variance (Reliability) of a Result

Evaluating the reliability of the regression solution is achieved most easily through the calculated variation about the mean (*RSquare*). Alternative to RSquare is the calculated RSquare Adjusted, which takes into consideration the number of coefficients and the number of Y values. RSquare or RSquare Adjusted values > 0.90 generally indicates an excellent fit of the data exists. Both of these values appear in the "*Summary of Fit*" portions of each page found in Appendix III.

Another criteria to look for lies in the analysis of variance (ANOVA) result of F Ratio. The F Ratio is the ratio of the mean squares for error in the regression (model) *versus* the mean squares for the error from duplicate experimental results (Table 6-1, Trials 25' through 31'). The variation among these seven duplicate experiments represents the 'pure error' in the system because all seven trials represent the same factor combination. Generally, F Ratios > 4 indicates that the variation in the model far exceeds the variation in reproducibility (i.e., pure error). Values near 1 indicate that the variation in reproducibility is comparable to the variation in the model. The ANOVA F Ratios appear in the "*Analysis of Variance*" portions of Appendix III.

Finally, each response surface model result in Appendix III contains a series of graphs ("*Prediction Profiles*") that show the best fit profile for each independent variable over the range of interest. These generally show whether or not the dependent variable of concern is increasing, decreasing, or both over the range of each independent variable.

6.2.2 Effects on Particle Size

6.2.2.1 General Overview

The results of the mean particle size measurements (D[4,3]) for each of the 31 response surface experiments are given in Table 6-2. Remember that these values represent an average of particulate mineral matter (when present) and bitumen. The mean particle size data range from < 10 µm to nearly 300 µm. In each instance the range of particle size was significantly larger and often not expressed by a normal distribution. In many instances particles larger than 600 µm, the maximum measurable by our laser diffraction methods, were formed. In most instances the distribution of particles were asymmetrical or bi-modal. Therefore, one must keep in mind that these data are averages and not necessarily representative of normal nor complete particle populations. Therefore, the utility of these data lie in their ability to reveal general trends rather than rates or absolute sizes.

In spite of this limitation some interesting observations can be made when the particle size data are examined in terms of their average values under different experimental conditions. These average particle sizes are shown in Table 6-3, which reveals some general noteworthy trends. For example, it is apparent that at any time during the 24-hour experiments the largest particles were consistently formed under the intermediate conditions (brackish water, medium Orimulsion concentrations,

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[4] Interaction is a measure of the effect that one independent variable has on Y as another independent variable changes. Variables are said to "interact" if the effect of one independent variable on Y changes as another independent variable changes.

[5] Curvature is a measure of the linearity of an effect that one independent variable has on Y.

medium energy, and medium clay content). The possible reasons for this are discussed in Section 6.2.2.4.

Another noteworthy trend is that, in most instances, the particle size tended to decrease over the course of the 24-hour experiments.

6.2.2.2 Response Surface Design Results

The mean particle size data in Table 6-2 was used to generate a response surface model for each time period measured. The results of these models are found in Appendix III and are summarized herein.

None of the response surface design model statistical results for particle size exhibit a very good fit of the mean particle size data. RSquared values range from only 0.76 to 0.54 and F Ratios ranged from 3.60 to 1.35. These results indicate that the mean particle size is difficult to predict from the four variables. This difficulty is derived from a combination of the error resulting from the extremely heterogeneous nature of the suspended material, the difficulty in representing the diverse population of particles by a single, mean diameter, and the limitations of the measurement method (i.e., particles > 600 microns not measured). These difficulties are evidenced in the seven replicate trials (25' to 31') in which mean particle size was shown to vary significantly (Table 6-2). Heterogeneity is further complicated by the presence of clay in the replicate experiments. Clay's broad particle size range could potentially confound the measurements due to the low reproducibility of these measurements. These results do not, however, preclude us from examining and ranking the variables that had the greatest impact on particle size. This impact can be measured by the significance of the term in the calculated model solution as determined from the t Ratio for each term and the prediction profiles for each variable (Appendix III).

Table 6-2. Summary of mean particle diameter (D[4,3]) measurements (in microns) after 1, 3, 8 and 24 hours – Response Surface Benchtop Experiments.

Trial	1 hr	3 hr	8 hr	24 hr
1'	20.6	18.8	13.5	10.1
2'	19.9	17.5	16.5	9.7
3'	20.0	12.9	12.8	10.8
4'	14.7	28.2	22.3	51.3
5'	20.2	17.7	14.3	9.8
6'	19.9	15.6	13.7	11.7
7'	17.1	21.2	18.2	15.0
8'	20.8	18.2	18.2	29.5
9'	19.2	23.2	15.5	17.8
10'	12.3	13.1	9.3	20.1
11'	26.7	16.3	25.3	NA
12'	25.7	19.8	23.8	87.3
13'	NA	NA	NA	NA
14'	22.9	21.6	15.9	14.4
15'	89.0	42.5	18.4	8.0
16'	71.2	45.6	18.9	20.2
17'	19.8	14.2	11.5	7.1
18'	164.0	21.8	64.5	13.7
19'	88.7	40.5	25.5	18.2
20'	186.9	95.0	87.0	119.2

Table 6-2 (continued)

Trial	1 hr	3 hr	8 hr	24 hr
21'	226.7	296.1	295.8	182.8
22'	158.1	123.4	120.2	195.2
23'	54.4	61.6	248.2	45.6
24'	60.0	168.8	113.2	15.8
25'	144.1	66.3	139.0	17.1
26'	121.7	165.7	96.6	15.2
27'	161.9	127.0	132.2	271.5
28'	18.3	53.4	45.2	30.6
29'	121.0	155.9	145.7	120.5
30'	106.3	78.6	56.1	172.3
31'	152.8	151.7	70.3	204.7
MIN.	**12.3**	**12.9**	**9.3**	**7.1**
MAX.	**226.7**	**296.1**	**295.8**	**271.5**
AVG.	**73.5**	**65.1**	**63.6**	**60.2**

NA- not available due to lack of measurable particles in suspension.

Table 6-3. Average particle diameter (D[4,3]) calculated for suspended particles under various average conditions during the response surface experiments.

Average Condition	1 hr	3 hr	8 hr	24 hr
Freshwater (0 ppt)	19	18	16	17
Brackish (17.5 ppt)	123	122	121	108
Saltwater (35 ppt)	54	25	24	26

1000 mg/L OR400	28	21	18	28
9000 mg/L OR400	116	114	118	99
17000 mg/L OR400	56	35	26	28

10 rpm	45	53	49	35
55 rpm	108	92	95	81
100 rpm	49	36	31	52

0 mg/L clay	33	27	46	17
135 mg/L clay	128	107	99	105
270 mg/L clay	30	39	28	29

An examination of t Ratios reveal that after 1 hour particle size was most influenced by the clay particle loading and to a lesser degree, by salinity effects. Examination of the prediction profiles reveals that both effects were curved such that, on average, the largest particles were observed at the intermediate particle loadings and salinities while, on average, smaller particles occurred at the extremes.

After three hours, the salinity had the greatest impact, again in a curved nature such that, on average, the largest particles were observed at the intermediate salinities. In this case, the water's energy level also had an impact on particle size. Its effect was also curved in the sense that on average the largest particles occurred at low and high energy levels.

After eight hours, salinity and initial Orimulsion concentration had the greatest effect, both exhibiting curved effects with the largest particle size predicted at intermediate values. Finally, after 24 hours the mean particle size was again attributable to the curved effects of salinity and water energy level.

A summary of these effects appears in Table 6-4. Also given in this table is the calculated solution for each time where the best-fit model would predict the maximum mean particle size. Remember the fit of the models to the data were rather poor (RSquared << 0.9), nonetheless, these results may offer some utility in predicting the fate of Orimulsion or in planning the flume experiments. All told, it is clear that following a spill of Orimulsion the water salinity and level of energy in the water will have the greatest impact on the growth of particles. The presence of clay (or presumably other) particles in the water has an effect only within the first couple of hours of the spill. The initial concentration of Orimulsion the water does not appear to play a significant role in particle growth.

Table 6-4. Summary of response surface results – mean particle diameter.

Time Since Spill	**Most Important Parameters**	**Interpretation**	**Maximum Values Predicted At**			
			Salinity (°/₀₀)	**OR400 (mg/L)**	**Energy (rpm)**	**Loading (mg/L)**
1 Hr	Clay loading	Particle size greatest at intermediate clay loading	23	20,643	52	127
3 Hr	Salinity and Energy	Particle size greatest at intermediate salinities and at intermediate energy	18	9,552	57	158
8 Hr	Salinity	Particle size greatest at intermediate salinities	18	9,230	58	153
24 Hr	Salinity and Energy	Particle size greatest at intermediate salinities and intermediate energy	18	9,054	53	136

6.2.2.3 Changes in Particle Size Observed at Different Salinities

The apparent importance of salinity in determining the particle size of suspended matter warrants some additional consideration, particularly as they may change over time. In this section the trends observed over the course of the experiments are presented in order to provide some indication of the particle size changes that might occur over the course of the first 24 hours following a release. The reader is reminded that the particle size values are average values, often from a non-normal distribution of particles. This is certainly a complicating factor in interpreting any trends.

Figures 6-1 through 6-3 show the changes in mean particle size over the course of 24 hours for the freshwater, brackish water, and seawater experiments conducted, respectively.

Under freshwater conditions particle size was generally observed to decrease from the original size of bitumen particles in fresh Orimulsion (~21 μm; Fig. 3-1) to approximately 10 μm after 24 hours. This result is generally consistent with the results observed in the freshwater PB screening experiments (Fig. 5-1) and further indicates that, under most freshwater conditions, particle growth does not occur.

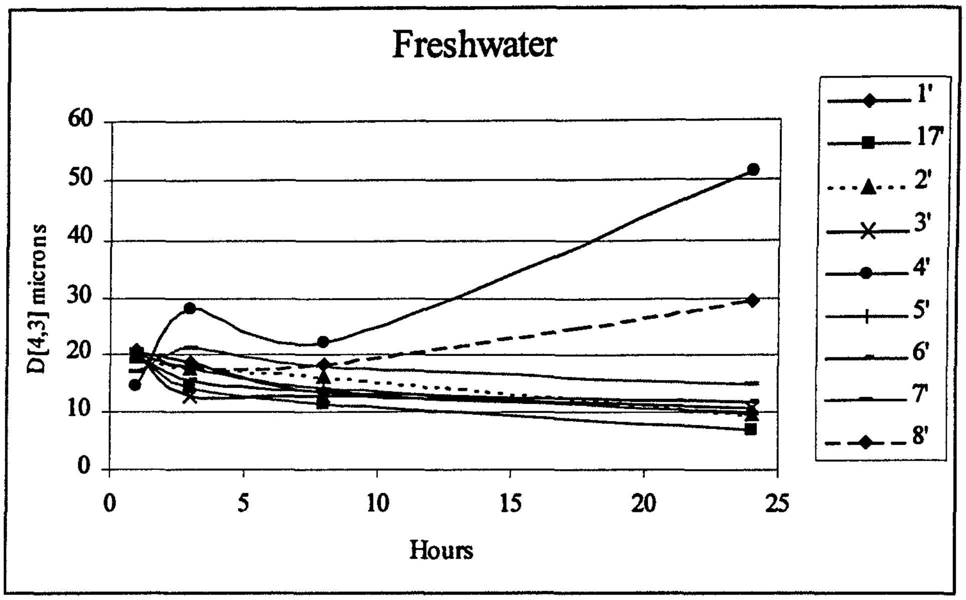

Figure 6-1. Changes in mean particle diameter during freshwater experiments.

However, particle growth was observed in two of the freshwater trials (Trials 4' and 8'; Fig. 6-1). These were the only two freshwater trials in which both high-energy conditions and high-clay content were present. A similar effect was observed in the Trial 7 in the PB screening experiments. It also had high energy and high mineral matter conditions (Fig. 5-1). Thus, one could expect that particle growth under freshwater conditions would only be expected when both high-energy conditions and high mineral matter were both present. Of course, the impact of suspended clay (alone) in these experiments could contribute to the increase in mean particle diameter.

Under brackish water conditions there are no clear trends to describe (Fig. 6-2) with the exception that particle diameters are generally larger than those of bitumen found in fresh Orimulsion (Fig. 3-1). This is consistent with the response surface models, which indicated that greater particle diameters generally occurred under intermediate salinities (Table 6-4). There is no comparison possible between these results and the screening results since the latter did not include any brackish water experiments.

The brackish water experiments conducted included the seven replicate experiments. Somewhat surprisingly these exhibited considerable variability in particle size (Trials 25 to 31; Table 6-2). We attribute this variability to the broad range of particle size in the clay present in these experiments. Regardless, this variability contributes to the error in the response surface model described above. Repeated measurements on the same sample yielded comparable results, therefore, we can only attribute this variability to the non-normal distribution of particles comprising the suspended matter, particularly resulting from the presence of clay.

Under most seawater conditions the mean particle size was generally observed to either (1) initially increase slightly from that of Orimulsion or (2) remain around the size of Orimulsion bitumen, regardless of the presence of clay in the water (Fig. 6-3). This was also observed in the early stages of the PB saltwater screening experiments (Fig. 5-2). Over the course of 24 hours the particle size was generally observed to remain around that of fresh Orimulsion bitumen (~21 μm) or to decrease slightly to around 10 μm. This trend was also common in the PB screening experiments. One exception to this trend was Trial 12' in which marked particle growth was observed after 24 hours (Fig. 6-3). A similar anomalous result was observed in Trial 2 of the PB screening experiments (Fig.

5-2). In that instance the growth of a bitumen 'network' was observed in the low energy, high OR400 concentration conditions. No such 'network' was formed in the Trial 12' results. Thus, at this time we have no obvious explanations for the particle growth observed in Trial 12'.

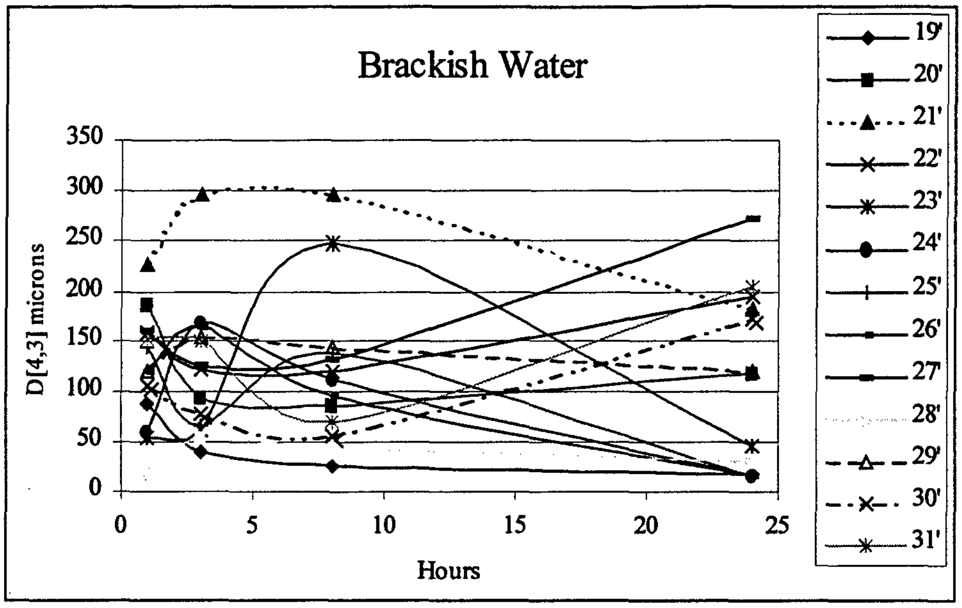

Figure 6-2. Changes in mean particle diameter during brackish water experiments.

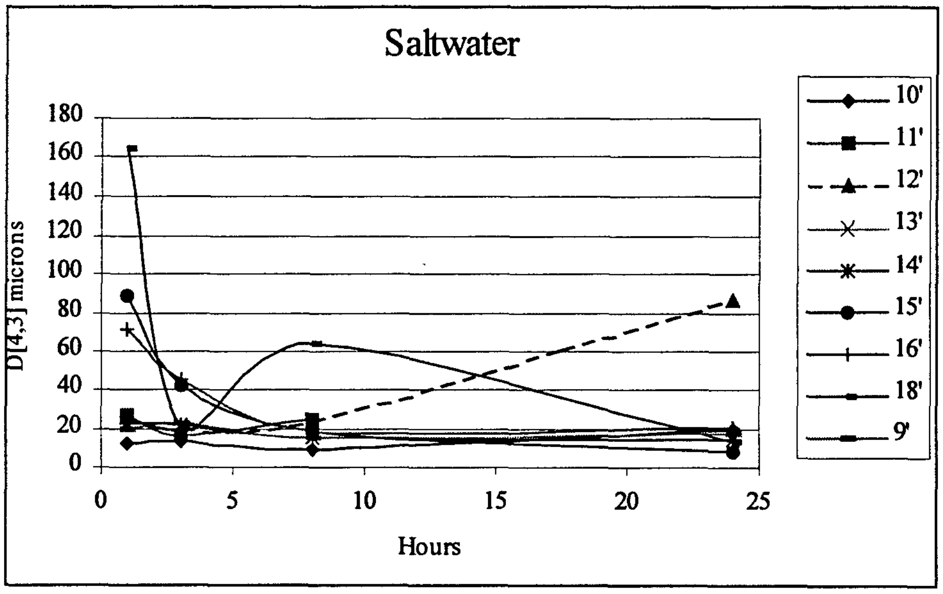

Figure 6-3. Changes in mean particle diameter during seawater experiments.

6.2.2.4 Summary of Particle Size Changes and Controls

The variables identified as playing the greatest role in particle growth over the course of these experiments were summarized in Table 6-4. In the initial hour following the release of Orimulsion the clay loading had the greatest 'statistical' effect. The effect of clay loading is intuitively reasonable in that the concentration of suspended clay, with its broad particle size distribution, would be highest early in the experiments (even the low energy experiments). However, because of its greater density the clay would tend to either (1) settle out over the first few hours of the low energy experiments or (2) form bitumen/clay particles due to collisions in the high energy experiments. In either case, the impact of clay (or other mineral matter in the water) is a complicating factor in measuring bitumen particle growth in these experiments. Its impact is limited to the early stages of the low energy experiments and is probably only important in the high-energy conditions when it would tend to remain in suspension longer.

In the longer term, salinity was 'statistically' determined to have the greatest effect on particle growth (Table 6-4). Statistically the greatest particle growth occurred under intermediate salinity (~ 18‰; Table 6-4). Comparison of the particle size observed after 24 hours in Figs. 6-1 through 6-6 provides further insight. In both instances the greatest variability and particle growth was observed under the intermediate conditions. With few exceptions, after 24 hours there were predominantly small particles (the same size or smaller than the bitumen in fresh Orimulsion) remaining in suspension in both freshwater and saltwater and in low and high initial Orimulsion concentrations. Significantly larger particles were often observed under brackish water and medium initial Orimulsion concentrations.

The observations of generally larger particles formed under intermediate conditions might be explained by:

(1) under brackish conditions bitumen particle may tend to remain in suspension longer and thereby increase the potential for collisions,

(2) under intermediate Orimulsion concentrations (~9000 mg/L) there is sufficient dilution of the surfactant yet the particles are not too dilute to prohibit collisions, and/or

(3) at low energy (10 rpm) collisions between bitumen particles are too few and weak to promote particle growth, at high energy (100 rpm) collisions with the wall are favored, but at intermediate energy levels (55 rpm) enough bitumen remains in the water column so that collisions are both frequent enough and strong enough to promote coalescence.

6.2.3 Effects on Total Petroleum Hydrocarbons in Water

6.2.3.1 General Overview

Measurements of the total petroleum hydrocarbons (TPH) suspended in the water after 1, 8 and 24 hours were made using gravimetric techniques and a modified EPA 8015 method (Appendix I). As described in Section 5.3.2.1, the TPH_{total} after 24 hours was comprised of the $TPH_{suspended}$ and $TPH_{dissolved}$. Table 6-5 contains the results of these TPH measurements for each response surface experiment.

Two trials (13' and 14') had difficulty measuring the TPH after 24 hours. The difficulty was akin to that observed in Trial 4 of the PB screening experiments. In these two trials, the only low energy, high Orimulsion concentration, saltwater experiments conducted, the spilled Orimulsion was observed to remain on or near the surface of the water throughout the 24-hour period. This led to relatively low TPH concentrations in the water column after 1 and 8 hours. However, after 24 hours, as the floating material was attempted to be recovered (and weighed), it quickly dispersed into the water column, thereby raising the measured TPH after 24 hours.

6.2.3.2 Response Surface Design Interpretations

The data in Table 6-5 was used to calculate a response surface model for each TPH measurement. The results of these are found in Appendix III and are described herein.

Table 6-5. Summary of total petroleum hydrocarbon (TPH) concentration (mg/L) in water 1, 8 and 24 Hours after an Orimulsion release – Response Surface Benchtop Experiments.

Trial #	TPH$_{total}$ 1 Hr	TPH$_{total}$ 8 Hr	TPH$_{suspended}$ 24 Hr	TPH$_{dissolved}$ 24 Hr
1'**	236.8	115.8	45.3	0.8
2'	315.8	140.0	70.0	0.7
3'	717.9	263.2	65.6	0.5
4'	370.0	13.9	72.4	0.4
5'	820.5	243.9	99.6	1.9
6'	850.0	472.2	130.0	1.7
7'	3,720.9	8,000.0	NA	2.4
8'	10,157.9	4,272.7	119.3	1.7
9'	26.3	15.8	7.4	0.3
10'	30.8	14.6	4.6	0.4
11'	166.7	16.2	0,1	0.4
12'	100.0	9.5	20.1	0.6
13'	2.4	2.3	3490.1*	3.2
14'	261.9	65.0	908.8*	3.3
15'	2,350.0	250.0	16.3	16.5
16'	1,441.9	133.3	4,468.4	3.9
17'	2,093.0	651.2	149.9	1.7
18'	95.2	28.6	113.2	2.9
19'	523.8	190.0	11.2	1.1
20'	5,756.1	1,952.4	302.8	4.7
21'	85.7	20.5	2143.1	3.2
22'	2,418.6	180.0	3,921.1	4.3
23'	944.4	2,611.1	82.0	3.6
24'	1,105.3	1,166.7	13.3	3.5
25'	842.1	1,405.4	26.0	3.9
26'	923.1	1,189.2	37.6	3.8
27'	174.4	47.6	401.0	3.0
28'	1,105.3	461.5	350.5	3.1
29'	186.1	6,256.4	787.9	3.3
30'	272.7	95.2	311.9	4.4
31'	95.3	105.3	257.7	3.9

NA - Sample lost due to laboratory problem.

* Results elevated; See text for description.

** 'prime' used to distinguish these trials from the screening trials.

The response surface design model results for TPH exhibited a variable range of fit quality, generally comparable to the particle size model fits (Appendix III). RSquared values range from 0.59 (TPH after 8 hours) to 0.79 (TPH after 1 and 24 hours). F Ratios ranged from 1.7 to 4.4, respectively.

These results indicate that the TPH in the water column is moderately predictable after 1 hour and after 24 hours and poorly predictable after 8 hours. The seven replicate trials (25' to 31') exhibited some range of error but this was outweighed by the variations due to experimental conditions (in all but the 8 hour TPH model).

An examination of the Ratios for each term in each solution reveals those which had the greatest effect on TPH. After 1 hour, TPH was strongly influenced by the interaction of water energy and Orimulsion concentration. Generally, as both of these parameters increased, so did the TPH concentration. The interaction of Orimulsion concentration with salinity also had a marginal effect in that higher TPH occurred when OR400 concentration was high and salinity was low. This also makes sense in that freshwater permitted greater dispersion of bitumen throughout the water column.

After 24 hours the TPH in suspension was strongly effected by the energy. In this case the effect was curved in the sense that higher TPH concentrations were predicted at both low energy and high energy while lower TPH concentrations were predicted at moderate energy. This is somewhat counterintuitive as one might expect a greater removal of bitumen (i.e. lowering of TPH concentration) from the water column to occur under high energy (due to increased collisions resulting in floating or sticking to walls) and low energy (due to floating or settling of bitumen particles). However, one can also envision how low energy might allow more of the smaller bitumen particles to remain suspended and how high energy could keep a broad range of particles in suspension (even clay particles). The model, therefore, must be influenced by other parameters. This is discussed a bit further in Section 6.2.3.5.

Interestingly enough, the TPH dissolved in water after 24 hours was most influenced by the interaction between the Orimulsion concentration and the water's salinity such that as both increased so did the concentration of dissolved hydrocarbons. This is intuitively opposite to what one would expect (increased salinity reduces solubility of organic matter) and may be due the single result of Trial 15', a saltwater experiment which contained a very high $\mathrm{TPH}_{\mathrm{dissolved}}$ concentration (Table 6-5).
A summary of the effects of different parameters on TPH measurements appears in Table 6-6. Omitted from this table are the calculated solutions for each time period in which the best fit model would predict the maximum TPH. These are omitted because the quadratic character of the models predicted the maximum TPH values to occur beyond the domain of reason, e.g., negative energy. (The JMP software cannot be constrained in performing this particular calculation.) In any case it is clear from the response surface model results (Appendix III) that the initial concentration of Orimulsion and the energy in the water will have the greatest impact on the concentration of petroleum hydrocarbons in the water. Oppositely, the presence of clay (or presumably other) particles in the water and the salinity of the water will have little influence on TPH in the water.

Table 6-6. Summary of response surface statistical model regarding the concentration of total petroleum hydrocarbons in the Water column.

Time Since Spill/ TPH form	Most Important Parameters	Interpretation
TPH 1 Hr -total	Initial Orimulsion concentration and energy	TPH greatest at higher OR400 concentrations and energy
TPH 8 Hr -total	Initial Orimulsion concentration and energy	TPH greatest at higher OR400 concentrations and energy
TPH 24 Hr -suspended	Energy	TPH greatest at lower and higher energy and lowest at medium energy
TPH 24 Hr -dissolved	Initial Orimulsion concentration and salinity	TPH greatest at higher OR400 concentrations and salinity

6.2.3.3 Changes in TPH Observed at Different Orimulsion Concentrations

The response surface design clearly identified the initial Orimulsion concentration as an important variable controlling the concentration of petroleum hydrocarbons that can be expected to occur in the water column following a release of Orimulsion. In this section the trends observed over the course of the response surface experiments are presented in order to provide some insight into the TPH concentrations that might occur over the course of the first 24 hours following a release. Because of the low concentration of dissolved TPH (Table 6-5), these concentrations are essentially a measure of the mass of bitumen particles in suspension.

Figures 6-4 through 6-6 show the TPH_{total} concentrations for the low, medium, and high initial concentrations of Orimulsion. Each of the low concentration experiments exhibited a maximum TPH within the first hour (avg. 277 mg/L) and an overall decrease in TPH after 24 hours (Fig. 6-4). This same trend was observed in the PB screening experiments (Fig. 5-3). In each case, the TPH_{total} concentration after 24 hours was < 73 mg/L and averaged only 33.5 mg/L. These results are also comparable to those of the PB screening experiments (Section 5.3.2.3). The implication of these results is that in waters receiving a low concentration Orimulsion (~1000 mg/L), the petroleum hydrocarbons remaining in the water column after 24 hours, under any salinity, turbidity or energy conditions, is less than 10% of the bitumen introduced[6].

The medium concentration OR400 spills exhibit several trends which resulted in decreases (Trials 17', 23', 24', 25', 26', 28'), increases (Trials 21', 27', 29', 31'), or consistency (Trials 18', 22', 30') in TPH concentrations over 24 hours (Fig. 6-5). After 1 hour the range of TPH concentrations is 2419 to 95 mg/L (avg. 790 mg/L) and after 24 hours it ranges from 3929 to 17 mg/L (avg. 665 mg/L). Close inspection of the trends does not reveal any particular reason for the decreases *versus* increases in TPH. Thus, the overall consistency in TPH concentration over the course of the medium Orimulsion concentration experiments, which included the seven replicate trials, is primarily a reflection of the error in the system. Thus, in total, the medium concentration experiments demonstrate that little change in TPH concentrations should be expected to occur over 24 hours under a range of water conditions. Notably, the average TPH_{total} concentration remaining in the water column after 24 hours represents again approximately 10% of the initial bitumen spilled (i.e., 665 mg/L is approximately 10% of 6300 mg/L, the concentration of bitumen in 9000 mg/L of Orimulsion).

The high initial Orimulsion concentration experiments generally exhibit an overall decrease in TPH over the course of 24 hours (Fig. 6-6). Trials 13', 14' and 16' are exceptional. The first two of these were unusual in that, under the low energy conditions, the bitumen remained floating near the surface until sampling occurred at 24 hours. When the surface slick was disturbed it dispersed into the water column leading to the sharp increase in TPH observed. This was considered somewhat unusual yet it offers some insight as to what could happen in low energy conditions where a surface slick is attempted to be recovered mechanically.

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[6] Since Orimulsion contains 70% by weight bitumen, an initial concentration of 1000 mg/L OR400 would result in a bitumen content in the water of 700 mg/L. These experiments have shown that a maximum of around 70 mg/L (or 10% of the original) bitumen may still be present in the water column after 24 hours.

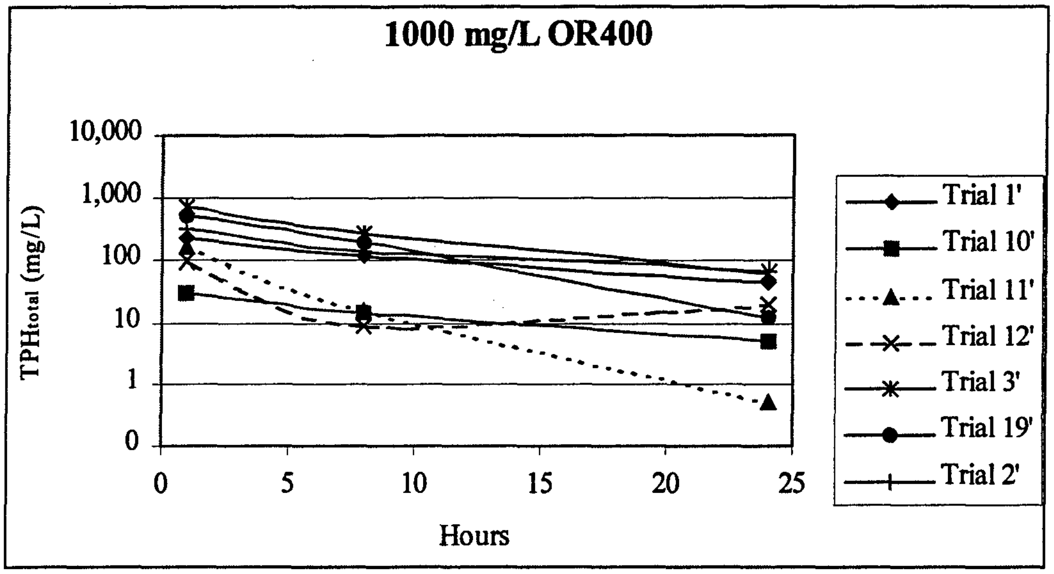

Figure 6-4. Changes in TPH_{total} in water column during low initial Orimulsion concentration (1000 mg/L) experiments.

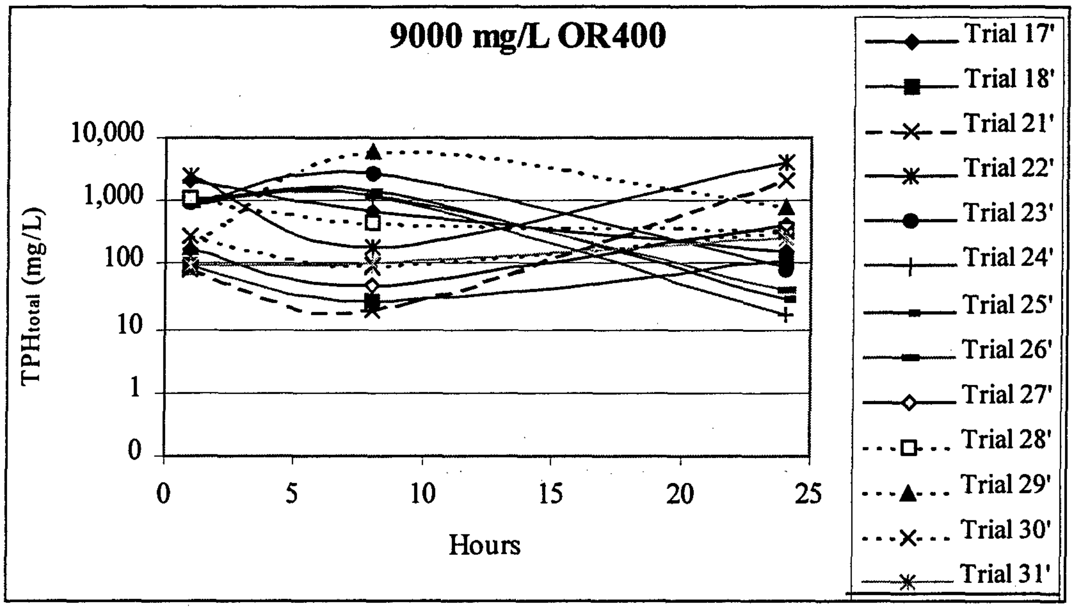

Figure 6-5. Changes in TPH_{total} in water column during medium initial Orimulsion concentrations (9000 mg/L) experiments.

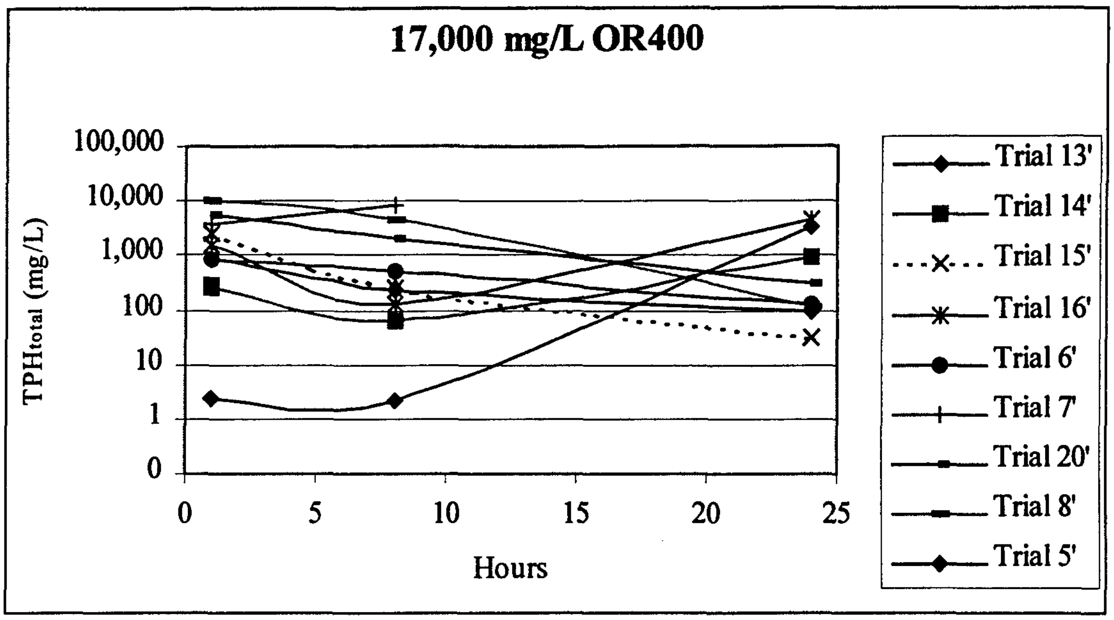

Figure 6-6. Changes in TPH$_{total}$ in water column during high initial Orimulsion concentration (17,000 mg/L) experiments.

The remaining high initial Orimulsion concentration trials exhibit TPH concentrations averaging 3943 mg/L after 1 hour with a maximum of 10,157 mg/L. These concentrations represent 33% (avg.) and 85% (max.) of the initial bitumen spilled (i.e., 17,000 mg Orimulsion contains about 11,900 mg of bitumen). However, after 24 hours the average TPH concentration is only 139 mg/L with a maximum of 308 mg/L (Table 6-5). This corresponds to less than 1% (avg.) and 3% (max.) of the initial bitumen introduced remained in suspension after 24 hours. This result is somewhat lower than was observed in the 17,000 mg/L Orimulsion PB screening experiments where about 10% of the original bitumen remained in suspension (Section 5.3.2.4).

6.2.3.4 Changes in TPH Observed at Different Energy Levels

The response surface design clearly identified the water energy as an important variable controlling the concentration of petroleum hydrocarbons in the water column following a release of Orimulsion (Table 6-6). In this section the trends observed over the course of the response surface experiments are presented in order to provide some insight into the TPH concentrations that might occur over the course of the first 24 hours following a release. Figures 6-7 through 6-9 show the TPH$_{total}$ concentrations for the low, medium, and high energy level experiments.

Most of the low energy experiments exhibited an overall decrease in TPH over the course of 24 hours (Fig. 6-7). Trials 13' and 14' are not included here due to the phenomenon involving the surface slick dispersion after 24 hours which markedly increase the TPH during sampling (see Section 6.2.3.3). Trial 21' showed the only true increase in TPH. The reason for this increase is unknown. The remaining six low energy experiments showed a marked decrease over the 24-hour experiments. These included four freshwater experiments (Trials 1', 2', 5' and 6') and two saltwater experiments (Trials 9' and 10').

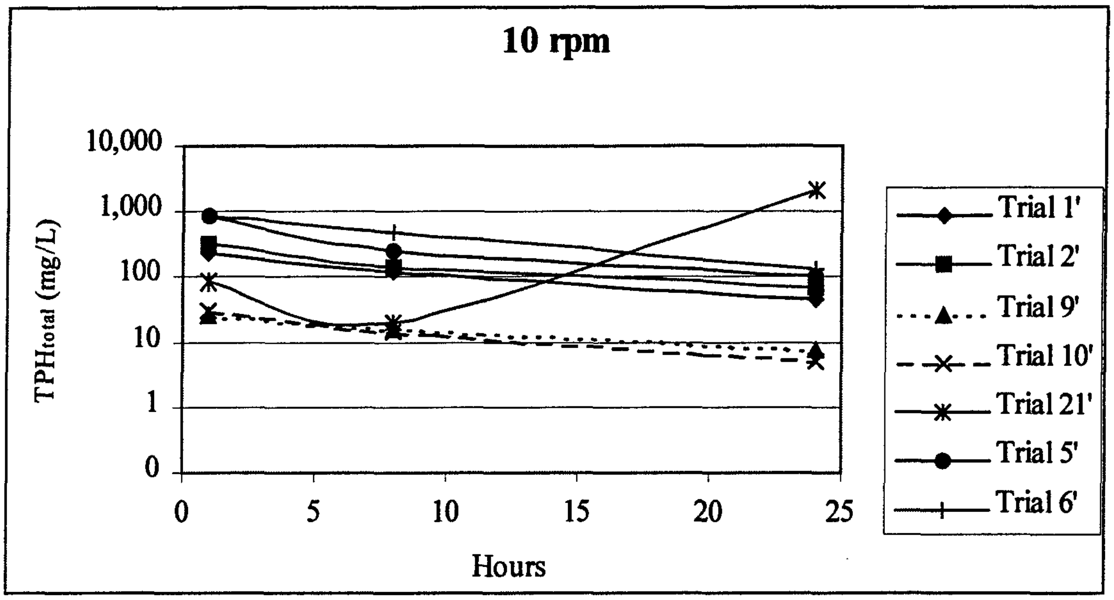

Figure 6-7. Changes in TPH_{total} in water column during low water energy (10 rpm) experiments.

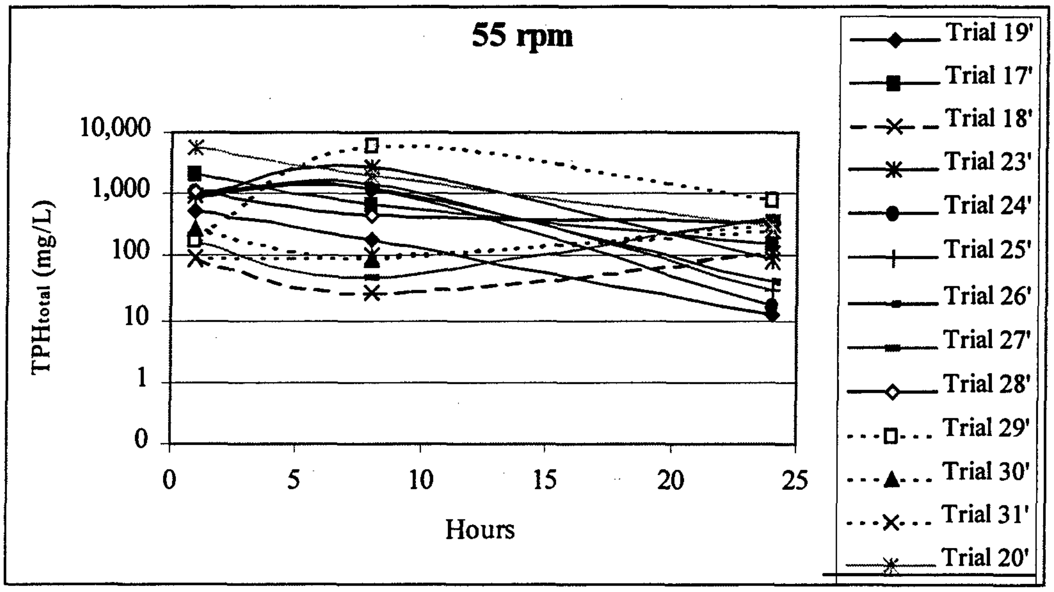

Figure 6-8. Changes in TPH_{total} in water column during medium water energy (55 rpm) experiments.

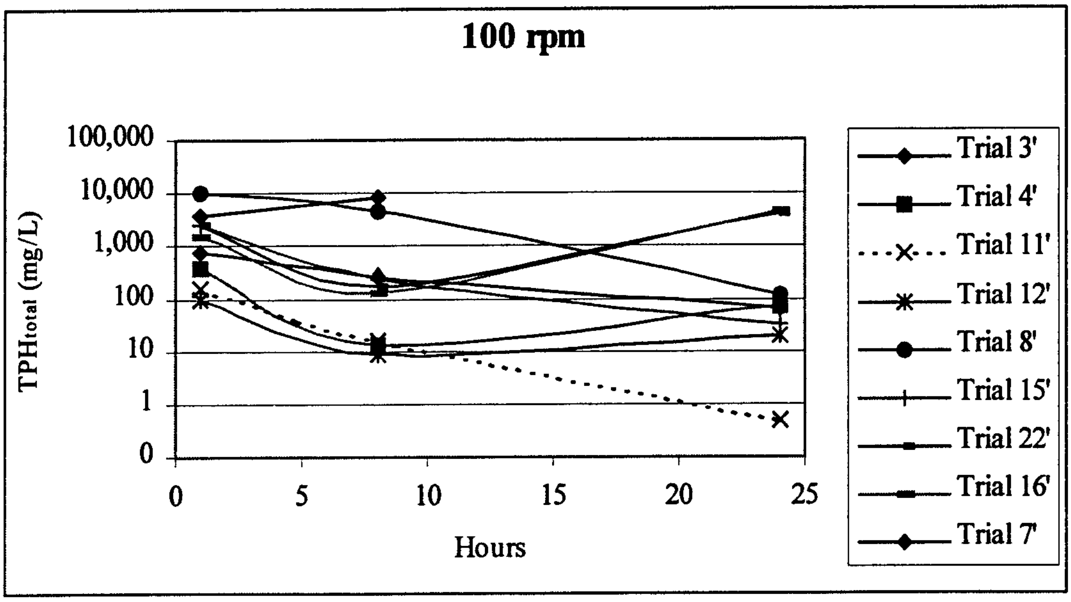

Figure 6-9. Changes in TPH$_{total}$ in water column during high water energy (100 rpm) experiments.

After 24 hours the average concentration of TPH$_{total}$ for the freshwater trials was 87.5 mg/L and only 6.4 mg/L for the saltwater trials (overall avg. of 60 mg/L for all salinities). These low values indicate that, regardless of the initial Orimulsion concentration, under low energy conditions very little bitumen would be expected to occur in the water column after 24 hours. The amount expected under freshwater conditions is higher than is expected under saltwater conditions. The reason for this difference may lie in the mechanism(s) of removal of the bitumen. For example, under freshwater conditions most bitumen seemed to gradually settle out of the water column while under saltwater conditions most bitumen seemed to float toward the top. In either case, under the low energy conditions of these experiments the water column itself became mostly clear after 24 hours.

The medium energy experiments exhibit most of the same trends observed in the medium initial Orimulsion concentration results (Figs. 6-8 and 6-5, respectively). This is due to the inclusion of the seven replicate trials in each. On average, after 24 hours the concentration of TPH in the water column was 222 mg/L. This is markedly higher than was observed on average under the low energy conditions described above and would be anticipated given the response surface model best fit (i.e., TPH increases with energy; Table 6-4).

The high-energy experiments generally exhibit two trends, increasing and decreasing (Fig. 6-9). The increasing TPH trends in Trials 16' and 22' were previously acknowledged and remain unexplained. For the remaining trials, after 24 hours the three saltwater trials (Trials 11', 12', and 15') exhibit an average TPH$_{total}$ of only 18 mg/L while the freshwater trials (Trials 3', 4', and 8') exhibit an average TPH$_{total}$ of 87 mg/L (52 mg/L overall). The average saltwater and freshwater TPH concentrations under high energy conditions after 24 hours are very comparable to those observed in the low energy experiments after 24 hours.

Unfortunately, the observations regarding TPH concentration after 24 hours described in this section are at odds with the statistical response surface model. For example, the response surface model for suspended TPH after 24 hours indicated the greatest TPH would occur at low and high energies (due to the curved effect of energy; Appendix II). However, on average, the highest TPH in suspension after 24 hours was observed under medium energy conditions (222 mg/L *versus* 52 and 60 mg/L).

The difference between these results lies in the strong effect that the few unusual trials had on the best fit modeled results (e.g., Trials 12', 13', 16', 21', and 22'). In other words, the response surface model relied upon the best fit for all of the data and not simply upon average values. However, in a practical sense this raises the issue of which approach is best capable of predicting what will happen in the "real world". This is discussed further in Section 7.

6.2.3.5 Summary of TPH Concentration Changes and Controls

The variables identified as playing the greatest role in the concentration of total petroleum hydrocarbons (TPH) suspended in the water column over the course of these experiments were summarized in Table 6-6. In a practical sense, the most relevant result is "*how clean is the water column after 24 hours?*". The parameter having the greatest 'statistical' effect on the answer to this question was the energy of the water. The effect was curved in that both higher and lower water energy levels would be predicted to produce the greatest TPH concentrations after 24 hours. As noted above, this seemed counterintuitive since one might expect a greater removal of bitumen (i.e. lowering of TPH concentration) from the water column to occur under high energy (due to increased collisions resulting in floating or sticking to walls) and low energy (due to floating or settling of bitumen particles). Our observations based upon Figs. 6-4 through 6-9 had revealed some general trends which were somewhat contrary to the response surface model in that higher average TPH was observed at intermediate energy levels (Fig. 6-8) than at low and high energy levels (Figs. 6-7 and 6-9). These figures also revealed the presence of several somewhat anomalous trials, that were contrary to the general trends. These anomalies undoubtedly influenced the response surface model solution. Therefore, any summary must include a hybrid interpretation of the response surface model and observed trends.

Consistent with the response surface model, after 24 hours the greatest average concentration of TPH_{total} was observed in the medium initial Orimulsion concentration trials (Fig. 6-5). In these trials an average of approximately 10% of the original bitumen remained in suspension after 24 hours. On the other hand, on average < 10% and < 3% of the original bitumen remained suspended at low and high initial Orimulsion concentrations, respectively (Figs. 6-4 and 6-6). Higher average TPH_{total} concentrations after 24 hours were also observed at medium energy levels (Fig. 6-8). We believe these average results reflect the loss of bitumen from the water column due to (1) a greater degree of settling (mostly in freshwater) or floating (mostly in saltwater) under low energy conditions and (2) a greater frequency of collisions with the walls (in both fresh and saltwater) and other bitumen particles (in saltwater) under high energy conditions (leading to the formation of buoyant/floating particles).

Regardless of the mechanisms involved, it is clear from these results that under a wide range of spill conditions the vast majority (>90%) of bitumen released during an Orimulsion spill will not remain suspended in the water column for more than 24 hours.

6.2.4 The Orimulsion Budget as Determined from Benchtop Studies

As described in Section 5.3.3, the "Orimulsion budget" is best addressed in considering the mass (weight) of bitumen which, over the course of these experiments, (1) floated to the surface of the water (float fraction), (2) sunk to the bottom of the glass vessel (settled fraction), (3) remained suspended in the water column (i.e., same as TPH_{total} after 24 hours), (4) dissolved into the water column (i.e. same as $TPH_{dissolved}$ after 24 hours), and (5) became stuck to the walls of the glass vessel.

The results of the mass balance measurements of the 31 response surface experiments are contained in Table 6-7. As was presented earlier in Table 5-5, these results show the weight (in grams) of air-dried bitumen that was recovered from these "five compartments" after 24 hours. Determination of the weight of the floating bitumen and bathtub ring bitumen was straightforward. The assumptions that went into deriving the weights of the other compartments are given beneath the table.

Table 6-7 also contains the total mass of bitumen recovered, the calculated mass of bitumen originally spilled, and the calculated percentage of original bitumen accounted for in the mass balance.

Most experiments indicate an over-recovery (>100%) of bitumen with the greatest over-recoveries occurring in trials containing the lower bitumen masses (i.e., the 1000 mg/L OR400 trials). The seven replicate trials (25' through 31') indicate over-recoveries averaging almost 200%. In these instances, as well as other over-recoveries, high recoveries is likely to be due to the presence of water trapped within the bitumen. Although drying times were extended to 3 days, it was impossible to completely dry the bitumen at room temperature. The effect of trapped water was greatest in trials, which had an excess of floating bitumen (e.g., the seven replicate trials) where water was trapped within the floating bitumen "patty". Regardless of the errors inherent in this mass balance these data provides important information on the fundamental aspects that govern the "Orimulsion budget" following a spill.

6.2.4.1 General Overview

Table 6-8 contains the normalized percentages of bitumen that occurred in each 'compartment' after 24 hours. Included in this table is the total percentage of bitumen that was not stuck to the sides of the vessel after 24 hours, i.e., the "bathtub ring" compartment. In Trial 11' essentially all of the bitumen was stuck to the vessel walls whereas in Trial 17' nearly all of the bitumen (98%) occurred in the other four compartments. On average, 73.1% was not stuck to the vessel walls. This high recovery is important since the vessel walls are an unavoidable consequence of these benchtop experiments, which are in stark contrast to open water.

Because of the effect of the vessel walls on these benchtop experiments it is perhaps best to focus on the fate of bitumen in the other four compartments. Inspection of these percentages reveals that in most trials >50% of the bitumen ended up either floating on the surface or settling to the bottom. Though exceptions existed, the primary control in these instances appeared to be salinity, i.e., mostly floating in saltwater and mostly settling in freshwater. This is addressed more thoroughly in Section 6.2.4.2.

In only one instance (Trial 22') was >50% of the bitumen suspended in the water column. This trial was extremely unusual in that approximately 40 bitumen "globules", about 1 cm in diameter, had formed and remained suspended after 24 hours. These globules appeared to be neutrally-buoyant and did not tend to stick to one another (but did stick to dry surfaces). (Some video was obtained of this phenomenon and is available for viewing.) Trial 22' was conducted in brackish water, with a medium initial Orimulsion concentration, a medium clay loading, and high water energy. This combination of parameters clearly produced a unique result.

6.2.4.2 Response Surface Design Interpretations

The percentages in Table 6-8 was used to calculate a response surface model for each 'compartment,' e.g., float, settle, stuck to walls, suspended, or dissolved. The results of these are found in Appendix III and are described herein.

Table 6-7. Masses of air-dried bitumen recovered from “five compartments” in the response surface benchtop experiments after 24 hours.

Trial	Floating (g)	Sunk[1] (g)	Bathtub Ring (g)	Suspended Particulate[2] (g)	Dissolved[3] (g)	Total Weight Bitumen Recovered (g)	Initial Weight Bitumen Added[4] (g)	% Recovery of Bitumen
1’	0.00	1.75	1.10	0.13	0.0022	2.98	2.19	136
2’	0.00	1.19	0.70	0.19	0.0019	2.09	2.19	95
3’	0.00	0.00	2.10	0.18	0.0014	2.28	2.19	104
4’	0.00	7.68	1.80	0.20	0.0011	9.68	2.19	442
5’	0.01	34.21	7.50	0.27	0.0052	42.00	37.25	113
6’	0.03	32.64	8.20	0.36	0.0047	41.23	37.25	111
7’	4.48	7.14	8.60	0.00	0.0066	20.23	37.25	54
8’	0.62	26.62	9.30	0.33	0.0047	36.87	37.25	99
9’	1.94	0.00	0.50	0.02	0.0008	2.46	2.19	112
10’	2.05	0.47	0.40	0.01	0.0011	2.93	2.19	134
11’	0.00	0.00	2.50	0.00	0.0011	2.50	2.19	114
12’	0.00	3.71	1.50	0.06	0.0017	5.27	2.19	241
13’	38.96	0.00	2.40	9.63	0.0088	51.00	37.25	137
14’	31.25	0.00	7.20	2.51	0.0091	40.97	37.25	110
15’	29.68	0.00	11.70	0.04	0.0455	41.47	37.25	111
16’	14.71	4.21	10.30	12.33	0.0108	41.56	37.25	112
17’	0.01	10.90	0.20	0.41	0.0047	11.52	19.71	58
18’	14.53	0.22	5.70	0.31	0.0080	20.78	19.71	105
19’	0.43	1.24	0.20	0.03	0.0030	1.90	2.19	87
20’	15.40	16.39	4.20	0.84	0.0130	36.83	37.25	99
21’	7.22	2.63	6.30	5.91	0.0088	22.07	19.71	112
22’	1.46	0.87	8.00	10.82	0.0119	21.16	19.71	107
23’	30.48	0.00	11.70	0.23	0.0099	42.42	19.71	215
24’	25.03	16.70	3.70	0.04	0.0097	45.48	19.71	231
25’	29.37	8.10	7.40	0.07	0.0108	44.95	19.71	228
26’	28.04	6.57	7.10	0.10	0.0105	41.82	19.71	212
27’	24.29	0.92	9.50	1.11	0.0083	35.83	19.71	182
28’	23.02	5.42	8.70	0.97	0.0086	38.11	19.71	193
29’	16.15	1.28	5.50	2.17	0.0091	25.11	19.71	127
30’	23.79	2.39	9.40	0.86	0.0121	36.45	19.71	185
31’	26.13	1.15	9.80	0.71	0.0108	37.80	19.71	192

[1] Dried weight of all material recovered from bottom of vessel minus the weight of the mineral matter added to that particular trial.

[2] Equals (TPH_{total} measured in water after 24 hrs x 2.76 L)-($TPH_{dissolved}$ measure after 24 hrs x 2.76 L).

[3] Equals measured $TPH_{dissolved}$ after 24 hrs x 2.76 L (Assumes that 240 ml of the original 3 L of water was removed in course of sampling at 1, 3, and 8 hr intervals).

[4] Equals mass of OR400 originally added x 0.73 (i.e., the bitumen content of OR400). Does not accommodate for losses due to sampling throughout the experiment.

Table 6-8. The “Orimulsion Budget” - Percentages of bitumen in different compartments after 24 hours - response surface experiments. All values are percentages.

Trial	Floating	Sunk	Bathtub Ring	Suspended	Dissolved	% not stuck to sides
1’	0.0	58.8	36.9	4.2	0.1	63.1
2’	0.0	57.1	33.6	9.3	0.1	66.4
3’	0.0	0.0	92.0	7.9	0.1	8.0
4’	0.0	79.3	18.6	2.1	0.0	81.4
5’	0.0	81.5	17.9	0.7	0.0	82.1
6’	0.1	79.2	19.9	0.9	0.0	80.1
7’	22.1	35.3	42.5	0.0	0.0	57.5
8’	1.7	72.2	25.2	0.9	0.0	74.8
9’	78.8	0.0	20.3	0.8	0.0	79.7
10’	69.9	16.0	13.6	0.4	0.0	86.4
11’	0.0	0.0	99.9	0.0	0.0	0.1
12’	0.0	70.4	28.5	1.1	0.0	71.5
13’	76.4	0.0	4.7	18.9	0.0	95.3
14’	76.3	0.0	17.6	6.1	0.0	82.4
15’	71.6	0.0	28.2	0.1	0.1	71.8
16’	35.4	10.1	24.8	29.7	0.0	75.2
17’	0.1	94.5	1.7	3.6	0.0	98.3
18’	69.9	1.1	27.4	1.5	0.0	72.6
19’	22.6	65.0	10.5	1.6	0.2	89.5
20’	41.8	44.5	11.4	2.3	0.0	88.6
21’	32.7	11.9	28.5	26.8	0.0	71.5
22’	6.9	4.1	37.8	51.1	0.1	62.2
23’	71.9	0.0	27.6	0.5	0.0	72.4
24’	55.0	36.7	8.1	0.1	0.0	91.9
25’	65.3	18.0	16.5	0.2	0.0	83.5
26’	67.1	15.7	17.0	0.2	0.0	83.0
27’	67.8	2.6	26.5	3.1	0.0	73.5
28’	60.4	14.2	22.8	2.5	0.0	77.2
29’	64.3	5.1	21.9	8.7	0.0	78.1
30’	65.3	6.5	25.8	2.4	0.0	74.2
31’	69.1	3.0	25.9	1.9	0.0	74.1

The response surface design models for each ‘compartment’ had quite good fits, much better than had been obtained in the mean particle size or TPH models (Appendix III). RSquared values were;

0.70 for % bitumen dissolved,
0.72 for % bitumen suspended,
0.85 for % bitumen stuck to the walls,
0.88 for the % bitumen which sunk, and
0.91 for % bitumen floating.

F Ratios ranged from 2.7 to 12.1, respectively. These results indicate that the gross “Orimulsion budget” under these experimental conditions is actually quite predictable. The seven replicate trials

(25' to 31') exhibited a smaller range of error than previously observed and this was far outweighed by the variations due to experimental conditions. An examination of t Ratios (Appendix III) for each term in each solution reveal those which had the greatest effect on the "Orimulsion budget".

The percentage of bitumen which floated after 24 hours was very strongly influenced by the interaction of water energy and salinity. In fact, this was the 2nd strongest effect of any term on any variable studied herein with a t Ratio of – 4.27. This interaction was somewhat complex in that as salinity increased so did the potential for bitumen to float whereas as energy increased the potential for bitumen to float increased, maximized at intermediate energies, and then decreased (Appendix III). This indicates that under comparable energy conditions, a higher percentage of bitumen would float in saltwater than would in freshwater. However at any given salinity, the amount of bitumen, which floated, would be lower at low and high energy than it would be at an intermediate energy level. Overall, the greatest potential to form floating bitumen would be predicted to occur at higher salinities and an intermediate energy level.

The potential for bitumen to settle through the water column after 24 hours was influenced by a variety of parameters. In order of decreasing importance these were salinity, the interaction of energy and particulate loading, the concentration of Orimulsion, and the interaction of salinity and Orimulsion concentration. In other words the interactions controlling the amount of bitumen which is predicted to settle through the water column are strong and therefore, one can only generalize about the trends. As salinity increased the amount of settling bitumen is expected to decrease. Intuitively speaking, a greater potential to settle through the water column under freshwater conditions is reasonable and consistent with the greater potential to float determined under saltwater conditions (noted above). As both water energy and particulate loading increase the amount of settled bitumen is expected to increase, maximize at intermediate levels, and then decrease at higher levels. This also make sense in that more clay (particulate) in the water, and a reasonable amount of energy in the water, collisions between clay and bitumen particles would occur more frequently leading to the formation of denser particles which would be prone to settling through the water column. If, however, the energy is too high these particles would remain in suspension and not settle through the water column.

The potential for bitumen to stick to a glass wall near the water's surface after 24 hours was most greatly influenced by the interactions of particulate loading with Orimulsion concentration and its interaction with water energy. This result was somewhat surprising in that salinity had virtually no impact indicating that the effect of salinity on the surfactant's effectiveness is not responsible for bitumen sticking to the vessel walls. Instead the amount of clay in the water had a greater effect. Again the interaction effects are rather complex but generally, as the concentration of clay increased the potential to stick to the vessel walls decreased. As energy increased the potential to stick to the vessel walls also increased. This makes sense in that a greater centrifugal force existed at higher energy levels thereby, allowing more frequent (and powerful?) collisions of bitumen particles with the vessel walls (and any bitumen already adhering to those walls). Finally, as the concentration of Orimulsion increased the potential to stick to the walls decreased. Intuitively speaking, this could result from a higher concentration of surfactant in the water at higher Orimulsion concentrations, which could tend to inhibit the bitumen particles from sticking to the walls.

The amount of bitumen suspended after 24 hours was very strongly influenced by the energy of the water. This effect was the strongest effect observed in any of these experiments (t Ratio = 5.6). However, the effect is not what one might anticipate in that the greatest potential for bitumen to remain suspended occurs at both low energy levels and high energy levels (and not just at high levels as might have been expected). The least amount of suspended bitumen would be expected at intermediate energy levels. This same phenomenon was apparent in the response surface model for the TPH_{total} after 24 hours (Section 6.2.3.2). This makes sense since TPH_{total} and the % of suspended bitumen should be highly correlated.

The amount of bitumen dissolved in the water after 24 hours was primarily influenced by the initial concentration of Orimulsion spilled. The effect was curved such that the highest concentration of dissolved bitumen is expected at both low and high initial Orimulsion concentrations. These results are somewhat unreliable given the very low percentages of bitumen dissolved under any conditions (Table 6-8).

A summary of the effects of the different parameters on the "Orimulsion budget" appears in Table 6-9. Included on this table are the calculated solutions for each 'compartment' which, according to the best fit response surface model, would yield the maximum percentage in that compartment. Because of the quadratic nature of the models some of the values are beyond the domain of reason, e.g., salinity of 58 $^{o}/_{oo}$ or particulate loading of –35. Nonetheless, they serve to further emphasize the response surface results (Appendix III).

Table 6-9. Summary of response surface benchtop results – "Orimulsion Budget" after 24 hours.

Compartment	Most Important Parameters	Interpretation	Maximum % Conditions			
			Salinity ($^{o}/_{oo}$)	OR400 (mg/L)	Energy (rpm)	Loading (mg/L)
% floating	Energy and Salinity	% is greatest at high salinity and intermediate energy; % is lowest at low salinity and low or high energy	48	12,872	27	160
% sunk	Salinity, Energy and Particulate Loading	% is greatest at low salinity, intermediate energy, and high loading	28	11,124	69	242
% stuck to vessel walls	Particulate Loading, OR400 conc. and Energy	% is greatest at low loading, low OR400, and high energy	27	13,169	64	359
% in suspension	Energy	% is greatest at low or high energy	20	10,057	54	142
% dissolved	OR400 concentration	% is greatest at low and high OR400	58	287	337	-35

6.2.4.3 Predicting the Formation of a Floating Bitumen Slick

Recovery of Orimulsion following a spill will probably be most effectively achieved in the case when most of the bitumen floats to the surface, e.g., mechanical recovery or special booms. Unfortunately, the greatest potential for damage to shorelines is also likely to occur when most bitumen floats. Therefore, it seems prudent to give this 'compartment' a little extra consideration.

Our experience indicates that the floating material is extremely 'sticky' and that it can occur as either semi-solid "patties" or as a semi-liquid "skin" or "mat". The latter is akin to the "skin" that forms over a bowl of cold soup. In either case, in our experiments the floating bitumen was easily recovered with a glass rod and, therefore, in the 'real world' any form of a bitumen 'slick' it should be recoverable by mechanical means amenable for recovery of heavy oils.

The response surface model clearly indicated that the energy and salinity of the water had a strong effect on the propensity for the formation of a floating bitumen slick. Furthermore, the response surface solution derived for the percentage of floating bitumen exhibited very good predictability (RSquared = 0.91). The quadratic solution for this model was:

$$\begin{aligned}\text{\% of Bitumen Floating After 24 Hours} = &- 0.1554 + 0.0331(\text{Salinity}) + 0.0131(\text{Energy}) + 0.0000322(\text{OR400}) - 0.0024(\text{Loading}) \\ &- 0.000335(\text{Salinity})^2 - 2.038\text{x}10^{-9}(\text{OR400})^2 - 0.000126(\text{Energy})^2 + 0.00001(\text{Loading})^2 \\ &+ 0.0000004(\text{OR400 x Salinity}) - 0.000173(\text{Energy x Salinity}) + 0.0000002(\text{Energy x OR400}) \\ &- 0.000007(\text{Loading x Salinity}) - 2.764\text{x}10^{-8}(\text{Loading x OR400}) - 0.000005(\text{Loading x Energy})\end{aligned}$$

where, Salinity = 0 to $35^{o}/_{oo}$; Energy = 10 to 100 rpm; Initial Orimulsion concentration = 1000 to 17,000 mg/L; and Clay Loading = 0 to 270 mg/L.

It is tempting to eliminate several of the terms in the solution due to the 'near-zero' values for the estimated b-coefficients. However, because of the large numbers these coefficients are being multiplied by, this is imprudent. Theoretically, this equation can be used to predict the percentage of bitumen that will be floating after 24 hours under any conditions within the range of values considered in these experiments. Of course, the difficulty lies in translating these terms to "real world" conditions. Nonetheless, with caution this equation could be used to predict the amount of bitumen that could be considered recoverable following an Orimulsion spill.

6.2.4.4 Chemical Nature of Hydrocarbons Dissolved into the Water Column

The dissolved hydrocarbon 'compartment' contained only a very small percentage of the total bitumen spilled in each trial (Table 6-8). Nonetheless, because the dissolved hydrocarbons are those with the greatest bioavailability, and therefore potential impact to biota, it is worthwhile to consider their chemical nature particularly in regard to the concentration of the more toxic polycyclic aromatic hydrocarbons (PAH).

The bulk nature of the dissolved hydrocarbons was consistent with that demonstrated in Fig. 5-7. That is to say that the dissolved hydrocarbons are comprised of the lighter (lower boiling) components found in fresh Orimulsion. This is undoubtedly due to the greater aqueous solubility of these lighter components (IUPAC, 1989). The PAH dissolved in water after 24 hours are also enriched in the more soluble PAH among those which occur in fresh Orimulsion. ("Dissolved" is operationally defined by the U.S. EPA and herein as the hydrocarbons that pass through a 0.45 µm filter.) This is demonstrated in a comparison of the PAH histograms for fresh Orimulsion and a typical dissolved water 24 hours after a spill (Fig. 6-10). Fresh Orimulsion contains bitumen relatively enriched in various three and four-ring PAH (e.g., phenanthrenes, dibenzothiophenes, and chrysenes) whereas the dissolved fraction is enriched in two-ring PAH (e.g., naphthalenes).

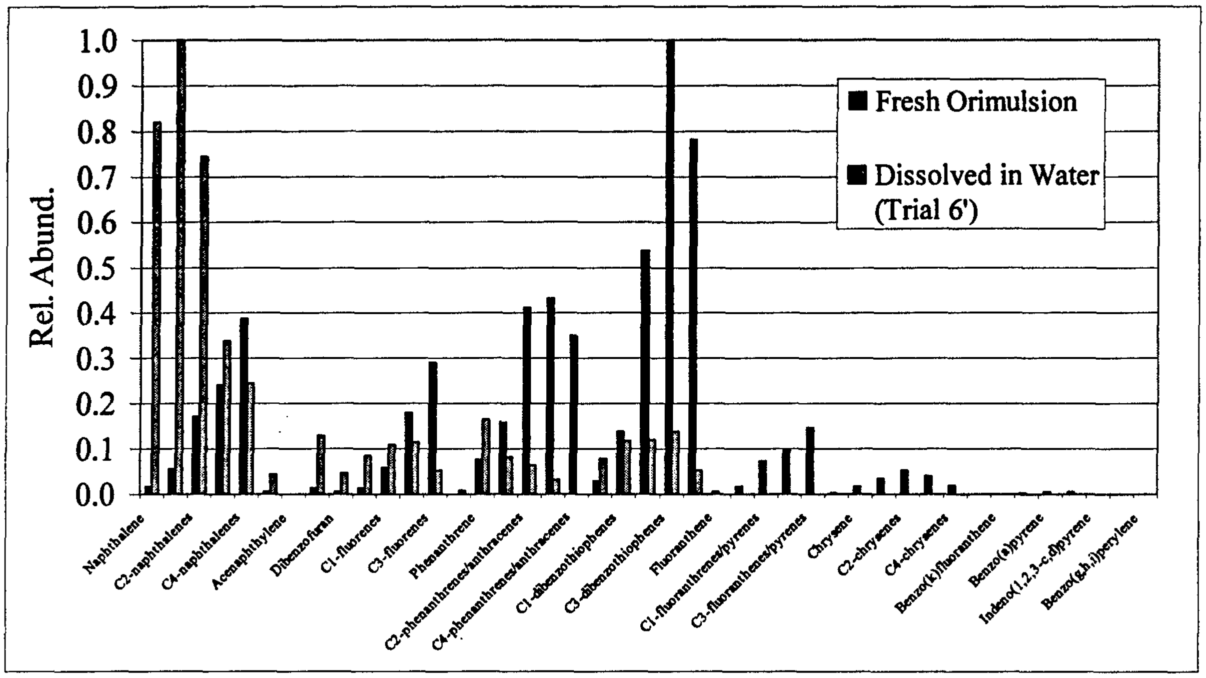

Figure 6-10. Histograms comparing the distribution of PAH in fresh Orimulsion and a representative distribution of PAH dissolved in water after 24 hours (Trial 6').

The results of our analysis on all of the filtered water samples are given in Appendix IV. The total PAH content of each sample is given in Table 6-10. As can be seen the concentrations varied between 25.84 ng/L and 60,904 ng/L. (The lower values are essentially background concentrations and can be ignored.) PAH occur in fresh Orimulsion 400 at a concentration of 2473 mg PAH/kg Orimulsion (Table 3-2). Trial 15' contained the largest concentration of PAH after 24 hours, nearly five times the concentration in any other experiment (Table 6-10). As was the case in the PB screening Trial 2 (Section 5.3.3.3), this is probably due to the breakthrough of some bitumen through the 0.45 μm filter during the filtering process. Irregardless, Trial 15' was a 17,000 mg/L OR400 experiment meaning that 126 mg of PAH was initially added to the water. After 24 hours, only about 0.18 mg of PAH was dissolved in the water. This is less than one percent of the original PAH (~0.15%). Thus, a very small percentage of the PAH present in Orimulsion will become dissolved in water under most circumstances.

The response surface model solution for the concentration of dissolved PAH (Appendix III) indicates that their concentration was not easily predicted from the four independent parameters. The RSquared value was only 0.68 and the F Ratio was only 2.48. Although no parameters had a significant influence on the concentration of dissolved PAH, the parameter showing the greatest influence was the interaction of initial Orimulsion concentration and particulate loading. Intuitively speaking, the initial concentration of Orimulsion would certainly influence the concentration of dissolved PAH while the impact of particulate loading is less clear. However, the model predicts that as the initial Orimulsion concentration is increased and as the loading is decreased the predicted concentration of dissolved PAH is increased. While it is difficult to place too much emphasis on this result (low RSquared) it is worth noting that the parameters affecting the total dissolved hydrocarbons ($TPH_{dissolved}$; Section 6.2.4.2 and Table 6-9) are different from those parameters effecting the concentration of dissolved PAH only.

The PB screening experiments had revealed a potential impact of salinity on the concentration of dissolved PAH (Fig. 5-8). This same relationship exists for the response surface experiments, especially if the dissolved PAH concentration result of Trial 15' is ignored. In all other trials the concentration of PAH is lower in saltwater than it is in freshwater. As was discussed in Section 5.3.3.3, this is consistent with the greater solubility that is expected in freshwater over saltwater (IUPAC, 1989). Not surprisingly, the concentration of dissolved PAH in the brackish water experiments was intermediate.

Table 6-10. Total PAH concentration dissolved in water after 24 hours – response surface experiments.

Trial	Total PAH's (ng/L)	Trial	Total PAH's (ng/L)
1'	8595.81	17'	10243.67
2'	9051.46	18'	879.75
3'	6026.74	19'	522.45
4'	7798.76	20'	1369.61
5'	11436.63	21'	2317.53
6'	9360.62	22'	125.73
7'	11966.33	23'	3606.57
8'	9351.58	24'	2589.75
9'	28.15	25'	1650.66
10'	25.84	26'	1549.44
11'	228.76	27'	2631.54
12'	407.53	28'	3060.95
13'	2428.83	29'	2795.73
14'	1674.64	30'	2403.93
15'	60904.54	31'	2157.47
16'	2514.80		

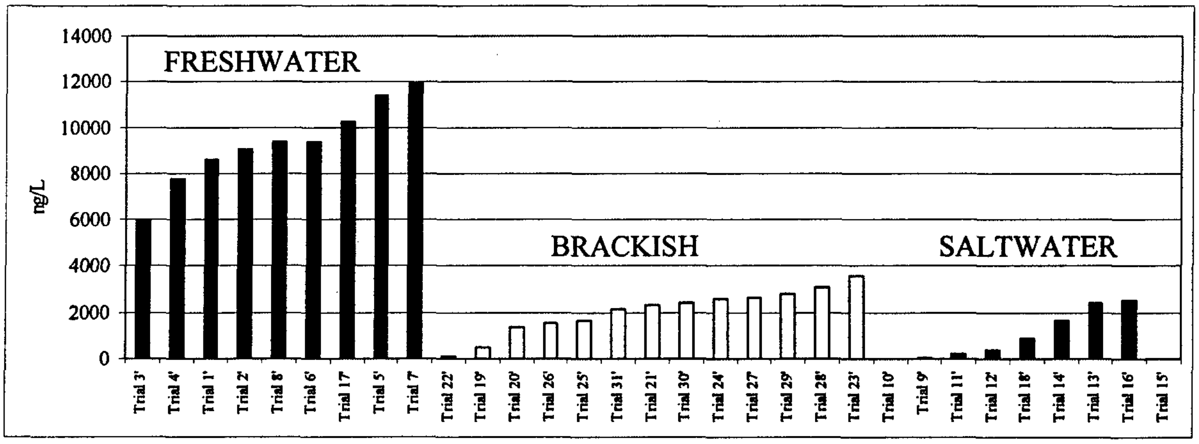

Figure 6-11. Concentration of dissolved PAH after 24 hours in freshwater, brackish water, and saltwater – Response Surface Benchtop Experiments.

7. PREDICTIONS SURROUNDING THE FATE OF ORIMULSION SPILLED IN WATER BASED ON BENCHTOP STUDIES

The results of the benchtop experiments presented above provide insight into the roles that various environmental parameters play in determining the behavior of Orimulsion. However, laboratory experiments in confined vessels (regardless of their size), cannot truly reflect behavior in an open water 'real world' spill. Spilling Orimulsion (or any petroleum product) in a confined container with a constant volume of water will be greatly influenced by the effects of the container walls and the prohibition of any dispersive processes. In the case of Orimulsion's bitumen behavior the balance between dispersion and coalescence processes that would exist in the 'real world' is abnormally skewed toward the coalescence processes (since dispersion is eliminated in the laboratory vessels). In the 'real world' increased energy in the receiving water would tend to promote dispersion yet in the confines of the benchtop vessels used herein, increased energy would tend to promote collisions of bitumen particles with either suspended mineral matter, other bitumen particles, or with the container walls. Thus, it is quite difficult to project the results from our laboratory benchtop experiments to the 'real world' in a quantitative fashion. The results presented above can, however, provide valuable insight into the fundamental processes at work and the relative importance of the independent variables evaluated in predicting the gross behavior of spilled Orimulsion.

In this section the results are discussed in an attempt to answer three questions relevant to containment, recovery and response planning, and modeling of spilled Orimulsion. The circumstances under which the majority (> 50% by weight) of the bitumen in Orimulsion (1) floats, (2) settles through the water column, or (3) remains suspended are discussed. Given the difficulty in extrapolating the benchtop data to the 'real world,' this gross approach is all that can be reasonably justified. Dissolved bitumen, while potentially important for its effect on biota, represented too small a fraction to discuss in terms of Orimulsion's gross behavior.

As noted above, the fraction of bitumen which adhered to the vessel walls is an artifact of the confined nature of the laboratory experiments, i.e., presence of a boundary which doesn't exist in open water conditions. It is unreasonable, however, to simply eliminate/ignore the "bathtub ring" bitumen fraction since it obviously contains bitumen that would have reported to one of the other "compartments" if the glass walls had not existed. Given the observed affect of salinity on the floating/ settling behavior of bitumen, a reasonable assumption would be that (in the absence of container walls) the 'bathtub ring' bitumen would have otherwise (1) floated or remained suspended in seawater or (2) settled or remained suspended in freshwater. In brackish water the true fate of the 'bathtub ring' bitumen is less clear, but given the experimental observations it would probably include a combination of floating, settling, and/or remaining suspended. To facilitate in these discussions a compilation of the screening results (Table 5-6) and response surface results (Table 6-8) is presented in Table 7-1.

An inspection of the percentages summarized in Table 7-1 reveals five results that might be considered anomalous given what we have observed. These results are identified by asterisks. Four of these occur in the screening phase experiments and only one occurred in the response surface experiments. Some additional comments on these anomalies are given below.

Table 7-1. **Summary of the mass balance results 24 hours after a spill compiled from PB screening (1-16) and response surface (1'-31') benchtop experiments. Percentages indicate the % of bitumen reporting to each of the five 'compartments.'**

Trial	Salinity (‰)	OR400 (mg/L)	Energetics (rpm)	Part. Load (mg/L)	Floating %	Sunk %	Bathtub Ring %	Suspended %	Dissolved %
1	35	1000	100	270	0	25	75	0	0
2	35	17000	10	270	40	7	21	32	0
3	0	17000	10	270	27	62	1	10	0
4	35	17000	10	0	NA	NA	NA	NA	NA
5*	35	1000	100	0	0	19	80	0	0
6*	35	1000	10	0	66	20	12	2	0
7	0	1000	100	270	0	59	40	1	0
8	0	17000	100	0	0	5	77	18	0
9	0	1000	10	270	0	92	0	8	0
10	35	17000	100	270	0	5	95	0	0
11*	0	17000	100	0	21	25	47	7	0
12	0	1000	10	0	0	98	0	2	0
13	35	50000	10	0	88	0	0	11	0
14	0	50000	100	0	4	23	26	47	0
15*	35	50000	100	0	0	87	12	1	0
16	0	50000	10	0	0	99	0	0	0
1'	0	1000	10	0	0	59	37	4	0
2'	0	1000	10	270	0	57	34	9	0
3'	0	1000	100	0	0	0	92	8	0
4'	0	1000	100	270	0	79	19	2	0
5'	0	17000	10	0	0	81	18	1	0
6'	0	17000	10	270	0	79	20	1	0
7'*	0	17000	100	0	22	35	43	0	0
8'	0	17000	100	270	2	72	25	1	0
9'	35	1000	10	0	79	0	20	1	0
10'	35	1000	10	270	70	16	14	0	0
11'	35	1000	100	0	0	0	100	0	0
12'	35	1000	100	270	0	70	28	1	0
13'	35	17000	10	0	76	0	5	19	0
14'	35	17000	10	270	76	0	18	6	0
15'	35	17000	100	0	72	0	28	0	0
16'	35	17000	100	270	35	10	25	30	0
17'	0	9000	55	135	0	95	2	4	0
18'	35	9000	55	135	70	1	27	2	0
19'	17.5	1000	55	135	23	65	11	2	0
20'	17.5	17000	55	135	42	44	11	2	0
21'	17.5	9000	10	135	33	12	29	27	0
22'	17.5	9000	100	135	7	4	38	51	0
23'	17.5	9000	55	0	72	0	28	1	0
24'	17.5	9000	55	270	55	37	8	0	0

Table 7-1 (continued)

Trial	Salinity (‰)	OR400 (mg/L)	Ener-getics (rpm)	Part. Load (mg/L)	Float-ing %	Sunk %	Bathtub Ring %	Suspend-ed %	Dis-solved %
25'	17.5	9000	55	135	65	18	16	0	0
26'	17.5	9000	55	135	67	16	17	0	0
27'	17.5	9000	55	135	68	3	27	3	0
28'	17.5	9000	55	135	60	14	23	3	0
29'	17.5	9000	55	135	64	5	22	9	0
30'	17.5	9000	55	135	65	7	26	2	0
31'	17.5	9000	55	135	69	3	26	2	0

NA – not available

*Trial with unanticipated results, see text for description.

Two anomalies, Trials 5 and 6, saw ~20% of the bitumen settling through the water column in saltwater in spite of the absence of any mineral matter. These occurrences were unexpected given density considerations of bitumen *versus* saltwater and are inconsistent with results observed in the comparable Trials 9' and 11' where no bitumen sunk (Table 7-1). However, visual inspection of the Trial 5 and 6 vessels after 24 hours definitely showed some very small bitumen particles had settled on the bottom of the glass vessels. The cause for the settling of these bitumen particles is presently unknown, but given the absence of any sunk bitumen in the comparable Trials 9' and 11', we believe that these screening trial results can be left unexplained.

The results of Trials 11 and 7' were also unexpected in that ~20% of the bitumen was found floating in freshwater experiments (Table 7-1). This is considered anomalous given what was more commonly observed in freshwater, i.e., most bitumen either settling through the water column or remaining suspended. A few other freshwater experiments resulted in very small percentages of bitumen floating (e.g., Trials 14 and 8'). Visual inspection of the vessels in all of these trials after 24 hours revealed the presence of small (< 1 cm) globules of bitumen floating on the surface. These globules are believed to have been bitumen that had been cast off from the sizable bathtub rings formed during these high-energy, freshwater experiments. Visual observations revealed that early in these experiments the high energy caused bitumen to stick to the dry glass walls. Over the course of the 24 hours the bitumen was cast-off/stripped from the walls by the action of the swirling water. It is possible that given more time the cast-off bitumen globules may have sunk. Alternatively, it is also possible that once these globules were formed near the surface that surface tension effects prevented them from settling through the water column in spite of the lower density of the freshwater. Thus, the floating bitumen in these freshwater experiments is considered an artifact of the bathtub ring.

The final unexpected result was that of screening Trial 15. In this very high Orimulsion concentration, saltwater experiment 87% of the bitumen was reported in the settle fraction. This was unusual given the observation of other high energy, saltwater conditions in which most bitumen had stuck to the vessel walls (Table 7-1). The exception to this more common result was Trial 12' in which, as with Trial 15, most bitumen was observed to settle. However, unlike Trial 15, Trial 12' included particulate matter, which could promote the settling of bitumen (having formed denser bitumen/mineral particles). This explanation, however, is inappropriate for Trial 15 where no mineral matter was present therefore, another cause must exist. Visual observations of Trial 15 showed that a black "cloud" of bitumen occurred throughout the water column after 24 hours. There was no recoverable floating material therefore, most of the bitumen was actually in suspension.

Unfortunately, due to our method of sampling the suspended bitumen by draining the water through the sampling port (located near the bottom of the vessel) we believe this led to the concentrating of the bitumen in the bottom of the vessel. This bitumen was subsequently 'assigned' to the settle fraction whereas it was more accurately reportable to the suspended bitumen fraction. Rather than change the data we chose to change the manner of sampling in the response surface experiments to eliminate this problem.

7.1 Under what conditions does most bitumen float?

As discussed in Section 6.2.4.3, the amount of bitumen which floats following an Orimulsion spill is perhaps the most important parameter considered because under this circumstance there is the greatest potential for both (1) recovery of the bitumen and (2) damage to shorelines. Therefore, it seems particularly important to be able to predict when most of the bitumen will float.

The nature of this floating material recovered from the benchtop trials ranged from semi-solid, free floating 'patties' or tar balls to a semi-liquid 'skin,' both of which were easily recovered from the surface of the water. Both PB and response surface statistics and our observational data indicated that water salinity and/or water energy were the greatest control(s) on the formation of floating bitumen. The other parameters (water temperature, particulate loading, particulate type, and Orimulsion concentration) had lesser effects. Therefore, predicting when most bitumen will float probably is best accomplished on the basis of water salinity and water energy. (This is further explored in Section 11.)

In 17 of the 47 benchtop experiments conducted more than 50% of the bitumen (by weight) originally spilled ended up floating on the surface of the water after 24 hours (Table 7-1). The maximum percentage of bitumen found floating was 88%. This occurred in a low energy, 50,000 mg/L initial Orimulsion concentration, saltwater screening experiment (Trial 13). In fact, all but one of the low energy, saltwater experiments conducted resulted in >50% of the bitumen floating. Oppositely, five of seven high-energy, saltwater experiments resulted in 0% of the bitumen floating. This difference clearly demonstrates the important interaction that salinity and energy have and indicates that low energy, saltwater conditions would seem to favor the formation of floating bitumen.

Notably, the high energy, saltwater conditions most often resulted in the greatest percentage of bitumen sticking to the walls of the vessel. In the real world's open water, comparable high energy conditions probably would tend to disperse the bitumen, thereby minimizing the frequency of collisions between particles and the formation of a floating bitumen slick. More on this in Section 7.4.

The interaction of salinity and energy was also demonstrated by the fact that the nine of 13 brackish water, medium energy experiments resulted in >50% of the bitumen floating (Table 7-1). Seven of these were the replicate trials performed in the response surface experiments, which had showed excellent reproducibility (60-69%). The only two brackish water experiments performed at low or high energy produced only 7% and 33% floating bitumen, respectively. Similarly, the only freshwater, medium energy experiment (Trials 17') yielded no floating bitumen. These results indicate that it is also likely that bitumen is favored to float in brackish water, medium energy conditions.

The interactive effect of salinity and energy on the formation of floating bitumen slick speaks to the combined effects that these variables have on (1) water density *versus* bitumen particle density, (2) the effectiveness of the surfactant in retarding coalescence in water with variable dissolved ion content, and (3) the frequency and energy of the collisions between bitumen particles. The interaction of these effects is undoubtedly complex and may warrant more detailed study of the physical-chemical processes involved.

In summary, the benchtop experiments indicate that highest percentage of bitumen might be expected to float under "low" energy, saltwater conditions or "medium" energy, brackish water conditions. In our benchtop experiments performed under these conditions this percentage was typically >50% of the bitumen spilled. However because our experiments are performed in a closed system, this percentage would probably be lower in the 'real world' where uninhibited dispersion would reduce the number of collisions between particles and thereby potentially reduce the volume (or at least, the particle size) of floating bitumen.

7.2 Under what conditions does most bitumen settle?

The amount of bitumen which settles through the water column following an Orimulsion spill is also important from the perspective of its potential impact on benthic communities, especially in nearshore areas. An additional concern in nearshore areas is the potential impact of sunk bitumen on shorelines, e.g., where waves and tides could carry the material to shore. This fraction of Orimulsion would seem to be particularly difficult to recover without advances in recovery technology. Therefore, it seems particularly important to be able to predict how much of a spill bitumen will settle in nearshore areas. In open water conditions the impact of settled bitumen would seem of little long term consequence.

The sunk bitumen in each of these trials occurred as discrete bitumen particles, often admixed and/or adhered to mineral matter (clay or limestone). There was never the formation of a sunk "patty" or "mat," only the discrete particles which, in most cases, could simply be rinsed from the bottom of the vessels with water. Any amount of turbulence in the water (e.g., stirring) disrupted the sunk bitumen. In the "real world," our knowledge of recovery techniques suggest that this sunk bitumen fraction would be very difficult or impossible to recover.

Both PB and response surface statistics and our observational data indicated that water salinity and the interaction of water energy with particulate loading had the greatest impact on the determining the amount of bitumen, which settles. The other parameters (water temperature, particulate type, and Orimulsion concentration) had lesser effects.

In 15 of the 47 benchtop experiments conducted >50% of the bitumen originally introduced ended up settling to the bottom of the vessels after 24 hours (Table 7-1). In four of these experiments >90% of the bitumen sank, with the maximum percentage settling being 99% (Trial 16). Three of these four were conducted in freshwater at low energy. In fact, of the 15 experiments in which >50% of the bitumen sank, 12 were conducted in freshwater and 8 of these 12 were conducted at low energy. These observations indicate that the majority of bitumen could be anticipated to settle under most low energy, freshwater conditions. This is consistent with the earlier observation that most bitumen would be expected to float under low energy, saltwater conditions (see Section 7-1).

The effect of particulate loading is less obvious from an inspection of Table 7-1. However, it is apparent that 10 of the 15 experiments in which >50% of the bitumen sank contained mineral matter. Half of these were conducted at low energy and half at high energy. It was observed that under low energy very little mineral matter remained in suspension for the full 24 hour experiment, i.e., it sank rather quickly due to its relatively high density. Therefore, the effect of mineral matter in low energy water conditions is minimal at best. The effect is greatest only when both mineral matter loadingand water energy are high. The effect is even greater when freshwater, high energy, and high mineral matter loading co-occur. In fact, in all three trials conducted under these conditions between 59 and

79% of the bitumen sunk (Table 7-1). Oppositely, the three freshwater, high-energy experiments conducted without any mineral matter present resulted in only 0% to 35% of the bitumen settling. Intuitively speaking, this makes sense since when water energy is high, and the mineral matter remains in suspension, the potential for collisions between bitumen particles and mineral particles is greater. Some of these collisions will create bitumen/mineral particles that would eventually settle through the water column due to the greater size and density. In one unanticipated trial (Trial 12') the co-occurrence of saltwater, high energy, and high mineral loading led to 70% of the bitumen settling. This suggests that high energy-promoted collisions between bitumen particles and clay particles in suspension must have created dense, mixed particles, which eventually sank.

The interactive effects of salinity, energy and mineral load have on the settling of bitumen speaks to the combined effects that these variables have on (1) water density *versus* bitumen particle density, (2) the effectiveness of the surfactant in retarding coalescence in water with variable dissolved ion content, and (3) the frequency and energy of the collisions between bitumen particles and suspended mineral matter. As above, the interaction of these effects are undoubtedly complex and may warrant more detailed study of the physical-chemical processes involved.

In summary, the benchtop experimental results might lead one to expect that the bitumen from spilled Orimulsion would settle through the water column under: (1) low energy, freshwater conditions and (2) high energy, high suspended mineral load (freshwater or saltwater) conditions. However, it could be argued that the latter may be an artifact of the closed nature of our benchtop experiments in which higher energy promotes greater bitumen-mineral collision frequency (rather than greater dispersion and less frequent collisions as it would in the 'real world').

7.3 Under what conditions does most bitumen remain in suspension?

The amount of bitumen which remains suspended in the water column following an Orimulsion spill is important from the perspective of its impact on pelagic communities. As with sunk bitumen, an additional concern for the suspended bitumen occurs in nearshore, shallow water areas where waves and tides could carry the material to shorelines. In open, deep water conditions the impact of suspended bitumen would seem of little long term consequence as it would likely simply diffuse to very low concentrations.

The percentage of bitumen that remained suspended after 24 hours was typically far less than the percentages, which float or sunk (Table 7-1). In fact, 31 of the 47 experiments resulted in <5% of the initial bitumen occurring in suspension after 24 hours. The typical form for the suspended bitumen, in all but two of these trials, was as small, discrete bitumen particles of variable size (average 54 microns, σ = 84 microns; Tables 5-4 and 6-2). In these instances where the suspended material was <5% the water appeared essentially clear. The exceptions occurred in Trial 22' and Trial 2. Trial 22' led to the formation of neutrally-buoyant "globules", approximately 1 cm in diameter. These tended to gently swirl around, rising and falling, but not sticking to one another. This was the only trial in which the majority of the bitumen remained in suspension and it was unique in being the only high energy, brackish water experiment conducted.

The other exception, Trial 2, led to the formation of a web-like, 'network' of bitumen that did not move but appeared to grow in place. At the end of the 24 hour test, as the vessel was drained the network collapsed. This trial was conducted under low energy, saltwater conditions. Any other tests in which a significant portion (but less than 50%) of the original bitumen remained in suspension were also conducted at either low or high energy levels. Oppositely, all of the trials conducted at intermediate energy levels resulted in an average of only 2.3% suspended bitumen. This result and the observations confirm the response surface model interpretation that the amount of suspended bitumen is strongly influenced by the energy level of the water.

For the most part, in order to remain in suspension bitumen must not exhibit significant particle growth (which would increase buoyancy and favor floatation) nor adhere to mineral matter (which would increase density and favor settling). These circumstances again involve the interactive effects of energy, salinity, and mineral load due to effects that these variables have on (1) water density *versus* bitumen particle density, (2) the effectiveness of the surfactant in retarding coalescence in water with variable salinity, and (3) the frequency and energy of the collisions among and between bitumen particles and suspended mineral matter.

In summary, the benchtop experiments suggest that it would be rare for >50% of the bitumen from spilled Orimulsion to remain suspended in the water column after 24 hours. The conditions most favorable for the occurrence of suspended bitumen are high energy, brackish or freshwater conditions. However, one has to imagine that without the confines of the laboratory vessels far fewer bitumen-bitumen (promoting floatation) and bitumen-mineral (promoting settling) particle collisions would occur. Thus, more bitumen would be expected to remain in suspension if it were not for the confined nature of the benchtop experiments. Thus, in the real world significantly more bitumen may remain suspended in the water column under any conditions. Nonetheless, these experiments demonstrate that a spill under high energy, fresh and brackish water would probably still yield the highest percentage of suspended bitumen.

7.4 Summary

The preceding sections have compiled the results surrounding the gross fate of bitumen following a spill of Orimulsion. These results can be summarized in Table 7-2 and can be used as guidelines in preparing for Phase III of this study, the flume experiments.

Naturally, caution is necessary in projecting the results of the benchtop study's Orimulsion "budget" to the real world, primarily due to the difficulties in comparing the closed system in the laboratory (glass walls) to the real world's open system (no glass walls). The primary influence of the closed system is to prohibit diffusion/ dispersion of the bitumen that would otherwise have occurred in the real world and thereby promote collisions between particles and with the vessel walls. This limitation exists to some degree in any laboratory-based experiments. The meso-scale experiments conducted in Phase III of this study, will reduce this condition due to the larger volume of water to be used, however, this limitation will still exist.

Table 7-2. Summary of the conditions most favorable for predicting the gross fate of bitumen following an Orimulsion spill as determined from the benchtop experiments.

Fate of Most Bitumen	Conditions Most Favorable
Float on/near Water Surface	low energy, saltwater; medium energy, brackish water
Settle to/toward Bottom	low energy, freshwater; high energy, high mineral matter
Remain Suspended in Water	high energy, freshwater; high energy brackish water

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8. ENERGETIC STUDIES CONDUCTED IN THE FLUME TANK

8.1 Overview

The benchtop studies revealed that water energetics played an important role in the fate of Orimulsion spilled on water (Sections 5, 6 and 7). Unfortunately, the measurement of "energy" on the benchtop scale was necessarily simplified to mean the rate of rotation (rpm) of the benchtop apparatus. The translation of just what "low" and "high" (rpm) energy from the benchtop experiments means in the "real world" is extremely difficult. While some mathematical approaches are possible, in an attempt to better understand and constrain the meaning of energy, a series of flume tests were conducted as an integral part of Phase II of this study.

The flume conditions of the earlier Orimulsion studies (Ostazeski et al., 1998) were arbitrarily set to match those previously used by IKU (Singsaas et al., 1995). These conditions were described by Fredriksson et al. (1996). Concern was expressed that these conditions were too energetic for the "real world". The basis for this concern was the fact that in the real world there is normally a decrease in the turbulent mixing with depth. However, it was observed that in the flume tank comparable levels of turbulence existed throughout the entire flume water depth leading to the complete mixing of the water mass. This was undoubtedly attributable in large part to the influence of the wave plunger.

To address this concern we conducted a series of measurements in the flume tank under a variety of wind vane and plunger settings. To address the concern mentioned above most measurements were conducted with the plunger static. During these studies we measured wind speed, wave height, and wave period, the results of which are described in the remainder of this section.

8.2 Flume Tank Test Conditions

The wind-vane generator was set to operate at 10 different revolutions per minute (rpm) settings between 70 rpm and 115 rpm in increments of 5 rpm. In introducing energy from the wind only it was thought to better mimic the decrease in turbulent energy with depth that occurs in the 'real world.' To further demonstrate this, two additional settings that included the use of the wave plunger were also investigated. At these two settings, the wind-vane generator was set to operate at 80 and 95 rpm and the wave plunger at 50 cycles per minute (cpm) with a stroke of 6 cm. The tank was filled to a level of 0.80 meters with filtered saltwater.

8.3 Wind Speed in the Flume Tank

For each setting the wind speed was measured at 25 cm above mean water level (MWL) and at three radial locations: in the center, and 5 cm from the inner and outer walls. Since the internal width of the tank is 54.2 cm, the measurement locations corresponded to 5.0 cm (Inside), 29.6 cm (Middle) and 49.2 cm (Outside). The results of these measurements are shown in Table 8-1 and Figure 8-1.

Table 8-1. Wind speed measurements (m/s) at a height of 25 cm above MWL.

Setting (rpm)	Inside (m/s)	Middle (m/s)	Outside (m/s)
70	3.8	6.0	7.9
75	4.1	6.4	8.7
80	4.3	6.7	9.2
85	4.7	7.3	9.8
90	5.1	7.7	10.5
95	5.5	7.9	11.3
100	5.8	8.0	11.7
105	6.2	8.5	12.1
110	6.8	8.6	12.8
115	7.4	8.9	13.0
80,50,6*	6.6	6.6	9.4
95,50,6*	7.6	7.6	11.1

*Correspond to wind-vane (rpm), wave plunger (cpm), and stroke (cm).

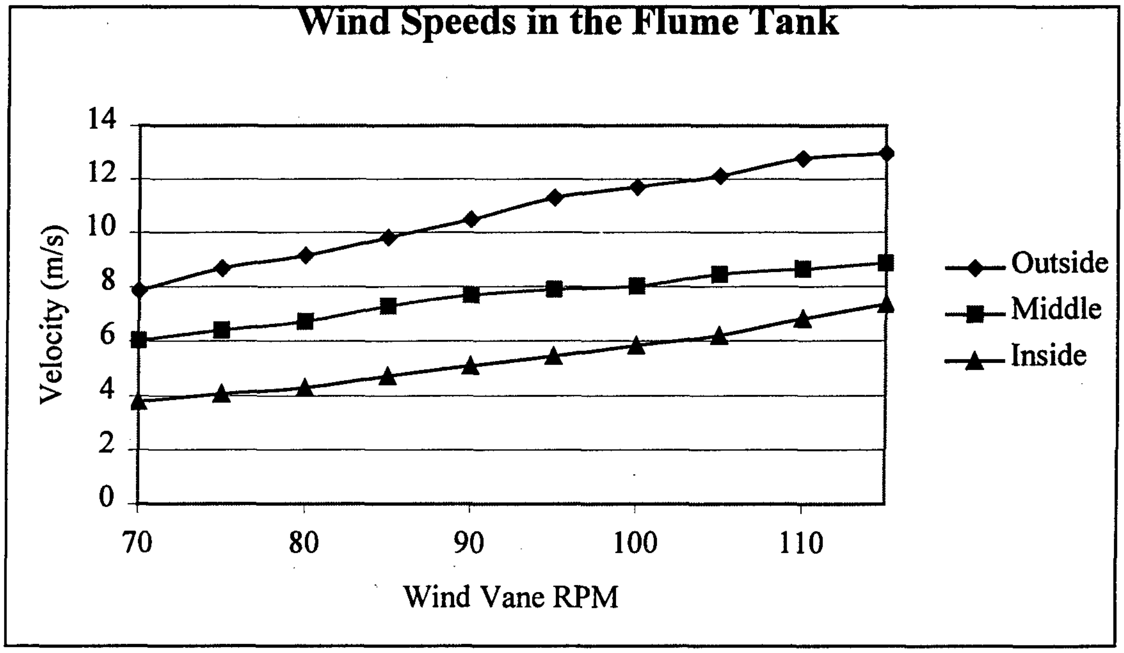

Figure 8-1. Wind vane velocities 25 cm above the mean water level.

8.4 Wave Height and Period Measurements

In addition to measuring wind speeds, a surface elevation times series was obtained for each setting for 5-6 minutes using a capacitance wave probe. These measurements were made after steady state conditions were achieved (i.e., approximately 15-20 minutes after the conditions were changed). The probe was placed at a distance of approximately 22 cm from the outside wall of the flume tank. Wave crest values were obtained from the surface elevation time series by finding the maximum elevation value after each zero up crossing. Wave trough values were found by obtaining the minimum elevation value after each zero down crossing. Wave heights were than calculated by adding successive crest and trough values. The significant wave height, H_s, was found by averaging the top third wave height values while the maximum wave height H_{max}, was considered to be the maximum value in the data set. Figure 8-2 shows the results obtained for each setting. The four independent points on the plot represent the H_s and H_{max} values for the settings that included the wave plunger (see also Table 8-2). The increase in H_s and H_{max} when the plunger was active clearly demonstrates the impact it can have on turbulence.

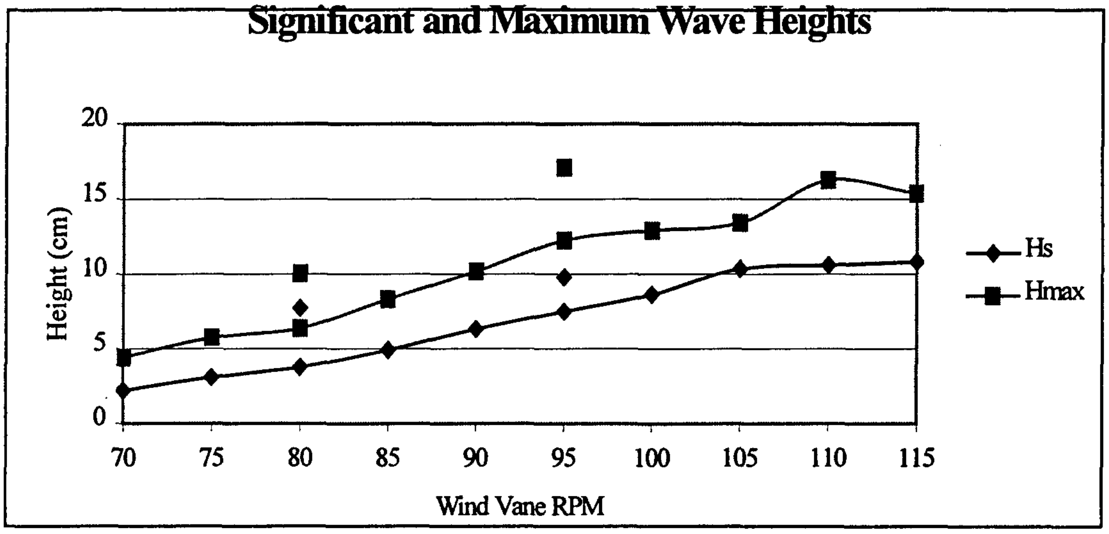

Figure 8-2. Resulting wave heights obtained at each wind vane setting. Points lying off each line are those values obtained with the wave plunger operating at 50 cpm (6 cm stroke).

At each setting, spectral analysis routines were performed on the surface elevation time series to obtain energy density spectra (cm^2/Hz) as a function of wave frequency (see Appendix V). The dominant frequency for each setting was found by identifying the peak value for each respective spectrum. Values for the dominant period, T_{max}, were then obtained by taking the inverse of the dominant frequency and are shown on Table 8-2.

Table 8-2. H_s, H_{max}, and T_{max} for each setting.

Setting (rpm)	H_s (cm)	H_{max} (cm)	T_{max}
70	2.2	4.4	0.60
75	3.1	5.7	0.68
80	3.8	6.6	0.76
85	4.9	8.3	0.82
90	6.3	10.2	0.93
95	7.5	12.3	0.98
100	8.6	12.9	0.98
105	10.4	13.4	0.98
110	10.6	16.3	1.14
115	10.8	15.4	1.28
80,50,6*	7.7	10.0	1.14
95,50,6*	9.8	17.1	1.08

*Correspond to wind-vane (rpm), wave plunger (cpm), and stroke (cm).

8.5 Qualitative Observations of Turbulence

The wind and wave data described above provide only minimal information in regard to the turbulence within the water column. For instance, it is apparent that turbulence in the flume tank is primarily a function of the size and frequency of waves characterized by spilling breakers. To help visualize the vertical distribution of turbulence at each setting, small plastic beads with a specific gravity of 0.96 were introduced onto the water surface. (Thus, under static conditions the beads floated.) Once breaking waves formed the turbulent energy created drove the plastic beads down into the water column. The greater the turbulent energy, the deeper the beads penetrated below the water. Thus, our visual observations surrounding the depth of penetration of the beads is a qualitative measure of the turbulence in the water at each of the settings studied.

A grid with known dimensions attached to the sidewall of the flume tank was used to roughly measure the depth of penetration of the plastic beads. Visual observations of the depth penetration of the plastic beads were noted during each test. The depth to which a significant number of beads penetrated and the maximum depth any one bead penetrated were recorded (Table 8-3).

Figures 8-3 and 8-4 are photographs taken at the wind-vane setting at 80 rpm with and without the wave plunger operating (50 cpm, stroke 6 cm). Additional photographs and video are available to view.

Table 8-3. Visual observations of the depth penetration of the plastic beads.

Setting (rpm)	Significant Penetration (cm)	Maximum Penetration (cm)
70	**negligible**	negligible
75	5	10
80	6	18
85	15	25
90	20	26
95	22	27
100	26	35
105	25	45
110	25	50
115	40	60
80,50,6	15	20
95,50,6	21	45

8.6 Measurement Differences – Current *versus* Past Flume Tests

The calibration information of the wind-wave flume tank presented in Sections 8.2 to 8.5 are representative of the physical conditions with the flume tank as currently configured. Some differences between the current configuration and those previously described (Fredricksson et al., 1996) exist. To avoid any confusion in comparing these results to previous ones, these differences and their implications are described below.

- Three less wind vanes: During the present study, three of the 15 wind vanes mounted on the rotor were removed because of damage during past experiments. Therefore, overall wind speed values obtained are reduced, thereby creating slightly different wave characteristics.
- Wind vane measurement locations: Wind speed measurements obtained during previous studies were made at a height of 15 cm above the MWL. In this study, the height of the wind measurement location was increased to 25 cm to minimize the chance of the anemometer becoming wet at the higher settings where larger waves and more spray occur.
- Wave height processing techniques: Wave processing techniques utilized during this study took into consideration the non-linear nature of the wave fields (for all settings). In past studies, departure from linear wave theory (especially at the lower wind-vane settings) was considered to be small so that simplified Airy (linear) theory could be utilized. Previous processing techniques reflected this assumption.

The current configuration of the flume tank remained in place for Phase III of this study.

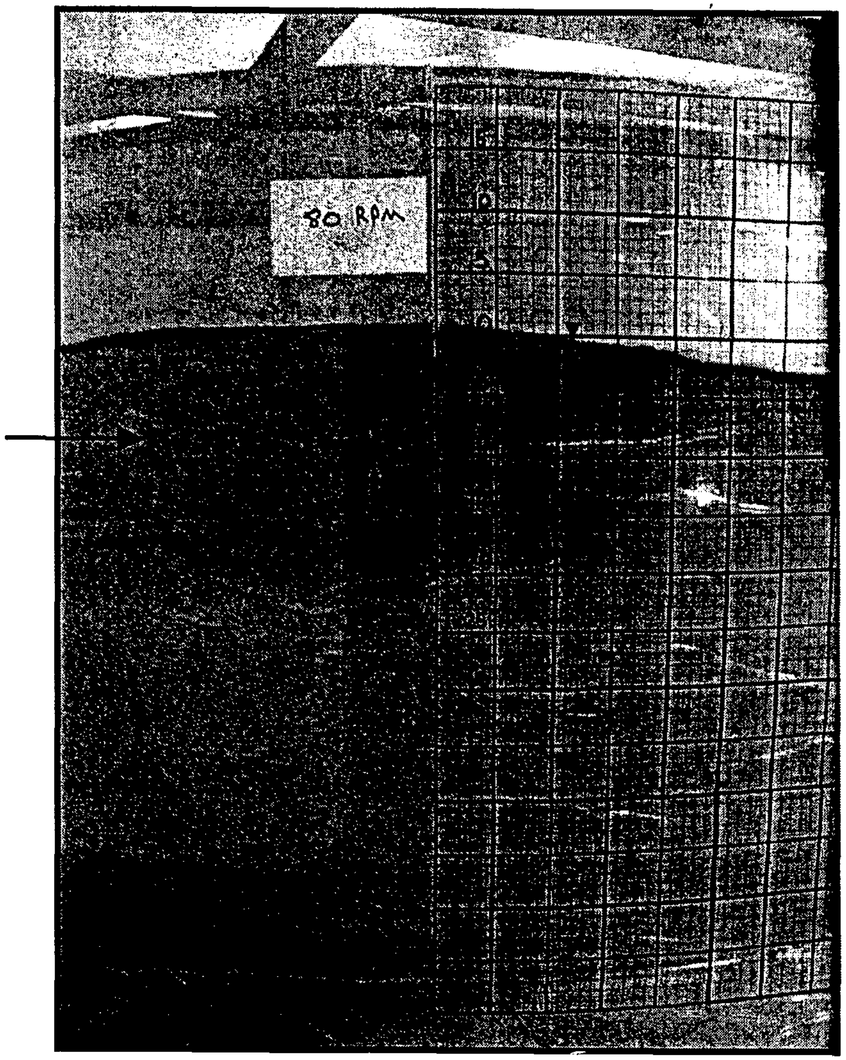

Figure 8-3. Bead penetration with wind vane at 80 rpm and no wave plunger. Grid is in cm; arrow shows depth of significant penetration.

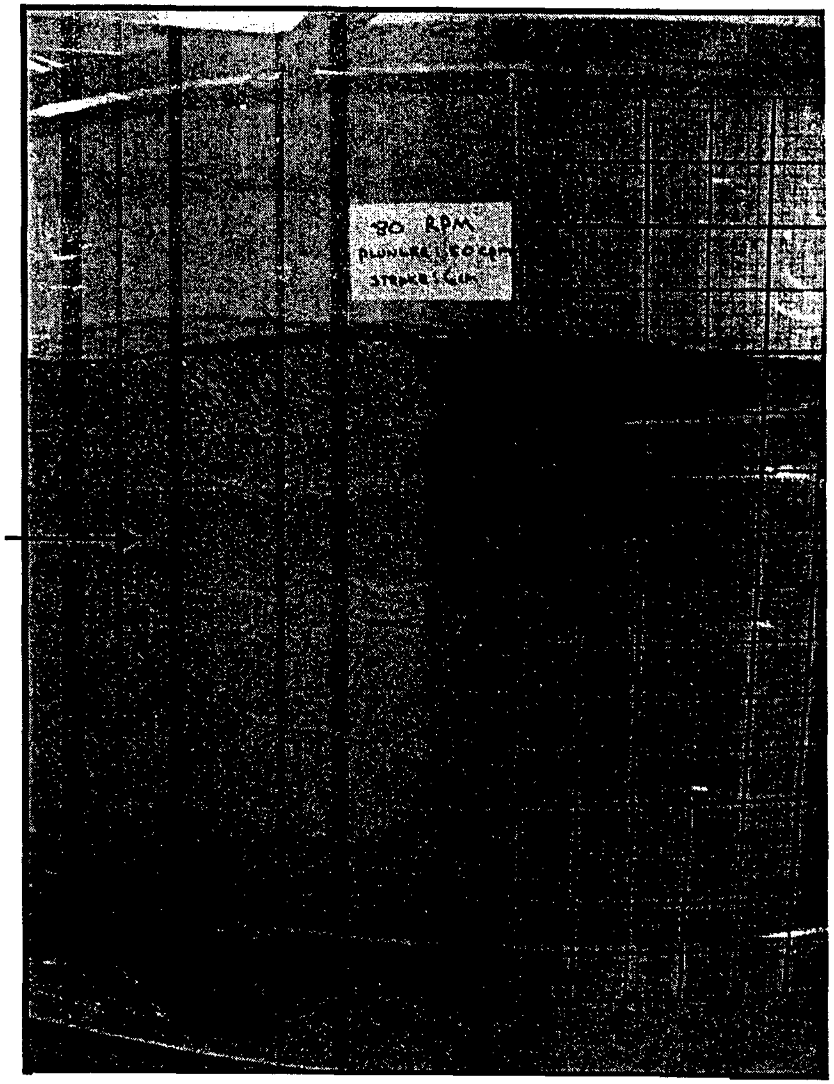

Figure 8-4. Bead penetration with wind vane at 80 rmp and wave plunger operating. Grid is in cm; arrow shows depth of significant penetration.

9. RECOMMENDED FLUME TEST EXPERIMENTS

The benchtop experiments and flume energy studies have provided a basis for recommending a limited set of flume experiments in which the fate of Orimulsion can be predicted. These recommendations cannot fully address the variety of possible experiments to conduct in the flume tank. The criteria that warrant consideration are; (1) the results of the benchtop studies, (2) conditions of the previous flume studies (Ostazeski et al., 1998), (3) the cost to perform a flume study, and (4) the available finances. (In a sense, this is a new 'multivariable problem' which could warrant statistical analysis!)

The benchtop experiments indicated that salinity and water energy had the greatest overall impact on most variables, particularly on the "Orimulsion budget" and on mean particle size. Therefore, the new flume studies should include some assessment of the interaction each of these variables.

The previous flume experiments involving Orimulsion were conducted in both saltwater and freshwater. They employed a single Orimulsion concentration based upon spilling 14.2L (3.75 gallons) of Orimulsion into the 4000L flume tank. This corresponded to an initial Orimulsion concentration of ~3550 mg/L, i.e., toward the low end of the range used in the benchtop experiments conducted herein. Therefore, it would seem prudent to conduct the flume studies at somewhat higher Orimulsion concentrations. We recommend that the intermediate Orimulsion concentration of 9000 mg/L (or 35.6 L or 9.4 gallons of Orimulsion be spilled into the 4000 L flume tank in each test). This will result in the addition of approximately 26.3 kg (70.5 lbs) of bitumen being added to each test (36,000 g of Orimulsion contain 73% bitumen by weight = 26,280 g of bitumen). If it is determined that this is too high a concentration to be reasonably spilled and cleaned-up in our flume tank, the concentrations for subsequent flume tests will be reduced to the earlier level (3550 mg/L).

These earlier studies were also conducted at energy levels that were quite high due to the use of the wave plunger. Therefore, it would seem prudent to conduct at least some of the new flume studies at lower energy levels using the wind vane only. This will assure that any turbulence is introduced from the wind (above) and that it should decrease with increasing depth (i.e., like the "real world"). However, it may also be useful to conduct selected flume experiments using the very high energy conditions which existed in the earlier studies (Ostazeski et al., 1998) since quantitative turbulence measurements exist for these conditions (Fredriksson et al., 1996). This would allow a direct comparison between any new results and those observed previously by Ostazeski et al. (1998).

The flume studies were originally planned for a duration of 168 hours and included chemical analyses on samples collected rather frequently over this time period (Appendix I). The benchtop studies have indicated that most changes had occurred in the first 24 hours following the release. This suggests that the duration of the flume studies could be reduced from 168 hours. The earlier studies on Orimulsion in the flume tank were conducted for 168 hours and most parameters were observed to stabilize after ~60 hours (Ostazeski et al., 1998). Therefore, we would recommend conducting the new flume experiments over the course of 72 hours (3 days). This reduction in experiment duration would reduce the number of samples for chemical analysis and also expedite the rate at which the flume studies can be performed.

We recommend that we attempt to acquire the "mass balance" information akin to the % of bitumen, which floated, sank, or remained in suspension in the benchtop studies. We believe that these mass balance data provide some very practical information in regard to the response and recovery of an Orimulsion spill (i.e., the "Orimulsion budget"). Given the large size and masses of water and Orimulsion involved in the flume tests, however, these mass balance measurements will not be easy to make. As noted above, the 9000 mg/L Orimulsion spill concentrations will result in the addition of 26.3 kg of bitumen (> 70 lbs.). We will undoubtedly face some technical challenges in achieving these measurements and therefore, they will need to be viewed as gross indicators of the Orimulsion budget. However, we believe it is worth pursuing so that our predictions for the gross fate of Orimulsion under various spill conditions based upon the benchtop (micro) scale can be investigated at the flume (meso) scale.

A final technical consideration surrounds the measurement of mean bitumen particle size in suspension. These measurements were undoubtedly confounded by the presence of mineral matter in some benchtop experiments. The same will occur in the flume tank experiments if clay is added to the water. This argues that since particle size growth remains an important parameter for modeling considerations, the use of mineral matter in the flume studies should be restricted to a few studies.

All told, we recommend that five flume studies be conducted as shown in Table 9-1.

Table 9-1. Recommended flume experiments to be conducted during Phase III.

	Salinity (o/oo)	Energy in RPM of wind vane (wind speed range/ signif. wave height)	Orimulsion Concentration (mg/L)	Particulate Loading (mg/L)	Objective
Test 1	0	80 rpm wind vane only (4.3-9.2 m/sec; 3.8 cm)	9000	0	Does most bitumen settle under low energy, freshwater conditions *sans* mineral matter?
Test 2	17.5	115 rpm wind vane only (7.4-13.0 m/sec; 10.8 cm)	9000*	0	Does most bitumen remain suspended or form globules under high energy, brackish conditions? Good particle growth data in brackish water.
Test 3	17.5	80 rpm wind vane only (4.3-9.2 m/sec; 3.8 cm)	9000*	0	Does most bitumen float under low energy, brackish conditions? Good particle growth data in brackish water.
Test 4	32	80 rpm wind vane & 50 cpm/12 cm wave plunger (5.5-11.3 m/sec; 13.4 cm)	9000*	270	Does suspended mineral matter cause settling of some bitumen under in very high energy, saltwater conditions (same conditions as used in 1997 experiments)?
Test 5	0	80 rpm wind vane & 50 cpm/12 cm wave plunger (5.5-11.3 m/sec; 13.4 cm)	9000*	270	Does suspended mineral matter cause greater settling even under very high energy, freshwater conditions (same conditions as used in1997 experiments)?

*To be reduced to 3550 mg/L if Test 1 clean-up is determined to be unmanageable.

While the objectives of these tests are certainly multi-fold, the primary objective of each test is shown in Table 9-1. Test 1 will determine whether or not under low energy, freshwater conditions most of the bitumen settles. Previous studies (Ostazeski et al., 1998) have shown that under higher energy, freshwater conditions that the bitumen will remain in suspension. Particle growth is not expected under these conditions but this will be confirmed. This test might be viewed as a proxy for spill in a freshwater lake or river. Test 2 is intended to test the effect of intermediate salinity at high-energy conditions on spilled Orimulsion. According to the benchtop results (e.g., Trial 22'), under these conditions we expect a large percentage of bitumen to remain suspended in some form, perhaps as 1 cm globules (as in Trial 22'; Section 6). We certainly expect some particle growth under high energy, brackish water conditions and this will be confirmed. This test might be viewed as a proxy for a spill in a brackish harbor or bay under high wind conditions.

Test 3 is intended to test the effect of intermediate salinity at medium energy. This will allow a direct comparison to Test 2 to see how lowering the energy effects Orimulsion. According to the benchtop results we anticipate the bulk of the bitumen to float under these conditions. The effect of energy on particle growth profiles will be obtained by a comparison between the Test 2 and Test 3 results. This test might be viewed as a proxy for a spill in a brackish harbor or bay under medium wind conditions.

Test 4 is intended to test the effect of mineral matter (kaolinite) under very high energy, saline conditions on spilled Orimulsion. These same conditions, except for the presence of mineral matter, were used in previous Orimulsion flume studies (Ostazeski et al., 1997; 1998). During these test the majority of the bitumen was observed to rise toward the surface and form floating patties. In Test 4 the effect of suspended mineral matter in the water column on bitumen's behavior will be determined. In this flume test we'd still anticipate most bitumen to float but, based on the benchtop studies, we'd also expect some bitumen to settle after forming denser, mineral-bitumen particles. However, the energy conditions might be too great to allow settling of these dense particles and we'd, therefore, expect them to remain in suspension. We anticipate particle growth under these conditions will occur. This test might be viewed as a proxy for a spill or Orimulsion in marine conditions as might exist during a storm, during a grounding, or near a river mouth where high concentrations of mineral matter suspended are likely.

Test 5 will introduce kaolinite as a suspended mineral material in order to determine the bulk effect it may have under very high energy, freshwater conditions. This test will be performed under the same test conditions as were used in the earlier Orimulsion flume tests (Ostazeski et al., 1997; 1998). During those tests the bitumen was observed to remain in suspension and experience no particle growth. Based upon our benchtop experiments some settling might be anticipated with the mineral matter in the system. However, as above, the energy may be too high to allow this. This test might be viewed as a proxy for a spill within a sediment-laden river.

Prior to the spilling of Orimulsion in Tests 4 and 5, but after the mineral matter (1.08 kg will yield a maximum of 270 mg/L TSS concentration) is added and steady state conditions are achieved, the concentration of total suspended solids (TSS; almost exclusively mineral matter) will be determined on aliquots of the water. This will give a measure of the TSS for comparison to real world conditions.

The sampling scheme and analyses to be obtained in the course of each of these tests are listed in Table 9-2. Notice that particle size measurements will be obtained on triplicate samples in order to assess the reproducibility and heterogeneity of the bitumen particle populations in suspension at any time under the test conditions. This measure of precision was lacking in previous studies but seems warranted given the potential that these data will be used in modeling particle growth.

The water samples for particle size, TPH, PAH, and SARA analysis from all time intervals will be collected from a depth of approximately 35 cm below the surface. Additional water samples for TPH measurement will be collected from three different depths (approximately 15, 35 and 55 cm) after 72 hours. Each of these samples will be collected in triplicate. The intention is to provide both an average TPH concentration (3 samples) from each depth in order to provide a more accurate measure of the TPH in suspension by acknowledging there may be some vertical distribution.

Table 9-2. Sampling and testing scheme for Phase III flume experiments. Each checkmark represents an individual sample to be taken.

	Bitumen Mass			Unfiltered Water				Filtered Water	
	Mass Floating	Mass Stuck to Walls	Mass Sunk (by difference)	SARA Analysis	TPH total	PAH total	Particle Size	TPH dissolved	PAH dissolved
0	—	—	—				✓✓✓		
15 min	—	—	—		✓		✓✓✓	✓	
30 min	—	—	—		✓		✓✓✓	✓	
1	—	—	—	✓	✓	✓	✓✓✓	✓	✓
2	—	—	—		✓		✓✓✓	✓	
4	—	—	—		✓		✓✓✓	✓	
6	—	—	—		✓		✓✓✓	✓	
12	—	—	—		✓		✓✓✓	✓	
24	—	—	—	✓	✓	✓	✓✓✓	✓	✓
48	—	—	—		✓		✓✓✓	✓	
72*	—	—	—		✓✓✓				
72**	—	—	—		✓✓✓				
72	✓	✓	✓	✓	✓✓✓	✓	✓✓✓	✓✓✓	✓

* samples to be collected from ~15 cm depth
** samples to be collected from ~55 cm depth

10. FLUME TEST RESULTS

The five flume tests recommended in Section 9 were conducted sequentially in Battelle's 4000L flume tank (Appendix I) between Oct. and Dec. 1998. Conditions for each test were consistent with those listed in Table 9-1 with the exception of the slightly increased energy conditions used during Tests 4 and 5. (This change was necessary in order to keep kaolinite in suspension; see below). The sampling and analysis performed in the course of these tests occurred as listed in Table 9-2. All of these tests were conducted at 13°C for a minimum of 72 hours. The results of each flume test are described in the following sections. Raw and tabulated data related to these tests are given in Appendix VI.

10.1 Test 1 – A Low Energy, Freshwater Spill

10.1.1 General Observations

Spill conditions for Test 1 were consistent with those listed in Table 9-1. The pH of the freshwater used in Test 1 was determined to be 7.5. The objective of this test was to determine the propensity for bitumen to settle to the bottom of a water column under low energy, freshwater conditions.

Upon the initial, slow spilling of Orimulsion, the bitumen cloud was observed to descend toward the bottom of the tank and spread laterally. With only minor energy in the water (induced by operating the wind vanes at 80 rpm), the cloud of bitumen slowly traveled around the tank within the first few minutes and diffused vertically. Within five minutes, however, the bitumen cloud was completely dispersed throughout the water column the entire way around the flume tank. This dispersed cloud of bitumen remained essentially unchanged to the naked eye for 24 hours. A small bathtub ring, approximately 1 cm high, had slowly formed over the course of the first 6 hours of the experiment. This was apparently caused by bitumen particles adhering to a 'dry' part of the flume tank walls (both inner and outer walls) at the water line. After 24 hours, there was a small (~10 cm) floating patty which had formed. It would appear to have formed from scavenging of bitumen from the thin, bathtub ring that had formed. Though only a small percentage of the total bitumen, the formation of the small, floating bitumen in freshwater, reveals the potential for some bitumen to float in spite of the apparently greater density. Some benchtop experiments had revealed this phenomenon. (In flume Test 5, below, this phenomenon is further exemplified; Section 10.5.)

Light could not penetrate the black, opaque water/bitumen mixture. As a result, we were unable to visually determine whether any bitumen had actually sunk to the bottom of the tank. The visual impression was that the vast majority of the bitumen had remained dispersed/suspended in the water column over the first 24 hours in spite of the very low energy in the water column.

Because Test 1 was intended to determine if bitumen would actually settle in low energy, freshwater conditions, it was decided to reduce the energy in the water further. Thus, between 24 and 48 hours following the spill the wind vane speed was reduced to 40 rpm, one-half of the original speed. Thus, far less energy was introduced into the water/bitumen mixture (see Section 8). Upon doing this, the surface of the water became essentially flat and free of any ripples though water continued to move around the flume tank. After 48 hours there still was no apparent settling of the bitumen, i.e., the opaque, black water column appeared unchanged. The floating bitumen patty had grown slightly due to continued scavenging of bitumen particles adhered to the flume tank wall. It was evident after 48 hours that the vast majority of the bitumen had remained in suspension.

Thus, it was decided to reduce the energy in the water further by turning off the wind vanes (0 rpm) between 48 and 72 hours following the spill. Within minutes of turning off the wind vanes completely, the floating bitumen patty had stopped moving. Within an hour the patty appeared to have dispersed to form a thin, bitumen slick on the surface of the water. Oily sheens and bitumen slicks formed in other areas of the tank. These, however, still represented a very small proportion of the total bitumen. Most bitumen appeared to remain in suspension. The bitumen/water mixture still appeared opaque after 72 hours as it had after only 30 minutes.

The high concentration of Orimulsion spilled in Test 1 (9000 mg/L) proved particularly problematic during the draining of the flume tank. The bitumen tended to clog the flume tank drains, filters, and hoses. This problem, in and of itself, demonstrates a difficulty for recovering bitumen in high concentrations. Because of these difficulties it was decided to reduce the concentration of the Orimulsion spilled in the remaining flume tests to levels equal to those employed in previous flume tests, namely 3550 mg/L (Table 9-1).

10.1.2 Bitumen Particle Size

The results obtained from particle size measurements obtained during Test 1 are shown in Table 10-1. (See Appendix I for laser diffraction measurement method description.) The values at t=0 represent those of the fresh Orimulsion spilled during this test. All of the water samples were collected from the middle of the water column in the tank, approximately 35 cm deep.

Table 10-1. Particle size (D[4,3] in microns) determined from water samples collected during flume Test 1. All samples collected from mid-water depth ~ 35 cm deep.

	Flume Test #1			
	Rep 1	Rep 2	Rep 3	Avg
t=0	21.9	23.3	22.1	22.4
t=15min	23.0	22.8	23.6	23.2
t-30min	22.2	23.8	22.1	22.7
t=1hr	22.2	23.0	22.4	22.5
t=2hr	24.6	23.8	22.6	23.7
t=4hr	23.0	23.2	22.0	22.8
t=6hr	22.4	22.9	22.6	22.7
t=12hr	21.5	20.9	21.7	21.4
t=24hr	20.5	18.8	19.0	19.4
t=48hr*	16.2	14.9	NA	15.6
t=72hr**	13.3	11.2	12.0	12.2

NA – not available

* wind-induced energy reduced to 40 rpm (1/2 original) for 24 hours prior to sample measurement

** wind-induced energy reduced to 0 rpm (static conditions) for 24 hours prior to sample measurement

It is apparent from the profiles of the particle distributions (not shown) that the bi-model character of the bitumen in suspension over the first 24 hours of this test was typical of fresh Orimulsion (Fig. 3-1). Thus, no particle growth was observed under the Test 1 conditions (i.e., high concentration Orimulsion, low energy, freshwater). This conclusion is consistent with the observations made in the course of the benchtop experiments conducted in freshwater in the absence of clay (Figs. 5-1 and 6-1).

It is notable that once the energy in the flume tank was reduced after 24 hours, and again after 48 hours, that the average particle size decreased slightly in the 48 and 72 hours samples (Table 10-1). Inspection of the particle profiles reveals a loss of the larger particles from the profile. We suspect that this loss was due to the settling of the larger bitumen particles toward the bottom of the tank. This indicates that there may be some 'settling' of bitumen in low energy, freshwater conditions, but that bitumen particle settling; (1) appears to be fairly slow process even in stagnant water and (2) tends to affect the larger bitumen particles in Orimulsion (Fig. 3-1).

10.1.3 Total Hydrocarbons and PAH

The results of the total petroleum hydrocarbon analysis for filtered and unfiltered water samples collected during Test 1 are shown in Table 10-2. TPH concentrations in the water remained approximately 5100 mg/L over the first 24 hours of the test, when the energy conditions were maintained by the wind vane operated at 80 rpm. If all of the bitumen initially added (26.3 kg; Section 9.0) was in suspension, the concentration in the 4000 L flume tank would be around 6575 mg/L. Since only ~5100 mg/L bitumen was measured over the first 24 hours, some percentage of the bitumen was lost during the early stages of the test. Some of this was lost to the thin bathtub ring and small floating patty that had formed while the bulk of it would appear to have been lost to/toward the bottom of the tank. As the energy in the water was further reduced (after 24 hours and 48 hours) the TPH_{total} concentrations were reduced. This further suggests that, indeed, some settling of bitumen had occurred, though quite slowly.

The eventual settling of bitumen was confirmed by the 72 hours samples collected from three depths within the tank (shallow ~ 15 cm, middle ~35 cm, and deep ~55 cm). These concentrations show that, on average, the highest concentration of bitumen was found in the deep sample and the lowest occurred in the shallow sample. The middle sample was intermediate in bitumen concentration. In other words, more bitumen was suspended in the bottom water than in the shallower water. This gradation confirms some bitumen settling had occurred by the end of the 72-hour experiment. The fact that the water contained approximately only 2252 mg/L after 72 hours, yet 6575 mg/L bitumen had been spilled, further argues for some settling of bitumen. (Remember that there was only a relatively small bathtub ring and floating material at the end of the test; Section 10.1). This will be further addressed in Section 10.1.4.

Table 10-2. Concentrations of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in unfiltered (total) and filtered (dissolved) water samples collected during flume Test 1.

TIME (hrs)	TPH(total) (mg/L)	TPH(dissolved) (mg/L)	PAH (total) (ug/L)	PAH (dissolved) (ug/L)
1	5063.29	2.30	20303.6	6.6
2	5328.95	NA	NA	NA
4	5064.94	NA	NA	NA
6	5197.37	NA	NA	NA
12	5031.85	NA	NA	NA
24	4200.00	3.05	16198.9	5.8
48	3184.00	NA	NA	NA
72Rep1(15cm)	2081.08	NA	NA	NA
72Rep2(15cm)	2062.50	NA	NA	NA
72Rep3(15cm)	1776.47	NA	NA	NA
72Rep1(35cm)	2187.50	2.62	NA	5.0
72Rep2(35cm)	2211.76	2.53	NA	NA
72Rep3(35cm)	2280.00	2.44	6285.3	4.1
72Rep1(55cm)	2617.45	NA	NA	NA
72Rep2(55cm)	2535.21	NA	NA	NA
72Rep3(55cm)	2518.52	NA	NA	NA

NA- not analyzed

The concentration of PAH_{total} was markedly decreased over the course of the test (Table 10-2). The initial concentration (20,303.6 ug/L) was very close to what would be predicted given the 36 kg of Orimulsion spilled and the concentration of PAH measured in Orimulsion (Table 3-2; 36 kg at 2472 mg/kg in 4000L = 22,248 ug/L). The decrease observed over the course of the test is correlated to the loss of TPH_{total} from the water column, i.e., due to settling of the bitumen.

The concentration of dissolved TPH and PAH was nominal throughout the test. The distribution of individual PAH compounds dissolved in the water were consistent with what had been observed earlier (e.g., Fig. 6-10), namely, the water became enriched in the most soluble PAH (Appendix VI). The concentration of $PAH_{dissolved}$ (~6000 ng/L) was within the range of concentration that had been observed in the freshwater, benchtop experiments (Figs. 5-8 and 6-11). Most importantly, the concentration of $PAH_{dissolved}$ was not observed to increase in the course of the test.

10.1.4 Mass Balance

The mass balance data obtained at the completion (72 hours) from Test 1 are shown in Table 10-3. These results are consistent with the visual observations made in the course of the test (Section 10.1.1). For example, very little (< 1%) bitumen floated and very little (< 1%) bitumen stuck to the walls of the flume tank. The abundance of bitumen which remained in suspension (9009 g or 34% of the bitumen added) produced the opaque, black bitumen cloud which prevented visual observation regarding the amount of bitumen which had sunk. However the mass balance results, along with the

TPH depth gradient (Table 10-2), confirms that approximately 65% of the bitumen had, in fact, settled to/toward the bottom of the tank.

Table 10-3. Results of mass balance for bitumen at conclusion of flume Test 1.

	Mass of Bitumen (g)	Percent of Bitumen
Initially Spilled (g)	26,280	--
Floated (g)[1]	45	0.2
Settled (g)[2]	17,211	65.5
Bathtub Ring (g)[3]	5	0.0
Suspended (g)[4]	9,009	34.3
Dissolved (g)[5]	10	0.0

[1] Weight of air-dried floating bitumen (corrected for water weight).
[2] Determined by difference.
[3] Weight of bitumen adhered to inside and outside liner over 1/5th of tank circumference x 5.
[4] Average TPH_{total} – average $TPH_{dissolved}$ x 4000L
[5] Average $TPH_{dissolved}$ x 4000L

These mass balance results are consistent with what was predicted based upon the benchtop results (Section 7.6). For example, flume Test 1 was intended to answer the question of whether or not the bulk of bitumen spilled into a freshwater, low energy environment would settle (Table 9-1). The likely answer based upon Test 1's mass balance results (Table 10-3) is yes. However, the caveat to this answer is that 'no energy' (i.e., static) conditions were necessary to observe any settling and even then, settling was extremely slow. (Remember, the energy in the system was reduced after 24 hours and then was eliminated after 48 hours.)

10.2 Test 2 – A High Energy, Brackish Water Spill

10.2.1 General Observations

Conditions for Test 2 were consistent with those listed in Table 9-1 with the exception of the lower initial Orimulsion concentration (3550 mg/L instead of 9000 mg/L; see Section 10.1.1). The pH of the water used in Test 2 was determined to be 7.6. The objectives of this flume test were to (1) determine the meso-scale response of bitumen spilled into brackish water and, in particular, (2) determine if high energy, brackish water conditions led to the formation of neutrally-buoyant, bitumen 'globules' (as had been observed in benchtop Test 22'; Section 7.3).

Upon spilling, the bitumen quickly dispersed throughout the water. Not surprisingly, given the high water energy induced by the wind vanes operating at 115 rpm (7.4 to 13.0 m/sec wind speed and spilling breaking waves up to 15.4 cm high; Sections 8.3 and 8.4), the water column became completely black with bitumen within the first minute of the spill. Bitumen was observed to begin sticking to the flume walls within minutes. Most of this bitumen became stuck to the dry areas of the walls, i.e., above the maximum wave level. The combination of spilling breakers and high wind speeds tended to 'cast' bitumen particles against the flume tanks outer wall forming a thick 'bathtub ring.' Within 30 minutes the bathtub ring was about 25 cm high and was continuous all the way around the tank's outer wall, again, mostly above the high water line. The ring was slightly thinner on the inner wall.

Coalescence of bitumen was rampant and numerous floating bitumen lumps had formed within the first several minutes of the spill. Most of these were initially only a few centimeters in diameter. These lumps were positively buoyant. In spite of the downward energy caused by the spilling breaking waves, the lumps remained near the water's surface. With every collision the lumps tended to stick to one another and within 30 minutes, one large, buoyant patty, approximately 0.1 m^2, had formed. This large patty tended to stick to the flume tank walls for minutes at a time before breaking lose and migrating further before sticking again. Within 6 hours the floating bitumen patty grew to approximately 1.0 m^2. The thickness of the patty was approximately 12 cm. It spanned the entire flume tank width and, being stuck to both the inner and outer wall, it tended to remain in one place for long periods of time. The energy level in the tank was significantly dampened (from the initial spill conditions) by the large patty.

As the patty formed, the amount of bitumen in the water column was visibly reduced. Within the first six hours of the spill the water column was translucent to light. After 24 hours, the water column was mostly 'clean.' After 72 hours, at the completion of the test, only a small amount of bitumen particles were still suspended in the nearly 'clean' water column. Clearly, most of the bitumen was present in the large, single floating patty or was adhered to the flume tank walls.

After the final samples were collected, the wind vanes were turned off. At this point, the static, floating patty tended to spread laterally and thin-out, presumably due to continued buoyant forces from bitumen toward the bottom of the thick (~12 cm) patty. The cohesive patty was easily recovered by 'folding' it onto itself until it could be scooped into a plastic pail. It was extremely sticky and 'tar-like.' The water column had become mostly clear although had a slight tan color to it. Unlike Test 1, the water and the small amount of suspended bitumen remaining in the water was easily drained through the flume's drainage system.

10.2.2 Bitumen Particle Size

The results obtained from particle size measurements obtained during Test 2 are shown in Table 10-4. The values at t=0 represent those of the fresh Orimulsion spilled during this test. All of the water samples were collected from the middle of the water column in the tank, approximately 35 cm deep.

It is readily apparent from D[4,3] data that a marked coalescence of bitumen particles occurred under the Test 2 conditions. Particle growth was observed visually almost immediately following the spill (Section 10.2.1) and this is evident in the particle size data. The coalescence of bitumen under brackish water conditions was anticipated based upon the results of the brackish water benchtop studies (Section 6.2.2.4 and Fig. 6-2).

The rate of particle growth is demonstrated by the curve shown in Fig. 10-1. Most particle growth had occurred within the first twelve hours of the spill after which time the no further growth was "evident" (see below). On average, particles in suspension after 12 hours were approximately 250 microns in size. However, it is critical to remember that the reported D[4,3] diameters represent the average of a broad population of bitumen particles. It is more important to remember that the laser diffraction method of particle size measurement (Section 5.2.2 in Appendix I) is limited to particles less than 600 microns. However, visual observations revealed the presence of larger suspended particles (Section 10.2.1). Therefore, the apparent 'leveling off' in the rate of particle growth after 12 hours (Fig. 10-1) is, at least in part, an artifact of the measurement technique. (In other words, if we were able to measure particles > 600 microns in size the average D[4,3] would probably have continued to increase throughout the experiment.) Thus, average particle data after the first twelve hours of the test are misleading.

Table 10-4. Particle size (D[4,3] in microns) determined from water samples collected during flume Test 2. All samples collected from mid-water depth ~ 35 cm deep.

	Flume Test #2			
	Rep 1	Rep 2	Rep 3	Avg
t=0	24.6	24.1	27.5	25.4
t=15min	73.7	73.5	70.6	72.6
t-30min	80.5	81.3	83.1	81.6
t=1hr	120.2	97.0	139.4	118.9
t=2hr	155.8	126.2	121.8	134.6
t=4hr	185.2	181.2	200.3	188.9
t=6hr	236.8	190.6	229.4	218.9
t=12hr	258.8	248.2	263.2	256.7
t=24hr	286.8	255.0	222.3	254.7
t=48hr	283.8	283.8	209.1	258.9
t=72hr	219.7	246.7	200.3	222.2

10.2.3 Total Hydrocarbons and PAH

The results of the total petroleum hydrocarbon analysis for filtered and unfiltered water samples collected during Test 2 are shown in Table 10-5. Total TPH concentrations in the water were quickly reduced from the initial levels. Consider that if all of the bitumen initially spilled had remained in suspension, the concentration in the 4000 L flume tank would be around 2600 mg/L (73% of Orimulsion spilled). However, within 1 hour of the spill the concentration of bitumen in suspension had been reduced to only 1263 mg/L, indicating about one-half of bitumen was no longer suspended in the water column. This measurement is consistent with the visual observations, which had indicated that a significant amount of bitumen was adhered to the flume tank walls or floating near the surface shortly after the spill (Section 10.2.1). The reduction in the concentration of TPH$_{total}$ continued throughout the remainder of the test and after 72 hours, an average of only 18.4 mg/L of bitumen remained in suspension (Table 10-5). This result is also consistent with the visual observation that the water column had become increasingly clear, but that some bitumen particles (most rather large) remained in suspension at the end of the test.

The concentration of PAH$_{total}$ was markedly decreased over the course of the test (Table 10-2). If all of the PAH spilled were in suspension the concentration would have been 8837 mg/L. The initial (t=1 hr) concentration (5178.1 ug/L) was lower than this, which is consistent with the removal of bitumen from the water column. The decrease in PAH$_{total}$ observed over the course of the test is correlated to the loss of TPH$_{total}$ from the water column, i.e., mostly due to the formation of the floating bitumen patty.

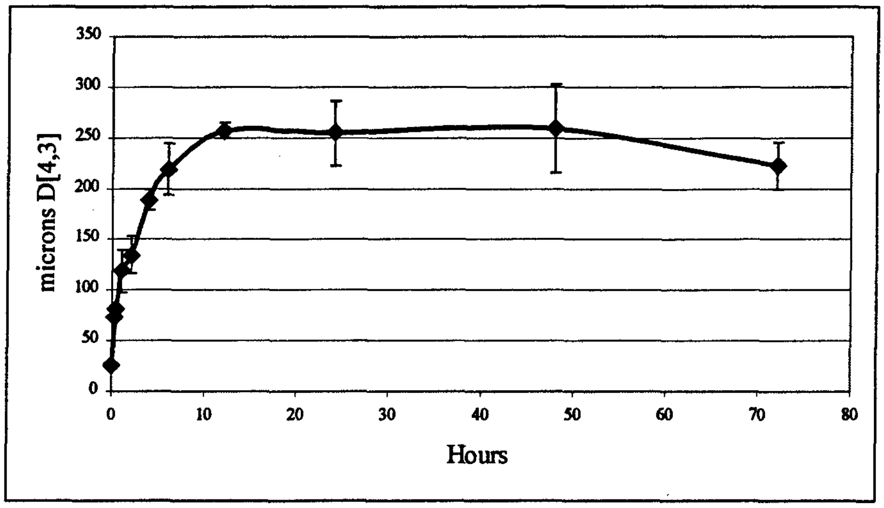

Figure 10-1. Particle growth trend observed during flume Test 2 – high energy, brackish water. Brackets reflect one standard deviation of the triplicate measurements (Table 10-4). Data after 12 hours are misleading; see text for description.

The concentration of dissolved TPH and PAH was nominal throughout the test. Again, the distribution of individual PAH compounds dissolved in the water were consistent with what had been observed earlier (e.g., Fig. 6-10), namely, the water became enriched in the most soluble PAH (Appendix VI). The concentration of $PAH_{dissolved}$ was gradually reduced, but in each case was between 4900 to 100 ng/L (Table 10-5). This range was essentially the range of concentrations observed in the brackish water, benchtop experiments (Fig. 6-11). Most importantly, the concentration of $PAH_{dissolved}$ was not observed to increase in the course of the test.

10.2.4 Mass Balance

The mass balance data obtained at the completion (72 hours) from Test 2 are shown in Table 10-6. These results are consistent with the visual observations made in the course of the test (Section 10.2.1). For example, most (>90%) of the bitumen had ended up in the large floating patty which had formed early and continued to grow in mass throughout the test. Given the high-energy conditions a notable amount (~ 8%) of bitumen had also become adhered to the flume tank walls, mostly above the water line. Also consistent with the "near-clear" water column at the end of the test, only a minor amount (< 1%) remained suspended.

Table 10-5. Concentrations of total petroleum hydrocarbons ad polycyclic aromatic hydrocarbons in unfiltered (total) and filtered (dissolved) water samples collected during flume Test 2.

TIME (hrs)	TPH(total) (mg/L)	TPH(dissolved) (mg/L)	PAH (total) (ug/L)	PAH (dissolved) (ug/L)
1	1263.16	1.89	5178.1	4.9
2	979.38	NA	NA	NA
4	705.13	NA	NA	NA
6	555.56	NA	NA	NA
12	372.34	NA	NA	NA
24	172.41	1.47	606.9	0.3
48	37.97	NA	NA	NA
72Rep1(15cm)	19.23	NA	NA	NA
72Rep2(15cm)	17.44	NA	NA	NA
72Rep3(15cm)	17.24	NA	NA	NA
72Rep1(35cm)	17.44	1.19	NA	NA
72Rep2(35cm)	17.44	1.27	2.7	0.1
72Rep3(35cm)	17.65	1.42	NA	NA
72Rep1(55cm)	20.00	NA	NA	NA
72Rep2(55cm)	18.99	NA	NA	NA
72Rep3(55cm)	18.75	NA	NA	NA

Table 10-6. Results of mass balance for bitumen at conclusion of flume Test 2.

	Mass of Bitumen (g)	Percent of Bitumen
Initially Spilled (g)	10,366	---
Floating (g)[1]	9,453	91.2
Sunk (g)[2]	0	0.0
Bathtub Ring (g)[3]	861	8.3
Suspended (g)[4]	74	0.7
Dissolved (g)[5]	5	0.0

[1] Weight of air-dried floating bitumen (corrected for water weight).

[2] Determined by difference.

[3] Weight of bitumen adhered to inside and outside liner over 1/5th of tank circumference x 5.

[4] Average TPH_{total} – average $TPH_{dissolved}$ x 4000L

[5] Average $TPH_{dissolved}$ x 4000L

These mass balance results are not surprising given the benchtop experiments. The benchtop experiments had clearly shown that under brackish water conditions (18 $^{o}/_{oo}$) that the bitumen particles were both positively buoyant and that they tended to coalesce (i.e., the surfactant was mostly ineffective at this salinity). Therefore, the formation of the sizeable floating bitumen patty was not unexpected.

The secondary objective surrounded the unusual result in benchtop Test 22'. This was the only one benchtop test conducted at what were considered "high energy, brackish water" conditions and it resulted in the formation of the neutrally-buoyant, bitumen globules which remained suspended (Section 7.3). Obviously, such globules were not formed during flume Test 2. One could easily envision that the benchtop apparatus (operated at 100 rpm) and the flume tank (operated at 115 rpm wind vanes) produced very different energy conditions (and motions). Therefore, the disparity between benchtop Test 22' and flume Test 2 is not too surprising. Perhaps a better comparison for flume Test 2 are the "medium energy, brackish water" conditions of benchtop Tests 23' through 31' in which > 50% of the bitumen ended up as floating material (Table 7-1).

Overall, Test 2's results are typical of what had been previously observed under "high energy, saltwater conditions" (Ostazeski et al., 1997; 1998). These earlier saltwater flume tests also resulted in the formation of a sizable floating patty.

10.3 Test 3 – A Low Energy, Brackish Water Spill

10.3.1 General Observations

The conditions for Test 3 were consistent with those listed in Table 9-1 with the exception of the lower initial Orimulsion concentration (3550 mg/L instead of 9000 mg/L; see Section 10.1.1). The pH of the brackish water used in Test 3 was determined to be 7.6. The original objective of flume Test 3 was to determine if most bitumen tended to float, as would be predicted based on the benchtop results (Table 9-1) under low energy, brackish water conditions. This answer was nearly guaranteed to be 'yes,' given the results of flume Test 2. Nonetheless, it was important to conduct flume Test 3 in order to determine the effect of the water energy has on a brackish water spill (i.e., direct comparison of flume Tests 2 and 3). Wind speeds and maximum wave height produced by the 80 rpm wind vane speed during flume Test 3 were 4.3 to 9.2 m/sec and 6.6 cm, respectively (Sections 8.3 and 8.4).

The spilled Orimulsion formed a continuous, black cloud of bitumen throughout the water column within the first few minutes of the spill. Contrary to Test 2, not nearly as much bitumen adhered to the flume tank walls during this test, presumably due to Test 3's lower energy. (The lower wind speed and wave heights cast less bitumen against the flume tank walls.) The bitumen mostly appeared to be positively buoyant and floating lumps of bitumen quickly formed. Presumably due to the abundance of bitumen near the water's surface, the energy within the water was significantly dampened within the first thirty minutes, i.e., the waves (H_{max} 6.6 cm) were reduced to ripples. Within four hours a large, single floating bitumen patty had formed and energy within the water column was markedly reduced from the initial spill conditions (estimated H_{max} 2 cm). The floating patty was approximately 1 m^2 and 12 cm thick.

As was observed in Test 2, the water column became increasingly clearer over time, i.e., visibly reduced in bitumen concentration. The water column was translucent to light. After 72 hours, the single large floating bitumen patty was present but the water column still contained some suspended bitumen. This suspended material might be considered to have been 'neutrally' buoyant. These suspended particles were fairly large (~ 1 mm diameter) in size. Some bitumen was stuck to flume tank walls near the water line, although not nearly as much as had been observed in flume Test 2. Curiously, some bitumen was also stuck to the flume tank walls well below the water line, mostly in creases in the flume tank's plastic liner.

The most unusual observation in Test 3 was the formation of six (?) bitumen "balls" approximately 15 cm in diameter. These were observed to have formed sometime between 48 and 72 hours. (They were not noticed after 48 hours but were after 72 hours.) After 72 hours these bitumen balls were observed rolling and bouncing along the bottom of the flume tank where they were clearly negatively (slightly) buoyant. Their roundness was undoubtedly due to their saltation along the bottom of the smooth tank.

10.3.2 Bitumen Particle Size

The results obtained from particle size measurements obtained during Test 3 are shown in Table 10-7. The values at t=0 represent those of the fresh Orimulsion spilled during this test. All of the water samples were collected from the middle of the water column in the tank, approximately 35 cm deep.

It is readily apparent from D[4,3] data that a marked coalescence of bitumen particles occurred under the Test 3 conditions. As in flume Test 2, the coalescence of bitumen under brackish water conditions was anticipated based upon the results of the brackish water benchtop studies (Section 6.2.2.4 and Fig. 6-2). Particle growth during flume Test 3 was observed visually almost immediately following the spill (Section 10.3.1) and this rapid growth is evident in the particle size data. The rate of particle growth is demonstrated by the curve shown in Fig. 10-2. Within only 15 minutes the bitumen particles in suspension increased in diameter to approximately ~110 microns. This was considerably faster than was observed in Test 2 (where at t= 15 min D[4,3] was only 73 microns).

However, after 1 hour the average bitumen particle size had reached its maximum diameter of approximately 120 microns (Fig. 10-2). Notably, during both flume Tests 2 and 3 the bitumen particles in suspension after 1 hour were both approximately 120 microns. However unlike flume Test 2 (Fig. 10-1), continued particle growth beyond the first hour of the flume Test 3 spill did not occur. Rather, the bitumen particles in suspension during flume Test 3 remained approximately 110-120 microns for the duration of the Test (Fig. 10-2). Remember that (1) the D[4,3] diameters reported are representing a population of bitumen particles and (2) the maximum particle size measurable was 600 microns (Appendix I). Thus, the 'leveling off' of the particle growth trend after 2 hours (Fig. 10-2) is due, at least in part, to the formation of particles larger than 600 microns that are not included in calculating the average D[4,3]. Also contributing to the leveling off in particle growth may be the removal of larger particles from the water column due to their greater buoyancy. Regardless, as was the case in the flume Test 2 particle size trend (Fig. 10-1), the average particle data after the first two hours of flume Test 3 are misleading.

Regardless of this limitation, the only difference between flume Tests 2 and 3 was the level of energy in the water. Therefore, the slightly faster rate of bitumen particle growth within the first hour in Test 3 (Figs. 10-1 and 10-2) must be due to the lower energy level. The faster particle growth during Test 3 led to the formation of (un-measurable and more buoyant) particles larger than 600 microns earlier (than in Test 2), and thus tended to reduce the average D[4,3] values more quickly. Thus, the D[4,3] maximum for Test 3 ended up being lower (~120 microns) than was measured during Test 2 (~250 microns). The bottom line is that particle growth occurred more rapidly in the lower energy, brackish water flume Test 3 than in the higher energy, brackish water flume Test 2. This result is somewhat counterintuitive if one considers the higher energy might promote more frequent collisions between particles. However, higher energy might also promote greater removal of larger, more buoyant particles from the water column and faster formation of a 'bathtub ring,' which reduces the concentration of bitumen in the water, and thereby decreases the frequency of collisions.

Table 10-7. Particle size (D[4,3] in microns) determined from water samples collected during flume Test 3. All samples collected from mid-water depth ~ 35 cm deep.

	Flume Test #3			
	Rep 1	Rep 2	Rep 3	Avg
t=0	23.0	21.5	NA	22.2
t=15min	113.9	102.7	109.3	108.6
t-30min	131.4	116.3	107.9	118.5
t=1hr	116.6	139.9	109.6	122.0
t=2hr	154.9	119.3	101.9	125.4
t=4hr	98.3	113.7	117.9	110.0
t=6hr	118.4	104.7	104.0	109.1
t=12hr	112.9	110.3	110.0	111.0
t=24hr	133.8	88.0	79.2	100.3
t=48hr	82.0	76.5	116.7	91.7
t=72hr	148.7	96.9	84.8	110.1

NA – not analyzed

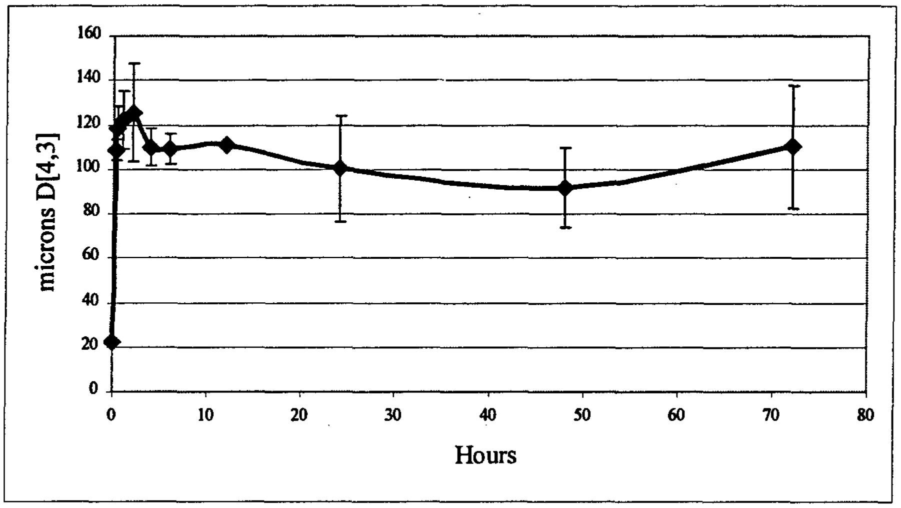

Figure 10- 2. Particle growth trend observed during flume Test 3 – low energy, brackish water. Brackets reflect one standard deviation of the triplicate measurements (Table 10-7). Compare to Fig. 10-2 (high energy, brackish water). Data after 2 hours are misleading, see text for description.

10.3.3 Total Hydrocarbons and PAH

The results of the total petroleum hydrocarbon analysis for filtered and unfiltered water samples collected during Test 3 are shown in Table 10-8. Total TPH concentrations in the water were quickly reduced from the initial levels. As was the case in flume Test 2, consider that if all of the bitumen initially spilled had remained in suspension, the concentration in the 4000 L flume tank would be around 2600 mg/L (73% of Orimulsion spilled). However, within 1 hour of the spill the concentration of bitumen in suspension had been reduced to only 1878 mg/L, indicating about 28% of the total bitumen was no longer suspended in the water column. Visual observations had indicated that bitumen was adhered to the flume tank walls or floating near the surface shortly after the spill (Section 10.3.1), which would explain the rapid loss of bitumen. The reduction in the concentration of TPH in suspension continued throughout the remainder of the test and after 72 hours, an average of only 81.5 mg/L bitumen (about 3%) remained in suspension (Table 10-8). This result is consistent with the visual observation that the water column had become increasingly clear, but that some bitumen particles (most rather large) remained in suspension at the end of the test.

Table 10-8. Concentrations of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in unfiltered (total) and filtered (dissolved) water samples collected during flume Test 3.

TIME (hrs)	TPH(total) (mg/L)	TPH(dissolved) (mg/L)	PAH (total) (ug/L)	PAH (dissolved) (ug/L)
1	1878.21	1.37	7090.1	1.3
2	1549.67	NA	NA	NA
4	741.75	NA	NA	NA
6	630.00	NA	NA	NA
12	361.14	NA	NA	NA
24	157.30	1.28	491.9	0.3
48	155.57	NA	NA	NA
72Rep1(15cm)	73.45	NA	NA	NA
72Rep2(15cm)	72.50	NA	NA	NA
72Rep3(15cm)	78.19	NA	NA	NA
72Rep1(35cm)	81.40	1.55	185.75	0.2
72Rep2(35cm)	79.07	1.68	NA	NA
72Rep3(35cm)	80.46	1.64	NA	NA
72Rep1(55cm)	77.53	NA	NA	NA
72Rep2(55cm)	107.47	NA	NA	NA
72Rep3(55cm)	83.72	NA	NA	NA

NA – not analyzed

It is worthwhile to compare the TPH results obtained in flume Tests 2 and 3. Figure 10-3 shows that concentration of TPH_{total} recovered from the water column throughout each test. (Given the low concentrations of $TPH_{dissolved}$ (Tables 10-5 and 10-8), the concentration of TPH_{total} is essentially equivalent to the total suspended bitumen.) Both brackish water flume tests saw a rapid reduction in the amount of bitumen remaining in suspension. However, it is apparent that the initial reduction occurred slightly faster in flume Test 2, the high energy test. This might be anticipated given the more rapid formation of the bathtub ring during Test 2. Between six and 24 hours following the spill the water from both tests contained comparable concentrations of suspended bitumen. After 48 and 72 hours the lower energy, Test 3 contained slightly higher concentrations of suspended bitumen. This would be consistent with the visual observations surrounding the occurrence of 'neutrally-buoyant' bitumen particles up to 1 mm in size still in suspension at the conclusion of Test 3 (Section 10.3.1).

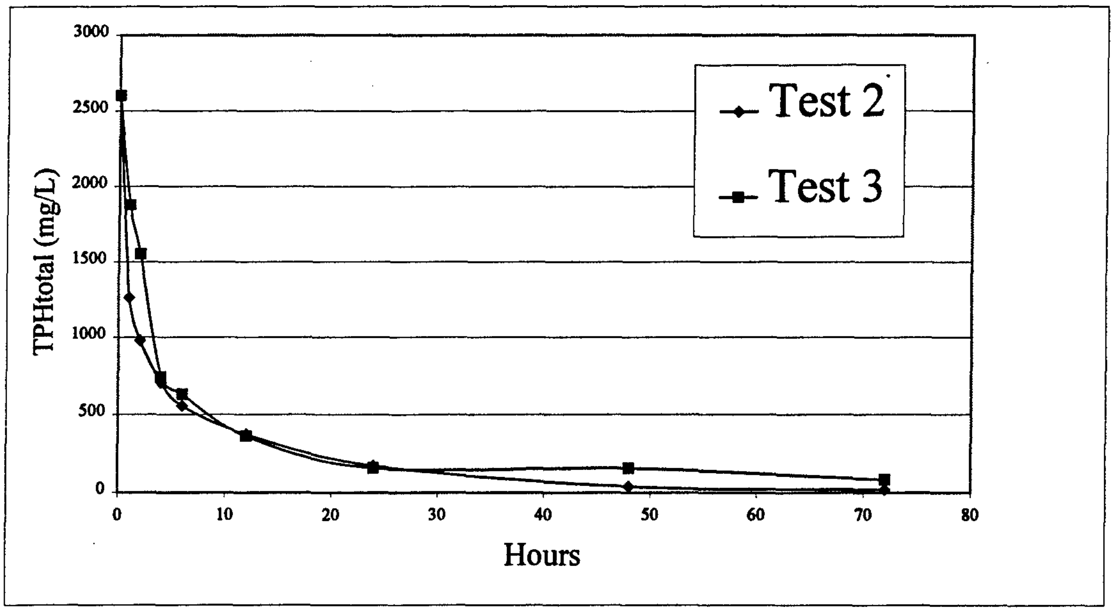

Figure 10-3. Concentration of total petroleum hydrocarbons in water column samples in the course of brackish water flume Tests 2 (high energy) and 3 (low energy). Data are from Tables 10-5 & 10-8.

As observed during flume Test 2, the concentration of PAH_{total} in the water was markedly decreased over the course of flume Test 3 (Table 10-8). This is consistent with the removal of bitumen from the water column (Fig. 10-3). The concentrations of $TPH_{dissolved}$ and $PAH_{dissolved}$ were nominal throughout the test. Again, the distribution of individual PAH compounds dissolved in the water were consistent with what had been observed earlier (e.g., Fig. 6-10), namely, the water became enriched in the most soluble PAH (Appendix VI).

10.3.4 Mass Balance

The mass balance data obtained at the completion (72 hours) from Test 3 are shown in Table 10-9. These results are consistent with the visual observations made in the course of the test (Section 10.3.1). For example, as would have been predicted based upon the benchtop tests, most (~ 77%) of the bitumen had ended up in the large floating patty which had formed early and continued to grow in mass throughout the low energy, brackish water Test 3. The mass of Test 3's floating patty was less than was formed during the high energy, brackish water flume Test 2 (~90%; Table 10-6). As expected, flume Test 3's lower energy conditions also resulted in a reduced amount of bitumen adhered to the flume tank walls (< 1%, as compared to 8% in flume Test 2).

The smaller percentages of bitumen which floated or adhered to the flume tank walls during flume Test 3 (as compared to flume Test 2), were offset by the higher mass of bitumen that remained in suspension (3% *versus* 1%) and the bitumen which had sunk (i.e., the 'balls' on the bottom of the tank; Section 10.3.1). The lower amount of bitumen which remained in suspension in Test 2 could be due to a greater frequency of particle collisions with one another and a greater force of bitumen particle collision with the flume tank walls. Both processes would tend to remove bitumen from the water column.

Table 10-9. Results of mass balance for bitumen at conclusion of flume Test 3.

	Mass of Bitumen (g)	Percent of Bitumen
Initially Spilled (g)	10366	---
Floating (g)[1]	8000	77.2
Sunk (g)[2]	2004	19.3
Bathtub Ring (g)[3]	29	0.3
Suspended (g)[4]	326	3.1
Dissolved (g)[5]	6	0.1

[1] Weight of air-dried floating bitumen (corrected for water weight).
[2] Determined by difference.
[3] Weight of bitumen adhered to inside and outside liner over 1/5th of tank circumference x 5.
[4] Average TPH_{total} – average $TPH_{dissolved}$ x 4000L
[5] Average $TPH_{dissolved}$ x 4000L

The greatest surprise/disparity between the two brackish water tests was the formation of numerous negatively-buoyant bitumen 'balls' which were observed to be rolling around the bottom of the tank at the completion of flume Test 3 (Section 10.3.1). They had not been noticed prior to their observation after 72 hours, so it is difficult to determine exactly when they had formed. It was determined that the sunk bitumen balls comprised approximately 19% of the bitumen spilled in Test 3 (Table 10-9). No sunk bitumen was observed in Test 2 (Table 10-6). The occurrence of the sunk bitumen in Test 3's brackish water is surprising given density considerations and could not have been predicted based upon the benchtop results. For example, the only brackish water benchtop tests in which bitumen was observed to have sunk also included suspended mineral matter (which was presumed to have caused the bitumen to settle; Section 7.2). The only brackish water benchtop test performed with no mineral matter (Test 23') produced no sunk bitumen (Table 7-1). Therefore, the formation of the sunk bitumen balls (19% of the bitumen spilled) in Test 3 was unique to the flume tank conditions of this spill.

10.4 Test 4 – A Very High Energy, Saltwater Spill - Suspended Particulate Matter

10.4.1 General Observations

The conditions for Test 4 were consistent with those listed in Table 9-1 with the exception of the lower initial Orimulsion concentration (3550 mg/L instead of 9000 mg/L; see Section 10.1.1). Test 4's conditions were similar to the conditions of the saltwater tests conducted by Ostazeski et al. (1997; 1998). These earlier flume tests had employed the wave plunger (operated at 50 cpm/12 cm stroke) and wind vanes (operated at 80 rpm). Flume Test 4 used the same wave plunger conditions but a slightly higher wind vane speed (115 rpm *versus* 80 rpm). The increased wind speed was determined to be necessary in order to keep any kaolinite in suspension. At only 80 rpm, nearly all of the kaolinite particles settled to the bottom of the tank. Therefore, in order to assess the effect of kaolinite/clay in suspension on spilled Orimulsion, the energy in the tank needed to be increased appropriately. Of all the flume tests conducted by Battelle to date, the energy within the tank for flume Test 4 (and Test 5; see below) were the highest ever used. The pH of the seawater used in Test 4 was determined to be 7.8.

The objective of flume Test 4 was to determine the effect that kaolinite in suspension might have on the bitumen in saltwater. In particular, it was of interest whether bitumen-kaolinite particles would form and settle due to their higher, combined density (Table 9-1). Kaolinite clay was introduced to the flume tank two hours prior to the spill of the Orimulsion. The kaolinite was allowed to distribute itself throughout the tank. The presence of kaolinite in the water gave the water a milky color. Visual observations indicated that, in spite of the high energy conditions, most of the kaolinite had sunk to the bottom of the tank. Water samples collected just prior to the Orimulsion spill were analyzed to determine the concentration of total suspended solids (TSS) according to a modified EPA Method 160.2 (Battelle SOP 5-053-02). The TSS of the water was determined to be 101.0 mg/L (average of three replicates; $\sigma = 7.9$ mg/L) indicating that only 37% of the kaolinite added (1.08 kg or 270 mg/L)[7] had remained in suspension. The water contained as much suspended kaolinite as it could.

During Test 4, floating bitumen particles formed and bitumen began adhering to the flume tank walls within the first minute of the spill. Energy within the system was dampened as numerous surface patties grew and began sticking to the walls. After 15 minutes a single, large surface patty had formed and a significant 'bathtub' ring (~20 cm thick) had formed on both the inner and outer walls of the flume tank. After 30 minutes the floating bitumen patty that had formed had grown to about 0.25 m^2. A large number of smaller floating lumps were formed or shed from the flume tank walls within the first hour of the Test. Thus, one hour after the spill there were a fair number of floating lumps and the single, larger floating patty (now about 0.5 m^2).

Sometime between 1 and 2 hours after the spill, the large floating patty that had formed earlier had essentially broken apart. The result was the formation of a large number (hundreds) of smaller, ovoid- to disk-shaped 'tar balls.' The majority of the tar balls were approximately 2 to 6 cm in their largest dimension. These tar balls were positively-buoyant and tended to not stick to one another or to the flume tank walls. The surface of the tar balls was smooth and when handled, they did not tend to stick so long as their surface was water-wet; i.e., as the tar ball surface dried they became increasingly sticky. Also, if a tar ball was squeezed between one's fingers its interior was extremely sticky. Thus, the tar balls tended to have a unique surface property, perhaps invoked by the kaolinite. Remember, earlier high energy, saltwater Orimulsion flume tests without kaolinite had resulted in the formation of a single, large floating patty (Ostazeski et al., 1997; 1998). Due to the need to keep the kaolinite in suspension, the energy during flume Test 4 was slightly higher than had been used by Ostazeski et al. Thus, the formation of the tar balls could be related to (1) the presence of the clay and/or (2) the slightly higher energy conditions used in Test 4.

The hundreds of positively buoyant, tar balls persisted (and did not coalescence) throughout the remaining 70 hours of the test.

It was difficult to visually determine the effect of the clay due to the opaque character of the water column early in the test and the milky color of the water later as the bitumen was removed from the water column. However, near the end of the test (when most bitumen was either stuck to the flume tank walls or present as floating tar balls) the water was still milky in color, suggesting some kaolinite was still in suspension.

Upon turning off the energy (wind and plunger) after 72 hours, the tar balls quickly rose to the surface demonstrating their positively buoyant character. All of these tar balls were skimmed from the surface and included in the 'float' fraction. Notably, as the tar balls floated at the surface their upper

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[7] The target concentration of 270 mg/L is based upon the average Mississippi River delta TSS values (Appendix I). Naturally, not all of the natural TSS is mineral matter.

surfaces became exposed to the air and became drier. As they dried the upper surface became increasingly sticky indicating that the non-sticky character of the tar balls during the test was due to their surfaces having remained water-wet. Once the surfaces dried, the tar balls began to stick to one another. As they coalesced, they remained positively buoyant. Thus, if there was any kaolinite incorporated into the floating tar balls, it was not present in high enough concentrations to cause them to settle through the water column.

As the tank was being drained, and one could see the tank bottom more clearly, it was apparent that some small tar balls were also present on the bottom of the tank. These tar balls were generally smaller than those observed to have floated. One would suppose that these 'settling' tar balls contained enough kaolinite (with its higher density) to increase their density sufficiently enough to cause their settling through the water column. Notably, a significant amount of kaolinite, still whitish in color, was observed on the bottom of the tank as the tank was drained. Much of this was undoubtedly there from the start of the test (remember 63% of the kaolinite introduced did not remain suspended), and another large proportion sunk shortly after the test had concluded (after turning off wind vane/plunger but prior to draining).

10.4.2 Bitumen Particle Size

The results obtained from particle size measurements obtained during Test 4 are shown in Table 10-10. The values at t=0 for bitumen represent those of the fresh Orimulsion spilled during this test. The t=0 values for the kaolinite introduced into the tank prior to the spill are also reported; these averaged around 16.6 microns in size but were represented by a bi-modal population particles ranging between about 0.5 and 70.0 microns with maxima around 2 and 25 microns. The introduction of the kaolinite mineral particles into the water column may have had some effect on the particle size measurements made in the course of the test. However, considering the overall low concentration of kaolinite in suspension (45.4 mg/L) as compared to bitumen (2600 mg/L), the effect which individual kaolinite particles had on individual or coalesced bitumen particles is considered minimal. All of the water samples were collected from the middle of the water column in the tank, approximately 35 cm deep.

The D[4,3] data indicate that a marked coalescence of suspended bitumen particles occurred under the Test 4 conditions. It is assumed that the coalescence observed is due to the growth of bitumen-bitumen particles as well as, bitumen-kaolinite particles. The apparent coalescence of bitumen particles in saltwater was anticipated based upon the results of the saltwater benchtop studies (Section 6.2.2.4 and Fig. 6-3) and previous saltwater flume tests (Ostazeski et al., 1997; 1998).

The rate of particle growth during flume Test 4 was visually observed to occur almost immediately following the spill (Section 10.4.1) and this rapid growth is evident in the particle size data (Table 10-10). The rate of particle growth is demonstrated by the curve shown in Fig. 10-4. Within only 15 minutes the bitumen particles in suspension increased in diameter to approximately ~55 microns. Continued particle growth was observed for the first six hours of the test until the maximum D[4,3] diameter was observed to be around 137 microns. After six hours the average particle size appears to decrease. This, however, is believed to be, at least in part, due to the formation of particles larger than 600 microns, the maximum particles measurable by the laser diffraction method employed (Appendix I). Thus, average particle data after the first six hours of the test are misleading.

Table 10-10. Particle size (D[4,3] in microns) determined from water samples collected during flume Test 4. All samples collected from mid-water depth ~ 35 cm deep.

	Flume Test #4			
	Rep 1	Rep 2	Rep 3	Avg
t=0 (kaolinite)	13.3	20.5	15.9	16.6
t=0 (bitumen)	23.2	23.1	NA	23.2
t=15min	37.9	52.8	74.5	55.0
t-30min	64.7	55.5	73.9	64.7
t=1hr	88.8	125.2	78.6	97.5
t=2hr	104.1	128.5	114.4	115.7
t=4hr	122.7	104.0	166.0	130.9
t=6hr	156.8	90.1	163.0	136.6
t=12hr	124.4	102.9	133.5	120.3
t=24hr	46.2	60.4	179.5	95.4
t=48hr	38.3	52.7	46.6	45.8
t=72hr	84.7	55.9	90.1	76.9

NA – not analyzed

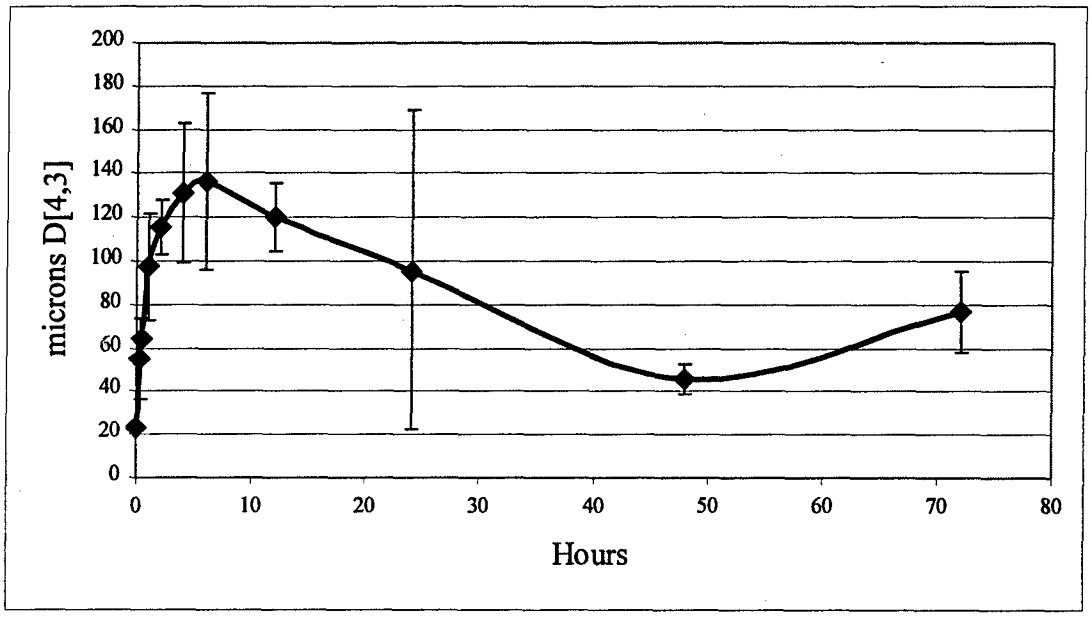

Figure 10-4. Particle growth trend observed during flume Test 4 – high energy, saltwater. Brackets reflect one standard deviation of the triplicate measurements (Table 10-10). Data beyond 6 hours are misleading, see text for description.

Unfortunately, any attempt to compare the flume Test 4 particle size results to those formerly available for the saltwater test conducted by Ostazeski et al. (1998) is confounded by the different focussing lenses used in acquiring the particle size data in both studies. The Ostazeski et al. dataset was acquired using the 100 mm focussing lens, which had a maximum measurable particle diameter of only 180 microns. Thus, particle larger than 180 microns were not included in the average D[4,3] values reported by Ostazeski et al. (1998).

10.4.3 Total Hydrocarbons and PAH

The results of the total petroleum hydrocarbon analysis for filtered and unfiltered water samples collected during Test 4 are shown in Table 10-11. Total TPH concentrations in the water were quickly reduced from the initial levels. The concentration of bitumen in the 4000 L flume tank was initially around 2600 mg/L (73% of Orimulsion spilled). However, within 1 hour of the spill the concentration of bitumen in suspension had been reduced to only 494 mg/L, indicating that most (~81%) of bitumen was no longer suspended in the water column. Visual observations had indicated that a significant amount of bitumen was adhered to the flume tank walls or occurred as floating lumps and tar balls near the surface within an hour of the spill (Section 10.4.1), which would explain the rapid loss of bitumen from the water column. The reduction in the concentration of TPH_{total} in suspension continued throughout the remainder of the test and after 72 hours, an average of only 183 mg/L of bitumen (~7% of the original bitumen spilled) remained in suspension (Table 10-11). This result is consistent with the visual observation that the water column had become increasingly clear.

Table 10-11. Concentrations of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in unfiltered (total) and filtered (dissolved) water samples collected during flume Test 4.

TIME (hrs)	TPH(total) (mg/L)	TPH(dissolved) (mg/L)	PAH (total) (ug/L)	PAH (dissolved) (ug/L)
1	493.98	1.36	1561.5	1.7
2	443.68	NA	NA	NA
4	382.93	NA	NA	NA
6	333.33	NA	NA	NA
12	235.63	NA	NA	NA
24	231.82	1.36	732.4	2.3
48	222.47	NA	NA	NA
72Rep1(15cm)	165.12	NA	NA	NA
72Rep2(15cm)	127.27	NA	NA	NA
72Rep3(15cm)	250.00	NA	NA	NA
72Rep1(35cm)	179.31	1.43	NA	NA
72Rep2(35cm)	221.69	1.76	NA	NA
72Rep3(35cm)	202.38	1.66	610.7	1.9
72Rep1(55cm)	152.94	NA	NA	NA
72Rep2(55cm)	170.45	NA	NA	NA
72Rep3(55cm)	174.42	NA	NA	NA

NA – not analyzed

The rate of removal of bitumen (as measured by TPH_{total}) from the water column under the high energy saltwater conditions of flume Test 4 was higher than in either of the brackish water flume tests (Fig. 10-3). This would be expected given the benchtop results which had indicated that high energy was a critical factor in removing bitumen from suspension (Table 6-6). Undoubtedly, the use of the wave plunger, in combination with high wind vane speed, in flume Test 4 caused a greater frequency of particle collisions with one another and with the flume tank walls. The high salinity, and its apparent detrimental effect on Orimulsion's surfactant effectiveness, allowed coalescence or sticking of the colliding particles, thus promoting their removal from the water column.

As observed during flume Tests 2 and 3, the concentration of PAH_{total} in the water was markedly decreased over the course of flume Test 4 (Table 10-11). This is consistent with the removal of bitumen from the water column. The concentrations of $TPH_{dissolved}$ and $PAH_{dissolved}$ were nominal throughout the test.

10.4.4 Mass Balance

The mass balance data obtained at the completion (72 hours) from Test 4 are shown in Table 10-12. These results are consistent with the visual observations made in the course of the test (Section 10.4.1). For example, most (~ 68%) of the bitumen ended up in the hundreds of floating tar balls which had formed within two hours of the spill. The mass of floating bitumen in flume Test 4 was lower than had been observed in either of the brackish water flume tests (Tables 10-6 and 10-9; 90% and 77%, respectively). This was, in part, due to the greater percentage of bitumen that became adhered to the flume tank walls in Test 4, presumably due to the higher energy.

Table 10-12. Results of mass balance for bitumen at conclusion of flume Test 4 (high energy, saltwater and clay).

	Mass of Bitumen (g)	Percent of Bitumen
Initially Spilled (g)	10366	---
Floating (g)[1]	7030	67.8
Sunk (g)[2]	1188	11.5
Bathtub Ring (g)[3]	1407	13.6
Suspended (g)[4]	734	7.1
Dissolved (g)[5]	6	0.1

[1] Weight of air-dried floating bitumen (corrected for water weight).
[2] Determined by difference.
[3] Weight of bitumen adhered to inside and outside liner over 1/5th of tank circumference x 5.
[4] Average TPH_{total} – average $TPH_{dissolved}$ x 4000L
[5] Average $TPH_{dissolved}$ x 4000L

It is interesting that nearly twice as much bitumen remained suspended in Test 4 (saltwater) as compared to the brackish water flume tests (Tables 10-6 and 10-9). Considering the higher density of saltwater (as compared to brackish water), which should have promoted greater buoyancy in suspended bitumen, the greater percentage of suspended bitumen in flume Test 4 must be due to either (1) the higher turbulent energy conditions in flume Test 4 or (2) the presence of kaolinite (e.g., some kaolinite-bitumen particles may be less buoyant than bitumen particles alone).

The addition of the kaolinite to the water in flume Test 4 was intended to test its effect on the mass balance. In particular, whether or not the formation of kaolinite-bitumen particles would cause some bitumen to settle through the water column in spite of the density/buoyancy considerations. The results of the mass balance exercise and the visual observations made in the course of draining the tank, clearly indicated that some bitumen has sunk to the bottom of the flume tank (~11.5% of the bitumen spilled; Table 10-12). The sunk bitumen was predominantly comprised of small tar balls (1-3 cm diameter). It is presumed that these tar balls had incorporated enough kaolinite into their 'bodies' so as to increase their density above that of seawater and thereby causing them to settle through the water column. Similar phenomenon was presumed to have occurred in several benchtop experiments (e.g., Tests 1 and 16'; Table 7-1). Whether the collision of bitumen and mineral matter occurred in the water column (i.e., collisions between suspended particles) or at/near the bottom of the tank (i.e., collisions between settled kaolinite and passing bitumen) is unknown. In any case the mass balance results suggest that some bitumen spilled into high energy, water containing suspended mineral matter may collide with the mineral matter to form neutrally- or negatively-buoyant bitumen-mineral particles.

10.5 Test 5 – A Very High Energy, Freshwater Spill – Suspended Particulate Matter

10.5.1 General Observations

The conditions for Test 5 were consistent with those listed in Table 9-1 with the exception of the lower initial Orimulsion concentration (3550 mg/L instead of 9000 mg/L; see Section 10.1.1). Test 5's conditions were similar to those of the freshwater test conducted by Ostazeski et al. (1997; 1998), the only differences being the presence of kaolinite and the higher wind vane speed used in Test 5 (115 rpm versus 80 rpm). (The latter was necessary in order to keep the kaolinite in suspension; see Section 10.4.1.) The pH of the freshwater used in Test 5 was determined to be 6.9. This was slightly lower than the freshwater without kaolinite (Section 10.1.1), suggesting that the presence of kaolinite in the water had some influence on its pH.

The objective of flume Test 5 was to determine the influence of suspended mineral matter (kaolinite) on the bitumen spilled in freshwater. In the absence of mineral matter, under high energy, freshwater conditions bitumen is expected to remain dispersed (Ostazeski et al., 1997; 1998). However, some high energy, freshwater benchtop experiments involving kaolinite resulted in significant settling of bitumen (e.g., benchtop Tests 7, 4', and 8'). Therefore, a meso-scale test of this phenomenon was necessary.

Kaolinite clay was introduced to the flume tank two hours prior to the spill of the Orimulsion. The kaolinite was allowed to distribute itself throughout the tank. Visual observations indicated that some of the kaolinite had sunk to the bottom of the tank in spite of the significant energy in the water. As was the case in flume Test 4, the presence of kaolinite in the water gave the water a milky color. A sample of water collected just prior to the Orimulsion spill was measured for the concentration of total suspended solids (TSS) according to a modified EPA Method 160.2. The TSS of the water was determined to be 45.4 mg/L (average of three replicates; $\sigma = 3.3$ mg/L) thus, only about 17% of the total kaolinite added (1.08 kg or 270 mg/L) remained in suspension. The reason for the higher the amount of TSS (kaolinite) in suspension prior to the start of Test 4 (saltwater; Section 10.4.1) than had occurred in Test 5 (freshwater), under the same energy conditions, can only be attributed to the higher density of the saltwater.

With the high energy conditions of this test, a bathtub ring formed very quickly following the spill. Most of the bitumen forming the bathtub ring appeared to have been blown off the wave crests. In spite of the presumed maintenance of the surfactant's effectiveness under freshwater conditions, the bitumen particles readily stuck to the flume tank walls, mostly above the water line. We envision the cause for this to be the combination of high energy conditions and the (relative) dryness of the upper flume tank walls. Recall, a small bathtub ring had formed in flume Test 1 (Section 10.1.1). Thus, it is not surprising that a larger ring formed during flume Test 5.

Within the first 2 hours the bathtub ring, mostly along the outer flume tank wall, was nearly 30 cm in height. Globules of bitumen were forming and breaking off of the ring. Eventually these globules collided to form a single floating patty. The patty grew to approximately 0.25 m^2 within over the first 24 hours of the test. It remained this same approximate size for the remainder of the 72 hour test.

The formation of a floating bitumen patty in this freshwater test might be explained as a secondary product of the bathtub ring, which we believe was formed due to the high energy used in the test. Recall the same phenomenon had been observed on a smaller scale in flume Test 1; Section 10.1.1. Furthermore, it will be recalled that two high energy, freshwater benchtop experiments also produced a considerable amount of floating bitumen, presumably by this same mechanism (Trials 7' and 11; Section 7.0). A component of this mechanism must include a factor(s) reducing the effectiveness of the surfactant. Recall, it had been previously understood that a lack of particle growth in freshwater indicated that Orimulsion's surfactant remained essentially intact in freshwater (Ostazeski et al., 1997; 1998; Section 6.2.2.3). It makes sense that the high energy of flume Test 5 (even higher than used by Ostazeski et al.) led to considerable amount of bitumen being cast against the flume tank walls above the water line where, due to the high wind speeds, it dried and became sticky. Over time, this bitumen grew into lumps, which were eventually eroded from the flume tank walls. What is perhaps more anomalous is the fact that the resulting bitumen lumps floated in freshwater (where one would predict them to have sunk). A reasonable explanation for this phenomenon is that air may be incorporated into the lumps of bitumen as they formed on the flume walls. The inclusion of air in the bitumen lumps, and eventually the patty, could invoke a positive buoyancy, in spite of the fact that bitumen is denser than freshwater.

In addition to the patty and the bathtub ring, a large amount of bitumen remained in suspension in Test 5. Thus, the water column remained opaque throughout the test. As a result, the effect of kaolinite on the bitumen in the water column was difficult to determine visually. The water column's opaqueness and the patty remained visibly unchanged after the first 24 hours of the test.

After the 72 hour test was completed and the final samples were collected and the floating patty was removed for drying and weighing, the wind/wave energy was left off for an additional 72 hours. The intention was to determine if the bitumen and kaolinite in suspension after 72 hours would settle through the water column. After 72 hours there was still no visible change in the water, i.e., it was still opaque with suspended bitumen. Recall, that the settling of bitumen in flume Test 1 had been very slow even under static conditions. Therefore, it is not too surprising to have not observed obvious settling of the bitumen out of the water column. Although it couldn't be observed, we suspect that any suspended kaolinite (with its higher density) did settle to the bottom of the tank. Thus, as flume Test 1 had demonstrated (Section 10.1.1), bitumen does not settle through the water column quickly in static freshwater.

10.5.2 Bitumen Particle Size

The results obtained from particle size measurements obtained during Test 5 are shown in Table 10-13. (See Appendix I for measurement method description.) The values at t=0 represent those of the fresh Orimulsion spilled during this test. The t=0 values for the kaolinite introduced into the tank prior to the spill are also reported; these averaged around 10.6 microns, slightly smaller than had been recorded prior to flume Test 4 (Table 10-10). It was evident that the kaolinite bi-modal population in the Test 5 water samples was shifted toward the 2 micron maxima, resulting in the lower average diameter. The reason for the disparity between the kaolinite populations in Tests 4 and 5 is unknown since the kaolinite was identical. Regardless, considering the overall low concentration of kaolinite in suspension (45.4 mg/L) as compared to bitumen (2600 mg/L), the effect, which the kaolinite particles had on bitumen particles, is considered minimal. All of the water samples were collected from the middle of the water column in the tank, approximately 35 cm deep.

Table 10-13. Particle size (D[4,3] in microns) determined from water samples collected during flume Test 5. All samples collected from mid-water depth ~ 35 cm deep.

	Flume Test #5			
	Rep 1	Rep 2	Rep 3	Avg
t=0 (kaolinite)	10.7	10.7	10.6	10.6
t=0 (bitumen)	22.7	22.5	22.5	22.6
t=15min	22.7	22.7	22.7	22.7
t-30min	23.0	22.0	21.8	22.3
t=1hr	22.6	21.6	22.0	22.1
t=2hr	22.6	22.9	21.0	22.2
t=4hr	22.3	22.4	22.6	22.4
t=6hr	23.3	22.2	22.7	22.7
t=12hr	21.4	28.4	24.1	24.6
t=24hr	26.8	27.7	25.0	26.5
t=48hr	27.3	25.1	26.8	26.4
t=72hr	23.2	24.1	23.6	23.6

It is apparent from the profiles of the particle distributions (not shown) that the bi-model character of the bitumen in suspension over the course of this test was typical of fresh Orimulsion (Fig. 3-1). There was a slight shift toward higher particle sizes after 24 hours, driven mostly by the formation of some particles (bitumen-bitumen or bitumen-kaolinite ?) in the 80 to 110 micron range. These particles increased the average D[4,3] slightly to around 26 microns. Overall, there was no significant particle growth observed under the Test 5 conditions (i.e., high energy, freshwater with kaolinite). This conclusion is somewhat inconsistent with the observations made in the course of the two of the three benchtop experiments conducted in high energy, freshwater in the presence of clay. Benchtop test 7 had showed no particle growth (Fig. 5-1) while benchtop tests 4' and 8' had showed slight growth (up to 50 microns; Fig. 6-1).

10.5.3 Total Hydrocarbons and PAH

The results of the total petroleum hydrocarbon analysis for filtered and unfiltered water samples collected during Test 5 are shown in Table 10-14. Total TPH concentration in the water was only slightly reduced from the initial levels of 2600 mg/L (based on the amount of Orimulsion spilled) to 2382 mg/L after only 1 hour. Visual observations confirmed that most bitumen was dispersed throughout the water column but that some bitumen was quickly adhered to the flume tank walls (Section 10.5.1). The bitumen loss to the walls, and subsequently to the floating patty, would explain the reduction in TPH_{total} in the water column, which occurred only gradually over the first 12 hours of the test (Table 10-14). The TPHtotal concentration was reduced markedly after the first 24 hours indicating a more rapid loss of bitumen from the water column. After 72 hours, only 1417 mg/L

TPH_{total} (~55%; on average) remained in suspension (Table 10-14). This result is consistent with the visual observation that the water column was still opaque due to the suspended bitumen.

Table 10-14. Concentrations of total petroleum by hydrocarbons and polycyclic aromatic hydrocarbons in unfiltered (total) and filtered (dissolved) water samples collected during flume Test 5.

TIME (hrs)	TPH(total) (mg/L)	TPH(dissolved) (mg/L)	PAH (total) (ug/L)	PAH (dissolved) (ug/L)
1	2381.72	1.91	6718.2	1.2
2	2396.74	NA	NA	NA
4	2144.44	NA	NA	NA
6	2135.87	NA	NA	NA
12	2134.41	NA	NA	NA
24	2122.34	2.12	2483.8	0.4
48	1552.69	NA	NA	NA
72Rep1(15cm)	1289.47	NA	NA	NA
72Rep2(15cm)	1364.13	NA	NA	NA
72Rep3(15cm)	1472.22	NA	NA	NA
72Rep1(35cm)	1366.48	3.25	273.87	0.5
72Rep2(35cm)	1381.11	3.19	NA	NA
72Rep3(35cm)	1385.96	2.62	NA	NA
72Rep1(55cm)	1467.74	NA	NA	NA
72Rep2(55cm)	1478.02	NA	NA	NA
72Rep3(55cm)	1548.94	NA	NA	NA

NA – not analyzed

The reason for the apparent increase in the rate of removal of bitumen from suspension after 24 hours (and again after 48 hours) is unknown. As will be demonstrated in the next Section, the loss is not due to any settling of bitumen to the bottom of the tank. Therefore, the increased rate of bitumen's removal from the water column after 24 and 48 hours must be due to its incorporation into the floating patty and/or the bathtub ring.

10.5.4 Mass Balance

The mass balance data obtained at the completion (72 hours) from Test 5 are shown in Table 10-15. These results are consistent with the visual observations made in the course of the test (Section 10.5.1). The majority of the bitumen (~55%) remained suspended throughout the test. This was consistent with the black, opaque water, which persisted throughout the test. The floating patty comprised about 35% of the initial bitumen spilled. As described above, the formation of patty was believed to have resulted as a secondary product of the significant bathtub ring that had formed early in the test. The final bathtub ring (~12%) was smaller, only slightly however, than was formed under the same energy conditions in saltwater (flume Test 4).

Table 10-15. Results of mass balance for bitumen at conclusion of flume Test 5 (high energy, freshwater with clay).

	Mass of Bitumen (g)	Percent of Bitumen
Initially Spilled (g)	10366	
Floating (g)[1]	3630	35.0
Sunk (g)[2]	-157	0
Bathtub Ring (g)[3]	1212	11.7
Suspended (g)[4]	5668	54.7
Dissolved (g)[5]	12	0.1

[1] Weight of air-dried floating bitumen (corrected for water weight).
[2] Determined by difference.
[3] Weight of bitumen adhered to inside and outside liner over 1/5th of tank circumference x 5.
[4] Average TPH_{total} – average $TPH_{dissolved}$ x 4000L
[5] Average $TPH_{dissolved}$ x 4000L

The formation of both a sizable bathtub ring and floating patty under freshwater conditions were somewhat surprising but not unprecedented. For example, two of the benchtop experiments conducted under high energy freshwater conditions resulted in formation of significant bathtub rings and floating bitumen material (e.g., Tests 11 and 7'; Table 7-1). These results had been considered anomalous and due primarily to the effects of the benchtop glass walls (Section 7.0). The same process has occurred in flume Test 1, but to a lesser degree (Section 10.1). The higher energy in Test 5 was expected to keep a relatively high concentration of bitumen in suspension. This was borne out by the mass balance results.

The addition of the kaolinite to the water in flume Test 5 was intended to test its effect on the mass balance. Would the kaolinite combine with bitumen, causing some bitumen to settle through the water column (Table 9-1)? This process was believed to have occurred in several high energy, freshwater benchtop experiments where clay was present (e.g., Tests 7, 4', and 8'). However, according to the mass balance results from flume Test 5 (Table 10-15), there was no bitumen which was not accommodated for in the suspended, floating, or bathtub ring. Thus, there was no significant impact resulting from the kaolinite. An explanation for the lack of formation of kaolinite-bitumen particles may lie in the decreased frequency of collisions resulting from the lower concentrations of both kaolinite and bitumen in flume Test 5 (as compared to the benchtop studies).

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11. SYNTHESIS OF BENCHTOP AND FLUME STUDIES

Synthesis of the large volume of data obtained in the course of this study is a difficult task. As is common in nature, there is seldom a phenomenon in which one can be definitive as to the expected result under all circumstances. The complexity surrounding the behavior(s) of Orimulsion spilled on water is no exception. Exceptions to "rules" surrounding (1) the coalescence of bitumen and (2) the "Orimulsion budget" seem to occur in every instance. Therefore, one is forced to generalize in order to achieve a reasonable understanding of the fundamental processes at work and the relative importance of the independent variables evaluated in determining the gross behavior of spilled Orimulsion.

This understanding allows some predictions to be made as to what Orimulsion will do under a variety of 'real world' spill conditions. Woven into any predictions must be an acknowledgement of the fundamental differences between what was observed in the laboratory and what might be observed in the 'real world.' As mentioned throughout the results presented, the most critical of these differences is the confined nature of the benchtop and flume experiments. Laboratory experiments in confined vessels (regardless of whether they are 3L or 4000L) cannot truly reflect behavior in an open water 'real world' spill. Spilling Orimulsion in a confined container with a constant volume of water will be greatly influenced by the effects of the container walls and the prohibition of any dispersive processes (after the initial minute(s) of the experiment). In the case of predicting Orimulsion's behavior, the balance between dispersion and coalescence processes that would exist in the 'real world' is abnormally skewed toward the coalescence processes (since dispersion is eliminated in the laboratory vessels). In the 'real world' increased energy in the receiving water would tend to promote dispersion yet in the confines of the benchtop vessels used herein, increased energy tends to promote collisions of bitumen particles with either suspended mineral matter, other bitumen particles, or with the container walls. Thus, projecting the results from our laboratory benchtop experiments to the 'real world' must be done cautiously. This is done in Sections 11.1 and 11.2.

11.1 Coalescence of Bitumen (Particle Growth)

An important phenomenon related to the behavior of Orimulsion spilled on water is the propensity of the bitumen particles to coalesce. Understanding this phenomenon is relevant to its physical recovery and to modeling the behavior of dispersed bitumen particles over time. Experience indicates that bitumen particle growth has two prerequisites, namely:

(1) the reduced effectiveness of Orimulsion's surfactant component and
(2) frequency and energy of collisions between bitumen particles.

Without both of these, no particle growth would be anticipated.

11.1.1 Role of Salinity and its Influence on Surfactant Effectiveness

Reduced effectiveness of the surfactant phase of Orimulsion requires changes in the bitumen particles' surface chemistry. These changes were consistently reflected by the bitumen particle growth, which took place in the saltwater (35 ‰) and brackish (17.5 ‰) water experiments performed at both the benchtop- and meso-scales. (Just as important in forming this conclusion was the fact that bitumen particle growth was consistently not observed to occur in the freshwater (0‰) experiments conducted.) This result is not surprising to surface chemists who know that the non-ionic surfactants, such as the alcohol ethoxylate surfactant present in Orimulsion 400, will have a reduced effectiveness as salinity increases (i.e., the hydrophobic/lipophobic balance is decreased). The mechanism(s) by which dissolved ions in water reduce this effectiveness are beyond this discussion. Nonetheless, the results of the benchtop and flume experiments are convincing as to salinity's role in particle growth.

Intuitively speaking, one might expect that particle growth would be greatest when salinity is greatest. However, our benchtop experiments indicated that particle growth was statistically greatest under brackish water conditions, rather than under saltwater conditions (Section 6.2.2). A similar result was obtained in the flume tests conducted in that the particle growth during the brackish water flume Tests 2 and 3 was slightly greater than observed during the saltwater flume Test 4. The slightly greater particle growth observed in our brackish water benchtop and flume experiments is believed to be the result of a longer residency time for suspended bitumen particles in brackish water than in saltwater (due to a smaller density disparity in brackish water causing smaller buoyancy forces). The reasoning is that the longer bitumen particles are in suspension, the greater the chances for particle collisions and coalescence and the greater the chances for us sampling the particles and measuring them. That is, in saltwater the larger particles are more quickly buoyed up toward the top of the water column (e.g., sometimes forming tar balls or floating patties) where they are not measured. Thus, the observation of larger suspended bitumen particles in brackish water may simply be an artifact of the sampling techniques.

Based on the benchtop and flume experiments, it is safe to assume that bitumen particle coalescence occurs at salinities above 17.5 $^{o}/_{oo}$. The only exception to this may be in instances of extremely high Orimulsion concentrations (~ 50,000 mg/L) where the concentration of surfactant is sufficiently high (i.e., the surfactant is not diluted enough) that it remains effective in spite of a high salinity (Section 5.3.1.4). A lack of coalescence was also observed at 20,000 mg/L in the benchtop experiments of Brown et al. (1995). Such high concentrations of Orimulsion would probably not exist in a 'real world' situation except for a short time in the immediate vicinity of the release. Thus, the question, which remains unanswered in our experiments, is the degree of surfactant effectiveness/particle coalescence at salinities between brackish water (17.5 $^{o}/_{oo}$) and freshwater (0 $^{o}/_{oo}$).

The rate of bitumen particle growth following an Orimulsion spill in brackish water and saltwater was observed to be nearly instantaneous. The best available data obtained surrounding the rate of particle growth was obtained in the course of the flume tests (Section 10).[8] For ease of comparison, the mean particle diameter trends for suspended particles, over the first two hours following the spill, for the brackish and saltwater flume tests conducted in this study are shown in Fig. 11-1. The comparable saltwater results from Ostazeski et al. (1998) are also shown. (These data have been limited to the first half-hour since they were collected using a different focussing lens than was used in the current study. Thus, all of the data shown are unaffected by the limitations of the laser diffraction measurement method.)

Flume Tests 2 and 3 (brackish water) exhibit slightly greater particle growth over the first two hours of the experiments than Test 4 (saltwater). This would be consistent with the discussion above involving the longer residency time for particles within a brackish water column. Notably, flume Test 3 (low energy, brackish) produced the largest suspended bitumen particles in the first half hour following the spill. This could be due to less frequent collisions with the walls (as may have occurred in Test 2's higher energy) which allowed greater frequency of collisions between particles (see below).

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[8] The benchtop experimental data, with the first sample having been collected 1 hour after the spill, simply did not provide the resolution necessary to see the particle size changes within the first hours of the spill.

11.1.2 Role of Water Energy and its Influence on Bitumen Particle Collisions

In instances of reduced surfactant effectiveness, the collisions between dispersed bitumen particles in the water column is the second prerequisite to bitumen particle growth. The primary control on the frequency and energy of collisions is undoubtedly the degree of energy in the water. This was borne out in the benchtop studies, which statistically demonstrated the importance of energy in particle growth (Section 6.2.2; Table 6-3). Secondary controls undoubtedly include Orimulsion concentration and salinity (see below).

Intuitively speaking, in the confined vessel experiments a higher water energy should increase the frequency and energy of collisions between dispersed bitumen particles. However, what was observed in the benchtop studies was that at too high an energy, collisions between bitumen particles and the vessel walls become the dominant type of collision (rather than collisions between particles).

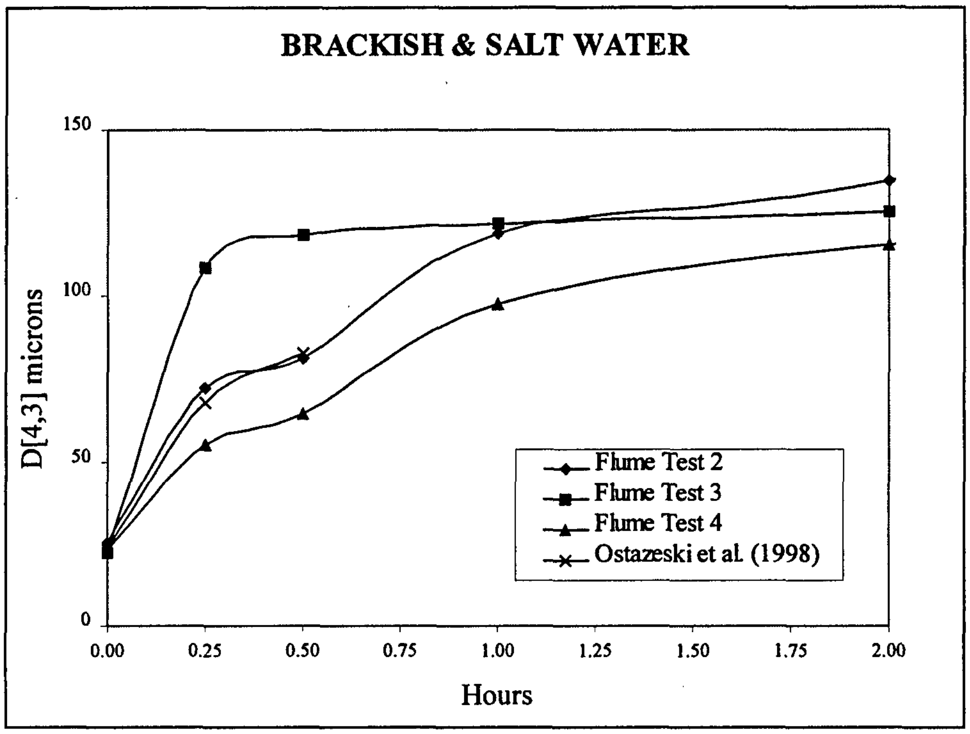

Figure 11-1. Mean bitumen particle diameters (D[4,3]) shortly after Orimulsion spilled into brackish and saltwater. (Tests 2 & 3 = brackish; Tests 4 and Ostazeski et al. = saltwater).

As a result, particle growth at the benchtop scale was statistically greatest at intermediate energy conditions (Table 6-3).

In the flume tests, where the influence of the flume tank walls on particle collisions should be reduced (relative to the benchtop experiments) due to the larger volume of water, the role of energy was demonstrated in the comparison of the brackish water flume Tests 2 and 3. These tests were conducted at high and low energy, respectively (Sections 10.2 and 10.3). Within the first hour of these spills, higher energy in the water produced smaller particles in suspension (Test 2) than the lower energy did (Test 3; Fig. 11-1). Thus, as was demonstrated at the benchtop scale, less particle growth occurred at the higher energy. Presumably, at the higher energy (Test 2) a greater frequency of collisions between bitumen particles and the flume tank walls occurred and thus, fewer bitumen-bitumen collisions within the water column occurred. Thus, even at the flume scale (4000L) the walls undoubtedly influence the particle growth phenomenon.

These results demonstrate that the role of receiving water energy in bitumen particle growth is obviously complex. Much of the complexity stems from the effects of the container walls, which are an unavoidable consequence of any laboratory experiments (see discussion in Section 11.2). One must ask, *would more rapid particle growth occur at lower/intermediate energies than at higher energies if no container walls existed*? Imagine a 'real world' Orimulsion spill in the absence of any walls. In this situation it is reasonable to expect that a higher water energy would result in more rapid dispersion/ diffusion of suspended bitumen particles. Thus, the frequency of collisions between suspended bitumen particles would be rapidly reduced as one moved away from the source of the spill. Under lower energy conditions, the bitumen may tend to remain in a higher concentration longer and thereby, the potential for collisions between suspended particles would be greater. Under these two situations, the propensity for bitumen particle growth is probably greatest in the lower energy environments. Generally speaking, this is consistent with what was observed in the laboratory experiments (larger suspended particles in lower energy conditions than in higher energy conditions) but for a different reason.

Secondary factors influencing the frequency of particle collisions must include (1) the concentration of the bitumen in the water and (2) the salinity. Obviously, higher bitumen concentrations will promote more collisions. However, too many bitumen particles will lead to very rapid particle growth that will quickly remove particles from suspension. This was statistically demonstrated in the benchtop experiments in which the greatest particle growth occurred at intermediate Orimulsion concentrations (Table 6-2). Less obviously, salinity creates density-driven buoyancy effects which, for example in saltwater, will promote higher concentrations of bitumen near the surface (due to the positively buoyant bitumen). Higher concentrations must promote greater frequency of collisions. This is probably the cause behind the formation of floating tar balls or bitumen patties in most saltwater and brackish water experiments.

The growth of bitumen particles was, in some circumstances, influenced by the presence of additional suspended particles in the water column (namely, mineral matter). This influence is believed to have occurred due to the increase that these additional particles had on the overall frequency of particle collisions in total. Once again, at the benchtop scale the presence of an intermediate amount of suspended mineral matter yielded a higher degree of particle growth (Table 6-3). It is presumed that a suspended mineral matter load actually decreased the mean particle size of suspended bitumen due to the more rapid settling of any relatively dense mineral-bitumen particles (Section 6.2; Table 6-3). At the benchtop scale, the effect of suspended mineral matter on particle growth was statistically limited to the first hour following the spill. After that time, energy and salinity were the controlling parameters (Table 6-4).

At the flume scale, the effect of suspended mineral matter in the water on bitumen particle growth was indiscernible from the Ostazeski et al. (1998) flume tests conducted without mineral matter. In the saltwater flume test containing mineral matter (flume Test 4; Section 10.4), there was only a slightly lower rate of particle growth immediately following the spill (Fig. 11-1). In the freshwater flume test containing mineral matter (flume Test 5; Section 10.5) and not containing mineral matter (Ostazeski et al., 1998), there was no particle growth observed among suspended bitumen particles. Thus, the effect that suspended mineral matter may have on the particle size of suspended bitumen particle size seems minor in saltwater (or presumably brackish water) and non-existent in freshwater. However, any effects may go unnoticed since any bitumen-mineral particles may quickly settle out of the water column.

11.2 The Orimulsion Budget

Careful interpretation of the results obtained from the benchtop and flume studies performed have provided significant insight into the gross fate of Orimulsion, specifically the bitumen component of Orimulsion. This insight provides the basis for development of a response plan and anticipating the fate of bitumen in the event of an accidental Orimulsion spill under various conditions. In this section, the results of the benchtop and flume studies are synthesized to yield a cohesive interpretation/prediction of what Orimulsion will do when spilled. As noted above, the effects of the confined nature of the laboratory results must be incorporated into any predictions.

The mass balance data collected for the five 'compartments' namely, floated, settled, suspended, dissolved, and stuck to the sides of the vessels, provide the basis for the "Orimulsion budget" (Sections 6.2.4 and 10). As mentioned above, this laboratory-based budget provides significant insight into the fate of Orimulsion spilled in the 'real world.' However, given the experience gathered from and the complexities inherent in these laboratory experiments, one cannot help but think that the behavior of Orimulsion in the 'real world' might actually be more easily predicted than the behavior observed during the artificial spills conducted within the constrains of a laboratory container (even a 4000L flume tank!). The two principal factors driving the additional complexities in the laboratory-derived Orimulsion budget are:

(1) the presence of container vessel walls and

(2) the absence of an infinite (or, at least, very large) volume of water.

These factors combine to prohibit any dilution effect in the laboratory benchtop and flume experiments conducted. In the absence of any dilution effect we are forced to consider formation of the 'bathtub ring' and the secondary products it can produce (e.g., shed bitumen lumps that otherwise would not have formed). We are also forced to consider formation of a floating bitumen patty, which one might assume may not even form in the 'real world.' (That is, lateral dispersion of the bitumen would reduce the frequency of bitumen particle collisions to the point where no floating patty would ever form in the 'real world'). Thus in the synthesis which follows, the limitation of projecting the laboratory-derived Orimulsion budget into the real world requires caution.

11.2.1 Floating Bitumen

The formation of floating bitumen is an important phenomenon since its formation offers the greatest potential for (1) recovery of the spilled bitumen and (2) impact to shorelines. Our laboratory Orimulsion spills under numerous instances led to occurrence of floating bitumen in numerous forms, e.g., patties, tar balls, surface skins and discrete (<100 μm) particles. Ultimately, the primary factor controlling the presence of floating bitumen, regardless of its form or mass, is the density of the bitumen *versus* the density of the receiving water. The density of fresh Orimulsion was determined to be 1.0104 g/ml at 15°C (Table 3-1). Previous measurements of fresh Orimulsion density at different temperatures indicated that it was slightly denser at 0°C (1.0176 g/ml) and slightly less dense at 25°C (1.0048 g/ml; Ostazeski et al., 1998). If and how the density of spilled bitumen may change in the course of a spill is unknown since no density measurements on spilled bitumen have been conducted.

The density of the receiving water is a function of both temperature and salinity. Water temperature, however, was shown to have no statistical effect on the mass of floating bitumen formed during the screening phase benchtop experiments (Section 5.3.3.2). Therefore, it is more likely that the salinity of the receiving water plays the largest role in determining the mass of floating bitumen (and sunk bitumen, see Section 11.2.2).

The importance of salinity in determining the mass of floating bitumen following a spill was indicated by the benchtop experimental results. These consistently demonstrated that an interactive effect between salinity and energy determined the mass of bitumen, which ultimately floated (Section 6.2.4.2). Simply stated, a greater mass of bitumen ended up floating at higher salinities, i.e., so long as the energy wasn't too high (which had led to greater bathtub ring formation). In the absence of container walls, as would exist in nature, one could predict that the higher the salinity the greater amount of bitumen would be anticipated to float simply due to a higher density disparity between the bitumen and the water. The greater this disparity the greater are the density-driven buoyancy effects.

The mass balance results for the five flume tests conducted in this study are summarized in Table 11-1. These results confirm the role of salinity in effecting the percentage of spilled bitumen, which will float. As would be predicted, flume Test 1 (low energy, freshwater) saw virtually no bitumen float over the course of the test. What little bitumen did float was believed to be a secondary product derived from the bathtub ring (Section 10.1.1). Flume Test 5 (high energy, freshwater with clay) produced a significant floating bitumen patty, however, this too was believed to be a secondary product of the significant bathtub ring formed by the high energy of this experiment. In the absence of the flume tank walls, one has to expect that the bitumen would have dispersed rather than form the ring/patty.

Table 11-1. Summary of mass balance results for flume tests described in Section 10. Data are percentage of the spilled bitumen in each compartment after 72 hours.

	Spill Conditions	Floated on/near Surface	Settled to/toward Bottom	"Bathtub Ring"	Suspended in Water Column	Dissolved into Water
TEST 1	low to no energy, freshwater	0.2	65.5	0.0	34.3	0.0
TEST 2	high energy, brackish water	91.2	0.0	8.3	0.7	0.0
TEST 3	low energy, brackish water	77.2	19.3	0.3	3.1	0.1
TEST 4	very high energy saltwater	67.8	11.5	13.6	7.0	0.1
TEST 5	very high energy, freshwater	35.0	0.0	11.7	54.7	0.1

The two brackish water flume Tests (2 & 3) showed that most bitumen spilled ended up floating. These results clearly indicated that water with a salinity of 17.5 °/₀₀ is more dense than spilled bitumen, and therefore, the bitumen will be buoyant and ultimately float. The higher energy of Test 2 produced a greater bathtub ring and, presumably due to greater frequency and energy of bitumen particle collisions, produced less suspended bitumen. Thus, the interactive effect of salinity with energy apparent in the benchtop experiments is also reflected in these results. In the absence of the flume tank walls one would suspect that nearly all of the bitumen spilled in brackish water (17.5°/₀₀) would ultimately float to or toward the surface.

In the lone saltwater flume test conducted (Test 5), less bitumen floated than in the two brackish water flume tests (Table 11-1). However, this is believed to be due to the higher energy of flume Test

5 (which produced a larger bathtub ring) and also the presence of clay (which produced some denser mineral-bitumen particles which either sank or remained suspended). In the absence of these differences, one would expect a higher percentage of bitumen to have floated in flume Test 5.

Both the benchtop and flume experiments have demonstrated that bitumen is prone to float at salinities greater than 17.5 ‰. Oppositely, at 0 ‰ most bitumen is not prone to floating. Therefore, at some salinity between 17.5 and 0 ‰ the density of spilled bitumen will equal the density of the water and bitumen would remain suspended (neutrally-buoyant). The experiments performed have not determined this important salinity. Whereas the effect which salinity has on surfactant effectiveness may be either a gradual effect or a 'stepped' effect (i.e., drastic change at a certain salinity), the effect which salinity has on density-driven buoyancy should be gradual. In other words, the percentage of bitumen that floats (in the real world where no wall effects exist) should be primarily driven by the salinity of the water. In those circumstances where suspended mineral matter may increase the density of bitumen particles (by coalescing with them) the percentage of bitumen which floats would be reduced (as it was in flume Test 4).

Another consideration of salinity's effect on the percentage of floating bitumen is the time that it takes for bitumen to float after a spill. In our experiments there were no measurements made as to the time it took to see bitumen bodies floating after a spill. At both 17.5 and 35‰ the time seemed to be rather short (minutes to hours). However, given that the disparity between the density of spilled bitumen and the density of the receiving water will determine the magnitude of the buoyancy force, it follows that the greater the disparity the faster the bitumen will tend to reach the surface. Thus, at some unknown salinity (lower than 17.5 ‰) the disparity will be so small that bitumen will rise very slowly to the surface. This should be a consideration in response planning since a spill at or near this salinity may require a longer time for the bitumen to reach the surface. In the real world, a longer time in suspension probably results in greater dispersion and thereby lower concentrations of bitumen at the surface once it does rise.

The physical form that the floating bitumen takes is very interesting and could influence its recovery. The formation of a single floating patty was the most common result observed in both the benchtop and flume experiments. One must believe, however, that in the absence of container walls that lateral dispersion would reduce the collisions between floating/buoyant bitumen bodies and thereby reduce the average size of the floating bitumen bodies. One can imagine that in low energy conditions (where dispersion would be lower) the size of the floating bitumen bodies would tend to be larger than those that would form in high-energy conditions (where dispersion would be greater). These floating bodies might range in size from floating patties (as observed in flume Test 2 or 3) to tar balls (as observed in flume Test 4) to discrete, individual bitumen particles (no larger than those in fresh bitumen; <80 microns). Notably, the very high energy conditions in flume Test 4 led to the physical breakup of an early-formed floating patty into the formation of the tar balls.

The degree of "stickiness" of any floating bitumen is also worthy of consideration. In the experiments conducted the floating bitumen bodies tended to become increasingly sticky as their surfaces (upper) were exposed to air. So long as their surfaces remained wet, they were far less sticky. This property could have an impact on the ability to recover floating bitumen.

11.2.2 Settled Bitumen

The amount of bitumen that settles to or toward the bottom after an Orimulsion spill is important because of its potential impact on sediment quality and benthic communities. The same arguments given in Section 11.2.1 regarding bitumen density *versus* receiving water density would again seem to be the primary factor in determining the potential for, and percentage of, bitumen that would settle through the water column following an Orimulsion spill. As argued above, the density of the receiving water is primarily a function of the salinity.

The importance of salinity in determining the percentage of sunk bitumen following a spill was clearly indicated by the benchtop experimental results (Section 6). These consistently demonstrated that, all things being equal, more bitumen sunk in freshwater than in brackish or saltwater (Section 6.2.4.2). Clearly, the density of spilled bitumen exceeds that of freshwater. However, the benchtop studies revealed that there were clear interactive effects between salinity and energy and between salinity and particulate loading. In freshwater, the percentage of bitumen that sunk generally increased as the water energy was decreased. This makes sense since a higher energy would keep more discrete bitumen particles suspended in the water column. In brackish water and saltwater, the percentage of bitumen which sunk generally increased as the amount of particulate (mineral matter) loading increased (this also depends on the energy; Section 6.2.4.2).

The flume test results further support the important roles of salinity, water energy, and mineral matter load in effecting the percentage of spilled bitumen that may settle through the water column. As would be predicted, flume Test 1 (low energy, freshwater) saw a significant proportion of the bitumen settle toward the bottom of the flume tank (Table 11-1). Qualitatively speaking, the rate at which this settling occurred was seemingly very slow and was very sensitive to the energy in the water column (Section 10.1.1). Even after allowing the water column to become static a significant amount of the bitumen did not settle through the water column after 72 hours. Translating flume Test 1's results to the real world suggests that bitumen probably would not settle through the water column in freshwater that has any degree of turbulence. Apparently the density difference between spilled bitumen and freshwater is so slight that any turbulence in the water column tends to keep the bitumen in suspension. Thus, in flowing freshwater bitumen would not be expected to settle through the water column. It can be imagined that only in confined, stagnant water bodies would a significant amount of bitumen actually end up settling to the bottom. It would be much more likely that following most freshwater spills, the bitumen would tend to remain dispersed in the water column and, without the restrictions of container walls, eventually diffuse throughout the available water volume/body.

The effect of suspended mineral matter has on the percentage of sunk bitumen was confirmed in flume Test 4 (high energy, seawater). In this test, as would be expected, the high salinity reduced surfactant effectiveness (Section 11.1.1). This permitted coalescence between suspended bitumen and kaolinite particles to occur within the water column. The frequency and energy of the collisions between the bitumen and kaolinite particles was promoted by the high energy in the water. The formation of some denser bitumen-kaolinite particles eventually led to their settling out of the water column. Any settling of bitumen in flume Test 5 (high energy, freshwater) by the same mechanism, was thwarted by the maintained effectiveness of the surfactant (which minimized formation of dense bitumen-kaolinite particles). One would expect that the combination of mineral matter and high energy, brackish water would have also yielded a considerable amount of sunk bitumen. However, in the absence of mineral matter (as in flume Test 2), no bitumen would be expected to settle through the water column under high energy, brackish water spill conditions.

Only one flume test result does not fit with the apparent relationship between salinity, energy and mineral matter in the formation of sunk (or floating bitumen). The formation of the sunk bitumen 'balls' in flume Test 3 (19.3% of the spilled bitumen; Table 11-1 and Section 10.3.1) were highly unusual and their formation cannot be explained by the salinity-density considerations described above. Their formation remains anomalous. Why did seemingly negatively-buoyant bitumen form in brackish water in the absence of mineral matter? We currently have no explanation for this other than the bitumen balls may not have truly been negatively buoyant. As described in Section 10.3.1, they tended to bounce along the bottom indicating they were nearly neutrally-buoyant.

By their nature, the benchtop vessels and the flume tank used in our experiments had a limited bottom surface area. The presence of the container walls had thereby forced any settling bitumen to settle onto this limited surface area. One has to imagine that in the unconstrained bottom surface areas available in most 'real world' situations, that settling bitumen would disperse vertically and laterally well prior to settling onto the bottom sediments. Under most circumstances then, the bitumen potentially reaching the sediments would be widely dispersed. We believe that the formation of a tarry bitumen mat would be highly unusual except perhaps following an Orimulsion spill in a shallow, restricted circulation (freshwater) area. In most open water conditions the impact of widely dispersed, individual, sunk bitumen particles would seem to be of little long-term consequence. By this thinking, an Orimulsion spill into a freshwater river would be expected to disperse bitumen along with the current. Any settling of bitumen onto the bottom would be minimal.

11.2.3 Bitumen Remaining in Suspension

The amount of bitumen that remains suspended in the water column after an Orimulsion spill is important because of its potential impact on pelagic communities and also because of the difficulty of recovering dispersed bitumen. The benchtop experiments had shown that the amount of bitumen which remained in suspension after 24 hours was typically far less than had either floated or sunk (or had stuck to the sides; Table 7-1 and Section 7.3). The energy in the water had the greatest statistical effect on the amount of bitumen that remained suspended at the benchtop scale. The role of energy was undoubtedly related to its effect on particle collisions with each other, mineral matter, and the vessel walls, all of which tend to remove bitumen particles from suspension. These effects combined to result in the water column becoming mostly clear after 24 hours in nearly every benchtop experiment. We believe this is largely due to scale and limitations of these confined experiments.

A better reflection on the propensity for bitumen to remain suspended following a spill was attained from the results of the flume tests conducted herein, and those conducted previously by Ostazeski et al. (1998). These tests were conducted for longer time periods and, due to the 4000 L volume, the effect of walls was reduced over the effect at the benchtop scale. The rate at which bitumen is removed from the water column is reflected in the TPH_{total} data. Of course, the final TPH_{total} value obtained at the end of the flume experiment was used to calculate the percentage of bitumen remaining in suspension (Section 10). These data have been compiled for the freshwater and brackish/saltwater flume tests conducted on Orimulsion 400 spills and are shown in Fig. 11-2.

A comparison of the TPH_{total} trends in Fig. 11-2 immediately reveals the important effect which salinity has on the concentration of suspended bitumen following a spill. The three freshwater experiments conducted each reveal an initial drop in the suspended bitumen concentration, presumably due to the relatively rapid formation of a bathtub ring (see Section 11.2.5.), followed by a gradual reduction in the concentration of suspended bitumen. The secondary role that water energy plays in determining the amount of suspended bitumen remaining the freshwater spills is revealed in the rate at which the gradual decrease occurs. In the low-to-no energy conditions of flume Test 1 (Section 10.1), the rate of bitumen removal from suspension is greater than in the high energy of flume Test 5 (Section 10.5) or the Ostazeski et al. (1998) test. This is undoubtedly due to the greater amount of settling of bitumen in the low-to-no energy of flume Test 1.

The four brackish and saltwater flume tests conducted all reveal a rapid loss of suspended bitumen from the water column within the first couple of hours following the spill. In these instances, the rapid loss is due to the formation of a bathtub ring and coalescence and floating of bitumen (due to reduced surfactant effectiveness; Section 11.2.1). 0 Notably, the lowest energy brackish or saltwater test conducted, flume Test 3, had the lowest loss rate early in the spill. Also, in the case of the highest energy brackish or saltwater test conduced, flume Test 4, there was the most rapid reduction observed (Fig. 11-2). This may have been due, in part, to the formation and settling of some dense kaolinite-bitumen particles. After the first 12 hours following the spill, the concentration of bitumen in the water column in each brackish and saltwater experiment remained mostly constant.

In the absence of vessel walls, as would exist in the event of a 'real world' spill, the concentrations of suspended bitumen in the water column would be expected to decrease even more rapidly than was observed in the initial hours following the spill in our flume experiments (Fig. 11-2). The concentrations of bitumen in suspension in the longer term would also decrease dramatically due to the continual dilution/dispersion of any bitumen that remained in suspension. Particles would continue to move further and further apart decreasing the potential for collisions and their concentration. Given a large body of water, one can imagine that the concentration of bitumen in suspension would continue to decrease with time. With this in mind, recovery of bitumen in suspension would seem impractical.

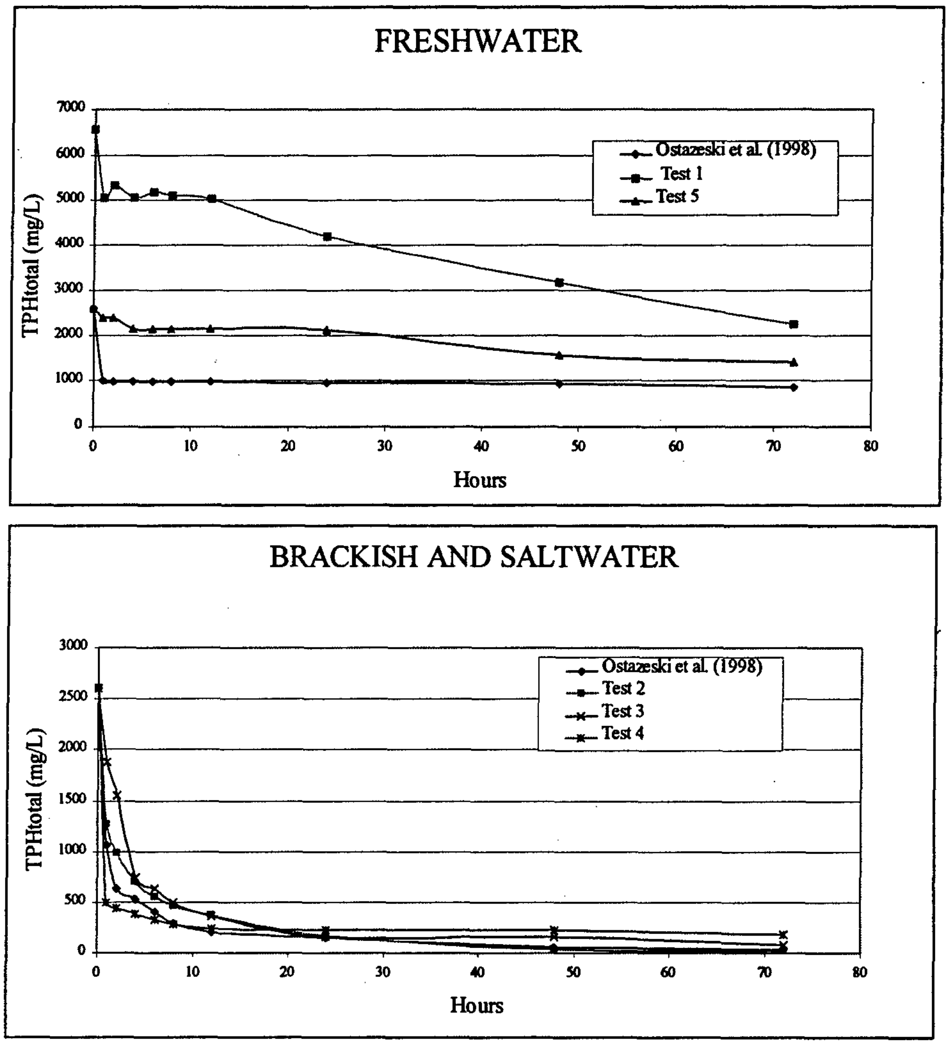

Figure 11-2. Trends showing amount of TPH_{total} (suspended bitumen) in the water column following Orimulsion spills in freshwater (top) and in brackish/saltwater (bottom).

Eventually, the density disparity between the widely dispersed bitumen particles and the water would determine their ultimate fate, i.e., moving up or down in the water column depending on the salinity. In freshwater with any degree of turbulence the bitumen would remain in suspension and continually disperse. In saltwater the bitumen would eventually float to/toward the surface. Theoretically, at some salinity between 0 and 17.5 $^{0}/_{00}$ the density disparity will be non-existent. (Again, any effect that temperature may have on water density are likely to be minor.) Under this situation bitumen will be neutrally-buoyant may remain suspended (although if the volume were unrestricted it would continue to disperse).

11.2.4 Bitumen Dissolving into Water

The soluble hydrocarbon component of spilled Orimulsion is only a very minor fraction of the bitumen. Thus, in terms of the Orimulsion budget it is essentially negligible. It is important to consider this minor fraction, however, because it represents the most bioavailable fraction. Our benchtop experiments revealed that the primary control on the concentration of dissolved hydrocarbons was the concentration of the Orimulsion spill (Section 6.2.4.2). The concentrations of dissolved hydrocarbons in any of the flume tests were consistently between 1 and 3 mg/L at any time following the spill, and under any spill conditions. These concentrations were achieved within the first hour following the spill and there was no apparent trend in concentration over the next 72 hours of the experiments (Section 10). Thus, there is little evidence that the concentration of dissolved hydrocarbons would increase significantly after the initial influx of bitumen into the water.

The flume experiments conducted by Ostazeski et al. (1998) obtained data at greater frequency than was done in this study. Their dataset revealed a rapid increase in $TPH_{dissolved}$ immediately following the spill (as observed herein) and a subsequent gradual increase in concentration in both freshwater and saltwater. The total and rate of increase in $TPH_{dissolved}$ concentration in freshwater exceeded those in saltwater, presumably due to the fact that there was more bitumen in suspension longer and more suspended particles with a greater surface areas in the freshwater flume experiment. It is envisioned that the suspended bitumen particles in freshwater had a longer time for, and greater surface area from which, hydrocarbons to dissolve into the water. Over time, the rate of increase in the concentration of $TPH_{dissolved}$ in both freshwater and saltwater slowed indicating a gradual 'saturation' of the flume tank water.

In the real world it can be imagined that the concentration of $TPH_{dissolved}$ would be far lower than the low values observed in these laboratory experiments due to the constant dilution that would occur in the absence of container walls.

11.2.5 Bitumen Adhering to Vessel Walls

As mentioned throughout the preceding sections, the container walls had a major effect on the Orimulsion budget (as reflected in the formation of a bathtub ring). The percentage of bitumen reporting to this compartment would, in the absence of a container wall, have reported to some other compartment. Therefore, discussion of the amount of bitumen that stuck to vessel walls cannot be readily translated to an open water, 'real world' situation.

In our experiments, the most important factors in increasing the formation of a bathtub ring were (statistically speaking) the energy of the water, the amount of clay in the water, and the concentration of Orimulsion spilled (Section 6.2.4.2). Energy was the most important factor. In the benchtop experiments there was sufficient centrifugal energy to cast bitumen particles against the vessel wall near and just above the water line. In the flume tank experiments bitumen became adhered to both the inside wall and the outside wall indicating that it was not only centrifugal energy at work in the flume tank experiments. However, consistent with the claim that energy is the most important factor in the formation of a bathtub ring(s), the greatest percentage of bitumen adhering to the walls occurred in the flume Tests 4 and 5, both of which were conducted at very high energy (Sections 10.4 and 10.5). We believe that the potential for bitumen to stick to the walls of both the benchtop vessels and the flume tank (inner and outer) walls was promoted by the relative dryness of the walls. This point is clearly indicated by the lack of bitumen adhering to any of the container walls below the water line.

Naturally, as noted above, no bathtub ring will form in nature. However, any body of water will have a shoreline and bitumen reaching the shoreline will probably tend to stick to it, just as it sticks to laboratory container walls. The primary reason for its sticking will simply be contact with a relatively dry surface. Any bitumen particle that is cast onto a surface will quickly become air-dried and very sticky. This phenomenon was observed on numerous occasions in our experiments but was most obvious in flume Test 3 (high energy, brackish). This was the test in which the hundreds of tar balls had formed during the test. Only after the test, when the tar balls surfaced and their upper surfaces became dry, did they begin to stick to one another. This phenomenon of dried bitumen particles sticking to relatively dry surfaces may even provide the potential to inhibit or reduce the volume of bitumen that might stick to a shorelines/surfaces by pre-treating (wetting ?) the shoreline/surface prior to the arrival of the bitumen.

Response to spills of Orimulsion into open bodies of water may include the use of booms or floating aprons. It is presumed that well-dispersed bitumen (i.e., bitumen below the air-water interface) coming into contact with these materials will probably not stick. This would be expected in freshwater. However, floating bitumen (i.e., bitumen at the air-water interface) will probably stick to these materials. This would be expected in brackish or saltwater.

The most important conclusion to be drawn from the formation of a bathtub ring is that bitumen tends to stick to dry surfaces, regardless of the salinity and the degree to which the surfactant is effective.

11.2.6 Other Factors

Although it was not measured in our studies, another 'compartment' to mention in the Orimulsion budget is the fraction of Orimulsion prone to evaporation. Spilled Orimulsion could potentially loose compounds with a significant vapor pressure. However, Orimulsion contains very little low boiling compounds (Section 3.3). In fact, analysis of Orimulsion for volatile organic compounds revealed a complete absence of VOC's typically found in petroleum (all VOC < 10 mg/kg according to Ostazeski et al., 1998). Therefore, the mass reduction due to evaporative losses in the event of an Orimulsion spill is expected to be nominal. From a response perspective, the presence of volatile hydrocarbons in the air immediately following an Orimulsion spill should be low compared to conventional oils.

Another 'compartment' not measured in our studies is the fraction of Orimulsion lost to microbial degradation. One has to imagine that since the bitumen component of Orimulsion is itself derived from an already, highly biodegraded crude oil, that microbial biodegradation following a spill of Orimulsion will be relatively minor. In other words, the most susceptible hydrocarbons present in Orimulsion have already been removed by biodegradation. Therefore, the mass reduction due to biodegradation in the event of an Orimulsion spill is expected to be nominal.

11.2.7 Fate of Surfactant Component

Finally, some mention of the surfactant component of Orimulsion is warranted. This component had been omitted from the mass balance (Orimulsion budget) described above primarily because of the existence of good data on the fate of the polyethoxylated alcohol surfactant in water provided by

Ostazeski et al. (1998). Their work had shown that in both freshwater and saltwater the concentration of polyethoxylated alcohol in filtered and unfiltered water samples increased immediately (to ~2.5 and 3.0 mg/L, respectively) following the release of 14.2 L Orimulsion 400 into the 4000L flume tank. The increase in concentration was proportional to the amount of Orimulsion spilled; in other words, there was a simple dilution of the surfactant into the receiving water. Surfactant concentrations remained essentially steady over the course of the 168 hour flume tests. Investigation of possible surfactant degradation products (e.g., total carboxylic acids) showed no evidence of surfactant degradation over the course of the 168 hour tests. Thus, the fate of the polyethoxylated alcohol surfactant component of Orimulsion 400 spilled in water appears to be one of simple dilution.

11.2.8 Projecting the Orimulsion Budget to the Real World

Throughout the previous sections, the Orimulsion budget results were continually projected to predict what would probably have happened if (1) there were no container walls (boundaries) and (2) the spilled Orimulsion were able to dilute into a large volume of water. In this section, a summary of the most likely fate of the bitumen component following an Orimulsion spill is offered as guidance in predicting the fate of most bitumen following a real world spill.

The details described above, and presented in Sections 6 and 10 of this report, have consistently revealed that the most important environmental parameters in determining the fate of spill Orimulsion, probably listed in order of their descending importance, are:

(1) receiving water salinity,
(2) receiving water energy, and
(3) presence/absence of suspended mineral matter.

The prediction of what will the bulk of the bitumen component of spilled Orimulsion do when spilled under the various combinations of these parameters is presented in Table 11-2. This table is divided into two sections, one in which the salinity is such that the surfactant component in Orimulsion remains mostly effective (top) and one in which the salinity is such that the surfactant component remains mostly ineffective (bottom). The actual salinity which 'divides' these two sections is unknown. Based on our experiments we can only state that the division lies somewhere between 0 and 17.5 $^{0}/_{00}$. Furthermore, whether the division between these sections is more gradual or more drastic is not known at present.

Under any "no energy" conditions, there is not expected to be any mineral matter in suspension and therefore this square is intentionally left blank. As can be seen, the prediction following a freshwater Orimulsion spill under most circumstances is that most bitumen will remain suspended in the water column as discrete particles. The size of the particles will be essentially unchanged from that of fresh Orimulsion (< 80 microns). Only under the rather rare "no energy" conditions would we predict most bitumen to settle through the water column (given ample time). If this "no energy" situation were to occur in a shallow restricted volume of water it is possible that a bitumen mat may form. Under most situations however, any bitumen remaining in suspension will be subject to continuous dilution when the volume of water is sufficiently large. The rate of dilution will increase with the energy of the water. Only in restricted circulation area, or small lake would the suspended bitumen not continuously dilute.

For Orimulsion spilled into water with a high salinity (> 17.5 $^{0}/_{00}$), we would predict that the vast majority of bitumen would float regardless of the other spill conditions (Table 11-2). When there is suspended mineral matter in the water column we would predict that some fraction of the bitumen would coalesce with the minerals and the resulting particles would either remain suspended or settle through the water column, depending on their density. The proportion of bitumen that ultimately floats, however, will far exceed the amount of bitumen that may remain dispersed or settle through the water column in saltwater. When energy is absent (stagnant water), we expect that some bitumen may remain suspended for a long period of time but that most bitumen would float.

The form that the floating bitumen will have will vary from discrete particles to sizable patties depending upon the concentration of the spill, proximity to the spill, and the rate of dilution. We'd predict that higher energy (where dilution is greatest) will yield smaller bitumen bodies (discrete particles or tar balls) whereas lower energy (where dilution is lowest) will yield larger bodies (patties).

Under both low salinity and high salinity settings, the potential for bitumen to reach a shoreline exists. When this occurs we predict that bitumen will eventually or immediately adhere to shoreline surfaces. The adhesion may be slower in a freshwater environment but once the bitumen comes into contact with a relatively dry surface or the bitumen becomes air-dried (e.g., on its upper surface), adhesion to the shoreline's surfaces will occur. In the case of a saltwater shoreline, we expect bitumen to immediately adhere to surfaces that it contacts.

Table 11-2. Summary of predictions surrounding the fate of most bitumen in the event of an Orimulsion spill under different conditions. See text for description.

	WATER ENERGY LEVEL			
	NO	LOW	HIGH	
LOW SALINITY		SUSPENDED - DILUTE (minor settled)	SUSPENDED HIGHLY DILUTE	MINERAL MATTER
	SETTLED TOWARD BOTTOM	SUSPENDED - DILUTE (minor settled)	SUSPENDED HIGHLY DILUTE	NO MINERAL MATTER

	WATER ENERGY LEVEL			
	NO	LOW	HIGH	
HIGH SALINITY		FLOATING - DILUTE (some suspended > some sink)	FLOATING HIGHLY DILUTE (some suspended > some sink)	MINERAL MATTER
	FLOATING NEAR SURFACE (some suspended)	FLOATING - DILUTE (some suspended > some sink)	FLOATING HIGHLY DILUTE	NO MINERAL MATTER

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