



Acquisition Directorate

Research & Development Center

Report No. CG-D-05-23

Guidance Document – Behavior of Diluted Bitumen in the Freshwater Environment

Distribution Statement A: Approved for public release; distribution is unlimited.

September 2023

NOTICE

This document is disseminated under the sponsorship of the Department of Homeland Security in the interest of information exchange.

For use outside the United States Government, the Government assumes no liability for its contents or use thereof.

The United States Government does not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the objective of this report.



Mr. M. J. Lewandowski
Chief, Environment & Waterways Branch
United States Coast Guard
Research & Development Center
1 Chelsea Street
New London, CT 06320



Guidance Document – Behavior of Dilbit in the Freshwater Environment

Technical Report Documentation Page

1. Report No. CG-D-05-23		2. Government Accession Number		3. Recipient's Catalog No.	
4. Title and Subtitle Guidance Document – Behavior of Diluted Bitumen in the Fresh Water Environment				5. Report Date September 2023	
				6. Performing Organization Code Project No. 4204	
7. Author(s) Benedette S. Adewale, Michele Fitzpatrick, Timothy J. Cooke, Michel C. Boufadel, Michael A. Wurl				8. Performing Report No. RDC UDI # 1953	
9. Performing Organization Name and Address U.S. Coast Guard Research and Development Center 1 Chelsea Street New London, CT 06320		U. S. Army Corps of Engineers Engineer Research and Development Center Cold Regions Research & Engineering Lab 72 Lyme Road Hanover, NH 03755		10. Work Unit No. (TRAIS)	
				11. Contract or Grant No. EPA/CG: DW-070-95965901 & 95983201 CG/CRREL: 70Z03222RA0000014 & 70Z0FT21KPE2S0400	
12. Sponsoring Organization Name and Address COMMANDANT (CG-MER) US COAST GUARD STOP 7516 2703 MARTIN LUTHER KING JR AVE SE WASHINGTON, DC 20593				13. Type of Report & Period Covered Final	
				14. Sponsoring Agency Code Commandant (CG-MER) US Coast Guard Stop 7516 Washington, DC 20593	
15. Supplementary Notes The R&D Center's technical point of contact is Dr. Benedette Adewale, 860-271-2849, email: Benedette.S.Adewale@uscg.mil					
16. Abstract (MAXIMUM 200 WORDS) The growth in oil production in North America is due in part to the increase in production and distribution of Canadian oil sands products. Recent spills of oil sands products (e.g., diluted bitumen (dilbit)) have demonstrated that they behave differently than conventional crude oil when spilled. The objective of this project is to study the behavior and response tools of dilbit spills in the freshwater environment. In addition, to provide the U.S. Coast Guard (USCG) Federal On-Scene Coordinator with decision-making guidance as they relate to the fate and transport of dilbit in the freshwater environment. The USCG Research and Development Center (RDC) led a three-experiment study at the U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) facilities in Hanover, NH to evaluate the behavior of dilbit products in freshwater. For these tests, researchers conducted weathering studies for 30-days using a set of open tanks containing freshwater. The research used two dilbit products, Cold Lake Blend (CLB) and Western Canadian Select (WCS) with different sediment concentrations and a control (no sediment). Throughout the experiments, the team visually assessed the oil slicks and collected samples for physical and chemical analysis. After 8 days of weathering, most dilbit product sank and refloated until it totally sunk. Dilbit density and viscosity increased over time during the weathering process. The presence of sediments contributed to the faster sinking of dilbit when compared with the control tanks. Evaporation of the diluents were faster in the warm weather than the cold weather. The chemical analysis results show that photo-oxidation was a major mechanism of the removal of aromatic compounds.					
17. Key Words diluted bitumen spill, dilbit, diluents, oil, hydrocarbon, oil-particle aggregates, weathering, unconventional oil, freshwater, oil spill, oil-sediment interaction, oil buoyancy		18. Distribution Statement Distribution Statement A: Approved for public release; distribution is unlimited.			
19. Security Class (This Report) UNCLAS// Public		20. Security Class (This Page) UNCLAS// Public		21. No of Pages 102	
				22. Price	



(This page intentionally left blank.)



EXECUTIVE SUMMARY

The growth in oil production in North America is due in part to the increase in the production and distribution of Canadian oil sands products (OSPs). Diluted bitumen (dilbit) is one example of an OSP that is currently transported from Canada to the United States. Recent dilbit spills have demonstrated that these OSPs behave differently than conventional crude oil during a spill. A major issue with the behavior of dilbit when spilled in a freshwater environment is the uncertainty in determining when it floats or sinks, especially in the presence of suspended particles and sediment. The buoyant behavior of dilbit is influenced by environmental conditions, the origin and manufacturer of the dilbit product, and the nature of the spill. Understanding the behavior of OSPs, especially the change in buoyancy over time, is critical for choosing the best response strategy when a spill occurs.

In 2021, the U.S. Coast Guard (USCG) Research and Development Center (RDC) received funding through the Environmental Protection Agency Great Lakes National Program Office's Great Lakes Restoration Initiative to investigate and better understand dilbit spill behavior and response strategies particularly in the Great Lakes and other freshwater environments. The RDC initially performed an in-depth literature review of dilbit research. Based on the knowledge gaps identified during the review, and to further characterize the behavior of dilbit products in freshwater, three experiments were performed by the USCG RDC at the U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) facilities in Hanover, NH. The physical and chemical properties of two common dilbit products, Western Canadian Select (WCS) and Cold Lake Blend (CLB) were assessed in the experiments. Seasonal environmental conditions (i.e., ambient temperature and sun angle/solar exposure) and sediment concentration were selected as factors to consider on spilled, dilbit behavior.

In the three mesoscale experiments, the dilbit products were placed in open, freshwater tanks which had sediment concentrations of 0 mg/L, 100 mg/L or 1,000 mg/L. Mechanical agitation was used to simulate the effects of natural mixing (as in a flowing stream). The experiments occurred outdoors in both cold weather (1.0°C-15.5°C) (November/December) and warm weather (10.0°C-25.0°C) (June) temperatures, allowing for diurnal and multi-day fluctuation in tank temperature. Throughout each 30-day experiment time, the tanks were visually assessed for surface oil slick amount, and samples of both surface and sunken oil were collected for physical and chemical analysis.

Based on the results of the experiments, researchers conclude:

- Dilbit weathers rapidly in freshwater, as compared to “traditional” crude oil. As the diluent evaporates, dilbit density and viscosity increase, and the remaining oil behaves like a heavy oil.
- The lighter hydrocarbon components evaporate faster in warm weather than in cold weather, resulting in increased density and viscosity.
- Dilbit may stay afloat for six to ten days in calm conditions with no agitation or sediment in the water. With suspended sediments in a high-energy mixing environment, dilbit will generally sink in a shorter timeframe.
- The oil appearance changed drastically over a week, suggesting an effective response window of opportunity could be only a few days.
- Higher sun angle/solar exposure increases the photo-oxidation process.



(This page intentionally left blank.)



TABLE OF CONTENTS

EXECUTIVE SUMMARY	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS.....	xii
1 INTRODUCTION.....	1
1.1 Background	1
1.2 Research Objectives	1
2 DILBIT CHARACTERISTICS.....	2
2.1 Physical Properties of Dilbit	2
2.2 Chemical Properties of Dilbit.....	3
2.3 General Behavior of Dilbit in Water	3
3 DILBIT WEATHERING EXPERIMENT	4
3.1 Research Facility	4
3.2 Materials and Methods	5
3.2.1 Experimental Set-up.....	5
3.2.2 Weather Instrumentation.....	7
3.2.3 Water Measurements	8
3.2.4 Visual Inspection and Photos.....	8
3.2.5 Sunken Dilbit	8
3.2.6 Physical Measurements of the Oils.....	9
3.2.7 Chemical Sampling and Analysis of the Oils	10
3.2.8 Laboratory Scale Experiment	11
3.2.9 Data Collected for Mesoscale Experiment	11
4 RESULTS	11
4.1 Weather Data.....	11
4.1.1 Cold Weather 2021	12
4.1.2 Warm Weather 2022	12
4.1.3 Cold Weather 2022	13
4.1.4 Weather Summary	14
4.2 Water Data.....	14
4.2.1 Water Temperature	14
4.2.2 Water Velocity	14
4.3 Visual Inspection, Photos, and Observations	14
4.3.1 CW21 Visual Inspection and Photos	14
4.3.2 WW22 Visual Inspection and Photos	15
4.3.3 CW22 Visual Inspection and Photos	17
4.3.4 Sunken Dilbit	19
4.3.5 Visual Inspection Summary	19



TABLE OF CONTENTS (Continued)

4.4	Physical Properties	20
4.4.1	Density	20
4.4.2	Viscosity	21
4.4.3	Physical Properties Summary	22
4.5	Chemical Properties	22
4.5.1	Saturates, Aromatics, Resins, and Asphaltenes	22
4.5.2	Polyaromatic Hydrocarbons.....	28
4.5.3	Chemical Properties Summary	28
5	CONCLUSIONS	29
5.1	Variations in Dilbit Products.....	29
5.2	Variations in Weather Conditions	29
5.3	Variations in Sediment Contents.....	30
5.4	Intersections/Interactions Between Multiple Variables	30
6	RECOMMENDATIONS.....	32
7	GUIDANCE ON DILBIT BEHAVIOR FOR PLANNERS AND RESPONDERS	33
8	REFERENCES.....	35
APPENDIX A. PROPERTIES OF DILUTED BITUMEN.....		A-1
APPENDIX B. ANALYTICAL TECHNIQUES.....		B-1
APPENDIX C. ADDITIONAL DATA.....		C-1



LIST OF FIGURES

Figure 1. Natural bitumen (left) and dilbit (right).....	1
Figure 2. SARA components of typical crude oils.	3
Figure 3. Experimental setup at CRREL.	5
Figure 4. Test tank schematic.	6
Figure 5. Three motors at the end of CW21.	7
Figure 6. Weather station.....	7
Figure 7. Sunken dilbit catchment trays.	8
Figure 8. Schematic of sunken dilbit sampling grid pattern and photo of trays in tank.	9
Figure 9. Density meter (left) and viscometer (right).	9
Figure 10. CRREL HPLC apparatus at CRREL.	10
Figure 11. GC-MS apparatus at CRREL.	10
Figure 12. Weather station data for the CW21 study.....	12
Figure 13. Weather station data for the WW22 study.	13
Figure 14. Weather station data for the CW22 study.....	13
Figure 15. Overtop image of the CW21 test tanks on day 4.....	15
Figure 16. Overtop image of the CW21 test tanks on day 12.....	15
Figure 17. WW22 study photos showing oil sunken and resurfaced.....	16
Figure 18. Day 8 photos of the high sediment CLB illustrating the consistency of the weathered oil.	17
Figure 19. Overhead photos of the oil surface at 1 hour (left) and 24 hours (right).....	17
Figure 20. CW22 day 8, showing the varying amounts of surface oil.....	18
Figure 21. CW22 day 12, showing little remaining surface oil for most tanks.	18
Figure 22. CW22 day 30 showing little oil remaining on surface.	19
Figure 23. Example trays from CW22 day 30.	20
Figure 24. Density graphs.	20
Figure 25. Viscosity graphs.	21
Figure 26. CW21 consolidated SARA.....	23
Figure 27. WW22 consolidated SARA.....	24
Figure 28. CW22 consolidated SARA.....	24
Figure 29. CW22 SARA correlation.....	25
Figure 30. WW22 laboratory scale SARA evaporation results.	25
Figure 31. WW22 laboratory scale SARA photo-oxidation results.	26
Figure 32. CW22 laboratory scale SARA evaporation results.	26
Figure 33. CW22 laboratory scale SARA photo-oxidation results.....	26
Figure 34. Correlation between the asphaltene fraction and the aromatics fraction.....	27
Figure 35. CLB observational results summary.	31
Figure 36. WCS observational results summary.....	31
Figure A-1. Density of pure water as a function of temperature.	A-2
Figure B-1. HPLC schematic.	B-1
Figure C-1. Tank water temperature data for the CW21 study.....	C-1
Figure C-2. Tank water temperature data for the WW22 study.	C-2
Figure C-3. Tank water temperature data for the CW22 study.....	C-2
Figure C-4. Time series of CW21 water velocity components.....	C-3
Figure C-5. Day 3 overhead image of the WW22 test tanks before the dilbit sank.	C-4
Figure C-6. Day 12 overhead image of the WW22 test tanks after a large portion of the dilbit had sunk... C-4	C-4



LIST OF FIGURES (Continued)

Figure C-7. Image from WW22 day 29 showing no oil remaining on surface.	C-5
Figure C-8. Total mass of dilbit products captured in five trays for CW21 days 15 and 30.	C-6
Figure C-9. CW21 ratio of dilbit recovered from the water surface and tank bottom on day 30.	C-6
Figure C-10. WW22 mass of oil collected in five catchment trays.	C-7
Figure C-11. CW21 individual tank density data.	C-9
Figure C-12. WW22 individual tank density data.	C-10
Figure C-13. CW22 individual tank density data.	C-11
Figure C-14. CW21 individual tank viscosity data.	C-12
Figure C-15. WW22 individual tank viscosity data.	C-13
Figure C-16. CW22 individual tank viscosity data.	C-14
Figure C-17. CW21 SARA results by tank.	C-17
Figure C-18. WW22 SARA results by tank.	C-20
Figure C-19. CW22 SARA results by tank.	C-23
Figure C-20. WW22 PAH tank 1 – CLB zero sediment.	C-24
Figure C-21. WW22 PAH tank 2 – CLB low sediment.	C-24
Figure C-22. WW22 PAH tank 3 – CLB high sediment.	C-25
Figure C-23. WW22 PAH tank 4 – WCS high sediment.	C-25
Figure C-24. WW22 PAH tank 5 – WCS low sediment.	C-26
Figure C-25. WW22 PAH tank 6 – WCS zero sediment.	C-26
Figure C-26. CW22 PAH tank 1 – CLB zero sediment.	C-27
Figure C-27. CW22 PAH tank 2 – CLB low sediment.	C-27
Figure C-28. CW22 PAH tank 3 – CLB high sediment.	C-28
Figure C-29. CW22 PAH tank 4 – WCS high sediment.	C-28
Figure C-30. CW22 PAH tank 5 – WCS low sediment.	C-29
Figure C-31. CW22 PAH tank 6 – WCS zero sediment.	C-29
Figure C-32. CW22 PAH tank 1 – CLB zero sediment.	C-30
Figure C-33. CW22 PAH tank 2 – CLB low sediment.	C-31
Figure C-34. CW22 PAH tank 3 – CLB high sediment.	C-31
Figure C-35. CW22 PAH tank 6 – WCS zero sediment.	C-32
Figure C-36. CW22 PAH tank 5 – WCS low sediment.	C-32
Figure C-37. CW22 PAH tank 4 – WCS high sediment.	C-33
Figure C-38. CW22 CLB ANOVA day 8.	C-33
Figure C-39. CW22 CLB ANOVA day 15.	C-34
Figure C-40. CW22 CLB ANOVA day 30.	C-34
Figure C-41. CW22 WCS ANOVA day 8.	C-35
Figure C-42. CW22 WCS ANOVA day 15.	C-35
Figure C-43. CW22 WCS ANOVA day 30.	C-36
Figure C-44. WW22 PAH CLB evaporation.	C-36
Figure C-45. WW22 PAH CLB photo-oxidation.	C-37
Figure C-46. WW22 PAH WCS evaporation.	C-38
Figure C-47. WW22 PAH WCS photo-oxidation.	C-39
Figure C-48. CW22 PAH CLB evaporation.	C-40
Figure C-49. CW22 PAH CLB photo-oxidation.	C-41
Figure C-50. CW22 PAH WCS evaporation.	C-42
Figure C-51. CW22 PAH WCS photo-oxidation.	C-43



LIST OF TABLES

Table 1. Ranges of physical properties for different oil types.	2
Table 2. Test parameters per tank.	6
Table 3. Weather data summary.	14
Table A-1. Summary of physical properties and chemistry data of selected dilbit products.	A-1
Table A-2. Coefficient of volume expansion for selected liquids.	A-2
Table C-1. Total mass of dilbit product measured in the CW21 catchment trays.	C-5
Table C-2. WW22 mass of dilbit product measured in the catchment trays.	C-7
Table C-3. Total mass of dilbit product measured in the CW22 catchment trays.	C-8
Table C-4. CLB CW21 SARA percentages by weight.	C-15
Table C-5. WCS CW21 SARA percentages by weight.	C-16
Table C-6. CLB WW22 SARA percentages by weight.	C-18
Table C-7. WCS WW22 SARA percentages by weight.	C-19
Table C-8. CLB CW22 SARA percentages by weight.	C-21
Table C-9. WCS CW22 SARA percentages by weight.	C-22



LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

°C	Degrees Centigrade
°F	Degrees Fahrenheit
β	Coefficient of volume expansion
ΔT	Change in temperature
ε	Energy dissipation rate
ρ	Density
τ	Correlation time scale
u'_{rms}	Root-mean-square of velocity fluctuations
ADV	Acoustic Doppler velocimeter
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
C(n)	Carbon number
CLB	Cold Lake Blend
cm	Centimeter
CRREL	Cold Regions Research and Engineering Laboratory
CW21	2021 Cold Weather Experiment
CW22	2022 Cold Weather Experiment
D9	USCG Ninth District
Dilbit	Diluted bitumen
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
FOSC	Federal On-Scene Coordinator
g	Gram(s)
g/cm ³	Grams per cubic centimeter
g/mL	Grams per milliliter
GC	Gas chromatograph
GC-MS	Gas chromatography – mass spectrometry
h	Hour(s)
Hz	Hertz
HPLC	High performance liquid chromatography
IR	Infrared (radiation)
K	Degrees Kelvin
kg	Kilogram
kg/m ³	Kilograms per cubic meter
L	Liter
m	Meter
m ³	Meters cubed
m/sec	Meters per second
m/z	Mass-to-charge
mg/L	Milligrams per liter
mL	Milliliter(s) (10 ⁻³ liter(s))



LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

mm	Millimeter(s) (10^{-3} meter(s))
mN/m	Milli-Newton/meter
mPa·s	Milli-Pascal-seconds
MS	Mass spectrometer
NAS	National Academies of Sciences
NASEM	National Academies of Sciences, Engineering, and Medicine
NH	New Hampshire
NRC	National Research Council
OPA	Oil-particle aggregate(s)
OSP	Oil sands product
Pa·s	Pascal-seconds
PAH	Polycyclic aromatic hydrocarbon(s)
PIV	Particle image velocimetry
ppm	Parts per million
R&D	Research and development
RDC	USCG Research and Development Center
SARA	Saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes
SDS	Safety Data Sheet
SIM	Selected ion monitoring
SR	Solar radiation
TC	Thermocouple
TPH	Total petroleum hydrocarbon(s)
U.S.	United States
USCG	United States Coast Guard
V	Volume
VOC	Volatile organic compound
W/m ²	Watts per square meter
WCS	Western Canadian Select
WW22	2022 Warm Weather Experiment



(This page intentionally left blank.)



1 INTRODUCTION

1.1 Background

Bitumen is an unconventional hydrocarbon that does not easily flow or pour. It is a semi-solid form of petroleum that is highly viscous and sticky. Bitumen is produced or extracted from natural oil sands (Environment Canada, 2013) (see Figure 1, left). As a result of bitumen's high viscosity and its abundance in landlocked Alberta, use of this oil sands product (OSP) as a reliable energy source is dependent on how it can be transported to distant refineries.



Figure 1. Natural bitumen (left) and dilbit (right).

OSPs can be transported if heated or if diluted with lighter hydrocarbons or natural gas condensates known as diluents. Diluted bitumen (dilbit), one type of OSP, is typically comprised of 70-80 percent bitumen and 20-30 percent diluent (Environment Canada, 2013) (see Figure 1, right). Producers normally transport dilbit by rail or pipeline, although they may also use vessels such as barges and tank ships. Every transportation method carries an inherent risk of spillage. Spills of dilbit have occurred in the past, and real-world experience demonstrates that dilbit behaves differently than conventional crude oil during an incident. The environmental factors, the type of dilbit, and nature of the spill all play a role in knowing how best to respond to a dilbit spill. To better understand the next steps in response, the U.S. Coast Guard (USCG) Research and Development Center (RDC) performed an in-depth literature review of dilbit research to determine gaps and identify needed research (Adewale et al., 2021).

This literature review identified several knowledge gaps. The exact conditions at the water surface and sub-surface that cause dilbit to submerge (i.e., type of sediment, sediment/oil interaction, high energy versus low energy conditions, seasonal temperature changes, etc.) in freshwater need further research. The precise length of time that dilbit stays afloat before sinking in freshwater is unpredictable. A single oil type may exhibit a range of behaviors depending on when a spill occurs due to environmental factors impacted by seasonal variability (Ortmann et al., 2020).

1.2 Research Objectives

Based on the knowledge gaps identified in the literature review, RDC developed and executed controlled tests to identify the conditions at the water surface and sub-surface that cause dilbit to submerge. The overall objective of this research was to gain a better understanding of dilbit behavior, including degradation and

buoyancy, in a freshwater environment with medium and/or high concentrations of sediment in the water column during both fall and summer conditions. Project goals included:

- Characterize physical and chemical properties of two different products, Cold Lake Blend (CLB) and Western Canadian Select (WCS) — representative of dilbit carried by pipelines across Great Lakes waterways — at various time intervals after a simulated spill to better understand how mechanisms of evaporation and photo-oxidation may change those properties over time.
- Study the effects of seasonal environmental variations and sediment concentration on the behavior of dilbit products in the freshwater environment.
- Provide the USCG Federal On-Scene Coordinators (FOSCs) with decision-making guidance related to the fate and transport of dilbit in the freshwater environment.

2 DILBIT CHARACTERISTICS

Dilbit and other crude oils generally contain the same classes of compounds, but the relative amount of those classes vary widely. These variations in composition are associated with wide differences in physical and chemical properties. APPENDIX A.1 provides a summary of physical properties and chemistry data of selected dilbit products.

2.1 Physical Properties of Dilbit

Table 1 shows a selection of the physical properties of dilbit – including density, viscosity, flash point, solubility in water, and interfacial tension – compared to a broad range of petroleum types. These are the main physical properties that affect the fate of spilled oil. The units in the table are kilograms per cubic meter (kg/m^3), degrees Centigrade ($^{\circ}\text{C}$), milli-Pascal-seconds ($\text{mPa}\cdot\text{s}$), parts per million (ppm), and milli-Newtons per meter (mN/m). APPENDIX A.2 provides definitions of these properties and more information on the physical properties of dilbit.

Table 1. Ranges of physical properties for different oil types.

Property	Units	Gasoline	Diesel	Light Crude	Heavy Crude	Dilbit (CLB)*	Dilbit (WCS)**
Density	kg/m^3 at 15°C	720	840	780 – 880	880 – 1000	923 – 933	921 – 928
Viscosity	$\text{mPa}\cdot\text{s}$ at 15°C	0.5	2	5 – 50	50 – 50,000	97-105***	211
Flash point	$^{\circ}\text{C}$	(-35)	45	(-30) – 30	(-30) – 60	< -5	Data not available
Solubility in Water	ppm	200	40	10 – 50	5 – 30	Negligible***	Data not available
Interfacial Tension	mN/m at 15°C	27	27	10 – 30	15 – 30	27.7	Data not available

Adapted from Hollebone, 2015

* Environment Canada, 2013

** Ortmann et al., 2020

*** From Safety Data Sheet



2.2 Chemical Properties of Dilbit

The chemical composition of petroleum dictates its physical properties (e.g., density and viscosity), behavior (e.g., spreading, sinking, and dispersion), biological impacts (e.g., toxicity and susceptibility to biodegradation), and fate in the environment (Lee et al., 2015). Conventionally, petroleum is separated into four major fractions for analysis: saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA). Saturated hydrocarbons are most abundant in light crude oils, which are the least dense and least viscous. Crude oils which are more dense and more viscous have greater concentrations of other components, including resins and asphaltenes. Resins and asphaltenes often include nitrogen, sulfur, and oxygen as well as carbon and hydrogen. Figure 2 shows the SARA components of typical crude oils, including dilbit (NASEM, 2016). See APPENDIX A.3 for a more detailed discussion of SARA content.

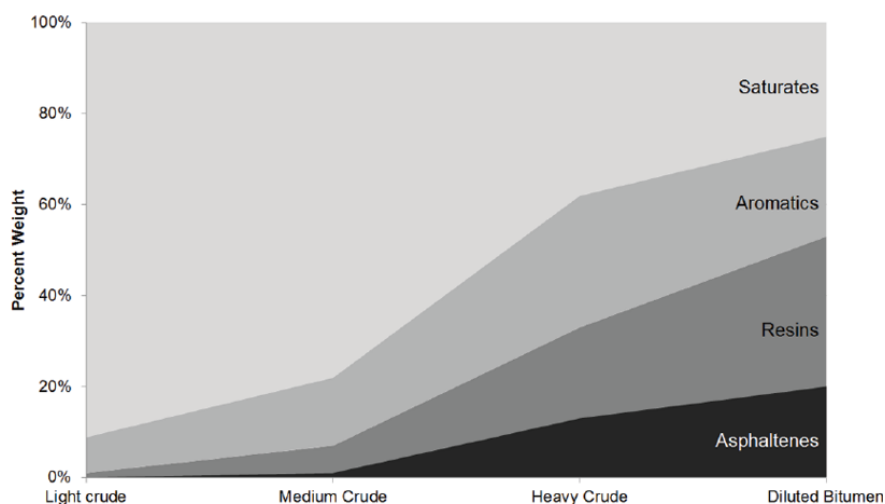


Figure 2. SARA components of typical crude oils.
(NASEM, 2016)

Dilbit products also contain several volatile organic compounds (VOCs):

- Benzene, toluene, ethylbenzene, and xylene (BTEX). BTEX makes up 0.8-1.2 percent of dilbit by volume (Environment Canada, 2013).
- Parent and alkylated polycyclic aromatic hydrocarbons (PAHs).
- Representative alkanes and petroleum biomarkers (e.g., hopanes, terpanes, and steranes).

2.3 General Behavior of Dilbit in Water

The properties of the starting bitumens vary widely, as do the diluents, resulting in highly variable dilbit products with highly variable behaviors (Fingas, 2015). Immediately following a spill, the behavior and toxicity of dilbit are similar to those of other commonly transported medium density crude oils. Since the density of dilbit is generally lower than the density of freshwater, freshly spilled dilbit will initially float on the surface.

However, the moment a spill occurs, exposure to the environment begins to change the spilled dilbit through various weathering processes. The net effect is a reversion toward properties of the initial bitumen or other heavy oil. Time is an important factor that determines when the dilbit will weather into an adhesive, dense,

viscous material. For any crude oil spill, lighter, volatile compounds begin to evaporate immediately. In the case of dilbit, as volatile compounds evaporate, a dense, viscous material with a strong tendency to adhere to surfaces begins to form as a residue. For this reason, dilbit spills pose particularly unique challenges when they occur in or reach water/freshwater environments. In some cases, the residues can submerge or sink to the bottom of the water body. It is important to note that the density of the residual oil does not necessarily need to reach or exceed the density of the surrounding water for this to occur.

The oil may combine with particles present in the water column to submerge, then remain in suspension or sink (NASEM, 2016). The U.S. National Research Council (NRC) proposed five major mechanisms for heavy oil sinking: evaporation; temperature variations with the day/night cycle causing cyclic sinking and refloating; uptake of solid matter, sand, and similar granular material; photo-oxidation; and water uptake (NRC, 1999).

Weathering alters the physical properties and chemical composition of dilbit products. These chemical and physical changes drive the behavior and fate of the oil in the environment. The weathering processes specifically addressed in this study include evaporation, photo-oxidation, and sedimentation. Weathering processes not addressed in this study include biodegradation, emulsification, spreading, dispersion, and dissolution. These processes happen at different rates when exposed to the natural elements (Fingas, 2013). Below is a brief overview of the processes addressed in this study.

- **Evaporation:** Evaporation is a weathering process where volatile compounds vaporize, leaving behind heavier hydrocarbons. Evaporation generally accounts for the greatest amount of loss compared to all other weathering processes (Environment Canada, 2013).
- **Photo-oxidation:** Photo-oxidation is a form of chemical weathering and occurs when spilled oil is exposed to large amounts of solar radiation and oxygen. It can transform individual hydrocarbon compounds, altering their chemical properties, including water solubility, which in turn may alter dissolution rates (Ortmann et al., 2011). It may also cause the viscosity, density, and adhesion properties of the oil to increase.
- **Sedimentation:** Sedimentation can lead to sinking after the attachment of sediment particles onto the oil, forming oil-particle aggregates (OPAs).

3 DILBIT WEATHERING EXPERIMENT

3.1 Research Facility

The RDC conducted mesoscale research at the U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH. This facility has a large footprint and open space to station test tanks. They also have on-site chemical analytical equipment for sample processing. Figure 3 shows the experimental setup at CRREL.



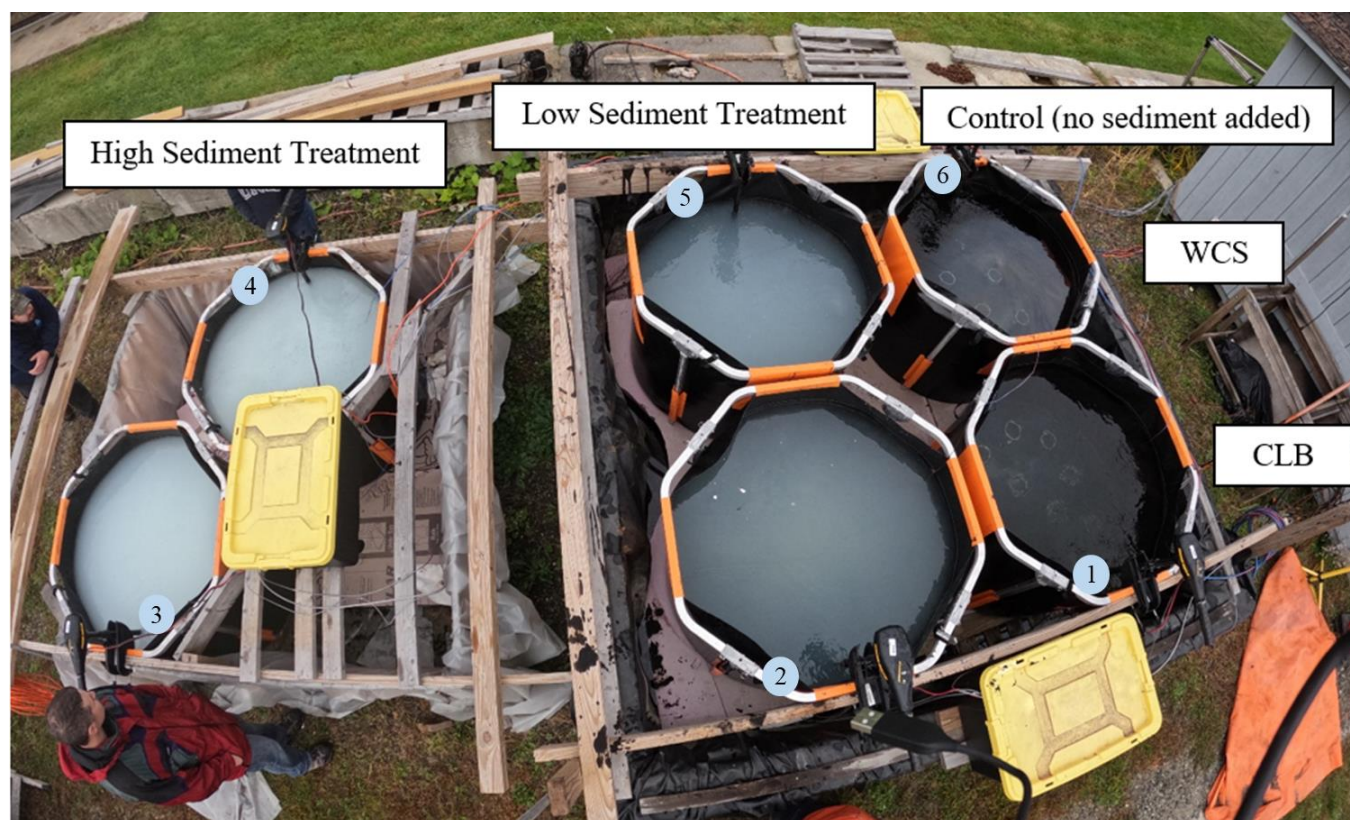


Figure 3. Experimental setup at CRREL.

3.2 Materials and Methods

RDC conducted weathering tests on two types of dilbit products as prioritized by freshwater environments, including Great Lakes region stakeholders and according to vulnerabilities related to oils carried by pipelines and rail cars:

- Cold Lake Blend (CLB).
- Western Canadian Select (WCS).

The team conducted three sets of experiments:

- Cold Weather 2021 (CW21) from 16 November to 15 December 2021 (included snow and ice).
- Warm Weather 2022 (WW22) from 13 June to 11 July 2022.
- Cold Weather 2022 (CW22) from 17 October to 15 November 2022 (ice-free conditions).

3.2.1 Experimental Set-up

The RDC researchers conducted a 30-day weathering test during each time frame. For each oil type, there was a control tank with no sediment, a tank with 100 milligrams per liter (mg/L) sediment, and a tank with 1,000 mg/L of sediment. These tanks had a diameter of 1.22 meters (m) and 0.7 m depth. Figure 4 shows a schematic of the set-up. Table 2 lists the contents of each numbered tank for each experiment.

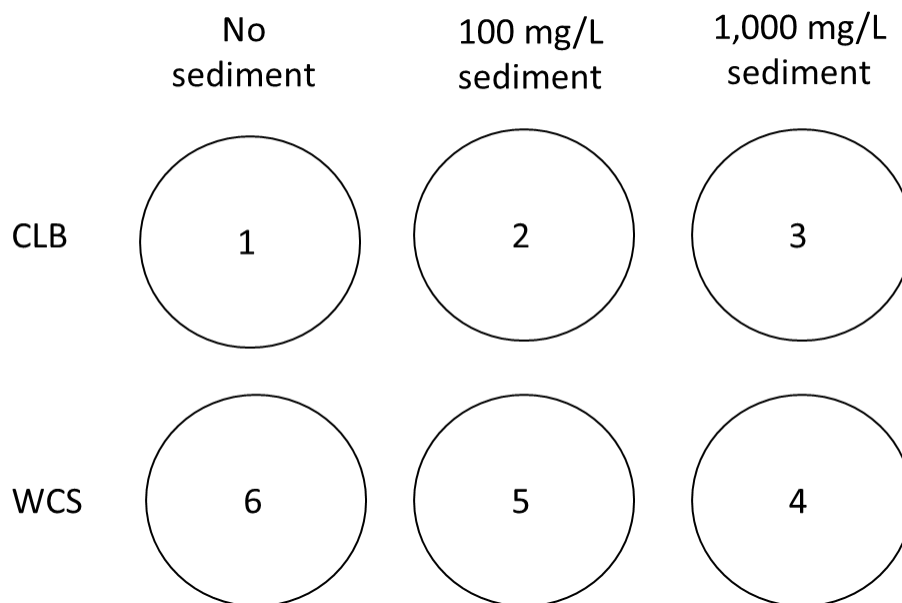


Figure 4. Test tank schematic.

Table 2. Test parameters per tank.

Tank	Dilbit	Oil mass (kilograms (kg))			Sediment (mg/L)		
		CW21	WW22	CW22	CW21	WW22	CW22
1	CLB	3.40	3.62	3.53	None	None	None
2	CLB	3.46	3.53	3.48	100	114	115
3	CLB	3.41	3.55	3.53	1,000	1,090	1,000
4	WCS	3.55	3.57	3.56	1,000	1,090	1,010
5	WCS	3.54	3.57	3.41	100	115	115
6	WCS	3.51	3.55	3.56	None	None	None

Researchers filled the tanks with freshwater (approximately 1,140 liters (L) per tank) and poured oil onto the water surfaces (sufficient mass for a three (3) millimeter (mm) slick, see Table 2) in the presence and absence of sediment in the water column. The 3-mm slick thickness represents conditions that would likely be found on open water during a dilbit spill. In this study, the dilbit products did not spread uniformly across the surface of the water due to their high starting viscosity.

For sediment, researchers used kaolin (hydrated aluminum silicate, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) from Sigma-Aldrich (Sigma-Aldrich, K7375). Kaolin is a clay mineral that has a low shrink-swell capacity. It was considered a good surrogate for natural sediments since it has been used in other dilbit studies in the past and can also be used in future studies for comparison. However, the kaolin may not provide a true representation of sediment conditions in all freshwater environments including Great Lakes, as natural sediment may have a different interaction with dilbit due to variation in polarity and particle size distribution. (Note: polarity refers to the distribution of electric charge across a molecule. Simplistically, polar compounds dissolve better in water (a polar solvent) than do non-polar compounds (Lee et al., 2015)). For this study, the sediment concentrations represent values that fall within a typical range for total suspended solids found in the Great Lakes. A turbid shoreline with many turbulent waves is represented by a concentration of 100 mg/L. Zones near the mouth of rivers and streams are represented by a concentration of 1,000 mg/L.

Researchers mixed the water in the tanks using small electric trolling motors (low energy) to simulate current that would be found at the mouth of a river or subsurface zones with undertow. Each tank was agitated for one minute “on” and four minutes “off” for the experiment duration. The “off” cycling was added to disrupt any homogenous conditions created during continuous flow time and to allow the weathered oil to settle to the bottom of the tanks. Figure 5 shows three motors at the end of CW21.



Figure 5. Three motors at the end of CW21.

3.2.2 Weather Instrumentation

Researchers collected meteorological data with a Campbell Scientific Weather Station, which included a wind speed sensor, temperature probe, and an NR01 four-component Net Radiation sensor (Campbell Scientific) (Figure 6). The weather station was located approximately 100 m north of the test tanks.



Figure 6. Weather station.

3.2.3 Water Measurements

Six K-type thermocouples (TCs) were used to measure the subsurface water temperature in each tank. The TCs were constructed with K-type TC wire and fused using an Omega Thermocouple and Fine Wire Welder “TL-Weld.” In CW21 only, the water velocity was measured at three locations in Tank #1 using an acoustic Doppler velocimeter (ADV). Only one tank was measured during one season. Researchers assumed that because each of the tanks has the same mixing mechanism the velocities were similar.

3.2.4 Visual Inspection and Photos

Researchers determined the time at which the dilbit oil sank through daily physical observations and time-lapse photographs taken throughout the study. Each tank was visually inspected for the dilbit slick every workday and photos were taken with a handheld camera. In addition, the surface of each tank was continuously monitored using GoPro® cameras set to take time-lapse photos every 30 minutes.

3.2.5 Sunken Dilbit

The amount of sunken dilbit was estimated using submerged catchment trays. Researchers assembled the trays using a 10-centimeter (cm) diameter aluminum pipe cut to 7.6 cm lengths. A 0.27 mm fine-mesh screen was attached across the bottom of the aluminum cylinders and was secured using hose clamps for easy removal (Figure 7). Ten catchment trays were distributed at the bottom of each tank in a grid pattern (see Figure 8). This allowed for random sampling of the sunken oil at the bottom of the tanks. Sunken dilbit was assessed over time by recovering five catchment trays from each tank on days 9, 12, and 15 (day 15 only in CW21). The mass of dilbit was measured in each tray and the trays were returned to the tanks. On day 29 or 30, all ten trays were removed from the tanks. In addition to the mass measurement, researchers took photographs of the trays and recorded visual observations of the texture of the sunken oil.



Figure 7. Sunken dilbit catchment trays.

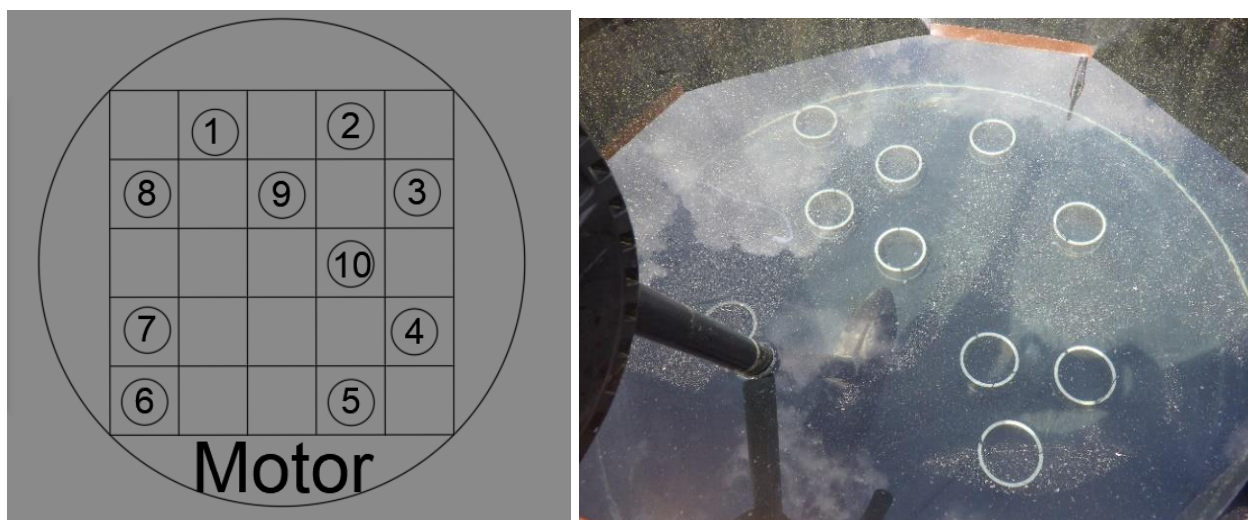


Figure 8. Schematic of sunken dilbit sampling grid pattern and photo of trays in tank.

The final fate of the dilbit was classified as being at the surface if skimmed off with a net, or at the bottom of the tank if it was scraped from the tank bottom, lower walls, or in the catchment tray.

3.2.6 Physical Measurements of the Oils

Researchers collected samples to measure density and viscosity twice per day (morning and afternoon) for the first five days, followed by once every other day for the first two weeks, and on the final day of the experiment. Approximately 80 milliliters (mL) of dilbit were collected from each slick using graduated beakers. The density was calculated by dividing the mass of the dilbit in the beaker to its volume. For samples with a lower density, an Anton Paar DMA 4200M density meter was used (see Figure 9, left). The viscosity was measured using a Brookfield DV-E rotary viscometer (see Figure 9, right). After the density and viscosity readings were collected, the dilbit was stored at four degrees centigrade (4 °C) to be used for chemical analysis.



Figure 9. Density meter (left) and viscometer (right).

3.2.7 Chemical Sampling and Analysis of the Oils

3.2.7.1 Sample Preparation

Researchers prepared the oil samples using a liquid-liquid extraction method modified from Environmental Protection Agency (EPA) Method 3510C. They extracted a small amount of oil, approximately 0.5 mL, using n-pentane. The asphaltenes, which are insoluble in n-pentane, were collected as a precipitate. The maltene fraction, which contains saturates, aromatics, and resins, was collected in the organic layer.

3.2.7.2 Saturates, Aromatics, Resins, and Asphaltenes Analysis

Researchers analyzed the oil samples for saturates, aromatics, resins, and asphaltenes (SARA). The maltene fractions were analyzed using high-pressure liquid chromatography (HPLC) on an Agilent 1260 Infinity II HPLC system with an Agilent 1260 Isopump and a Thermo Scientific Hypersil Gold Amino column (250x4.6) (see Figure 10). See APPENDIX B for more discussion of the chemical analysis process.



Figure 10. CRREL HPLC apparatus at CRREL.

3.2.7.3 Polyaromatic Hydrocarbon Analysis

Researchers analyzed the polyaromatic hydrocarbon (PAH) concentrations using a modified EPA Method 8260 in a gas chromatography–mass spectrometry (GC-MS) apparatus (Figure 11). A small aliquot of the extracted maltenes was analyzed using an Agilent 8890 gas chromatograph (GC) and Agilent 5977 mass spectrometer (MS) in selective ion plus scan mode. In CW22, an external lab was used for additional PAH analysis. At the external lab, GC–MS was conducted using an Agilent 5973N benchtop GC having a 30 m × 0.25 mm ID film column DB-5ms, Millipore Sigma.



Figure 11. GC-MS apparatus at CRREL.

3.2.8 Laboratory Scale Experiment

During WW22 and CW22, researchers set up a semi-controlled lab-scale experiment with no sediment to assess how the chemical properties of the dilbit changed over time as a function of evaporation and photo-oxidation. Controlling for these independent variables is very challenging at the mesoscale. The smaller-scale study was conducted adjacent to the 1,000 L test tanks for similar exposure to environmental conditions. Researchers filled eight (8) mason jars with dilbit and subjected them to the following treatments:

- **Evaporation** – The jars were placed in a covered area without a lid to allow atmospheric exposure and reduce exposure to solar radiation.
- **Photooxidation** – The jars were covered with glass and placed in sunlight to increase solar exposure.

3.2.9 Data Collected for Mesoscale Experiment

Researchers collected the following data:

- Weather data: continuous.
- Water data: velocity (CW21) and temperature.
- Visual inspection and photos:
 - Tanks were visually inspected every working day during testing.
 - Overhead photos for each tank collected every 30 minutes during daylight hours.
- Density and viscosity measured:
 - (CW21) 0, 2, 4, 8, 20, 24, 48, and 72 hours (h), then every 48 h for 11 days.
 - (WW22 and CW22) 0, 3, 21, 25, 45, 49, 71, and 74 h, then every 48 h for 10 days.
- Chemical analysis sampling:
 - (CW21) Days 1, 2, 3, 4, 6, 8, 10, 14, and 30.
 - (WW22) Days 1, 2, 3, 4, 5, 6, 8, 10, 12, 15, and 29.
 - (CW22) Days 1, 2, 3, 4, 5, 6, 8, 10, 12, 15, and 30.
- Catchment trays:
 - (CW21) Five catchment trays from each tank on day 15. All ten trays from each tank on day 30.
 - (WW22) Five trays from each tank on days 9, 12, and 15. All ten trays from each tank on Day 29.
 - (CW22) Five trays from each tank on days 9, 12, and 15. All ten trays from each tank on Day 30.
- Lab-scale tests (physical and chemical measurements):
 - (WW22 and CW22) Days 1, 8, 15, and 30.

4 RESULTS

4.1 Weather Data

Meteorological data was collected continuously, then averaged over 15-minute time intervals to generate a single average data point for each time interval. Overall average values for temperature and wind speed were calculated by averaging all data points during the full experiment. Daily average values for solar radiation (SR) and infrared radiation (IR) were only calculated between times 07:00 and 17:00. This time



interval was selected to capture only daylight hours during all phases of the experiment. For this study, only direct SR and IR were of interest because they represent the amount of radiation the diluted bitumen slick received. The uncertainties with the numerical results are based on the standard deviation.

4.1.1 Cold Weather 2021

From 16 November to 15 December 2021, the mean air temperature was $-0.02 \pm 4.6^{\circ}\text{C}$, with a high temperature of 16.7°C and a low temperature of -11.4°C . On 24 November (day 8), overnight temperatures dropped to around -8°C (Figure 12(a)). During this time, a 2.5 cm thick ice sheet developed on the surface of each tank. The ice sheet fluctuated in thickness and persisted through the remainder of the experiment. The ice sheet was broken each day to assess the dilbit slick. The mean wind speed during testing was 0.72 ± 0.61 meters per second (m/sec) (Figure 12(b)). The mean daily SR during testing was 80.3 ± 73.0 Watts per square meter (W/m^2) (Figure 12(c)) and the mean daily IR was $33.4 \pm 50.8 \text{ W}/\text{m}^2$ (Figure 12(d)).

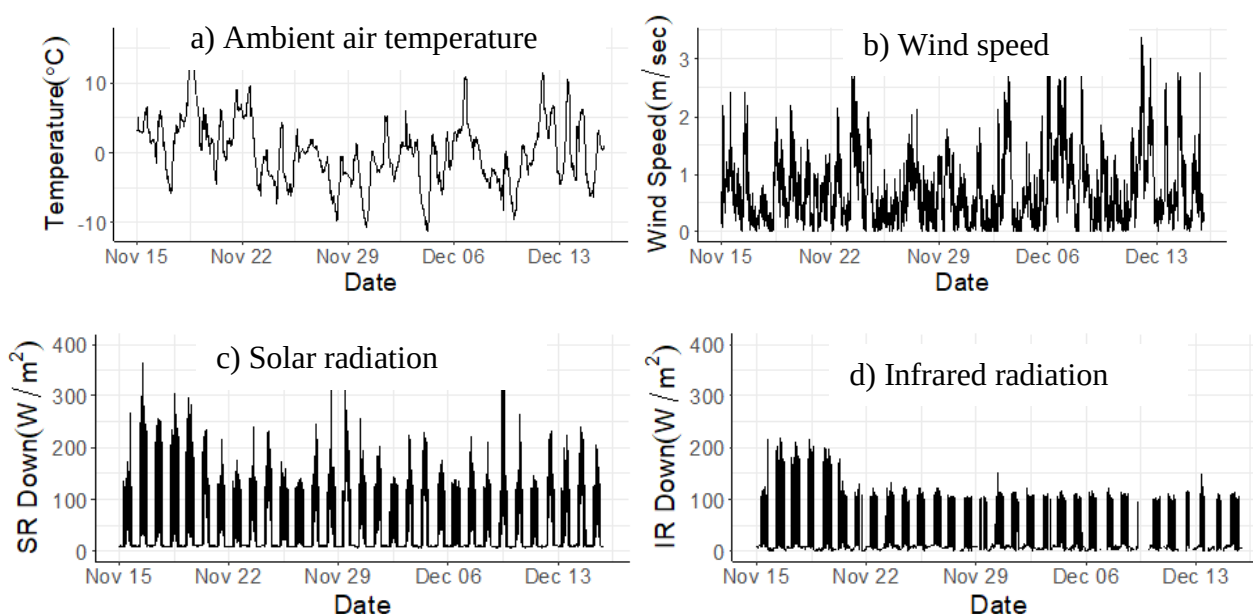


Figure 12. Weather station data for the CW21 study.

4.1.2 Warm Weather 2022

From 13 June to 11 July 2022 the mean air temperature was $19.3 \pm 5.7^{\circ}\text{C}$, with a high temperature of 33.4°C and a low temperature of 4.90°C . (Figure 13(a)). The mean wind speed during testing was 0.88 ± 0.68 m/sec (Figure 13(b)). The mean daily SR during testing was $136.8 \pm 69.7 \text{ W}/\text{m}^2$ (Figure 13(c)) and the mean daily IR was $63.7 \pm 50.8 \text{ W}/\text{m}^2$ (Figure 13(d)).

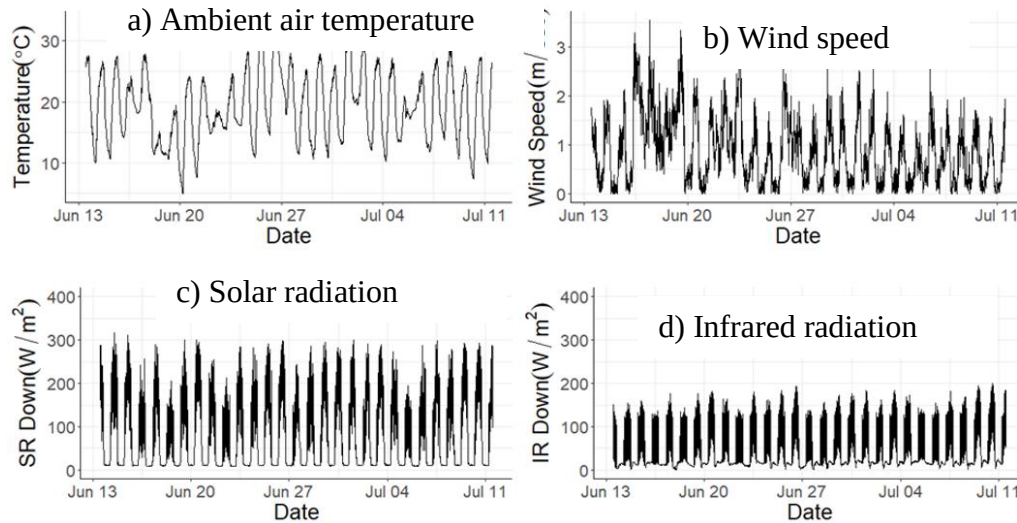


Figure 13. Weather station data for the WW22 study.

4.1.3 Cold Weather 2022

From 17 October to 15 November 2022 the mean air temperature was 8.4 ± 7.1 °C, with a high temperature of 24.2 °C and a low temperature of -7.0 °C (Figure 14(a)). The mean wind speed was 0.67 ± 0.63 m/sec (Figure 14(b)). The mean daily SR during testing was 83.0 ± 63.6 W/m² (Figure 14(c)) and the mean daily IR was 35.4 ± 46.0 W/m² (Figure 14(d)).

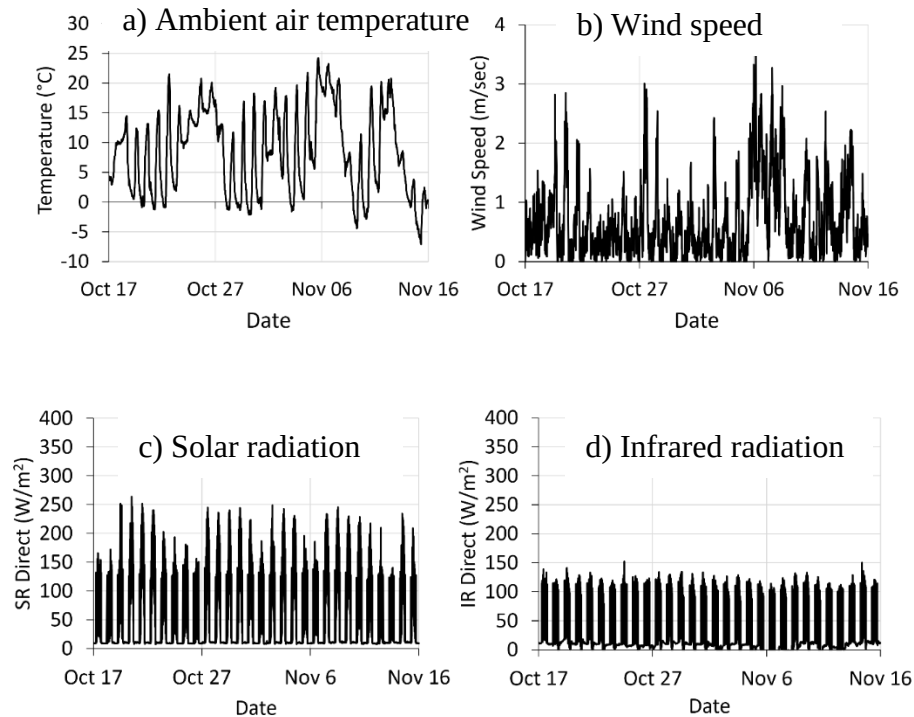


Figure 14. Weather station data for the CW22 study.

4.1.4 Weather Summary

Environmental conditions during this study were typical of the northeastern U.S., with low solar exposure and subfreezing temperatures during the cold weather studies and higher solar exposure with moderate temperatures during the warm weather study. CW21 experienced the coldest average temperatures, which led to ice buildup in the tanks despite efforts to prevent the water from freezing. CW22 experienced slightly higher temperatures and the tanks remained ice free throughout the experiment. As expected, temperatures and solar exposure were both greater during WW22. Average wind speeds were similar during all phases of the study. Table 3 provides a summary of the weather data.

Table 3. Weather data summary.

	Air Temperature (°C)	Wind Speed (m/s)	Solar Radiation (W/m ²)	Infrared Radiation (W/m ²)
CW21	-0.02 ± 4.6	0.72 ± 0.61	80.3 ± 73.0	33.4 ± 50.8
WW22	19.3 ± 5.7	0.88 ± 0.68	136.8 ± 69.7	63.7 ± 50.8
CW22	8.4 ± 7.1	0.67 ± 0.63	83.0 ± 63.6	35.4 ± 46.0

4.2 Water Data

4.2.1 Water Temperature

APPENDIX C.1 contains the water temperature plots. The water temperature was seasonal as expected compared to the air temperature.

4.2.2 Water Velocity

The water velocity was measured at three locations in Tank #1 using an acoustic Doppler velocimeter (ADV), which provided three components of the water speed. From these speeds, the mixing energy of the water was estimated, and found to be comparable to non-breaking wave conditions. See APPENDIX C.2 for details of the water velocity measurements.

4.3 Visual Inspection, Photos, and Observations

This section provides a summary and/or examples of the results from visual inspection of the tanks, photo documentation, measurements of the sunken dilbit, and observations associated with handling the oils. Photo documentation from the full three phases is available from the RDC.

4.3.1 CW21 Visual Inspection and Photos

Visual inspection and photography of the tanks in CW21 showed that ice began to develop on the surface of the tanks around day 8 of testing. Figure 15 shows the tanks at day 4, which was prior to the ice formation. After day 8, the ice was routinely broken into moderate-sized pieces each day to allow for inspection of the dilbit slick. It was estimated that between days 9 and 10 a large portion of the slick sank for both the CLB and WCS across all treatments. This event occurred on a Friday night (day 9) and was captured with the overtop cameras on Saturday morning (day 10). However, the tanks were not able to be sampled until the following Monday (day 12). On day 12, researchers verified that a large amount of the slick was no longer at the surface, and the ice sheet was broken up to take adequate photos of the event (Figure 16). The



Guidance Document – Behavior of Dilbit in the Freshwater Environment

observational assessment determined that the CLB and WCS high sediment tanks had the largest amount of dilbit at the surface on day 12.

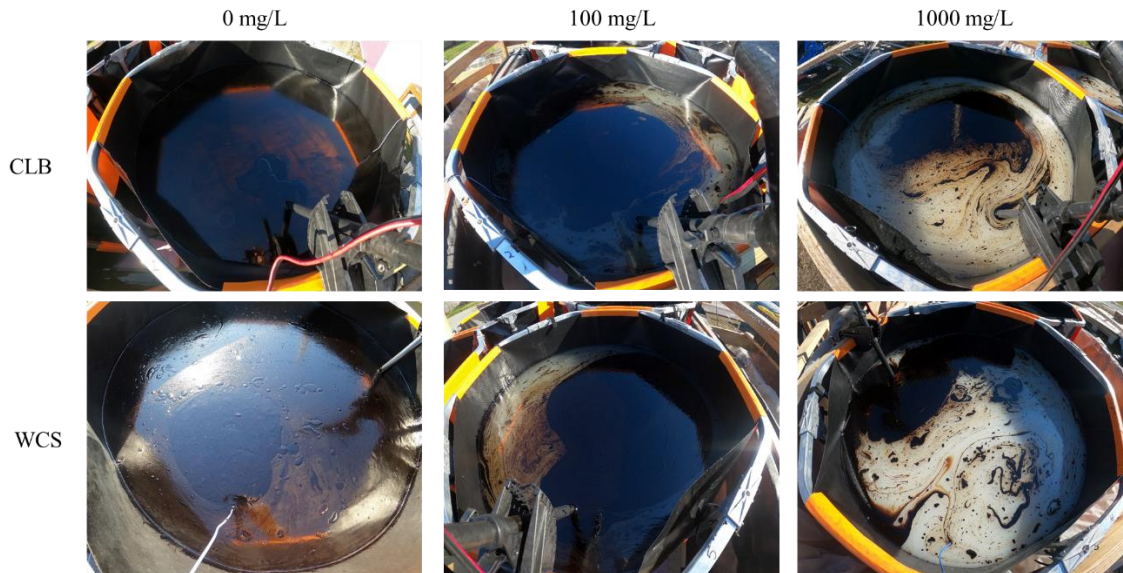


Figure 15. Overtop image of the CW21 test tanks on day 4.

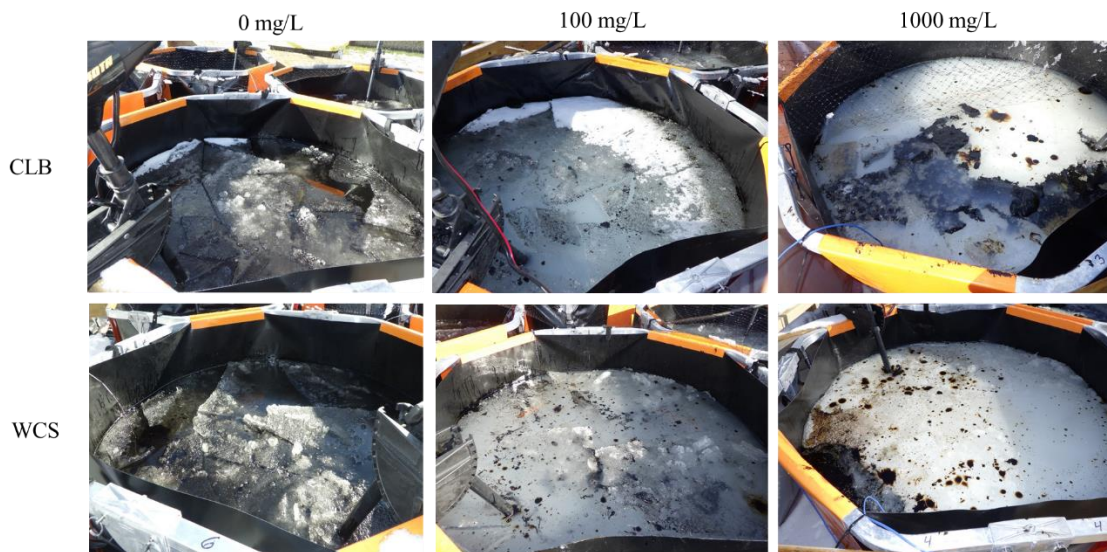


Figure 16. Overtop image of the CW21 test tanks on day 12.

4.3.2 WW22 Visual Inspection and Photos

From observation during visual inspection and photography of the tanks in WW22, researchers determined that a significant portion of the oil slick was suspended below the water surface as early as day 3. In the mornings, it was observed that the slick resembled an iceberg; a significant amount of the slick was present under the surface of the water, but still as one large globule. As time passed throughout the day, it was noted that the slick spread out and appeared to return to the surface (Figure 17). This phenomenon of sinking was noted to happen with cooler temperatures at night, followed by rising with warmer temperatures during the



Guidance Document – Behavior of Dilbit in the Freshwater Environment

days. By day 8, the oil slick was scarce in the high sediment tanks, and it was challenging to collect surface samples, as most of the oil had sunk. A change in the consistency of the CLB in the high sediment tank was also noted. In the high sediment tank, the CLB surface oil did not resemble a liquid, rather it felt solid and exhibited a gritty, stringy consistency shown in Figure 18. By day 12, a large portion of the diluted bitumen had sunk in all tanks and by day 30, no amount of appreciable oil slick was left at the surface.

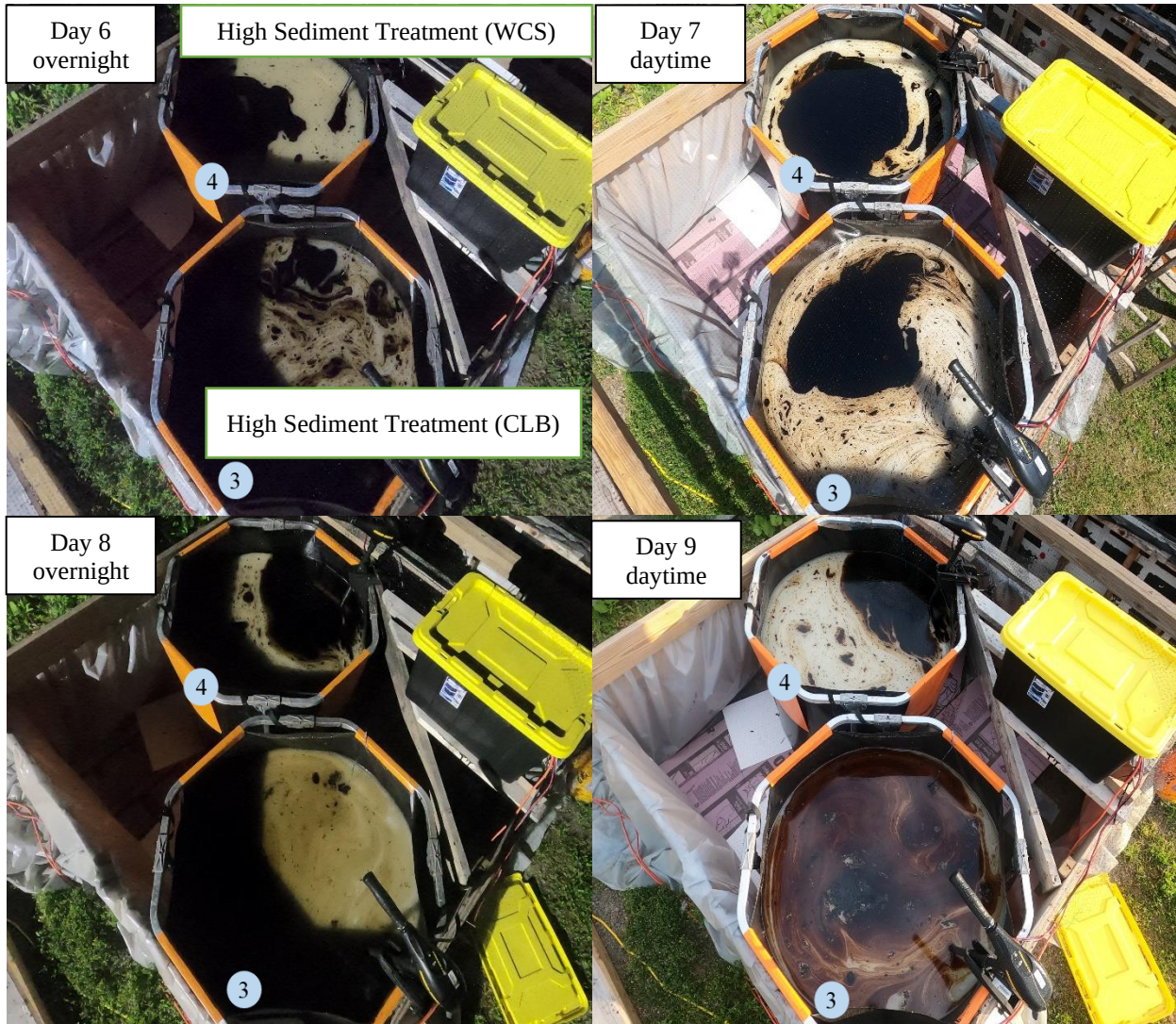


Figure 17. WW22 study photos showing oil sunken and resurfaced.



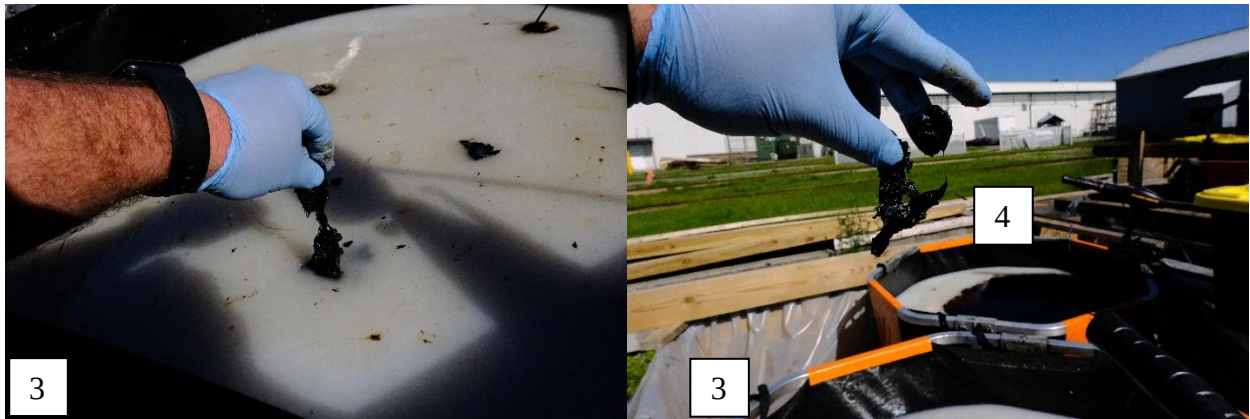


Figure 18. Day 8 photos of the high sediment CLB illustrating the consistency of the weathered oil.

4.3.3 CW22 Visual Inspection and Photos

In CW22, the overhead photographs showed that within 24 hours, the oil slick was no longer thin and diffuse, but had thickened and aggregated. Figure 19 shows overhead photos of the oil surface at one hour (left) and 24 hours (right).

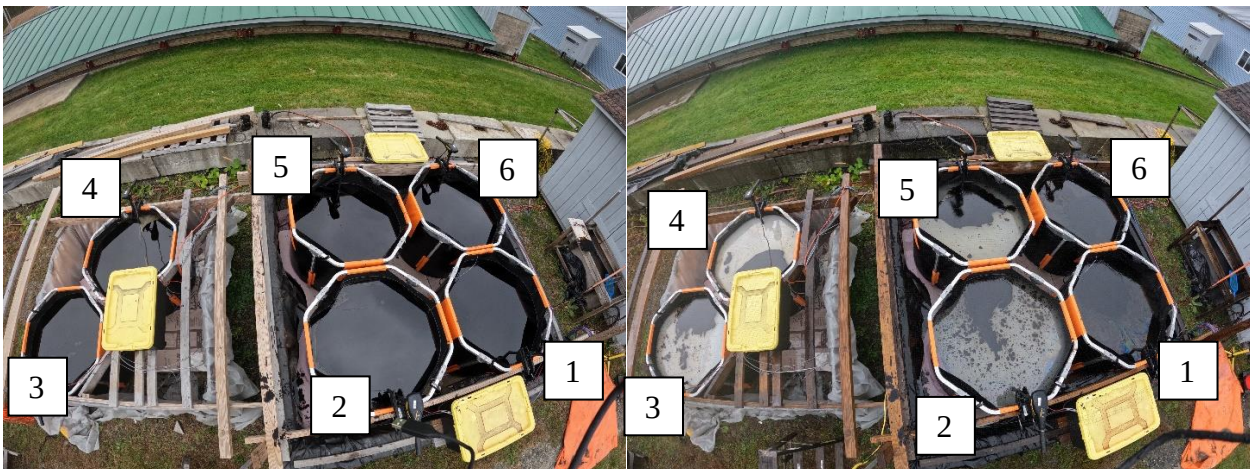


Figure 19. Overhead photos of the oil surface at 1 hour (left) and 24 hours (right).

Figure 20 shows the tanks on day 8. Tanks containing high sediment, seen in Figure 20 as the leftmost tanks #3 and #4, were observed with little surface oil while the control tanks, seen as the rightmost tanks #1 and #6, show oil remaining on the surface.

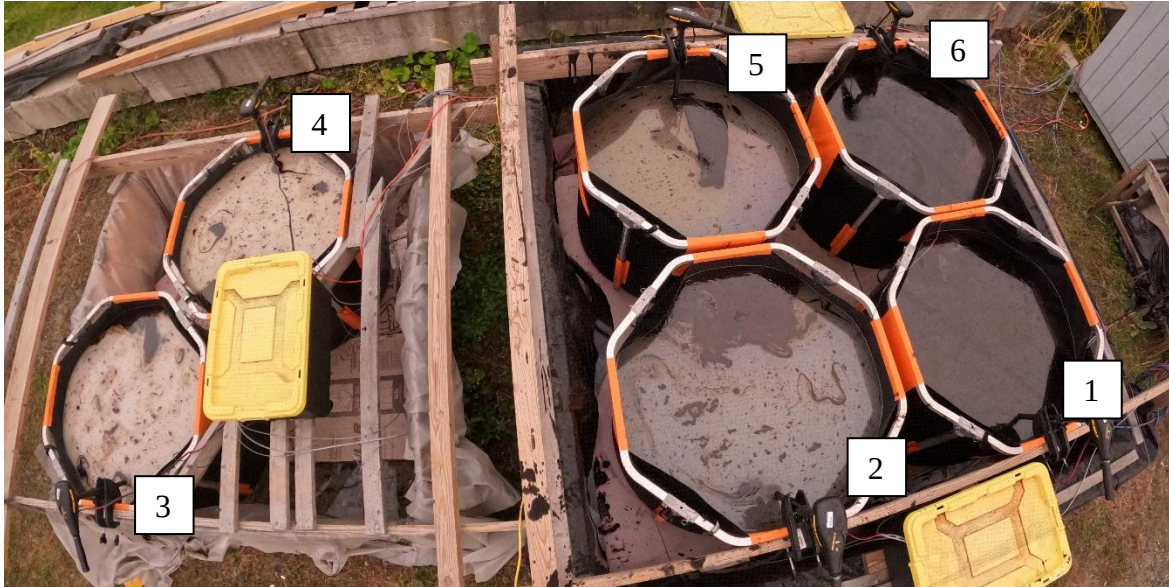


Figure 20. CW22 day 8, showing the varying amounts of surface oil.

By day 12, most of the oil in the CLB tanks, shown in the bottom row of the photographs in Figure 21, had sunk. The WCS high sediment tank (Figure 21, top left) also shows little remaining surface oil. Low and no sediment WCS tanks show oil remaining on the surface. After 30 days, the CLB control and low sediment tanks had small pancake oil slicks remaining, while the CLB high sediment tank had no oil slick remaining. The WCS control and low sediment tanks still had an oil slick remaining at the surface, while the WCS high sediment tank had only a smaller pancake slick remaining (Figure 22). All surface oil was gritty and putty-like in consistency.

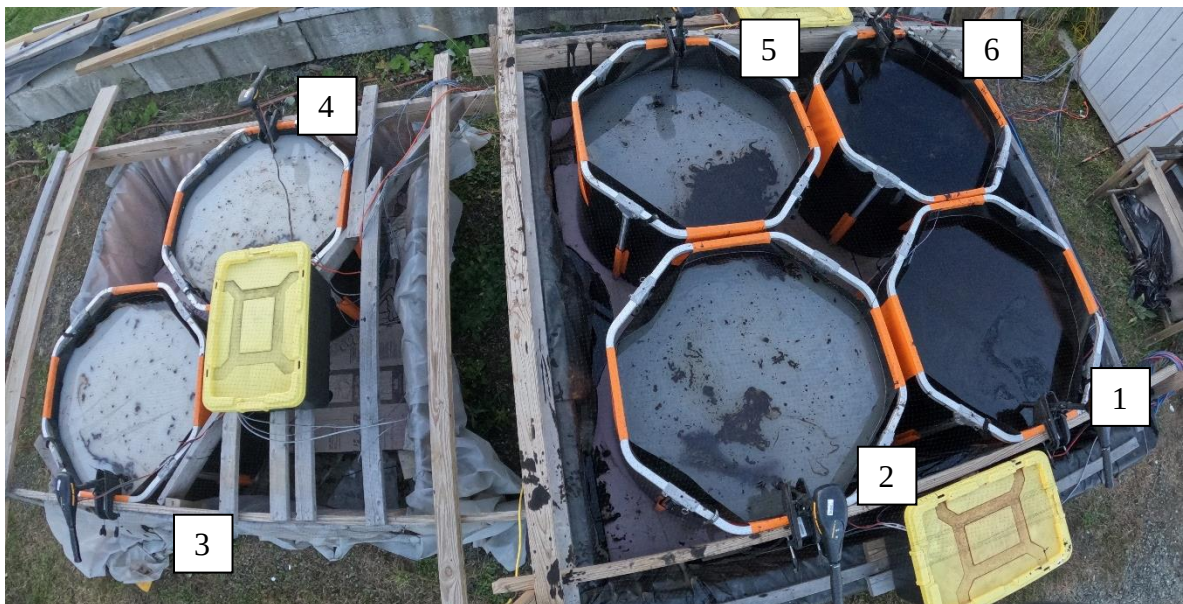


Figure 21. CW22 day 12, showing little remaining surface oil for most tanks.

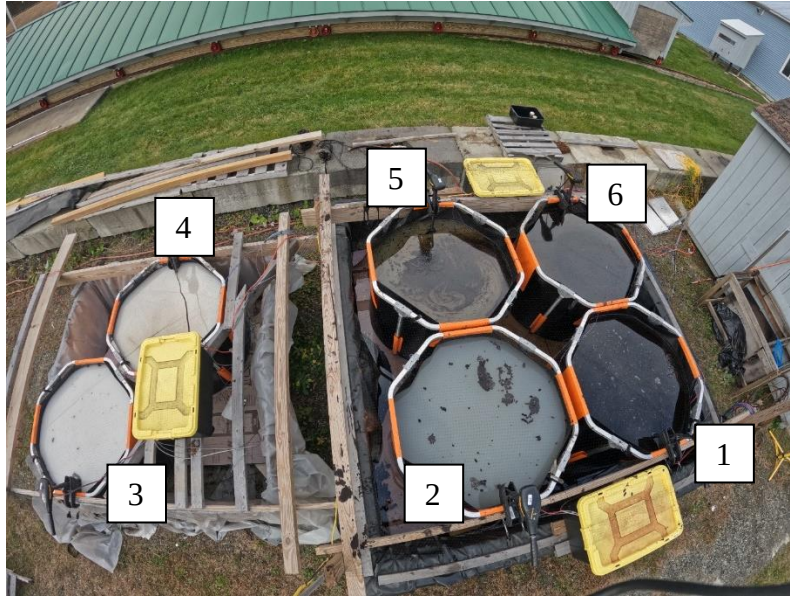


Figure 22. CW22 day 30 showing little oil remaining on surface.

4.3.4 Sunken Dilbit

As discussed in Section 3.2.5, researchers estimated the amount of sunken dilbit using submerged catchment trays. On all days but the last, the mass of dilbit product in each tray was recorded without removing the product from the tray. All trays were then returned to their respective tanks. In CW21, five catchment trays were recovered from each tank on day 15 and all ten trays were recovered on day 30. In WW22, five catchment trays were recovered from each tank on day 9, 12, and 15 and all ten trays were recovered on day 29. In CW22, five catchment trays were recovered from each tank on day 9, 12, and 15 and all ten trays were recovered on day 30. APPENDIX C.4 includes the data from all three phases.

4.3.5 Visual Inspection Summary

During both cold weather studies, some oil remained on the surface of the water after 30 days, whereas no surface oil remained on the surface during the warm weather study. Data collected from the sunken dilbit trays in CW22 appears to support the observation that sediment concentration plays a role in the sinking of the oil. Both oil types appear to show more oil recovered from the trays with a higher sediment concentration.

Figure 23 shows the texture of the dilbit in the catchment trays after 30 days of weathering during CW22.



(a) CLB no sediment (tank #1)

(b) CLB high sediment (tank #3)

Figure 23. Example trays from CW22 day 30.

4.4 Physical Properties

4.4.1 Density

Figure 24 shows the summary density graphs for the three experiments. Following the graphs are the summaries for each season. The beginning values for both oils are comparable to other reported densities for CLB and WCS of 0.928 ± 0.005 grams per cubic centimeter (g/cm^3) and 0.929 ± 0.005 g/cm^3 , respectively (POLARIS Applied Science, Inc. 2013). APPENDIX C.5.1 contains density graphs for the individual tanks.

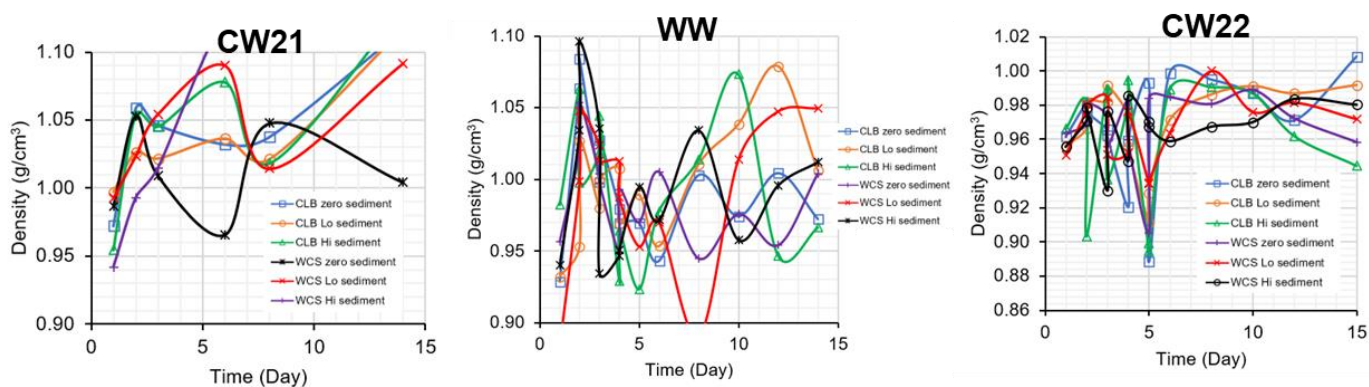


Figure 24. Density graphs.

At the beginning of CW21 and before weathering, the CLB had a density of $0.94 \text{ g}/\text{cm}^3$ and WCS had a density of $0.95 \text{ g}/\text{cm}^3$. The dilbit density increased rapidly at the beginning of the experiment for all treatments and stabilized after three days. During the first 24-48 h of environmental exposure, densities increased to around $1.00 \text{ g}/\text{cm}^3$ for both CLB and WCS and remained at or above this value for the remaining 28 days of the study (Figure 24, left).

At the beginning of WW22 and before weathering, the CLB had a density of 0.94 g/cm^3 and WCS had a density of 0.95 g/cm^3 . The dilbit density increased rapidly at the beginning of the experiment for all treatments and stabilized after 3 days. During the first 24-48 h of environmental exposure, densities increased to approximately 1.05 g/cm^3 for both CLB and WCS. Density values remained around 1.0 g/cm^3 for the rest of the study (Figure 24, middle).

At the beginning of CW22 and before weathering, the CLB had a density of 0.94 g/cm^3 and WCS had a density of 0.95 g/cm^3 . The dilbit density increased rapidly at the beginning of the experiment for all treatments and stabilized after 3 days. During the first 24-48 h of environmental exposure, densities increased to approximately 0.98 g/cm^3 for both CLB and WCS. Density values remained around this value for the remainder of the study (Figure 24, right).

4.4.2 Viscosity

Figure 25 shows the summary viscosity graphs for the three experiments using a logarithmic scale for viscosity. Following the graphs are the summaries for each season. APPENDIX C.5.2 contains viscosity graphs for the individual tanks.

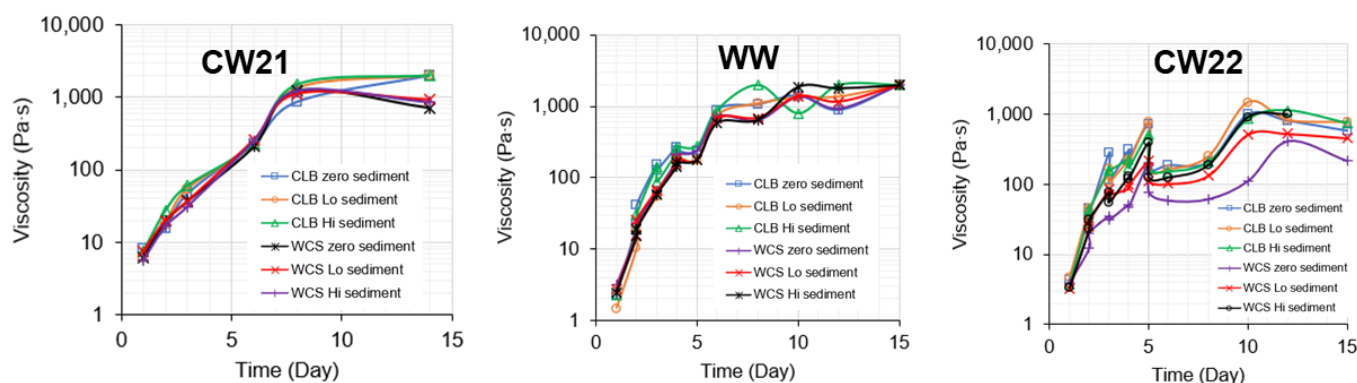


Figure 25. Viscosity graphs.

In CW21, the starting viscosity for the CLB was 0.55 Pascal-seconds (Pa·s). For all sediment treatments, the CLB viscosities increased steadily from zero to six days reaching 250 Pa·s, then from 6-8 days, the CLB viscosities increase rapidly reaching 750-1,500 Pa·s. The control tank had the lowest viscosity at this time. Between 8-13 days CLB viscosities climbed steadily and peaked at 2,000 Pa·s. CLB viscosities then decreased between 13-15 days. The starting viscosity for the WCS was 0.6 Pa·s. For all sediment treatments, the WCS viscosities increased steadily from zero to six days reaching 250 Pa·s, then from 6-8 days, the WCS viscosities increase rapidly reaching 1,116-1,244 Pa·s. WCS viscosities then decreased slightly between 8-15 days (Figure 25, left).

In WW22, the starting viscosity for the CLB was 0.55 Pa·s. For all sediment treatments, the CLB viscosities increased rapidly over the first three days, reaching 273.5 Pa·s in the control tank after 72 hours. By day 8, CLB viscosity in the control tank is above 1,000 Pa·s, while the high sediment tank was measured at above 2,000 Pa·s, the limit of our instrument. By day 15, all CLB tanks were measured at above 2,000 Pa·s (Figure 25, middle). The starting viscosity for the WCS was 0.60 Pa·s. After the first three days, the viscosity was 150 Pa·s; about half the increase in viscosity when compared to the CLB. By day six, WCS viscosities for

all sediment types are above 500 Pa·s, and above 1,000 Pa·s by day 10. Similar to CLB, by day 15 all WCS tanks were measured at above 2,000 Pa·s.

In CW22, the starting viscosity for the CLB was 0.36 Pa·s, increasing to 4.3 Pa·s after 4 hours. For all sediment treatments, the CLB viscosities increased rapidly over the first three days, reaching 282 Pa·s in the control tank after 72 hours. By day 10, CLB viscosity in the control tank was above 1,000 Pa·s. By day 15, all CLB tanks were measured at above 2,000 Pa·s, the limit of CRREL's instrument. The starting viscosity for the WCS was 3820 Pa·s, increasing to 3.82 Pa·s after 4 hours. After the first three days, the viscosity was 35.2 Pa·s; roughly an eighth the increase in viscosity when compared to the CLB. For both WCS and CLB, the viscosities in the control tanks are consistently below the viscosities in the low sediment tanks, and the viscosities in the low sediment tanks are consistently below the viscosities in the high concentration tanks (Figure 25, right).

4.4.3 Physical Properties Summary

Figure 24 (center (WW22) and right (CW22)) indicates obvious density fluctuations for both CLB and WCS (likely due to diurnal heating and cooling) that correlate to the visual observations.

These results demonstrate that the physical properties (density and viscosity) of dilbit in fresh water can rapidly change, resulting in the submergence and subsequent resurfacing, and later sinking of dilbit. The primary difference between the CLB and WCS oils was in CW22, when there seemed to be a rapid increase in viscosity for CLB and a slower increase for WCS.

4.5 Chemical Properties

4.5.1 Saturates, Aromatics, Resins, and Asphaltenes

Researchers used HPLC to measure the SARA content of the oils at various points in the experiment to help understand the oil component changes with different sediment concentrations. Generally, measurements are standard where large changes in the asphaltenes are expected because the asphaltenes cannot be measured using common gas chromatography (the temperature in those columns does not rise sufficiently high). Figure 26 through Figure 28 show the SARA summary graphs for the three experiments. APPENDIX C.6 contains individual tank data.

4.5.1.1 SARA Results from CW21 Mesoscale Tanks

In CW21 (Figure 26) the saturates manifest essentially no decrease with time, reflecting the fact that little evaporation or degradation took place. The resins show fluctuations with time, and one may assume that their fraction did not change. The aromatics show a consistent decrease in mass percent from around 60 percent to around 50 percent. The fraction of asphaltenes rose from around 8 percent to around 22 percent, suggesting an inverse relation with the aromatics. The difference between various tanks (e.g., oils and/or sediment content) is too small to distinguish between them, considering the uncertainty in the SARA quantification method (and all SARA methods).



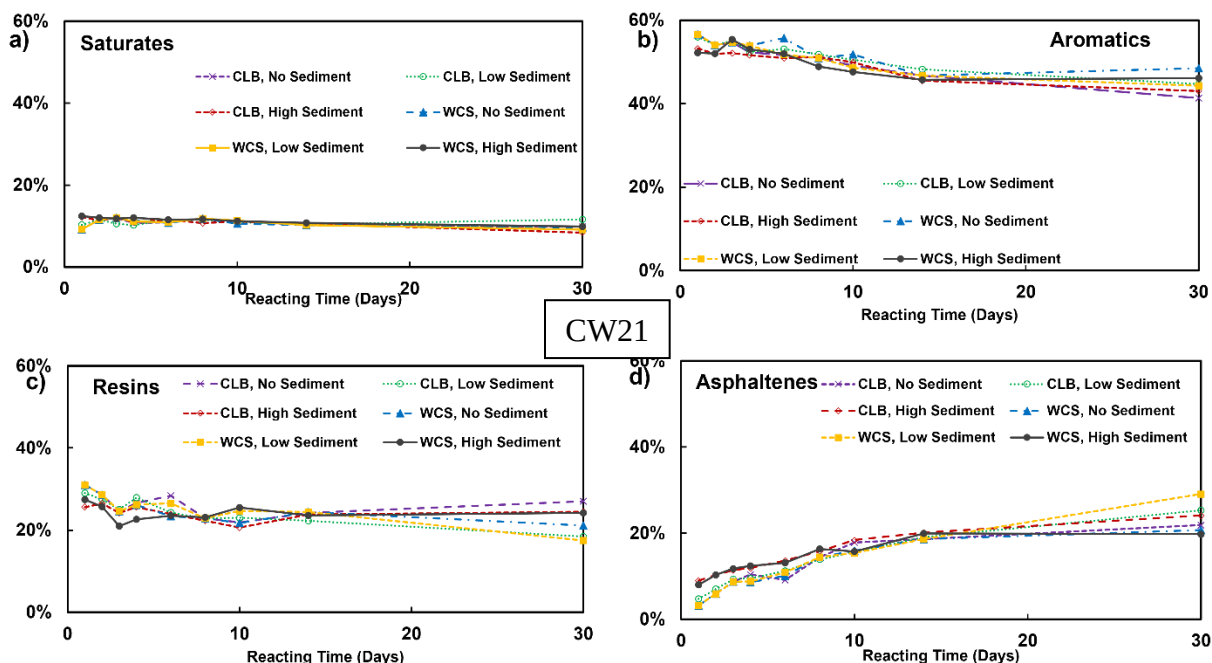


Figure 26. CW21 consolidated SARA.

4.5.1.2 SARA Results from WW22 Mesoscale Tanks

In the warm weather experiment (Figure 27), no oil was present on the water surface on Day 29, so the sample was obtained from the bottom of the tanks. The fraction of saturates decreased rapidly within five days and then decreased more gradually over time. The total decrease was around 5 percent. It is assumed the fraction of resins increased initially as if to compensate for the evaporation of some saturates. The variability with time suggests that these changes are not conclusive to the fate of the saturates. The fraction of aromatics decreased from around 60 percent to around 25 percent within five days then fluctuated for 10 days before essentially leveling off on Day 29 at around 25 percent. The fraction of asphaltenes rose from around 5 percent to around 40 percent within 10 days and then leveled off.

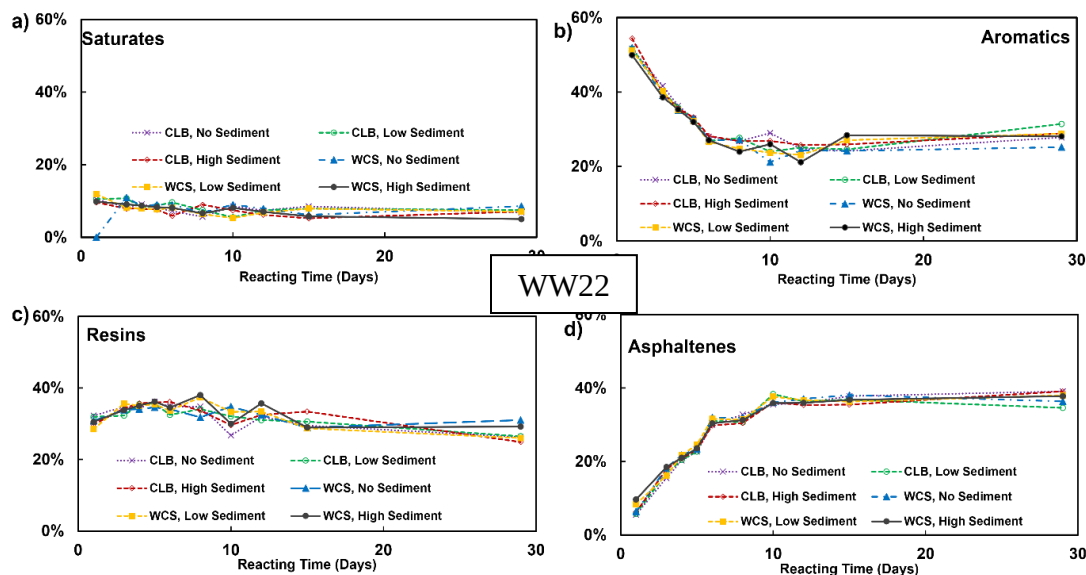


Figure 27. WW22 consolidated SARA.

4.5.1.3 SARA Results from CW22 Mesoscale Tanks

Figure 28(a) indicates that the saturates concentration slightly fluctuated with the mixing time, and the changes were not significant, showing that there was little evaporation or degradation. Figure 28(b) for aromatics shows that the fraction of aromatics decreased significantly from over 50 percent to lower than 30 percent with the treatment time, regardless of the sediment concentration for both CLB and WCS oils. This confirmed that photo-oxidation happened in the experiment setup. Figure 28(c) shows little change in fraction of resins throughout the experiment. Figure 28(d) indicates that the increase in the fraction of asphaltenes from 20 percent to around 40 percent with the treatment time at various sediment concentrations for both CLB and WCS oils. The fraction of asphaltenes is inversely correlated to the changes of aromatics.

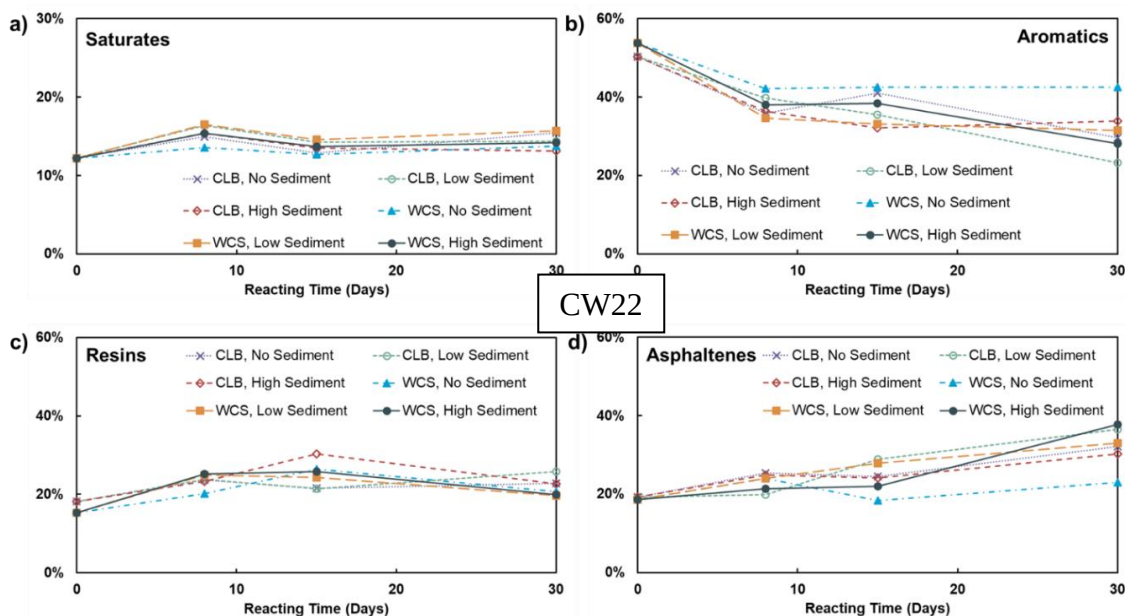


Figure 28. CW22 consolidated SARA.

Of interest in Figure 26 through Figure 28 is the behavior of resins, which was not consistent across seasons. However, the changes were small, except for CW22, which exhibited a clear initial increase within the first 15 days and then a decrease with time until it stabilized. In general, photo-oxidation is expected to increase the fractions of both asphaltenes and resins (Garrett et al., 1998; Radović et al., 2014; and Aeppli et al., 2022).

Figure 29 shows the correlation between the fraction of aromatics and the fraction of asphaltenes for CLB and WCS oil during CW22. The coefficient value (R^2) is 0.80 for the CLB oil and is 0.68 for WCS oil. The slope for CLB and WCS oils were -0.59 and -0.57, respectively, indicating the evaporation of the aromatics resulted in the asphaltene making up a greater fraction of the sample, with only some asphaltene evaporating or degrading.

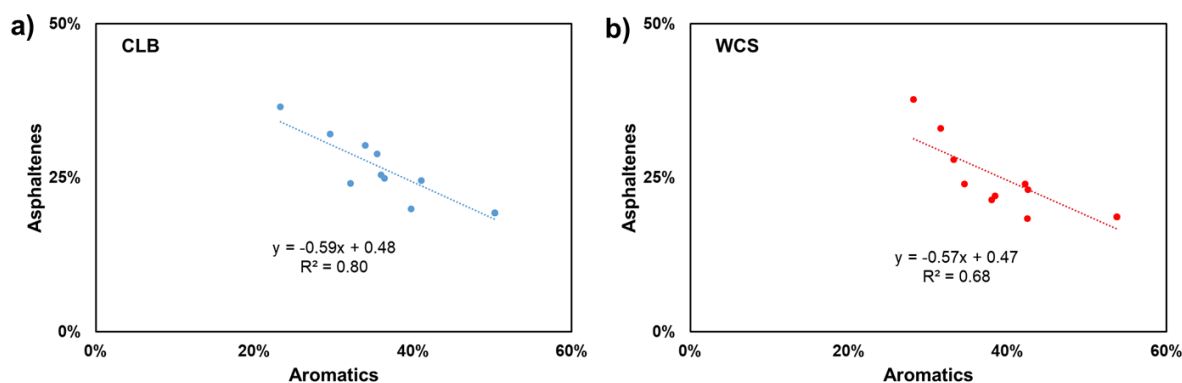


Figure 29. CW22 SARA correlation.

4.5.1.4 SARA Results from Laboratory Scale for WW22 and CW22

The laboratory scale tests involved exposing un-weathered (raw) dilbit products in glass jars outdoors for 30 days to measure evaporation and photo-oxidation. One jar was removed for analysis on days 1, 8, 15, and 30. Figure 30 shows the WW22 SARA evaporation results and Figure 31 shows the WW22 SARA photo-oxidation results. Figure 32 shows the CW22 SARA evaporation results and Figure 33 shows the CW22 SARA photo-oxidation results.

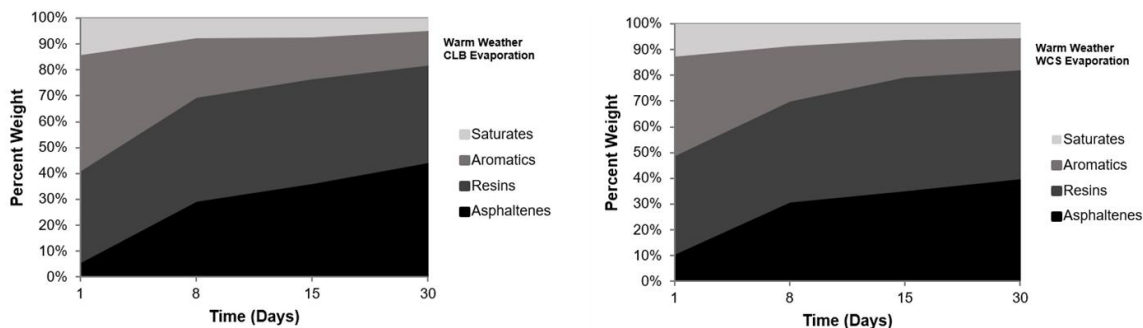


Figure 30. WW22 laboratory scale SARA evaporation results.

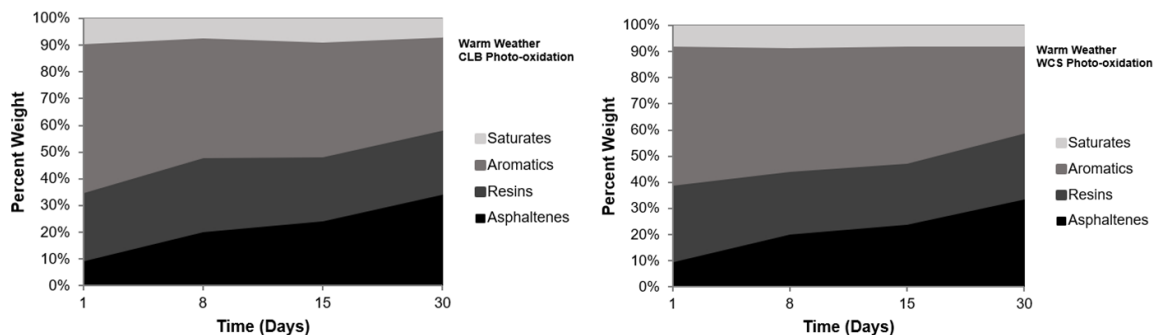


Figure 31. WW22 laboratory scale SARA photo-oxidation results.

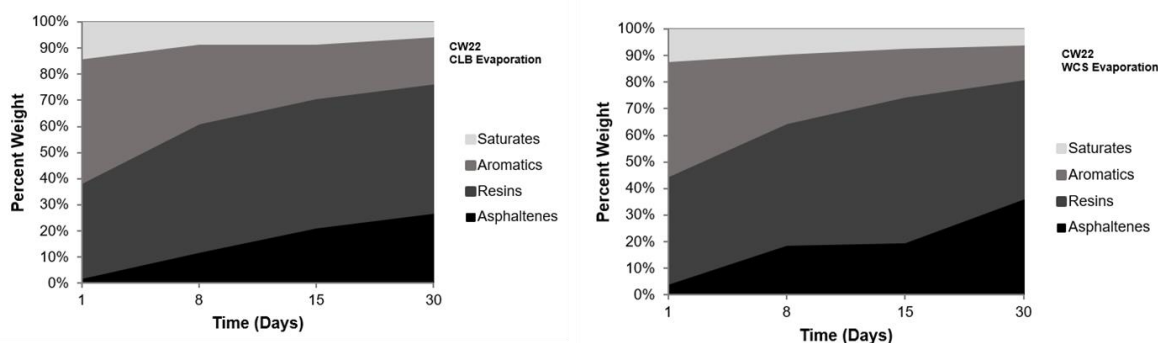


Figure 32. CW22 laboratory scale SARA evaporation results.

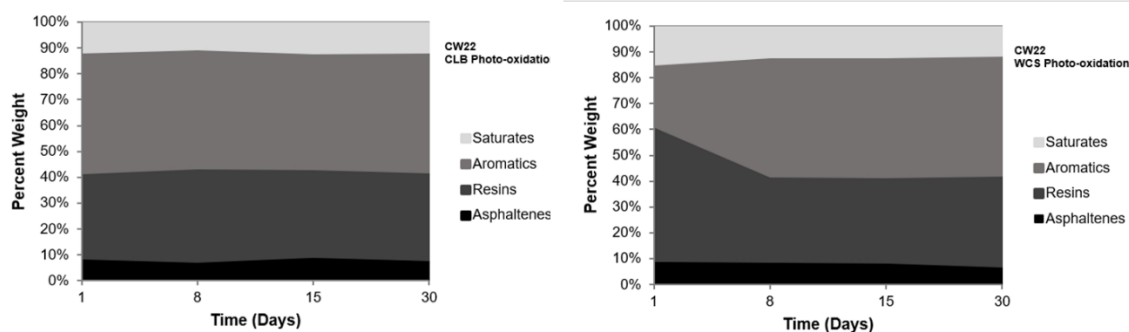


Figure 33. CW22 laboratory scale SARA photo-oxidation results.

4.5.1.5 SARA Discussion

The SARA results are important because the results demonstrate that the chemical composition of dilbit changes over time. The change in chemical composition over time is correlated to the sinking of dilbit over time. For the WW22 lab-scale results, evaporation was observed for both CLB and WCS samples. On day 1, the aromatics comprised the greatest weight percent of the samples. The weight percent of resins marginally increased until day 30. The weight percent of saturates decreased from 13.7 percent to 4.5 percent for CLB and 12.3 percent to 5.2 percent for WCS. The weight percent of aromatic compounds decreased over time until day 30. Aromatic compounds are highly volatile. The weight percent of asphaltenes increased significantly over time from 6.2 percent to 44.5 percent for CLB and 11.0 percent to 40.3 percent for WCS. Asphaltenes have a polar substitute, which may cause the asphaltenes to be less volatile and not subject to loss during evaporation.

For the photo-oxidation treatment in WW22, compared to the WW22 evaporation samples, a higher weight percent of aromatics was observed in both the CLB and WCS samples. However, overall, the weight percent of aromatics still decreased over time; the weight percent of aromatics decreased from 55.6 percent to 34.9 percent for CLB and from 53.3 percent to 33.3 percent for WCS. Like the WW22 evaporation results, the weight percent of asphaltenes increased for the duration of the 30 days, from 9.7 percent to 34.6 percent for CLB and 10.0 percent to 34.1 percent for WCS. The weight percent of resins and saturates remain constant in their range percentages for the duration of the 30 days.

The SARA weight percentages in the CW22 study for evaporation and photo-oxidation treatment were generally similar to those observed during the WW22 study. However, the results of the CW22 evaporation experiment show greater total percentages for resins and aromatics, indicating the rate of evaporation was slower in cold weather than in warm weather. In the CW22 evaporation samples, the weight percent of resins increased from 36.4 percent to 49.5 percent for CLB and slightly increased from 40.4 percent to 45.0 percent for WCS. The weight percent of aromatics decreased from 47.7 percent to 18.1 percent for CLB and from 43.2 percent to 13.1 percent for WCS. The weight percent of saturates decreased from 13.7 percent to 5.3 percent for CLB and from 11.8 percent to 5.5 percent for WCS. The weight percent of asphaltenes increased from 2.3 percent to 27.1 percent for CLB and from 4.6 percent to 36.4 percent for WCS.

Comparing the WCS and CLB results for the CW22 photo-oxidation treatment, it showed a different result when compared with the evaporation treatment. The aromatics had the greatest weight percentages, 46.6 percent to 46.3 percent for CLB and 16.6 percent to 46.4 percent for WCS. Figure 33 shows an anomalous behavior for WCS photo-oxidation where aromatics increased and resins decreased. The cause of behavior is unknown.

It is important to note that aromatics increase rapidly for WCS from day 1 (16.6 percent) to Day 8 (46.3 percent) and then final day 30 (46.4 percent). On day 1, WCS contained less aromatics. By day 30, it has increased to the same percent as CLB. Unlike WW22, resins in CW22 have greater percentages, 33.1 percent to 34.2 percent for CLB and 36.4 percent to 35.1 percent for WCS. Asphaltenes and saturates are in the lower ranges. The hypothesis is that evaporation is the primary mechanism causing the aromatic compounds to lose mass.

SARA analysis was also performed on both dilbit products, CLB and WCS samples from the mesoscale tanks in each of the three experiments. Figure 34 shows scatter plots of these quantities from the mesoscale samples, where a negative linear relationship could be posited based on the relatively high value of the coefficient of determination, R^2 (> 0.80). The slope was -1.06 in WW22, -1.46 in CW21 and -0.67 in CW22. This correlation between aromatics and asphaltenes is similar to what is shown from the laboratory-scale SARA results.

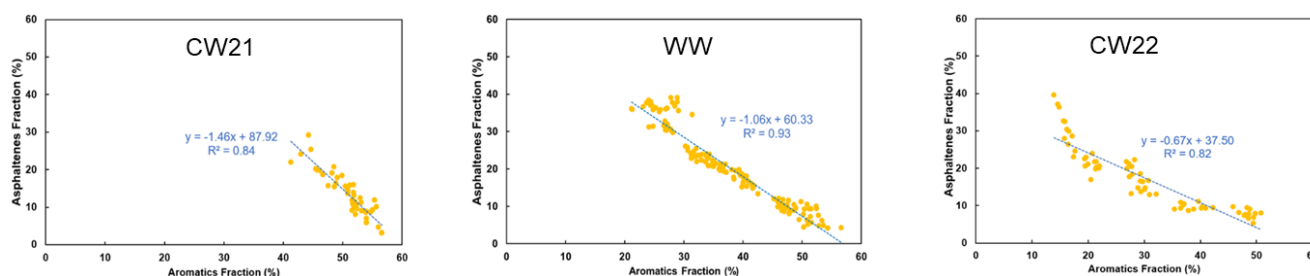


Figure 34. Correlation between the asphaltene fraction and the aromatics fraction.

Biodegradation is also expected to be small for the bitumen components, since bitumen consists of large molecules of saturates and aromatics. In addition, since tap water was used, including its chlorine content and with limited availability of nutrients (nitrogen and phosphorus), the percent loss of petroleum hydrocarbons due to microbial degradation is expected to be small.

4.5.2 Polyaromatic Hydrocarbons

The GC-MS data represents both linear and cyclic hydrocarbons. Saturates have low molecular weight and are non-polar compounds. Aromatics are cyclic and ringed compounds (example: Benzene). The PAHs highlighted in this study are Naphthalene, C1-C4 Naphthalene, Fluorene, C1-C4 Fluorene, Phenanthrene, C1-C4 Phenanthrene, Dibenzothiophene, C1-C4 Dibenzothiophene, Chrysene, C1-C4 Chrysene.

APPENDIX C.7 contains the PAH results for the individual tanks and lab-scale samples for WW22 and CW22 (researchers did not analyze PAH in CW21). Naphthalene is a 2-ring compound with a molecular formula $C_{10}H_8$. Both Fluorene and Phenanthrene are 3 ringed compounds. Fluorene has an ortho-fused tricyclic component with a molecular formula of $(C_6H_4)_2C_2H_2$. Phenanthrene is fused with three benzene rings and has a molecular formula of $C_{14}H_{10}$. Dibenzothiophene is a heterocyclic aromatic and an organosulfur compound with a central thiophene ring and two benzene rings. Chrysene is an aryl hydrocarbon, a 4-ringed compound with a molecular formula of $C_{18}H_{12}$. These PAHs are on the United States Environmental Protection Agency pollutant list, some are toxic, mutagenic, carcinogenic, or persistent properties in the environment.

The GC-MS data indicates a total increase in the aromatic compounds Phenanthrene and Dibenzothiophene in the samples from the photo-oxidation experiment. For WW22, the mass percent of C2 dibenzothiophene and C1 Fluorene increased in the samples from the evaporation experiment. For CW22, the samples from the evaporation experiment contain almost twice the mass of dibenzothiophene and C2- Phenanthrene when compared to the samples from the photo-oxidation experiment. The mass fraction of C2-C3 dibenzothiophene is highest in the samples from the photo-oxidation experiment. The mass fraction of C1-C4 Chrysene, a 4-ringed compound, is low in samples from both the evaporation and the photo-oxidation experiments.

4.5.3 Chemical Properties Summary

The aromatics that evaporate under normal environmental conditions are usually the naphthalenes and fluorenes, whereby the evaporation rate decreases with the degree of alkylation (i.e., C2-Naphthalene evaporates slower than C1-Naphthalene) (Abou Khalil et al., 2021). The evaporation of dibenzothiophene and phenanthrenes (especially the parent ones) could also occur, but at a much slower rate (Abou Khalil et al. 2021).

Photo-oxidation by sunlight is very effective at oxidizing three-, four- and five-ring aromatics in floating slicks and stranded oil, whereby the molecules are not destroyed, but become polymerized and incorporated into the resin and polar fractions of the oil (Aeppli, 2022). Photo-oxidation has the opposite effect on aromatic hydrocarbons relative to evaporation and biodegradation since photo-oxidation rate increases with the degree of alkylation (Garrett et al. 1998, Dutta and Harayama, 2000). There are several methods to investigate if photo-oxidation took place in a sample. One is to conduct SARA analysis, whereby the weight percent of aromatics should decrease with time and the weight percent of the resins and asphaltenes should increase with time. Another method would be to investigate the percent depletion of individual polycyclic aromatic hydrocarbons, particularly the depletion of chrysenes and pyrenes (both parent and alkylated) since



these compounds don't evaporate under normal environmental conditions. If the percent depletion increases with the degree of alkylation, then it can be assumed that photo-oxidation was the predominant mechanism (Garrett et al. 1998 and Dutta and Harayama, 2000). However, if the percent depletion decreases with the degree of alkylation, then it can be assumed that evaporation was the predominant mechanism.

In CW22, for CLB with no sediment, around 40 percent loss of the alkanes and aromatics occurred by day 15, but a large loss occurred by day 30, and was more than 60 percent loss for most components. For WCS with no sediment, the loss of components by day 15 was more than 50 percent for the alkanes and less than 40 percent for the aromatics (in general). However, the loss increased only slightly at Day 30. In general, the loss of components could not be attributed to one process, but to a combination of evaporation and photo-oxidation.

For the CW22 data only, Analysis of Variance (ANOVA) tests were conducted to evaluate the impact of sediment concentration using the loss of total petroleum hydrocarbons (TPH). At day 15, it was found that CLB with zero sediment had a higher loss by comparison to CLB with high sediment concentration. It is likely that the binding of the CLB to sediment and subsequent settling reduced oil loss. There was no statistical difference between the WCS samples from the zero sediment tanks and the high sediment concentration tanks. The SARA results show a trend over time of decreased weight percent of aromatics and increased weight percent of asphaltenes. A linear correlation for all tanks showed that 0.5 g of asphaltenes was produced for every loss of 1.0 g of aromatics.

5 CONCLUSIONS

The RDC conducted field experiments to address several knowledge gaps regarding the sinking or floating of dilbit products in the freshwater environment, with the objective of providing a more informed strategy to the emergency response actions during dilbit product spills. The experiments focused on the weathering of two common dilbit products, CLB and WCS, representative of oil-sands products which originate in Canada and are transported through the United States, including across Great Lakes waterways.

5.1 Variations in Dilbit Products

CLB and WCS have many similarities but also differ. When comparing the initial properties, the CLB product is thicker and adheres to itself, while the WCS product is more fluid and spreads across the surface of the water. During the physical characterization, the CLB density and viscosity was higher than for WCS. During weathering, the viscosity in the CLB mesoscale tank increased rapidly than when compared to the viscosity in the WCS mesoscale tank. This makes the texture different as evaporation occurs and the oil product thickens. Viscosity rapidly increased for the first three days and then continued to slowly increase through day 30. CLB and WCS sank at slightly different rates.

5.2 Variations in Weather Conditions

Ambient temperature plays an important role in the behavior of dilbit. The mesoscale experiments occurred during three time periods – Fall 2021, Summer 2022, and Fall 2022. The results from the three experiments indicate that the dilbit products in fresh water will sink in both warm and cold seasons – including extremely cold seasons with the presence of ice or snow.



Results of the experiments identified that weathering of dilbit begins immediately upon spillage and evaporation occurs more rapidly in warm weather than cold weather. In all tested conditions, the dilbit sank within the 30-day test period. The sunken oil was collected in the tanks using catchment trays and then measured for mass balance.

Dilbit generally sinks faster in the warm weather compared to the cold weather responding to a floating dilbit in the warm weather will require a faster response.

5.3 Variations in Sediment Contents

During the literature review, past studies showed that dilbit tends to sink in the presence of suspended particles. At the water surface, the presence of sediment causes the products to lose fluidity and adopt a colloidal or solid consistency. The increase in suspended particles will cause more rapid sinking of the dilbit products. This phenomenon was observed in both the fall and summer experiments. The dilbit products in the high sediment tanks sank more rapidly than the dilbit products in the control and low sediment tanks. The results from this study during cold (ice and ice-free) weather demonstrate that dilbit will sink in both the presence and absence of sediment. A compounding factor is that below 4 °C, water density *decreases* slightly while dilbit density increases.

5.4 Intersections/Interactions Between Multiple Variables

The interactions between variables or the statistical significance of those interactions were not studied in this research. However, additional experiments were carried out to study the effects of evaporation and photo-oxidation on the behavior and composition of the dilbit products. The results from the chemical analyses show that the CLB with no sediments lost more alkanes and aromatics, and WCS with no sediment lost more alkanes and less aromatics. The loss of components in the dilbit can be attributed to both evaporation and photo-oxidation.

The research indicates that dilbit spills in fresh water can be treated as conventional, heavy oil spills for the first few days while the dilbit remains buoyant on the surface of the water, provided the effects of mixing and sediments do not impair the buoyancy.

Figure 35 provides a summary of the observational results for CLB. Figure 36 provides a summary of the observational results for WCS. The cold weather data, referenced in Figure 35 and Figure 36, is based on CW22 (ice-free) where the mean air temperature was 8.4 ± 7.1 °C, with a high temperature of 24.2 °C and a low temperature of -7.0 °C.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

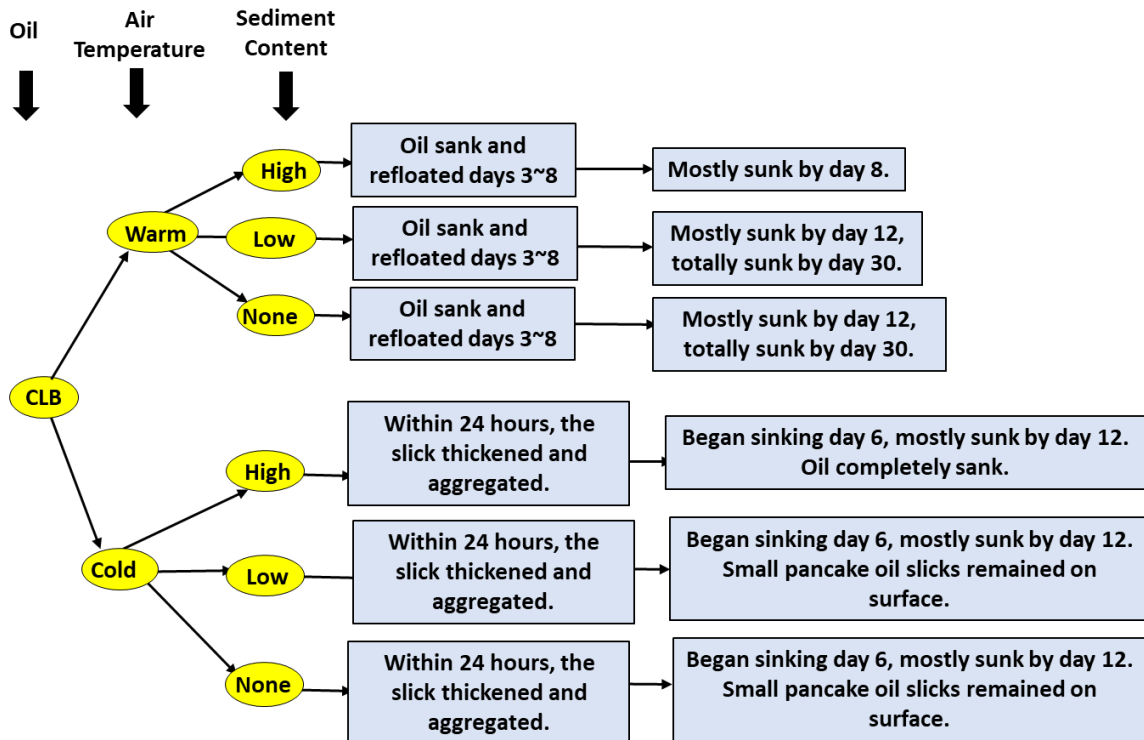


Figure 35. CLB observational results summary.

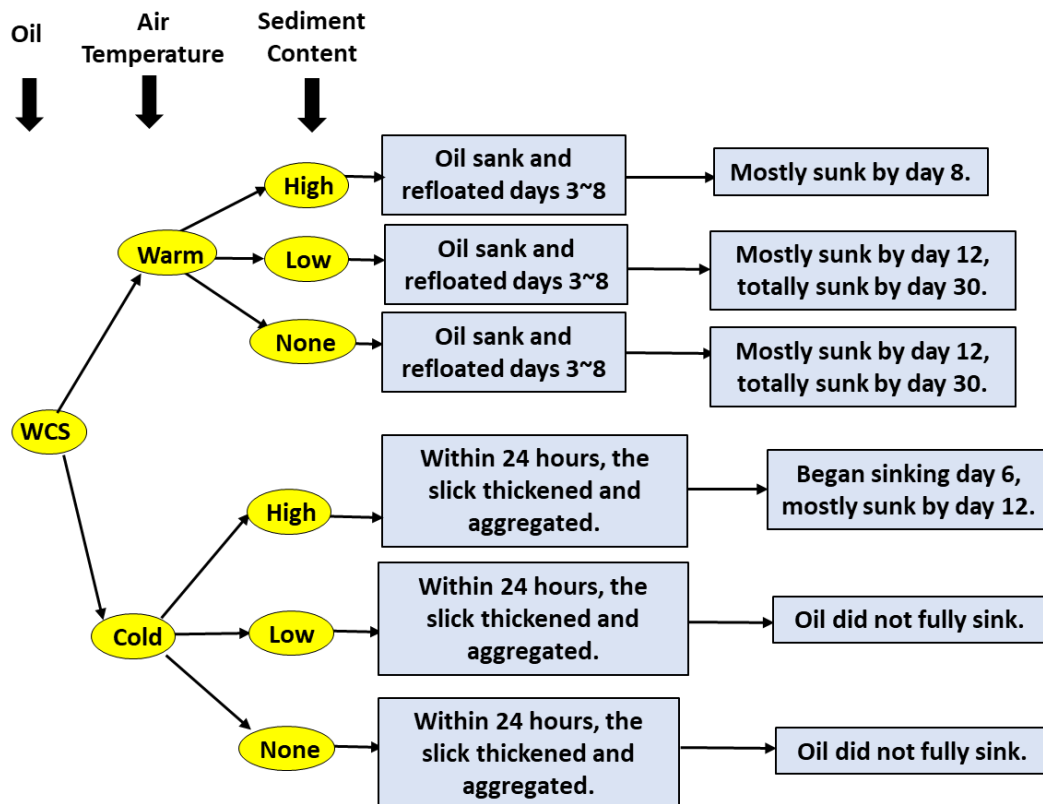


Figure 36. WCS observational results summary.



Additional notes:

- Visual observations revealed that the oil appearance changed drastically by day 8, which suggests that the window of opportunity for effective response could be a few days.
- The physical properties of dilbit products for the three field experiments show that the lighter components of the hydrocarbon evaporate faster in warm weather than in cold weather. The densities and viscosities of all tested dilbit products changed over time, as the diluents degraded, and increased to greater than 1 g/cm³ and greater than 2000 Pa·s, respectively, after 14 days.
- The comparison of fall and summer solar exposure serves to highlight the importance of photo-oxidation under specific environmental conditions.
- The effects of dilbit on aquatic organisms are not well understood (Adewale et al., 2021).

6 RECOMMENDATIONS

For the study of dilbit behavior, future work should be performed to determine which mechanism – evaporation or photo-oxidation – has a more dominant effect on the degradation of dilbit.

More work is needed to understand the effects of nutrients on biodegradation, and on different types of pure bitumen and dilbit product (e.g., rates of anaerobic biodegradation, or what factors effect long-term and short-term biodegradation). Precise rates of photo-oxidation changes to dilbit are also needed.

Improvement to tools for detection, mapping, and mitigation of sunken dilbit (and other oil), particularly containment and recovery, continues to be a well-identified area for further study and technical development.

Regardless of the level of understanding of dilbit behavior, the project recommends renewed effort for examining multiple tools for detection, characterizing, and mapping dilbit. Further, we recommend renewed effort to find an effective method for containment, recovery, and mitigation of the effects of sunken oil, including dilbit.

Preparedness and response entities should use and share the information in Figures 35 and 36 and in Section 7 (below) as basic planning and response guidance for dilbit incidents.



7 GUIDANCE ON DILBIT BEHAVIOR FOR PLANNERS AND RESPONDERS

The actual fate of spilled dilbit will depend on the type of dilbit and its characteristics, the environmental conditions during and after a spill, and the nature of the body of water itself, i.e., the amount of suspended sediment. Response plans should focus on containing and removing the surface slick before it weathers sufficiently to sink or become more difficult to collect with skimmers.

The guidance here is based on a research experiment that studied the behavior of *two types* of diluted bitumen when spilled during cold (iced and ice-free conditions) and warm weather. The Western Canadian Select (WCS) and Cold Lake Blend (CLB) used in the test have light ends in the range of 17-22% by volume; other common blends could have a greater percentage of light ends, e.g., 21-26% by volume.

When comparing unweathered physical properties for the two dilbit types, the CLB was thicker and adhered to itself, while the WCS was more fluid and spread across the surface of the water. Both density and viscosity were higher for CLB than for WCS.

The earlier literature review noted that dilbit generally floats after initial release into freshwater. However, dilbit weathers rapidly in freshwater as compared to traditional crude oil. As the diluent evaporates, the density and viscosity increase, and the remaining oil exhibits behavior of heavy oil. When conditions are calm with no agitation or sediment in the water, dilbit may generally stay afloat for six to ten days in freshwater environments. The same containment and recovery tools used for medium-to-heavy crude oil can be used on dilbit when floating.

Initially, spilled dilbit generally behaves like a medium/heavy oil that would tend to float on the surface of the water. However, the diluents evaporate rapidly, affecting both chemical and physical characteristics of the product.

- Diluent can be expected to evaporate within 24-72 hours depending on weather conditions. Air quality should be monitored in the vicinity of the spill.
 - In warm weather, rapid diluent evaporation will occur with noticeable fumes that may require responder respiratory protection.
 - In cooler weather, the evaporation rate is not as great, however it is still occurring.

As dilbit weathers and diluent evaporates, viscosity and density of the remaining product both increase.

- With increasing viscosity, the floating dilbit becomes stickier, and acquires a thickened or toothpaste-like texture, depending on the weather conditions.
- During weathering, the viscosity for the CLB increased more rapidly than the viscosity for the WCS.
 - Higher viscosity product will spread more slowly.
 - Highly viscous oils are difficult to disperse.
 - Viscous oils typically form more stable emulsions.
 - More viscous oils are generally more difficult for mechanical skimmers to recover, generally do not have the ability to spread, and present pumping challenges.
 - In a highly viscous state, the remaining product will not likely penetrate soil or sediment.



- Though weathering has the major role in changing density, temperature changes can affect the relative densities between a dilbit product and the surrounding water to cause submergence and refloating.
 - During experiments, diurnal heating and cooling of the tanks caused dilbit to submerge and refloat until enough weathering had occurred to where the density change caused the product to sink and remain on the bottom.
 - During warm-weather tests, sinking began on day 3, with some refloating occurring until day 8 when it did not resurface; most of the dilbit completely sank by day 12.
 - Submergence and refloating will likely be dictated by the thermal inertia of the body of water where a spill occurs.
 - Heavy petroleum generally expands or contracts at three to five times the rate of water, depending on the temperature. Since density is inversely proportional to volume, the density of oil decreases approximately four times faster than water as the temperature rises and increases four times faster than water when the temperature drops.
 - In conditions where water temperature is below 4 °C, water density decreases slightly while dilbit density increases, possibly causing dilbit to sink before significant weathering occurs.

Suspended sediments directly affect dilbit behavior.

- At the water surface, the presence of sediment causes the products to lose fluidity and adopt a colloidal or solid consistency.
- In a high sediment tank, all the dilbit sank by day 8, while in the control (no sediment) tanks, most dilbit sank by day 12, all products sank by day 30.
- In a control tank, even with mixing action the same as in the suspended sediment tanks, the dilbit did not readily sink.



8 REFERENCES

- Abou Khalil, C., Fortin, N., Prince, R.C., Greer, C.W., Lee, K., and Boufadel, M.C. (2021). "Crude Oil Biodegradation in Upper and Supratidal Seashores." *Journal of Hazardous Materials* 416: 125919, 2021.
- Adewale, B., Cisternelli, M., Gonin, I., Wurl, M., and Tusia, M. (2021). *Literature Review of Diluted Bitumen (dilbit)*, USCG Research and Development Center, Report No. CG-D-03-21, June 2021.
- Aeppli, C. (2022). "Recent Advance in Understanding Photooxidation of Hydrocarbons after Oil Spills." *Current Opinion in Chemical Engineering* 36: 100763, 2022.
- Aeppli, C., Mitchell, D.A., Keyes, P., Beirne, E.C., McFarlin, K.M., Roman-Hubers, A.T., Rusyn, I., Prince, R.C., Zhao, L., and Parkerton, T.F. (2022). "Oil Irradiation Experiments Document Changes in Oil Properties, Molecular Composition, and Dispersant Effectiveness Associated with Oil Photo-Oxidation." *Environmental Science & Technology* 56(12): 7789-7799.
- Braga, N.C. (2022). *Coefficients of Volume Expansion*, <http://www.incbtech.com/index.php/articles/78-clues-and-ideas/714-coefficients-of-volume-expansion-of-solids-ip041e>, accessed 15 August 2022.
- Cui, F., Geng, X., Robinson, B., King, T., Lee, K., and Boufadel M.C. (2020). "Oil Droplet Dispersion under a Deep-Water Plunging Breaker: Experimental Measurement and Numerical Modeling." *Journal of Marine Science and Engineering* 8(4): 230, 2020.
- Dutta, T.K. and Harayama, S. (2000). "Fate of Crude Oil by the Combination of Photooxidation and Biodegradation." *Environmental Science & Technology* 34(8), pp. 1500-1505, 2000.
- Environment Canada (2013). *Federal Government Technical Report: Properties, Composition and Marine Spill Behavior, Fate and Transport of Two Diluted Bitumen Products from the Canadian Oil Sands*, Environment Canada, 2013. Retrieved on 12 February 2020 from <https://canadianenergynetwork.org/federal-government-technical-report-properties-composition-and-marine-spill-behaviour-fate-and-transport-of-two-diluted-bitumen-products-from-the-canadian-oil-sands/>.
- Fingas, M. (2013). "Modeling Oil and Petroleum Evaporation." *Journal of Petroleum Science Research*, 2 (3), pp. 104–115, 2013.
- Fingas, M. (2015). "Review of the Properties and Behaviour of Diluted Bitumen." *Proceedings, 38th Arctic and Marine Oil-Spill Program Technical Seminar*, Vancouver, BC, Canada, pp. 470–494, June 2015.
- Garrett, R.M., Pickering, I.J., Haith, C.E., and Prince, R.C. (1998). "Photooxidation of Crude Oils." *Environmental Science and Technology*, 32 (23): pp. 3719–3723, 1998.
- Hollebone, B.P. (2015). "The Oil Properties Data Appendix." In *Handbook of Oil Spill Science and Technology*, Fingas, M., Ed. John Wiley and Sons Inc.: NY, 2015; pp 577-681.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

- Holzmann CFD (2022). Temperature-Dependent Thermophysical Properties for Pure Water, <https://holzmann-cfd.com/community/blog-and-tools/cae-blog/thermophysical-properties-water>, accessed 15 August 2022.
- Ji, W., Boufadel M.C., Zhao, L., Robinson, B., King, T., and Lee, K. (2021). “Formation of Oil-particle Aggregates: Particle Penetration and Impact of Particle Properties and Particle-to-oil Concentration Ratios,” *Science of the Total Environment*, 760: 144047.
- King, T.L., Robinson, B., Cui, F., Boufadel, M.C., Lee, K., and Clyburne, J.A.C. (2017). “An Oil Spill Decision Matrix in Response to Surface Spills of Various Bitumen Blends.” *Environmental Science: Processes and Impacts*, 19(7): 928-938, DOI: 10.1039/C7EM00118E, May 2017.
- Lee, K., Boufadel, M.C., Chen, B., Foght, J., Hodson, P., Swanson, S., and Venosa, A. (2015). *Expert Panel Report on the Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments*. Royal Society of Canada, Ottawa, ON, Canada, 2015. ISBN: 978-1-928140-02-3.
- Li, C., Miller, J., Wang, J., Koley, S., and Katz, J. (2017). "Size Distribution and Dispersion of Droplets Generated by Impingement of Breaking Waves on Oil Slicks." *Journal of Geophysical Research: Oceans* 122(10): 7938-7957, 2017.
- Meyer, V (2022). *Practical High-performance Liquid Chromatography*, https://en.wikipedia.org/wiki/High-performance_liquid_chromatography#/media/File:HPLC_apparatus.svg, accessed 15 March 2022.
- Michel, J. and Galt, J. (1995). “Conditions under which floating oil slicks can sink in marine settings.” *Proceedings of the 1995 International Oil Spill Conference*, pp. 573–576. Washington, D.C.: American Petroleum Institute.
- National Academies of Sciences, Engineering, and Medicine (NASEM). (2016). *Spills of Diluted Bitumen from Pipelines: A Comparative Study of Environmental Fate, Effects, and Response*. Washington, DC: The National Academies Press, 2016. <https://doi.org/10.17226/21834>.
- National Research Council (NRC) (1999). *Spills of Non-Floating Oils, Risk and Response*. National Academy Press, Washington, D.C. <https://nap.nationalacademies.org/catalog/9640/spills-of-nonfloating-oils-risk-and-response>.
- Ortmann, A.C., Cobanli, S.E., Wohlgeschaffen, G., MacDonald, J., Gladwell, A., Davis, A., Robinson, B., Mason, J., and King, T.L. (2020). “Measuring the Fate of Different Bitumen Products in Coastal Surface Waters.” *Marine Pollution Bulletin*, 153, DOI: 10.1016/j.marpolbul.2020.111003, April 2020.
- POLARIS Applied Science, Inc. (2013). “A Comparison of the Properties of Diluted Bitumen Crudes with Other Oils.” Retrieved on 21 February 2020 from https://crrc.unh.edu/sites/crrc.unh.edu/files/comparison_bitumen_other_oils_polaris_2014.pdf.
- Radović, J.R., Aeppli, C., Nelson, R.K., Jimenez, N., Reddy, C.M., Bayona, J.M., and Albaigés, J. (2014). "Assessment of Photochemical Processes in Marine Oil Spill Fingerprinting." *Marine Pollution Bulletin* 79(1): 268-277.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

- SL Ross (2020). *Comparison of the Behaviour of Spilled Conventional and Non-Conventional Crude Oils through Laboratory and Meso-Scale Testing: Full Data Report*. SL Ross Environmental Research Limited, 2020. <https://crudemonitor.ca/tools/Comparison%20of%20Conventional%20and%20Non-conventional%20Oils%20%20Final%20Data%20Report%20v106.pdf>.
- Sparkman, D.O., Penton, Z., and Kitson, F.G. (2011). *Gas Chromatography and Mass Spectrometry: A Practical Guide*. Academic Press. ISBN 978-0-08-092015-3.
- ThermoFisher Scientific (2022a). *HPLC Basics*, <https://www.thermofisher.com/us/en/home/industrial/chromatography/chromatography-learning-center/liquid-chromatography-information/hplc-basics.html>, accessed 15 March 2022.
- ThermoFisher Scientific (2022b). *Gas Chromatography-Mass Spectrometry (GC-MS) Information*, <https://www.thermofisher.com/us/en/home/industrial/mass-spectrometry/mass-spectrometry-learning-center/gas-chromatography-mass-spectrometry-gc-ms-information.html>, accessed 15 March 2022.
- Venosa, A.D. and Xueqing, Z. (2003). “Biodegradation of Crude Oil Contaminating Marine Shorelines and Freshwater Wetlands,” *Spill Science and Technology Bulletin*, 8: 163-178.
- Wickley-Olsen, E., Boufadel, M. C., King, T., Li, Z., Lee, K., and Venosa, A. D. (2008). “Regular and Breaking Waves in Wave Tank for Dispersion Effectiveness Testing.” *International Oil Spill Conference Proceedings*, pp 499-508, Savannah, GA, United States, 2008. <https://doi.org/10.7901/2169-3358-2008-1-499>
- Zhao, L., Boufadel, M.C., Conmy, R., Wang, N.B. and Armanante, P. (2015). "Evaluation of mixing energy in the EPA baffled flask using PIV." *Journal of Environmental Engineering*, ASCE, 2015.



(This page intentionally left blank.)



APPENDIX A. PROPERTIES OF DILUTED BITUMEN

A.1 Dilbit Composition

Table A-1 shows the summary properties of four different bitumen blends based on gas condensate as the diluent. These diluents are generally either pure condensates, or butane/pentane enhanced condensates obtained from the gas well at the production facility (Fingas, M. (2015).)

Table A-1. Summary of physical properties and chemistry data of selected dilbit products.

Name	Diluent/Source	Density (kg/m ³)	Sediment (ppm)	Light Ends* (vol%)	BTEX (vol%)
Standard Dilbit - (gas condensates)					
Access Western Blend	Condensate	918 - 928	80 - 98	22 - 26	1.1- 1.4
Christina Dilbit Blend	Condensate	920 - 930	47 - 129	21 - 25	1.0 - 1.3
Cold Lake Blend	Condensate	923 - 933	52 - 136	19 - 22	0.9 - 1.2
Western Canadian Select	Condensate	924 - 932	261 - 307	17 - 20	0.7 – 1.0

*Light Ends compromise the sum of all butanes through decanes, inclusive.

Source: Environment Canada, 2013; Fingas 2015.

A.2 Physical Properties

The properties defined below are the main properties that affect the fate of spilled oil.

Density is the mass per unit volume of the oil (or emulsion) and determines how buoyant the oil is in the water. The common unit of density is grams per milliliter (g/mL). The SI unit is kg/m³, which is numerically 1,000 times the value in g/mL. The density of spilled oil increases with weathering and decreases with rising temperatures. If the density of the oil approaches or exceeds 1,000 kg/m³, the oil becomes subject to temporary submergence and possible sinking in freshwater (SL Ross, 2020).

Viscosity is a measure of the resistance of oil to flow, once in motion. The SI unit of measurement of viscosity is the milli-Pascal second (mPa·s). The viscosity of spilled oil increases as weathering progresses and decreases with increasing temperature.

Flash point of crude oil is the temperature at which the oil produces sufficient vapors to ignite when exposed to an open flame or other ignition source. Flash point increases with increasing evaporation and is an important safety-related spill property, especially in the early stages of a spill when the oil is fresh. Any liquid with a flash point less than 60°C is categorized as flammable (SL Ross, 2020).

Solubility in water is the measure in parts per million (ppm) of the how much oil will dissolve in the water column on a molecular basis. Solubility is important in that the soluble fractions of the oil are sometime toxic to aquatic life, especially at higher concentrations. Most bitumen products have a very low solubility in water. However, diluted bitumen products contain several soluble fractions (Fingas, 2015).

Interfacial Tension is a measure of the surface forces that exist between the interfaces of the water and oil, and the oil and air. The common unit of interfacial tension is the dyne/cm; the SI unit is the milli-



Newton/meter (mN/m), which is numerically equivalent to the dyne/cm. Interfacial tensions (oil/air and oil/water) are fairly insensitive to temperature but are affected by evaporation. Interfacial tension affects the following processes (SL Ross, 2020):

Temperature Dependence of Density

The density of both water and oil depends on temperature, but each to a different degree. Figure A-1 shows the temperature dependence of the density of pure water (Holzmann CFD, 2022).

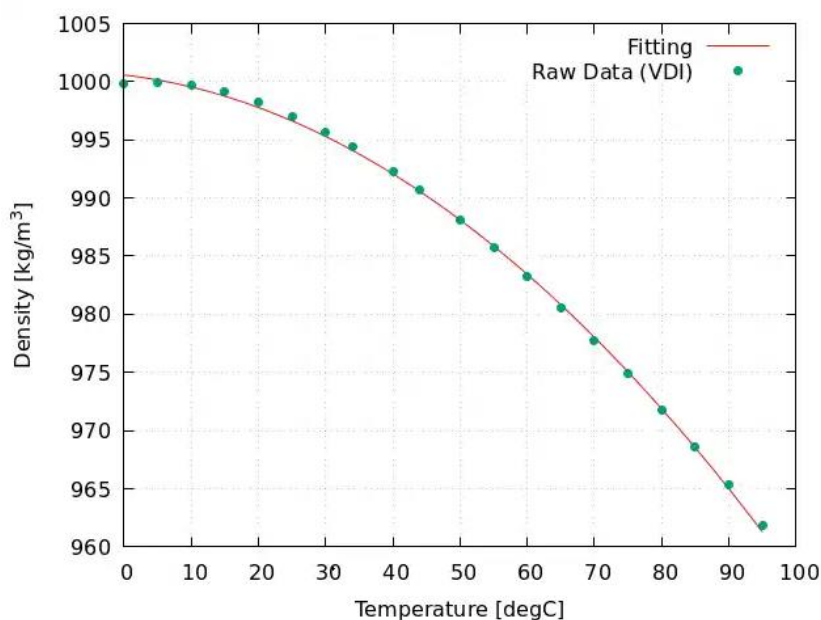


Figure A-1. Density of pure water as a function of temperature.

In general, the temperature dependence of a liquid's density can be inferred from its volumetric change with temperature:

$$\Delta V = \beta V \Delta T.$$

In this equation, V is the volume, ΔT is the change in temperature, and β is the coefficient of volume expansion. Table A-2 gives some common values of these coefficients, with the units being inverse temperature in degrees Kelvin (K) (Braga, 2022).

Table A-2. Coefficient of volume expansion for selected liquids.

Liquid	β (10^{-4} K^{-1})
Acetone	14.3
Benzene	10.6
Ethyl alcohol	11.0
Kerosene	10.0
Petroleum (crude oil)	9.2
Toluene	10.8
Water (5 to 10°C)	0.53
Water (10 to 20°C)	1.56
Water (20 to 40°C)	3.02

As can be seen in the table, oil (petroleum) generally expands or contracts at three to five times the rate of water, depending on the temperature. Since density (ρ) is inversely proportional to volume ($\rho = \text{mass}/\text{Volume}$), the density of oil decreases approximately four times faster than water as the temperature rises and increases four times faster than water when the temperature drops.

NRC (1999) suggests three mechanisms for refloating oil: (1) still-buoyant oil can separate from the sand, (2) wave-generated currents can loosen and resuspend pieces of buoyant oil from the bottom, and (3) increases in water and/or oil temperature can make the oil less viscous and/or more buoyant. Michel and Galt (1995) note that once the oil is on the seafloor, the small differential in density due to short-term changes in temperature are unlikely to cause the oil to refloat. However, as seen in the WW22 dilbit experiment herein, when the oil has only sunk to just below the surface, it can refloat. It is valuable to note that the water temperature in the WW22 tanks was subject to greater changes in air temperature than large water bodies, which tend to have a greater thermal inertia. Thus, the temperature increase in the tank is likely the major factor for the decrease in density of oil and the subsequent refloating.

A.3 Chemical Components

The chemical composition of petroleum dictates its physical properties (e.g., density and viscosity), behavior (e.g., spreading, sinking, dispersion), biological impacts (e.g., toxicity, susceptibility to biodegradation) and fate in the environment. Thus, petroleum chemistry is important to oil spill responders for predicting hazards, such as fire and explosion, and for selecting suitable cleanup and remediation approaches. It is also important to regulators for forensic purposes, monitoring and determining acceptable endpoints for spill remediation (Lee et al., 2015).

Most crude oil constituents can be divided into four major chemical classes known by the acronym SARA: saturates, aromatics, resins and asphaltenes, as described below. Together these fractions contribute to the bulk properties of petroleum, such as viscosity, specific gravity, and susceptibility to biodegradation (Lee et al., 2015). These four main groups of chemicals influence the behavior of oil, including evaporation and emulsification, as well as implications on the effects of oil spills, including toxicity of the oil (Environment Canada, 2013). Information about the SARA constituents, and their influence on the behavior of oil, is important to both the oil production and refining industries.

Saturates: This chemical class is typically the major component of petroleum. It exclusively comprises hydrocarbon molecules having single carbon-carbon bonds, with all remaining bonds being saturated with hydrogen atoms (i.e., no double- or triple-bonded carbon). Three subclasses are defined within this fraction: paraffins and isoparaffins having straight or branched chain structures, respectively; naphthenes (cycloparaffins, also called alicyclic hydrocarbons) having one or more saturated ring structures; and fused-ring aliphatics, including hopanoids and steroids, having large, complex structures combining paraffinic and naphthenic structures (Lee et al., 2015).

Aromatics: The aromatic compounds include at least one benzene ring of six carbons. Three double carbon-to-carbon bonds float around the ring and add stability. Because of this stability, aromatic rings are very persistent and can have toxic effects on the environment. The most common smaller and more volatile compounds found in oil are often referred to as BTEX, or benzene, toluene, ethyl-benzene, and xylenes. Polyaromatic hydrocarbons or PAHs are compounds consisting of at least two benzene rings. PAHs make up between 0 percent and 60 percent of the composition of oil (Hollebone, 2015).



Resins: Resins are polar compounds consisting predominantly of high molecular weight compounds with high carbon-to-hydrogen ratios. Polar compounds are those that have a significant molecular charge as a result of bonding with atoms such as sulfur, nitrogen, or oxygen, known collectively as heteroatoms. The “polarity,” or charge that the molecule carries, results in behavior that is different than unpolarized compounds (Hollebone, 2015). Unlike saturates and aromatics that can be defined by their chemical structures, petroleum resins (and asphaltenes) are defined on the basis of their solubility in hydrocarbon solvents rather than on discrete structures, with the resins fraction being soluble in *n*-pentane or *n*-heptane but insoluble in liquid propane (Lee et al., 2015).

Asphaltenes: Asphaltenes are not hydrocarbons because they contain S-, N- and O-heteroatoms, like the resins. Asphaltenes have greater average molecular weight than resins. This chemical class represents a myriad of individual chemicals and is defined on the basis of insolubility in *n*-alkanes, such as pentane and heptane, but solubility in toluene (Lee et al., 2015). When there are more asphaltenes in an oil, the oil is more viscous and more prone to form water-in-oil emulsions (Hollebone, 2015).

Waxes: Waxes are a subgroup of saturate compounds. The waxes are the straight-chain alkanes from a carbon number of 20 and above. They are important in that they can precipitate out of an oil solution, interact as a group to form a crust or internal matrix, and alter the interfacial properties of the oil, which can significantly affect oil behavior (Hollebone, 2015).



APPENDIX B. ANALYTICAL TECHNIQUES

B.1 High Performance Liquid Chromatography

High-performance liquid chromatography (HPLC) is a broad analytical chemistry technique used to separate compounds in a chemical mixture. These separations utilize the pressure-driven flow of a mobile phase through a column packed with a stationary phase. The mobile phase carries a liquid sample through the column to the detector, and compounds or analytes separate due to varying degrees of interaction with the stationary phase. A detector measures the analytes after elution from the column, and a chromatography data system translates the detected signal (ThermoFisher Scientific, 2022a).

The schematic of an HPLC instrument (Figure B-1) typically includes a degasser, sampler, pumps, and a detector. The sampler brings the sample mixture into the mobile phase stream which carries it into the column. The pumps deliver the desired flow and composition of the mobile phase through the column. The detector generates a signal proportional to the amount of sample component emerging from the column, hence allowing for quantitative analysis of the sample components. A digital microprocessor and user software control the HPLC instrument and provide data analysis. Some models of mechanical pumps in an HPLC instrument can mix multiple solvents together in ratios changing in time, generating a composition gradient in the mobile phase. (Meyer, 2022)

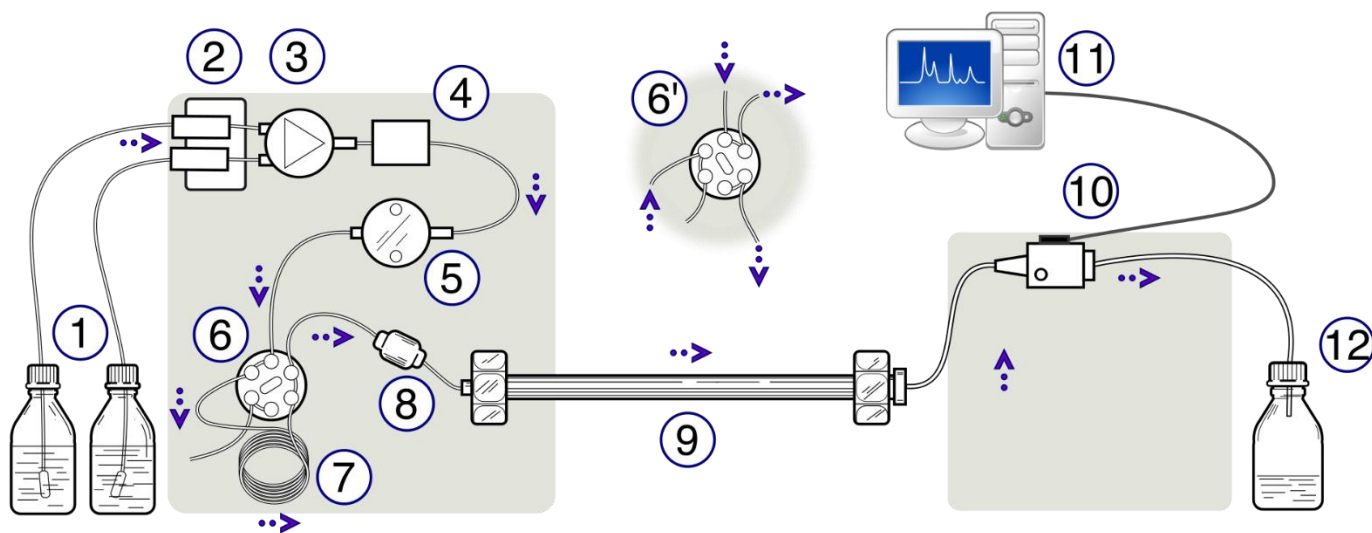


Figure B-1. HPLC schematic.
(from Meyer, 2022)

Schematic representation of an HPLC unit. (1) Solvent reservoirs, (2) Solvent degasser, (3) Gradient valve, (4) Mixing vessel for delivery of the mobile phase, (5) High-pressure pump, (6) Switching valve in "inject position", (6') Switching valve in "load position", (7) Sample injection loop, (8) Pre-column (guard column), (9) Analytical column, (10) Detector (i.e., IR, UV), (11) Data acquisition, (12) Waste or fraction collector.

B.2 Gas Chromatography-Mass Spectrometry

Gas chromatography–mass spectrometry (GC-MS) is an analytical method that combines the features of gas-chromatography and mass spectrometry to identify different substances within a test sample and quantify their amounts (Sparkman et al., 2011).

GC-MS can be used to study liquid, gaseous or solid samples. Analysis begins with the gas chromatograph, where the sample is effectively vaporized into the gas phase and separated into its various components using a capillary column coated with a stationary (liquid or solid) phase. The compounds are propelled by an inert carrier gas such as helium, hydrogen, or nitrogen. As components of the mixture are separated, each compound elutes from the column at a different time based on its boiling point and polarity. The time of elution is referred to as a compound's retention time. GC has the capacity to resolve complex mixtures or sample extracts containing hundreds of compounds (ThermoFisher Scientific, 2022b).

Once the components leave the GC column, they are ionized and fragmented by the mass spectrometer using electron or chemical ionization sources. Ionized molecules and fragments are then accelerated through the instrument's mass analyzer, which quite often is a quadrupole or ion trap. It is here that ions are separated based on their different mass-to-charge (m/z) ratios. GC-MS data acquisition can be performed in either full scan mode, to cover either a wide range of m/z ratios, or selected ion monitoring (SIM) mode, to gather data for specific masses of interest (ThermoFisher Scientific, 2022b).

The final steps of the process involve ion detection and analysis, with fragmented ions appearing as a function of their m/z ratios. Peak areas, meanwhile, are proportional to the quantity of the corresponding compound. When a complex sample is separated by GC-MS, it will produce many different peaks in the gas chromatogram and each peak generates a unique mass spectrum used for compound identification. Using extensive commercially available libraries of mass spectra, unknown compounds and target analytes can be identified and quantified (ThermoFisher Scientific, 2022b).



APPENDIX C. ADDITIONAL DATA

This Appendix includes a sample of the data collected in this study. For access to more of the data, contact the USCG RDC.

C.1 Water Temperature

For Figures C-1 through C-3, tank reference is:

Tank #	Dilbit	Sediment Treatment
1	CLB	Control
2	CLB	Low
3	CLB	High
6	WCS	Control
5	WCS	Low
4	WCS	High

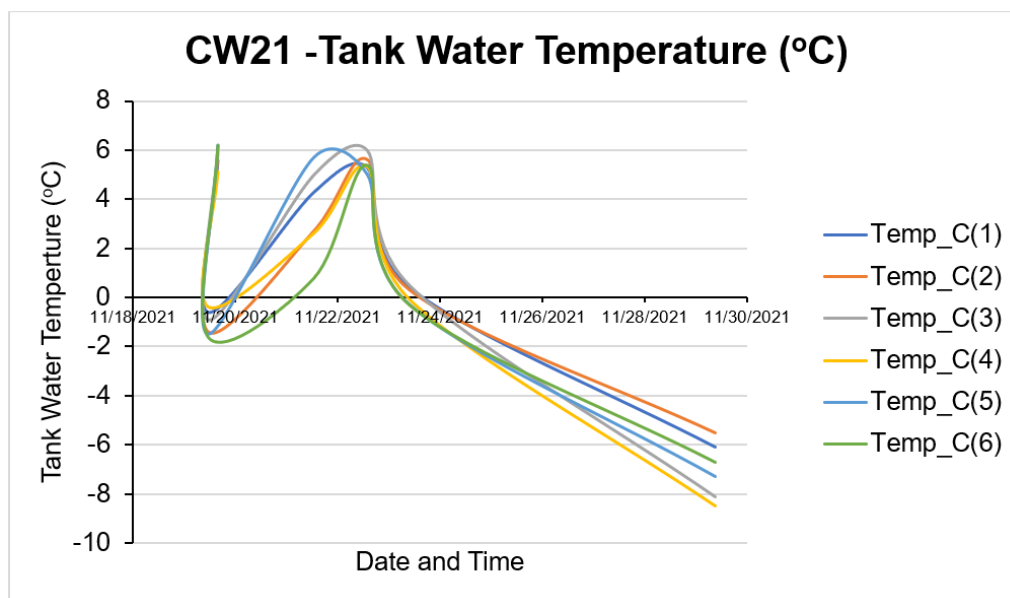


Figure C-1. Tank water temperature data for the CW21 study.



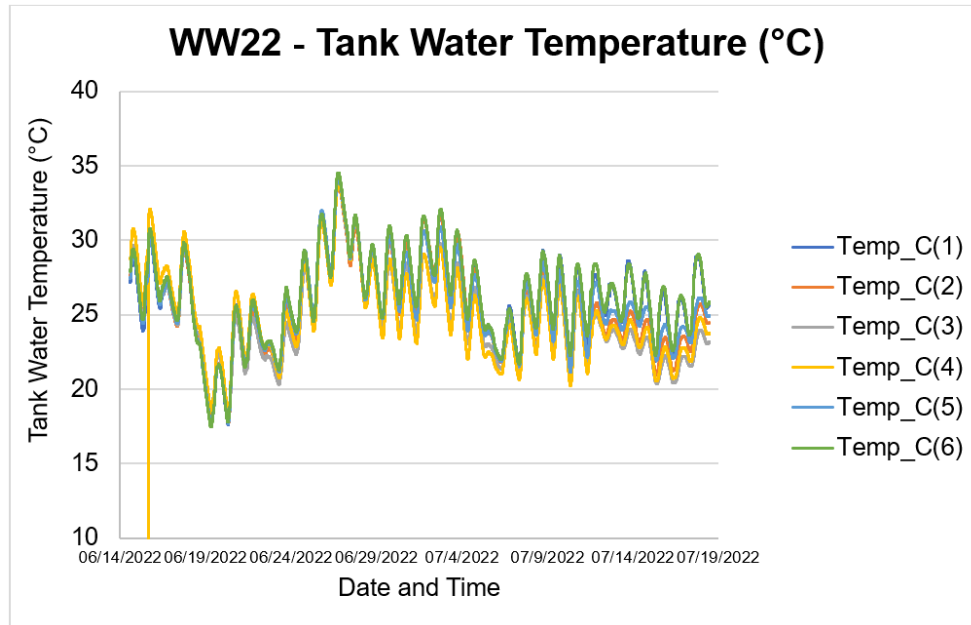


Figure C-2. Tank water temperature data for the WW22 study.

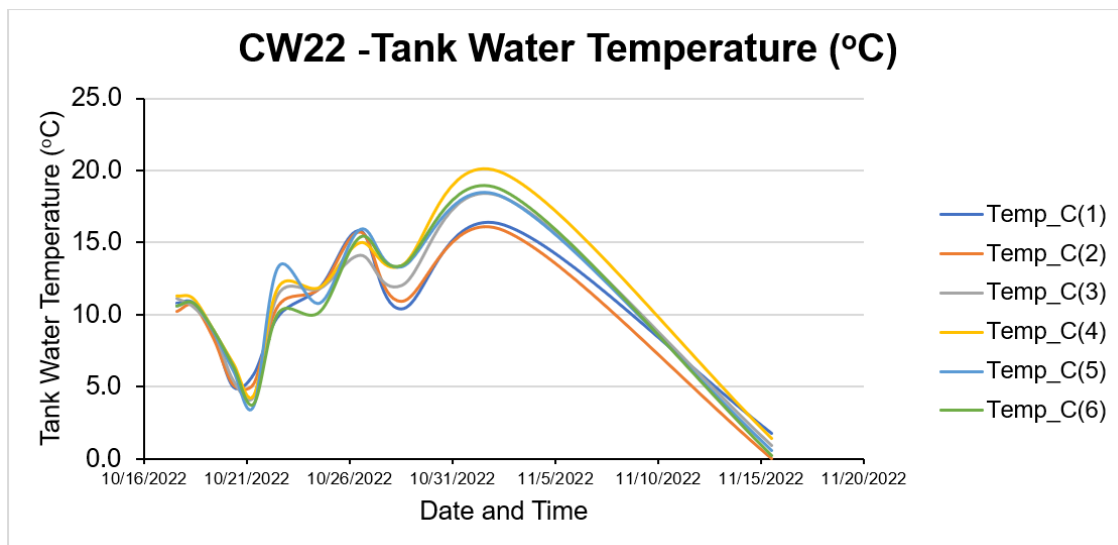


Figure C-3. Tank water temperature data for the CW22 study.

C.2 Water Velocity

In CW21 only, an acoustic Doppler velocimeter (ADV) measured the vertical water velocity (scalar) at three levels in Tank #1. Since all the tanks had the same mixing mechanism, it is assumed that the velocity in each tank is similar. Figure C-4 shows the water velocity time series, at upper-, mid-, and lower levels as a function of time in seconds. Measurements were taken at an interval of 0.0625 second (16 Hertz (Hz)).



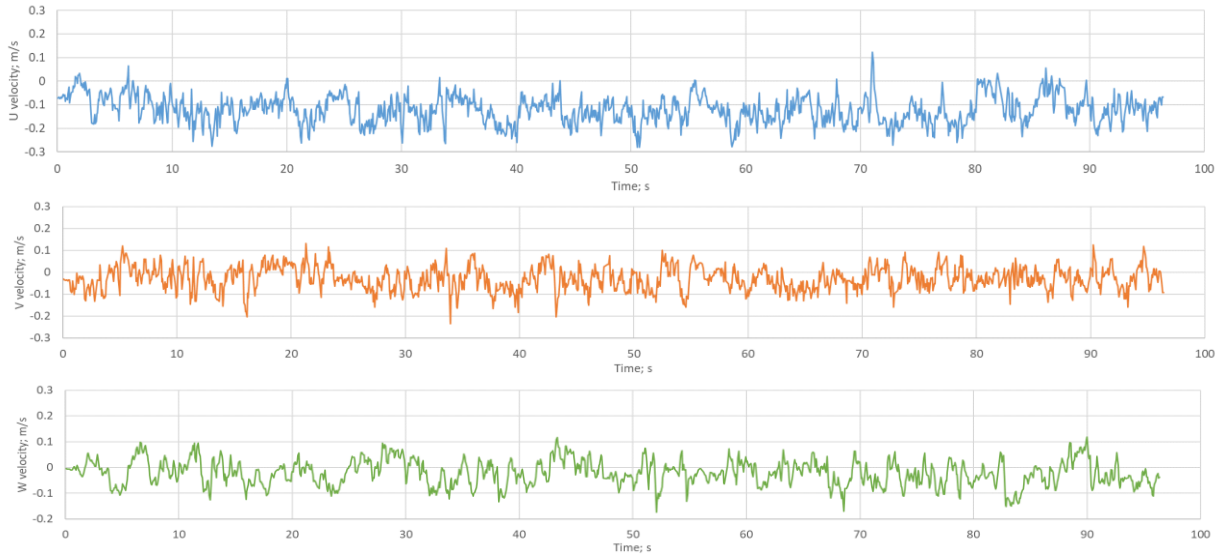


Figure C-4. Time series of CW21 water velocity components.

The energy dissipation rate (ε) based on the expression (Zhao et al. 2015) was calculated as:

$$\varepsilon = A \frac{(u'_{rms})^2}{\tau}$$

where A is a constant on the order of unity, u'_{rms} is the root-mean-square of velocity fluctuations (due to turbulence), and τ is the correlation time scale obtained based on the temporal correlation function. Based on the data obtained in this study, they found that $\tau \cong 0.9$ s and $\varepsilon \cong 2 \times 10^{-4}$ watt/kg. The value 2×10^{-4} watt/kg represents non-breaking wave conditions at the water surface or mixing at a depth of 2 to 3 m in normal seas (i.e., with some whitecaps) (Wickley-Olsen et al. (2008) and Zhao et al. (2015)). The energy dissipation rate within a breaking wave is on the order of 0.05 to 1.0 watt/kg (Li et al. (2017) and Cui et al. (2020)).

It is worth noting that the mixing energy at the impeller could be even larger than 1.0 Watt/kg but the interaction between oil and sediment is expected to occur throughout the tank, and thus the team believes the computed value is more representative of the overall mixing in the tanks.

C.3 Additional Visual Observations

C.3.1 WW22

Figure C-5 shows an overhead image of all six test tanks at 3 days of testing and before the dilbit sank. Figure C-6 shows an overhead image of all six test tanks on day 12 of testing and after a large portion of the dilbit had sunk. After 30 days, no amount of appreciable oil slick remained at the surface (Figure C-7).



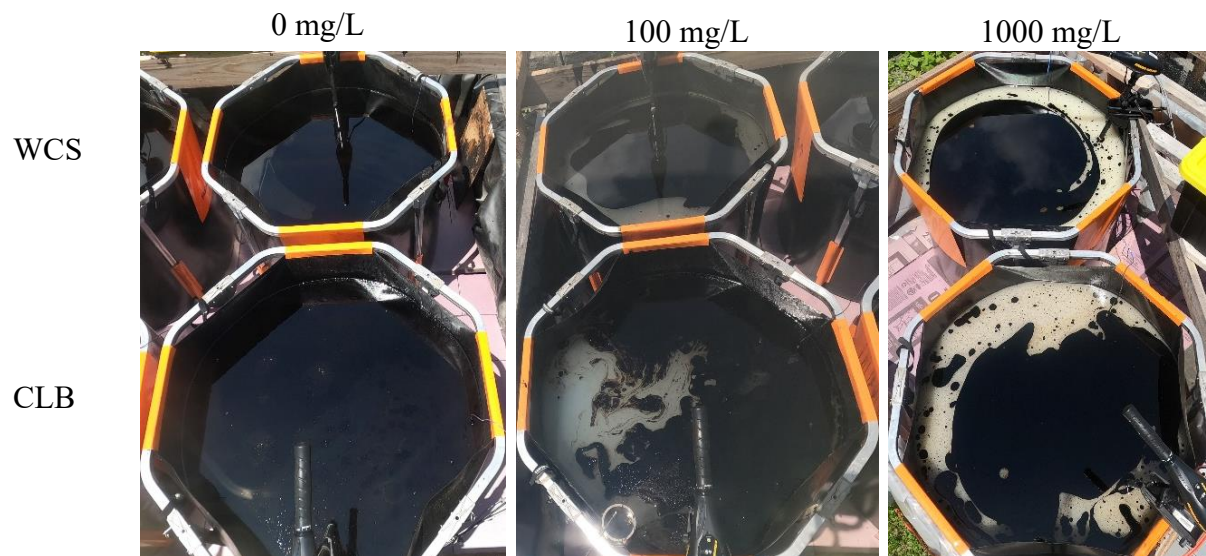


Figure C-5. Day 3 overhead image of the WW22 test tanks before the dilbit sank.

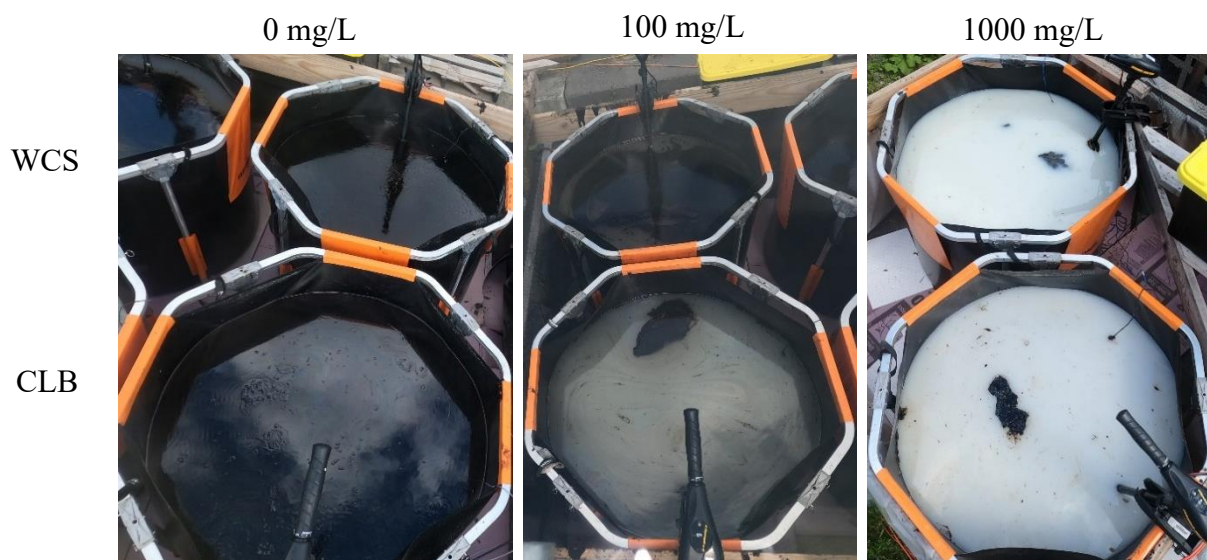


Figure C-6. Day 12 overhead image of the WW22 test tanks after a large portion of the dilbit had sunk.



Figure C-7. Image from WW22 day 29 showing no oil remaining on surface.

C.4 Sunken Dilbit

C.4.1 CW21 Sunken Dilbit

On day 15, researchers recovered five catchment trays from each tank. The mass of the dilbit product in each tray was measured and recorded without removing the product from the trays, then all trays were placed back in their respective tanks. Table C-1 shows the total amount of product collected for all tanks. Figure C-8 shows the total mass of dilbit products captured in five trays for CW21 days 15 and 30. For CLB on day 15, the low sediment tank had 277.72 grams (g) more dilbit than the control, and the high sediment tank had 242.72 g more than the control. For CLB on day 30, the low sediment tank had 942.84 g more than the control and the high tank had 1014.24 g more than the control. For WCS on day 15, the low sediment tank had 36.36 g more dilbit than the control, and the high sediment tank had 15.04 g less than the control. For WCS on day 30, the low sediment tank had 209.15 g more than the control and the high sediment tank had 717.88 g more than the control.

Table C-1. Total mass of dilbit product measured in the CW21 catchment trays.

Tank #	Dilbit	Sediment Treatment	Day 15 (g) (5 trays)	Day 30 (g) (10 trays)
1	CLB	Control	460.41	945.16
2	CLB	Low	738.13	1888
3	CLB	High	703.7	1959.4
6	WCS	Control	515.12	1094.97
5	WCS	Low	551.48	1304.14
4	WCS	High	500.08	1812.85



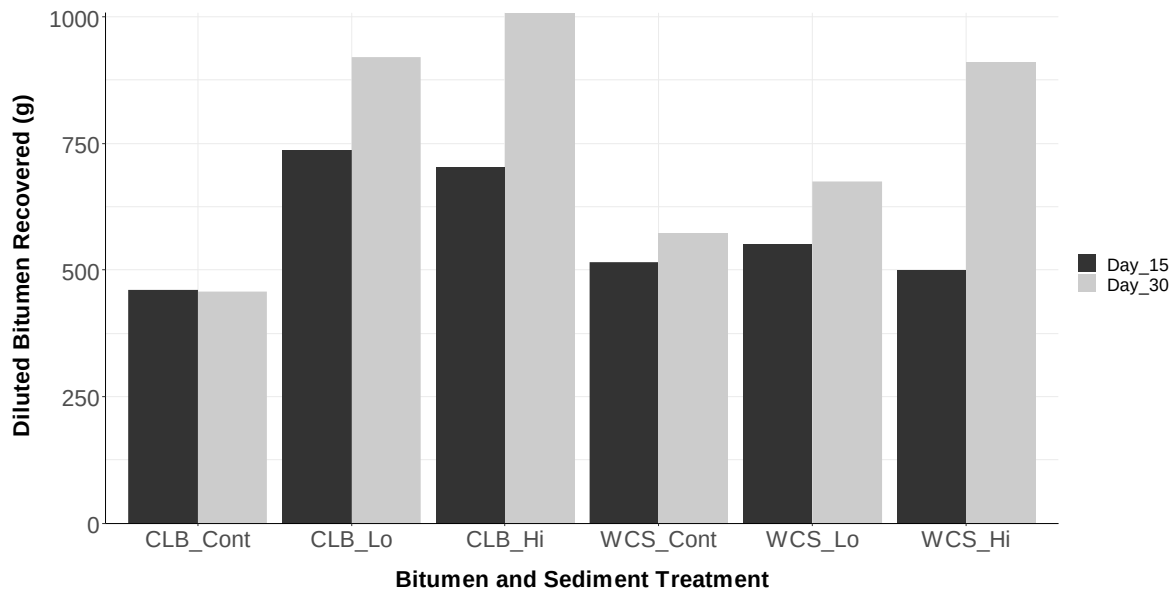


Figure C-8. Total mass of dilbit products captured in five trays for CW21 days 15 and 30.

A direct comparison of the amount of sunken dilbit product in the catchment trays from day 15 to day 30 could not be made due to the additional number of catchment trays collected on day 30. To facilitate this analysis, five catchment trays from day 30 were randomly selected and compared to the total mass of the five trays collected on day 15. For CLB, the amount of dilbit in the catchment trays did not increase for the control tank from day 15 to day 30. The low sediment treatment increased by 182.7 g and the high treatment increased by 305.19 g. For WCS, the control treatment increased by 57.67 g, the low sediment treatment increased by 123.33 g, and the high treatment increased by 410.38 g.

After 30 days, for both the CLB and WCS samples and all sediment concentrations, over 60 percent of the dilbit was at the bottom of the tank (Figure C-9).

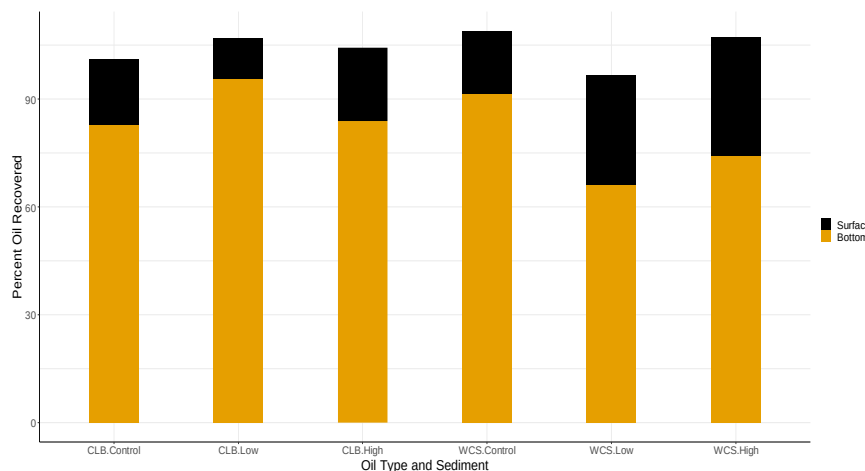


Figure C-9. CW21 ratio of dilbit recovered from the water surface and tank bottom on day 30.

C.4.2 WW22 Sunken Dilbit

For all six tanks, five catchment trays were recovered on day 9, 12, and 15. The mass of dilbit product in each tray was measured and recorded without removing the product from the tray. Then all trays were returned to their respective tanks. Ten trays were collected from each tank on day 29. Table C-2 and Figure C-10 show the total mass of dilbit product collected in five trays for all tanks.

Table C-2. WW22 mass of dilbit product measured in the catchment trays.

Tank #	Dilbit	Sediment treatment	Day 9 (g)	Day 12 (g)	Day 15 (g)	Day 29 (g) (5 trays)
1	CLB	Control	158.83	920.62	506.78	439.07
2	CLB	Low	407.55	967.11	829.54	541.41
3	CLB	High	387.75	1033.95	790.34	511.04
6	WCS	Control	525.09	1631.92	768.27	274.73
5	WCS	Low	660.62	1347.87	764.9	640.97
4	WCS	High	106.55	207.1	150.2	536.46

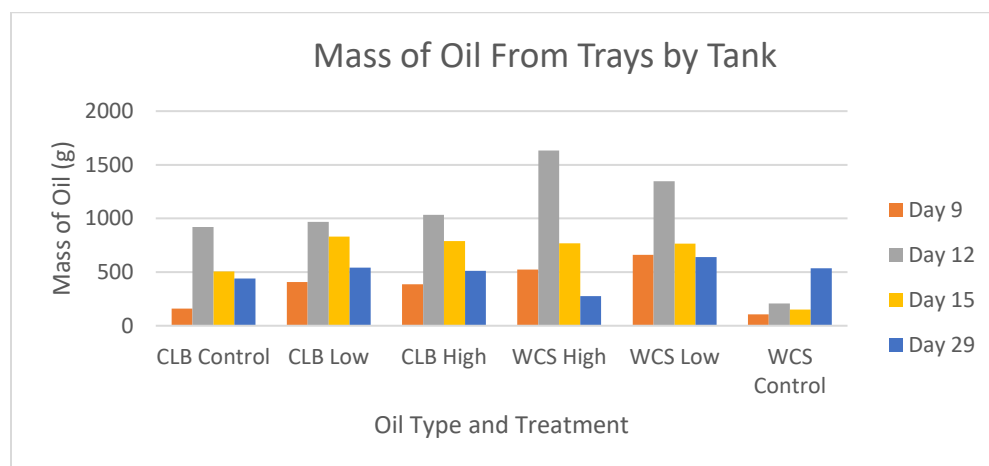


Figure C-10. WW22 mass of oil collected in five catchment trays.

For CLB on day 9, the low sediment tank had 248.72 g more dilbit than the control, and the high sediment tank had 228.92 g more than the control. On day 12, the low sediment tank had only 46.49 g more than the control and the high sediment tank had 113.33 g more than the control. On day 15, the low sediment tank had 322.76 g more than the control and the high sediment tank had 283.56 g more than the control. On day 29, the low sediment tank had 942.84 g more than the control and the high sediment tank had 1014.24 g more than the control.

For WCS on day 9, the low sediment tank had 554.07 g more dilbit than the control, and the high sediment tank had 418.54 g more than the control. For WCS on day 12, the low sediment tank had 1140.77 g more dilbit than the control, and the high sediment tank had 1424.82 g more than the control. On day 15, the low sediment tank had 614.7 g more than the control, and the high sediment tank had 618.07 g more than the control. On day 29, the low sediment tank had 104.51 g more than the control and the high sediment tank had 261.73 g less than the control.



C.4.3 CW22 Sunken Dilbit

Five trays were collected from each tank on days 9, 12 and 15. Ten trays were collected from each tank on day 30. The mass of dilbit product in each tray was measured and recorded without removing the product from the tray. All trays were then returned to their respective tanks (except day 30 after which the experiment concluded). Table C-3 shows the total mass of dilbit product collected from all tanks.

Table C-3. Total mass of dilbit product measured in the CW22 catchment trays.

Oil Type	Sediment treatment	Day 9 Total (g)	Day 12 Total (g)	Day 15 Total (g)	Day 30 Total (g)	Day 9 Average (g)	Day 12 Average (g)	Day 15 Average (g)	Day 30 Average (g)
CLB	Control	140.11	108.65	386.6	2188.15	28.022	21.73	77.32	218.815
CLB	Low	166.24	334.27	709.11	1646.72	33.248	66.854	141.822	164.672
CLB	High	370.56	393.39	1646.1	3084.06	74.112	78.678	329.22	308.406
WCS	High	274.53	253.41	780.81	2849.58	54.906	50.682	156.162	284.958
WCS	Low	60.49	67.05	70.47	798.24	12.098	13.41	14.094	79.824
WCS	Control	55.83	63.18	86.4	266.1	11.166	12.636	17.28	26.61

For CLB on day 9, the low sediment tank had only 26.13 g more dilbit than the control, and the high sediment tank had 230.45 g more than the control. On day 12, the difference between the sediment treatments and the control increases. The mass of dilbit in both the high sediment and low sediment tanks is roughly 200 g more than the control. By day 15, the mass of dilbit in the high and low sediment tanks continues to diverge; 936.99 g more oil was recovered from the high sediment tank compared to the low sediment tank, and 1259.5 g more oil was recovered from the high sediment tank than the control.

C.5 Physical Properties

In this section, graphs for density and viscosity show individual data points as well as fitted curves using the formulas from King et al. (2017). For density, the equation for the fitted curve is,

$$\rho(t) = \left\{ \rho_0 + (\rho_f - \rho_0) \times \frac{t^n}{t^n + T^n} \right\},$$

where ρ_0 is the initial density, ρ_f is the final density, and T is the total time.

For viscosity, the equation for the fitted curve is,

$$\ln \mu = \left[\ln \mu_0 + \left\{ (\ln \mu_f - \ln \mu_0) \times \frac{t^n}{t^n + T^n} \right\} \right]$$

where μ_0 is the initial density, μ_f is the final density, and T is the total time.



C.5.1 Density

CW21 Individual Tank Density

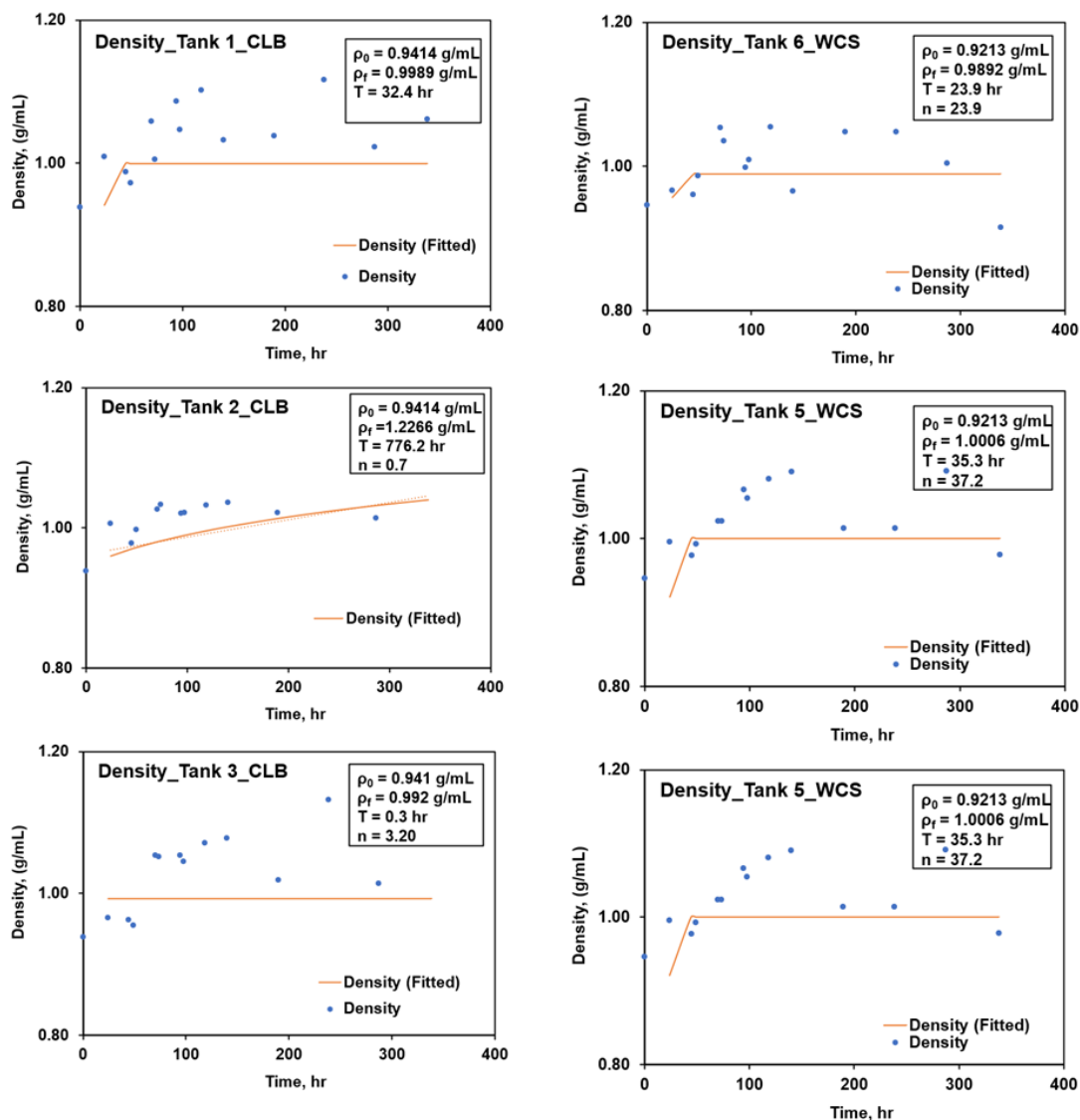


Figure C-11. CW21 individual tank density data.



WW Individual Tank Density

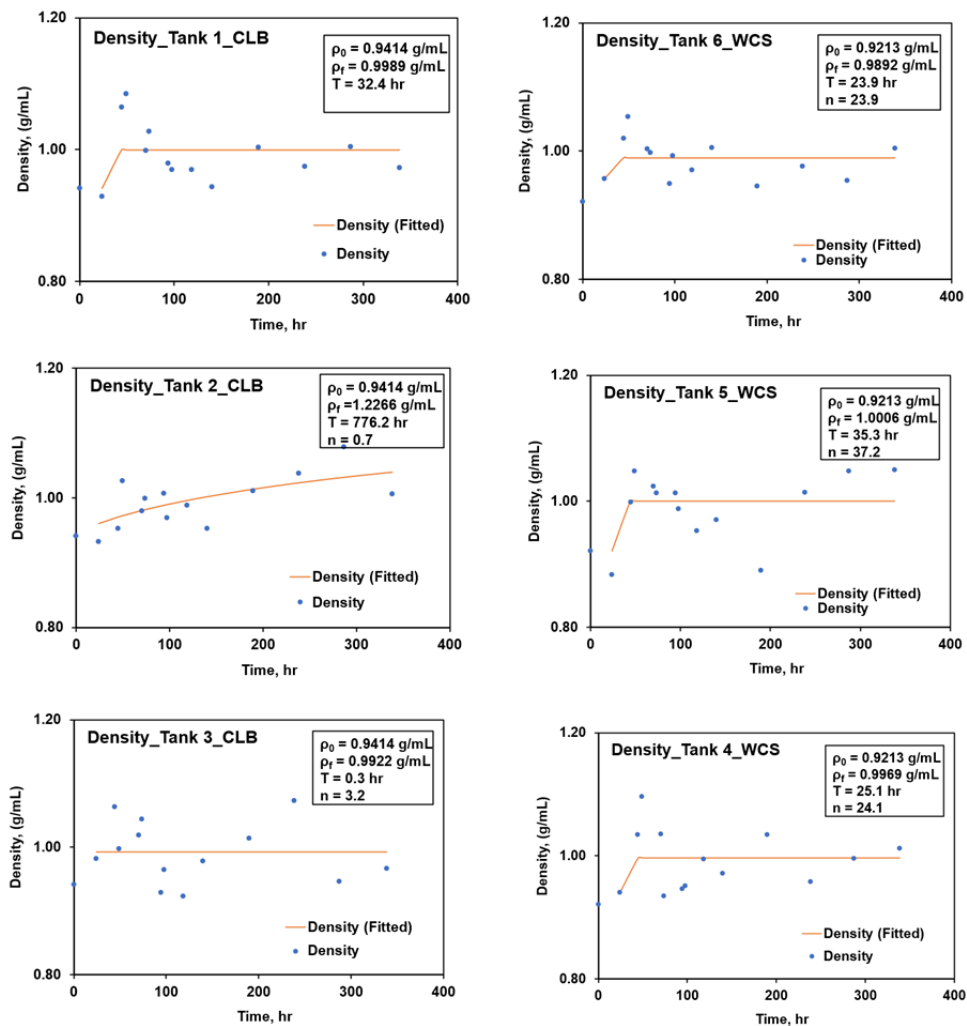


Figure C-12. WW22 individual tank density data.

CW22 Individual Tank Density

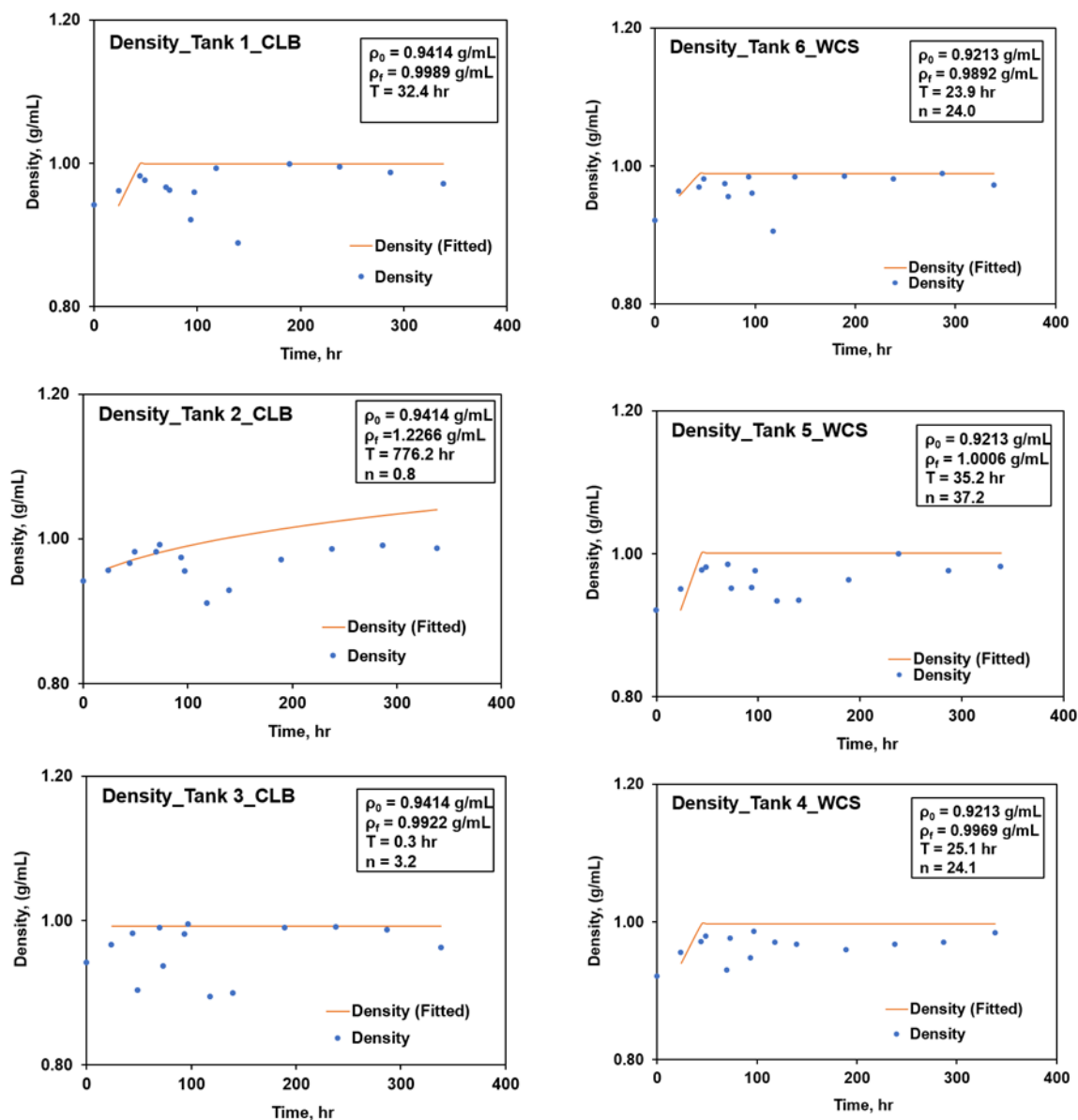


Figure C-13. CW22 individual tank density data.

C.5.2 Viscosity

CW21 Individual Tank Viscosity

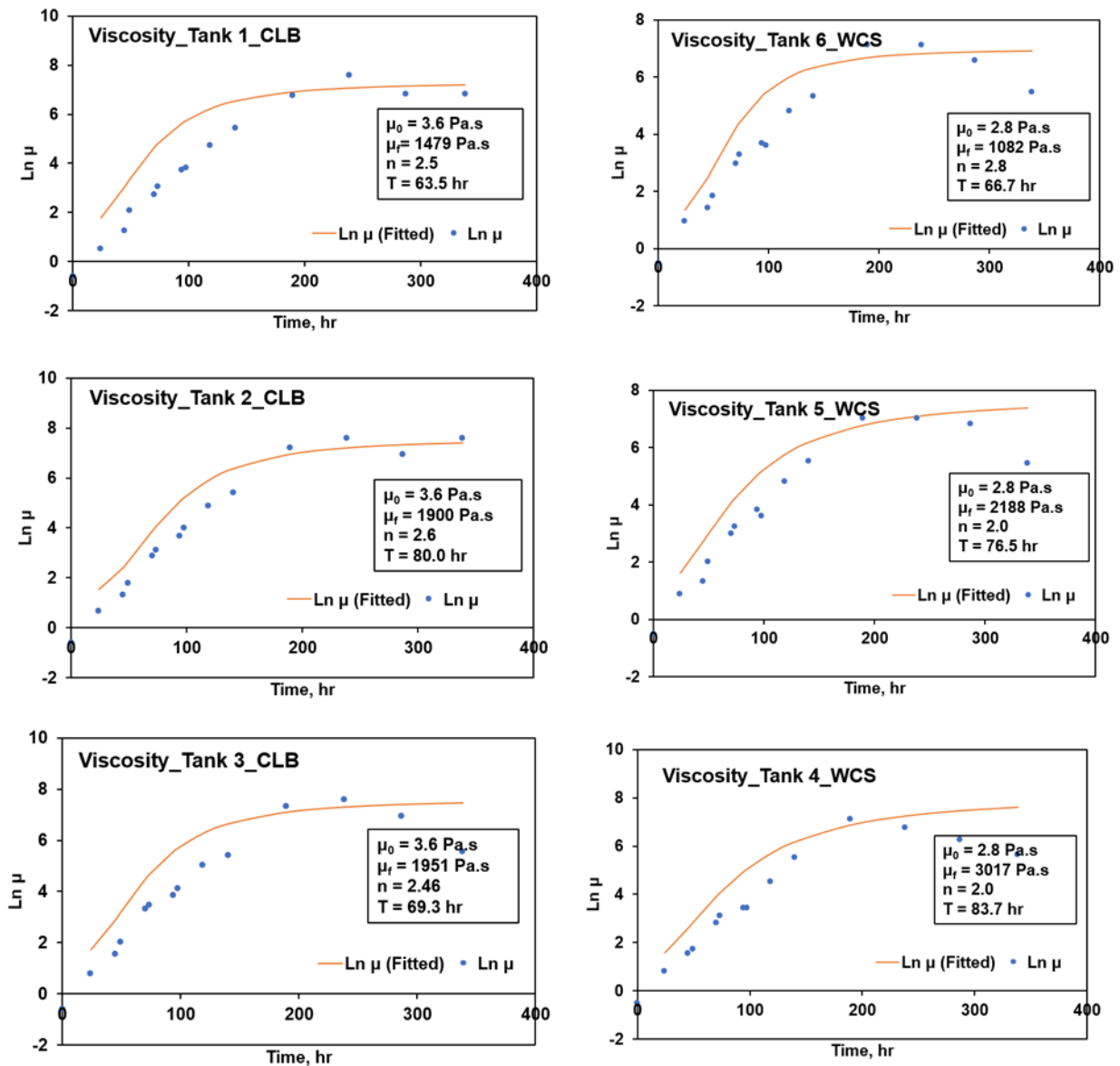


Figure C-14. CW21 individual tank viscosity data.

WW Individual Tank Viscosity

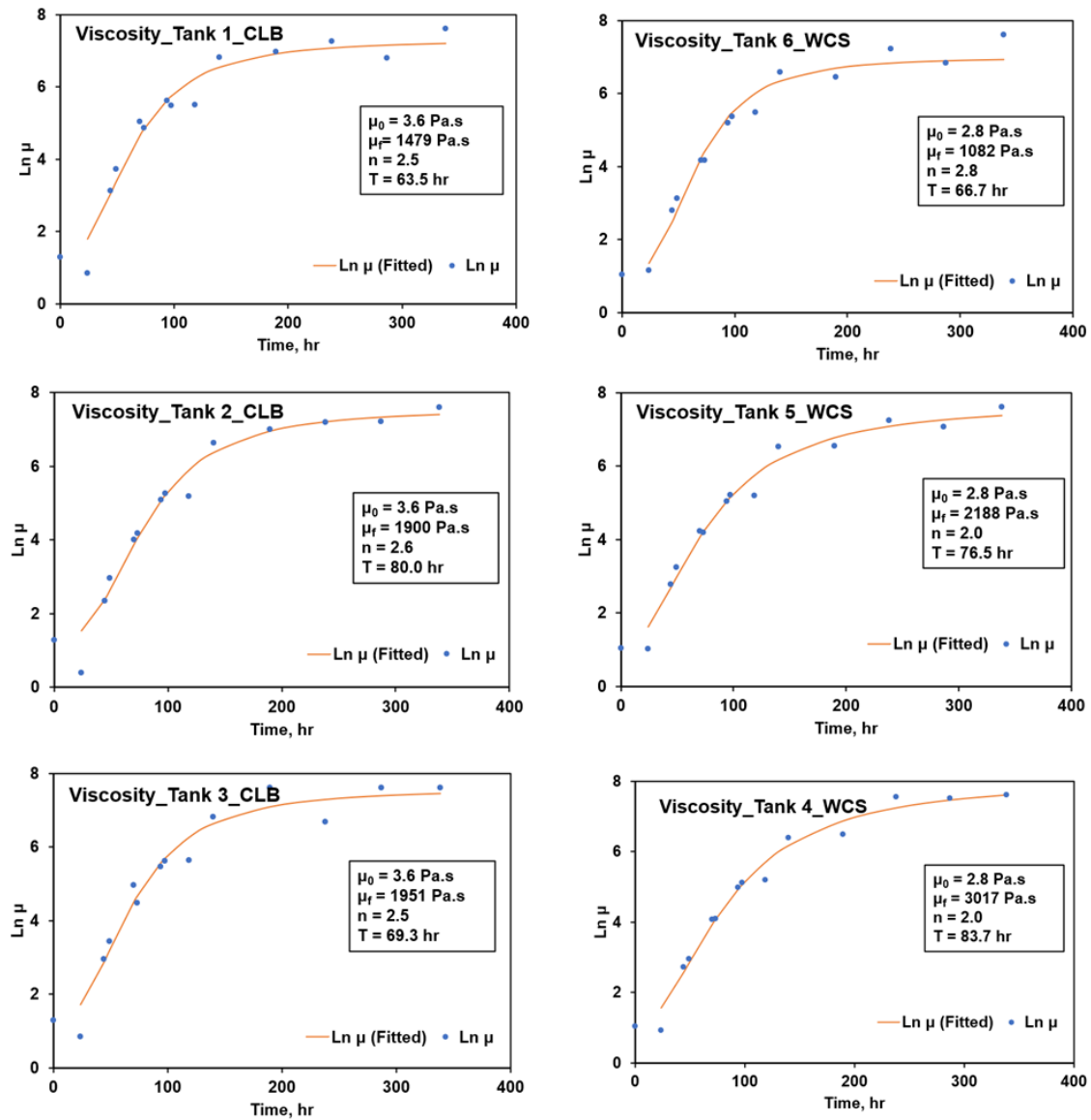


Figure C-15. WW22 individual tank viscosity data.



CW22 Individual Tank Viscosity

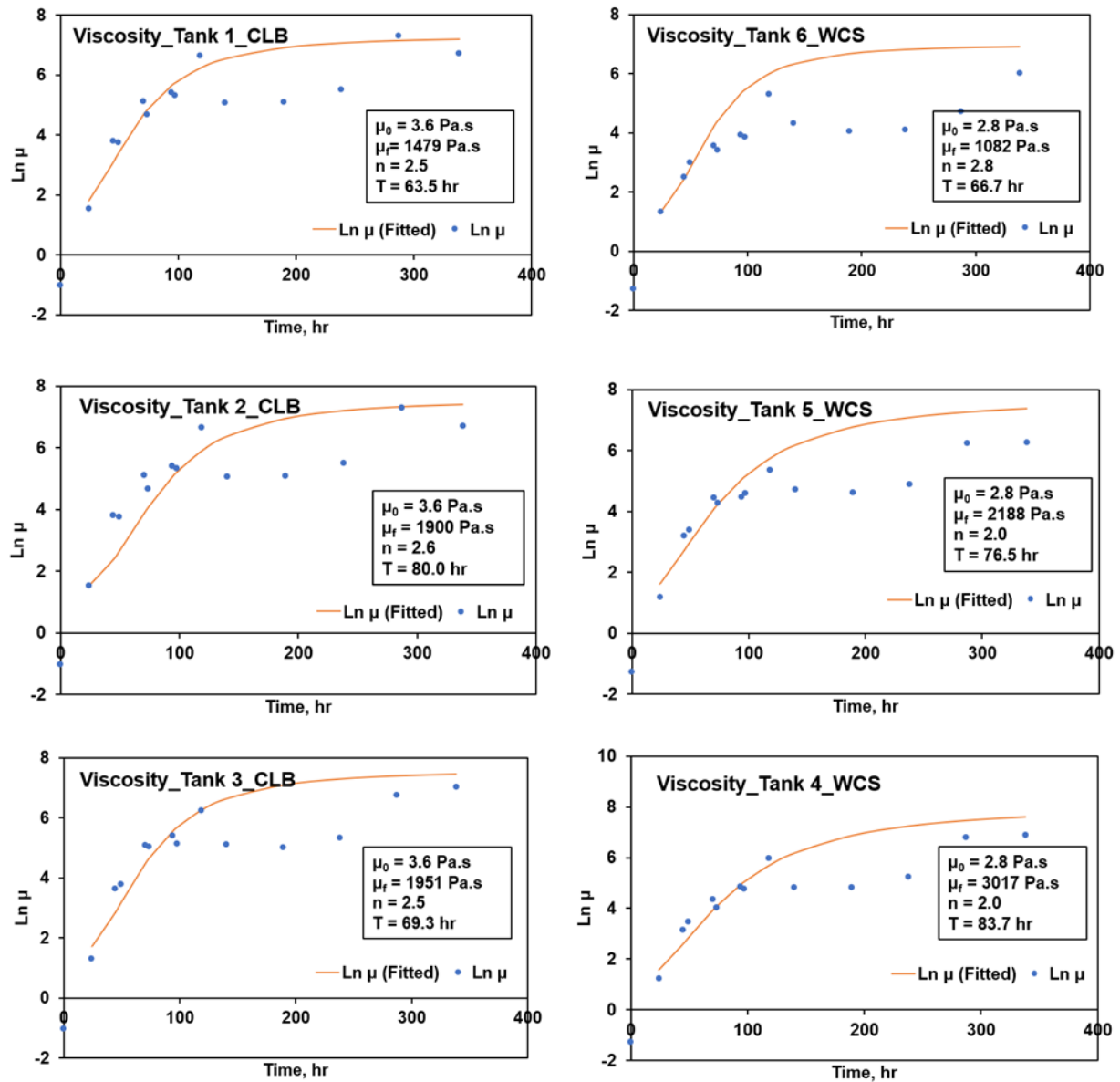


Figure C-16. CW22 individual tank viscosity data.

C.6 SARA

C.6.1 SARA Results from CW21 Mesoscale Tanks

Table C-4 and Table C-5 list the CW21 SARA data for CLB and WCS, respectively. Figure C-17 provides the graphical presentation of these data by tank.

Table C-4. CLB CW21 SARA percentages by weight.

Tank 1 - CLB Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	9.2	56.6	31	3.2
2	11.5	54.0	28.6	5.9
3	12.0	54.7	24.6	8.7
8	11.8	50.9	22.9	14.4
14	10.2	46.7	24.4	18.6
Tank 2 – CLB Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	10.3	56.0	29	4.7
2	11.5	54.0	27.5	7.0
3	10.6	55.1	25	9.3
8	11.5	51.8	22.8	13.9
14	10.4	48.2	22.3	19.1
Tank 3 -- CLB High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	12.2	53.2	25.6	9.0
2	11.3	51.9	26.5	10.3
3	12.1	52.1	24.4	11.4
8	10.7	51.2	22.3	15.8
14	10.6	45.5	23.8	20.1



Table C-5. WCS CW21 SARA percentages by weight.

Tank 4 – WCS High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	12.4	50.2	26.4	11.0
2	13.0	51.2	24.6	11.2
3	10.2	55.4	21.0	13.4
8	14.5	47.8	22.1	15.6
14	13.8	47.2	23.6	15.4
Tank 5 – WCS Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	15.4	46.8	24.0	13.8
2	13.6	48.3	24.9	13.2
3	15.2	50.5	20.6	13.7
8	14.7	47.9	21.0	16.4
14	15.2	46.5	20.4	17.9
Tank 6 - WCS Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	11.4	45	27.2	16.4
2	12.1	46.2	25.8	15.9
3	15.4	44.9	22.3	17.4
8	13.7	45.2	22.2	18.9
14	11.9	46.7	21.3	20.1



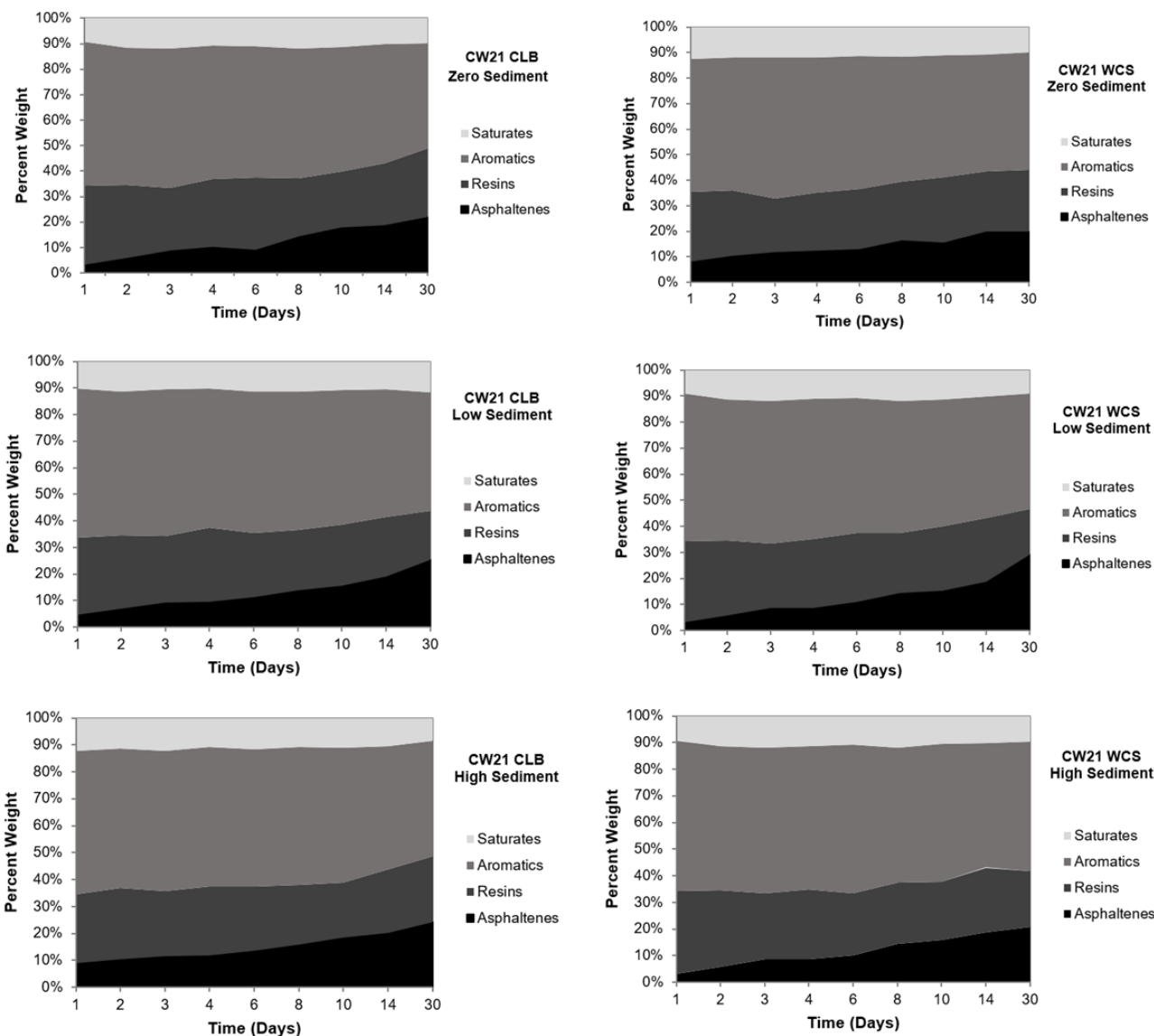


Figure C-17. CW21 SARA results by tank.

C.6.2 SARA Results from WW22 Mesoscale Tanks

Table C-6 and Table C-7 list the WW22 SARA data for CLB and WCS, respectively. Figure C-18 provides the graphical presentation of these data by tank.

Table C-6. CLB WW22 SARA percentages by weight.

Tank 1- CLB Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	10.5	51.7	32.3	5.5
2	10.7	46.6	32.9	9.8
3	8.2	41.6	34.7	15.5
4	9.1	36.3	34.3	20.3
5	8.2	32.9	36.2	22.7
6	7.2	28.0	34.8	30.0
8	5.6	26.8	34.8	32.8
10	8.5	29.0	26.8	35.6
12	7.4	24.8	31.9	35.9
15	8.5	24.2	29.5	37.8
29	6.8	27.8	26.3	39.1
Tank 2 – CLB Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	10.6	51.7	31.9	5.8
2	11.3	47.9	31.6	9.3
3	10.7	40.2	32.3	16.8
4	8.2	35.8	35.5	20.5
5	8.7	32.9	35.6	22.7
6	9.6	26.9	32.5	31.1
8	7.5	27.7	34.1	30.7
10	5.5	24.0	32.1	38.4
12	7.5	25.1	31.0	36.4
15	7.9	24.6	30.6	36.9
29	7.5	31.4	26.5	34.6
Tank 3 – CLB High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	9.6	54.4	29.8	6.2
2	10.1	47.0	32.7	10.2
3	7.9	39.8	34.3	17.9
4	7.9	35.6	35.7	20.8
5	7.6	33.2	35.9	23.2
6	5.9	28.2	36.1	29.8
8	9.0	26.8	33.7	30.5
10	7.4	26.9	29.6	36.1
12	6.2	25.8	32.5	35.4
15	5.2	25.9	33.4	35.5
29	7.1	28.9	24.9	39.1



Table C-7. WCS WW22 SARA percentages by weight.

Tank 4 – WCS High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	9.8	49.9	30.5	9.7
2	10.1	47.2	32.0	10.6
3	9.1	38.6	33.8	18.5
4	8.7	35.3	35.1	21.0
5	8.3	32.0	36.2	23.6
6	8.1	27.1	34.5	30.4
8	6.6	24.0	38.0	31.3
10	8.1	26.0	30.0	35.9
12	7.0	21.2	35.7	36.0
15	5.8	28.4	28.9	36.8
29	5.0	28.1	29.2	37.8
Tank 5 – WCS Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	11.9	51.2	28.5	8.4
2	9.3	47.9	31.8	11.0
3	8.1	40.2	35.6	16.2
4	8.0	35.2	35.1	21.7
5	7.7	32.2	35.4	24.6
6	8.1	26.6	33.7	31.6
8	6.4	24.8	37.4	31.4
10	5.3	23.7	33.3	37.7
12	6.8	23.1	33.4	36.7
15	7.9	27.1	28.7	36.3
29	7.1	28.8	26.0	38.0
Tank 6 – WCS Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	10.9	51.9	30.8	6.4
2	8.8	48.3	33.5	9.4
3	8.6	39.1	33.9	18.3
4	9.0	35.1	34.1	21.8
5	8.9	33.0	34.6	23.5
6	6.8	27.1	34.1	32.0
8	9.0	27.2	31.8	32.0
10	7.9	21.2	34.8	36.1
12	6.2	24.3	32.4	37.1
15	8.6	24.4	28.9	38.1
29	7.4	25.2	31.0	36.4



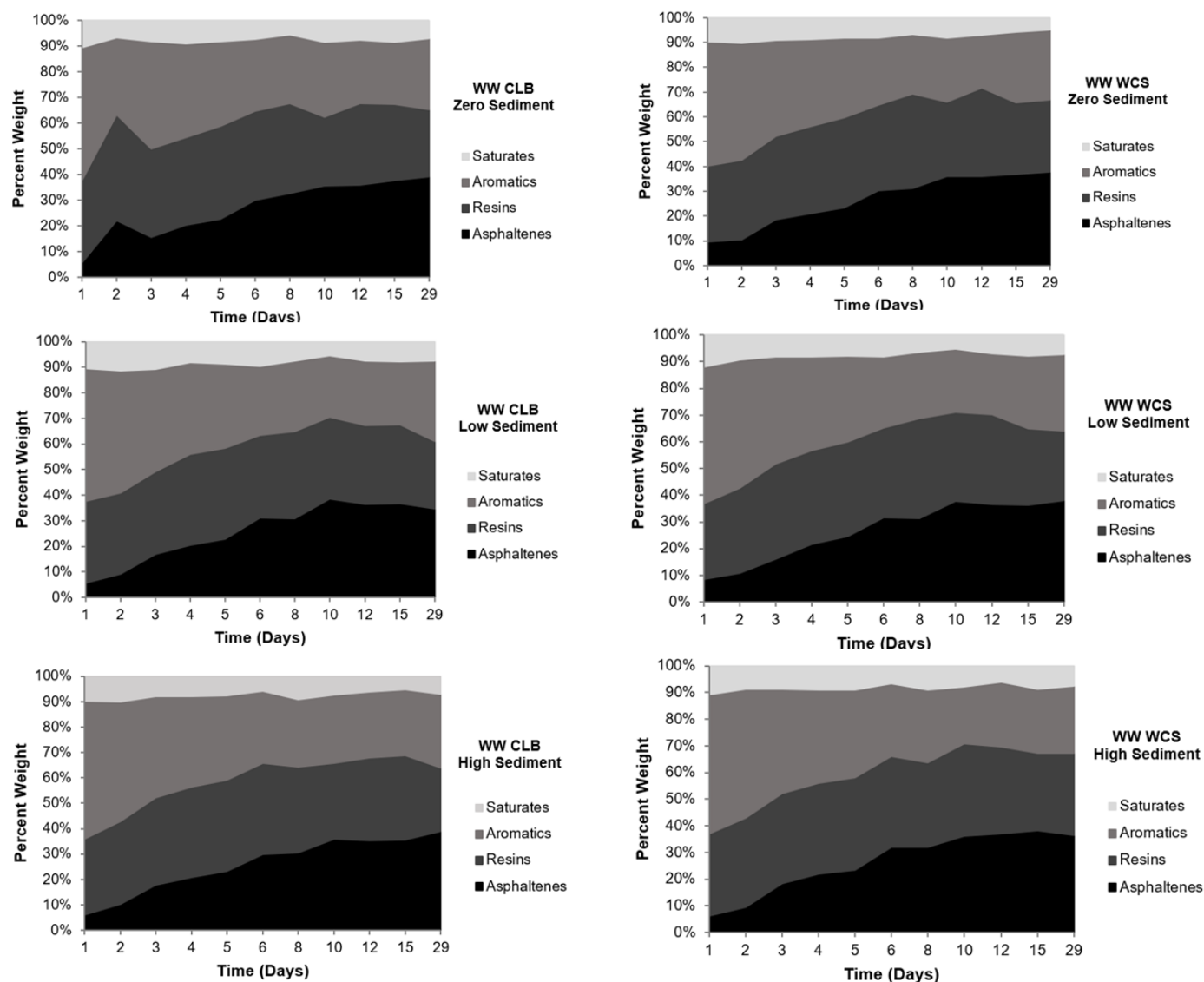


Figure C-18. WW22 SARA results by tank.

C.6.3 SARA Results from CW22 Mesoscale Tanks

Table C-8 and Table C-9 lists the CW22 SARA data for CLB and WCS, respectively. Figure C-19 provides the graphical presentation of these data.

Table C-8. CLB CW22 SARA percentages by weight.

Tank 1 - CLB Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	13.1	48.7	30.5	7.7
2	12.1	48.1	32.2	7.6
3	11.2	40.2	39.4	9.3
4	11.2	37.2	41.1	10.4
5	9.6	30.8	43.0	16.7
6	8.0	27.9	45.9	18.3
8	9.2	27.4	45.7	17.7
10	7.2	22.0	50.8	20.0
12	8.5	21.2	48.5	21.7
15	7.7	17.5	51.8	23.0
30	6.6	16.5	50.5	26.4
Tank 2 – CLB Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	11.2	48.9	30.9	9.1
2	13.7	49.6	29.9	6.8
3	12.7	38.8	39.4	9.1
4	12.3	36.5	40.4	10.8
5	12.4	30.2	42.7	14.7
6	12.8	29.7	41.1	16.4
8	10.0	26.9	43.2	19.9
10	11.3	21.5	47.1	20.1
12	10.2	19.5	49.7	20.5
15	9.0	16.2	44.4	30.3
30	9.8	15.8	46.4	28.0
Tank 3 – CLB High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	11.6	48.3	30.7	9.4
2	12.9	49.5	32.3	5.3
3	11.4	40.9	38.4	9.3
4	13.1	35.4	42.5	9.0
5	11.8	29.4	45.1	13.7
6	12.5	27.7	46.6	13.1
8	10.5	28.3	39.1	22.2
10	10.7	21.5	46.1	21.8
12	10.6	19.4	47.6	22.4
15	9.8	16.6	43.9	29.8
30	9.7	15.6	42.1	32.6



Table C-9. WCS CW22 SARA percentages by weight.

Tank 4 – WCS High Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	12.0	50.8	29.1	8.0
2	13.4	49.8	29.0	7.9
3	11.8	40.4	38.1	9.7
4	12.2	37.1	40.5	10.2
5	11.1	29.3	43.0	16.6
6	10.8	31.0	45.3	13.0
8	10.0	27.3	41.5	21.2
10	9.9	21.4	48.9	19.8
12	9.7	20.0	49.2	21.1
15	9.3	17.1	45.0	28.6
30	8.6	15.9	43.1	32.4
Tank 5 – WCS Low Sediment Treatment				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	12.3	48.6	32.5	6.6
2	11.9	45.8	32.5	9.7
3	10.4	39.7	38.9	11.0
4	12.4	37.9	41.1	8.6
5	11.5	32.1	43.4	13.0
6	12.5	30.1	43.1	14.4
8	11.0	27.8	40.9	20.4
10	9.6	20.7	45.8	23.9
12	10.1	20.5	52.5	16.9
15	9.0	14.6	39.3	37.1
30	7.9	14.9	40.9	36.3
Tank 6 - WCS Control (no sediment added)				
Day	Saturates	Aromatics	Resins	Asphaltenes
1	12.9	46.9	32.1	8.1
2	12.7	47.8	32.2	7.3
3	11.9	42.3	36.3	9.5
4	11.4	36.5	42.8	9.3
5	11.3	29.3	41.0	18.4
6	11.3	28.9	45.1	14.7
8	10.7	26.8	40.8	21.7
10	10.1	22.1	47.3	20.5
12	9.8	19.7	47.7	22.9
15	9.9	17.7	47.9	24.6
30	9.0	14.0	37.5	39.6



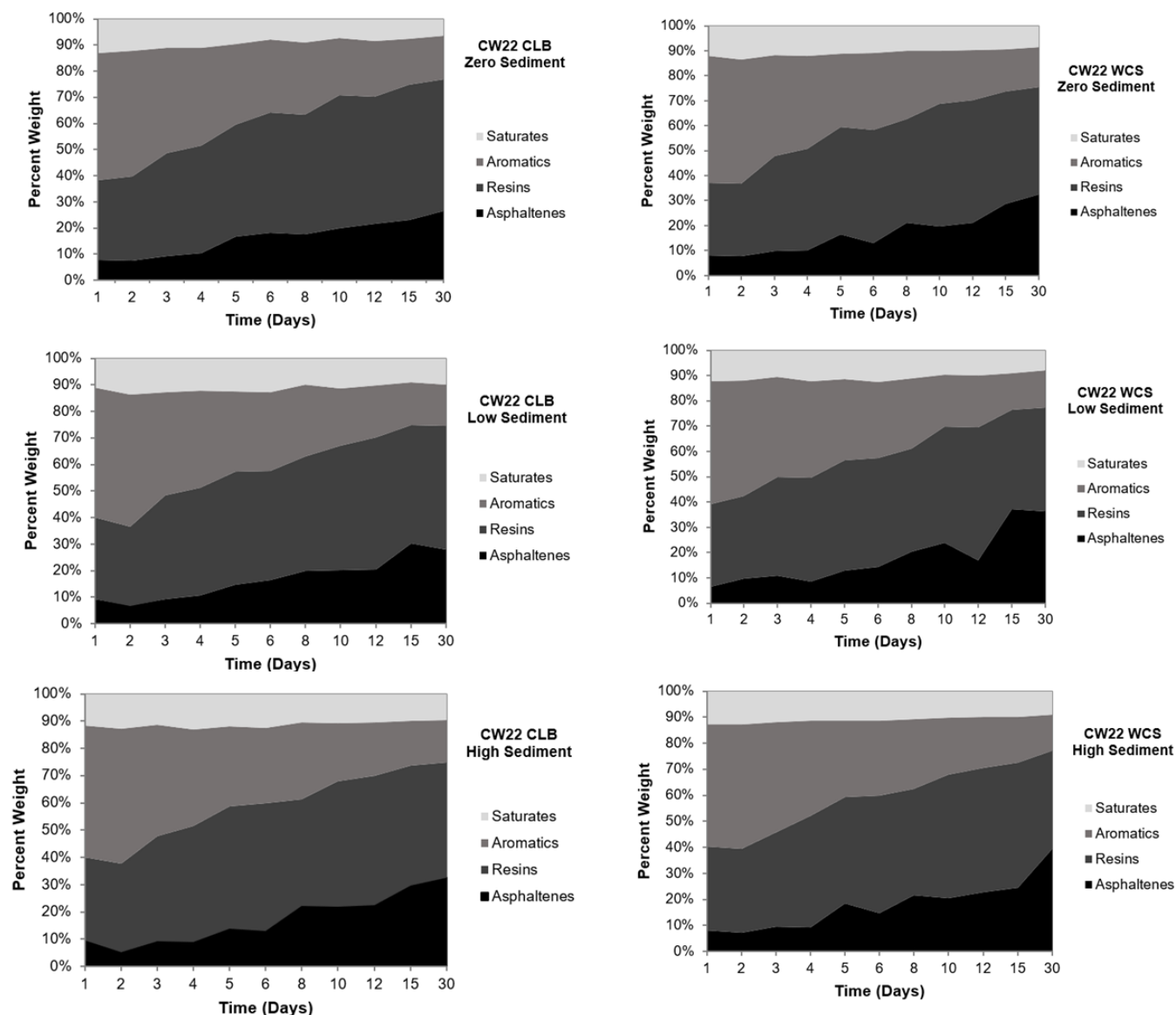


Figure C-19. CW22 SARA results by tank.

C.7 PAH

For WW22 and CW22, the samples were analyzed to determine the amount of selected PAHs.

C.7.1 PAH Results from WW22 Mesoscale Tanks

Figures C-20 through C-25 show the PAH analysis for the individual WW22 tanks.

WW PAH Tank 1

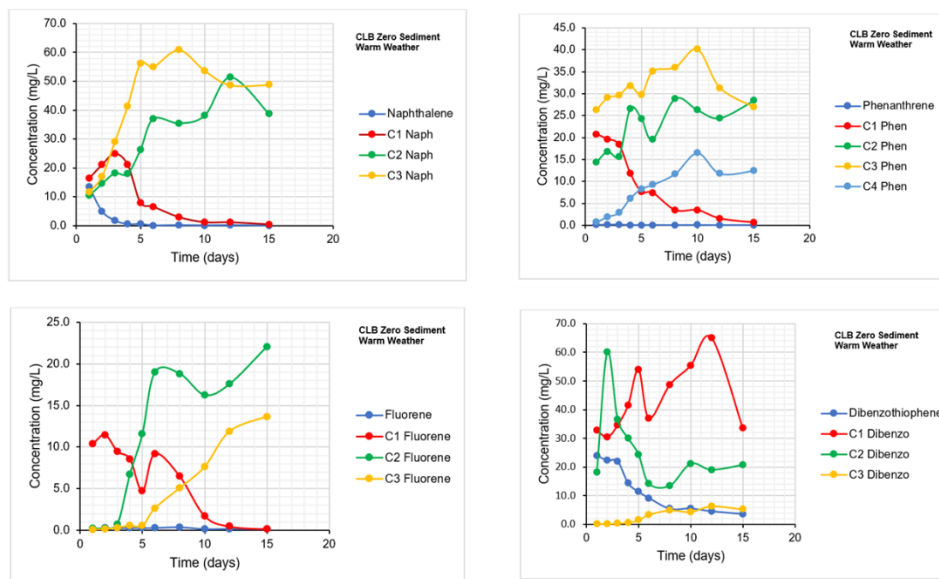


Figure C-20. WW22 PAH tank 1 – CLB zero sediment.

WW PAH Tank 2

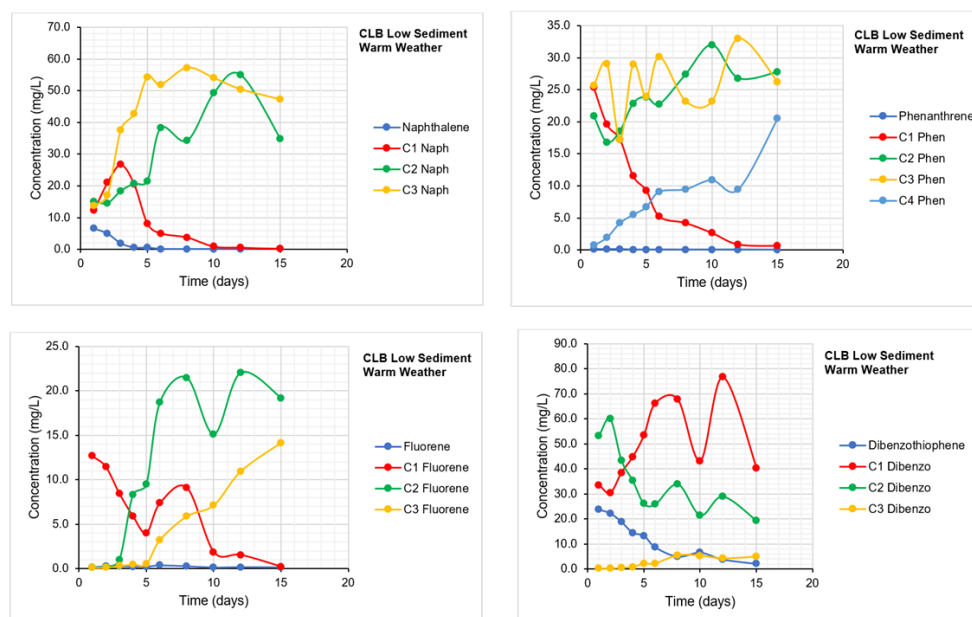


Figure C-21. WW22 PAH tank 2 – CLB low sediment.

WW PAH Tank 3

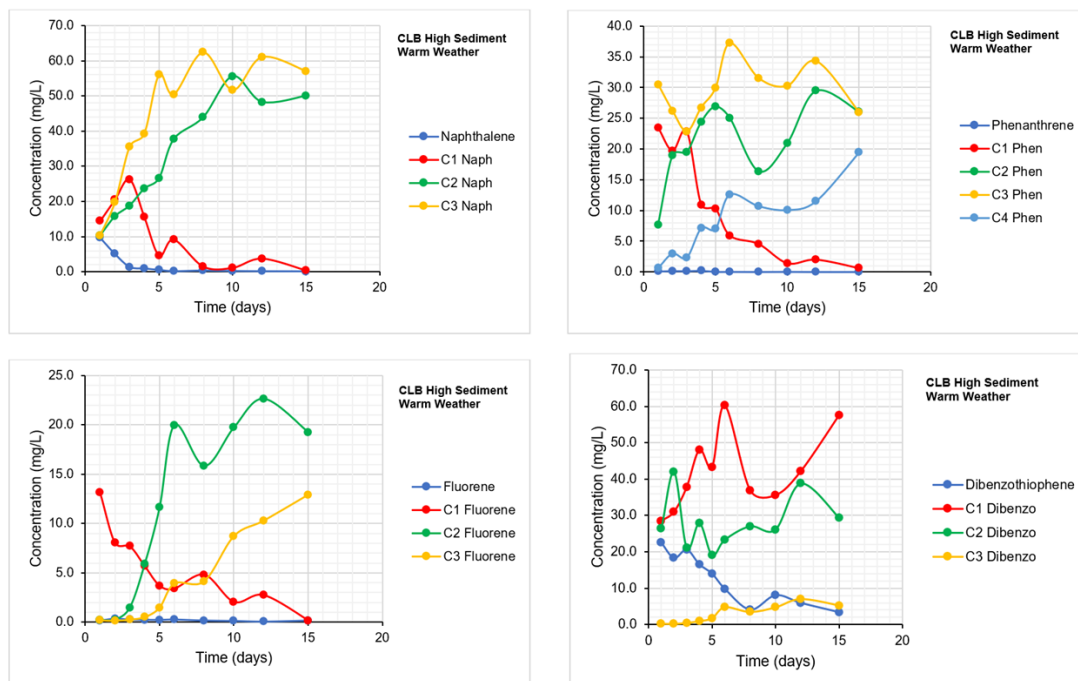


Figure C-22. WW22 PAH tank 3 – CLB high sediment.

WW PAH Tank 4

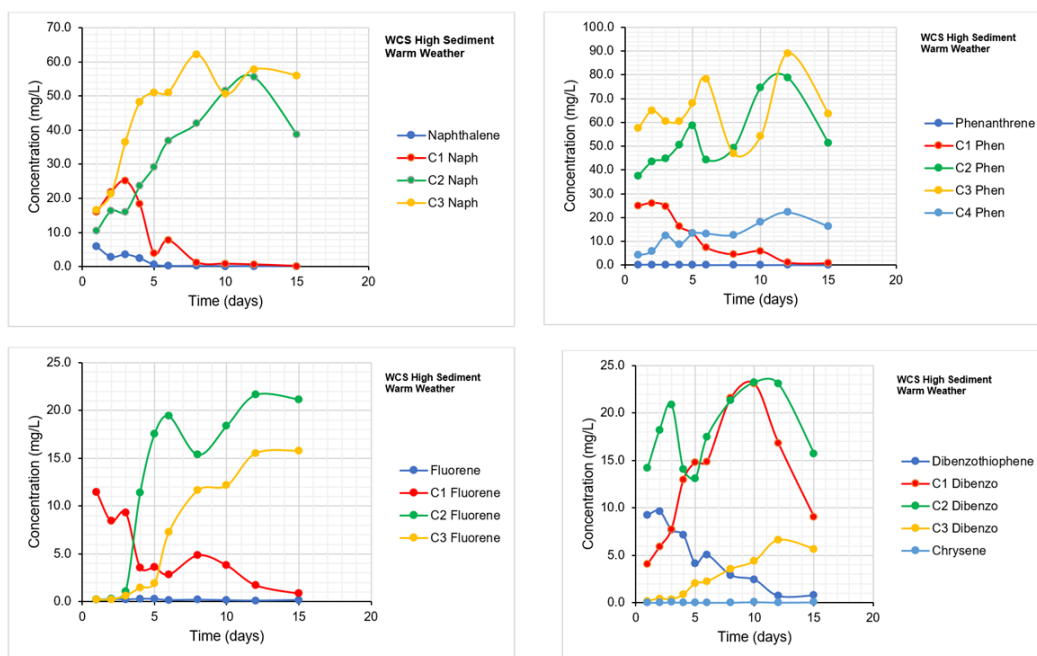


Figure C-23. WW22 PAH tank 4 – WCS high sediment.

WW PAH Tank 5

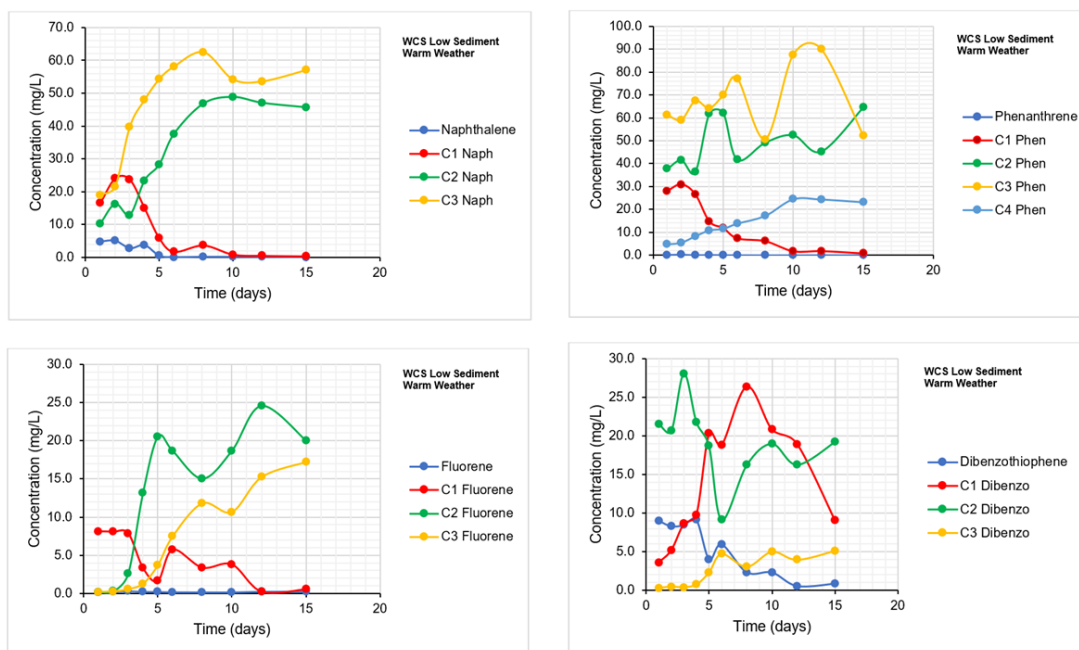


Figure C-24. WW22 PAH tank 5 – WCS low sediment.

WW PAH Tank 6

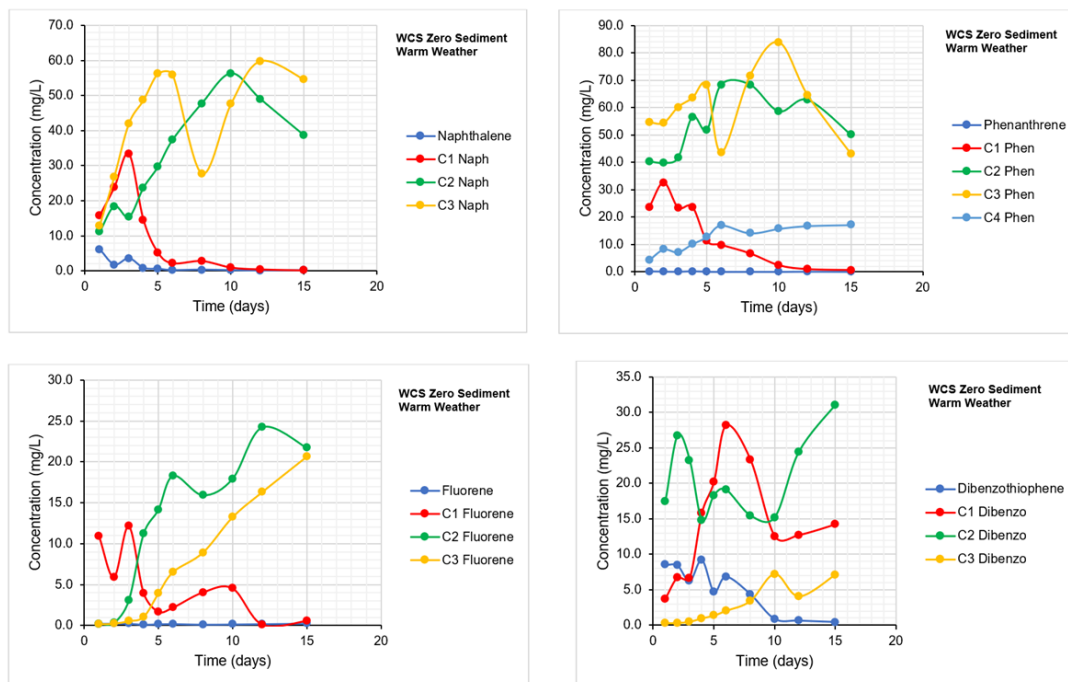


Figure C-25. WW22 PAH tank 6 – WCS zero sediment.

C.7.2 PAH Results from CW22 Mesoscale Tanks

Figures C-26 through C-31 show the PAH analysis for the individual CW22 tanks using the same analysis process as used for the WW22 tanks.

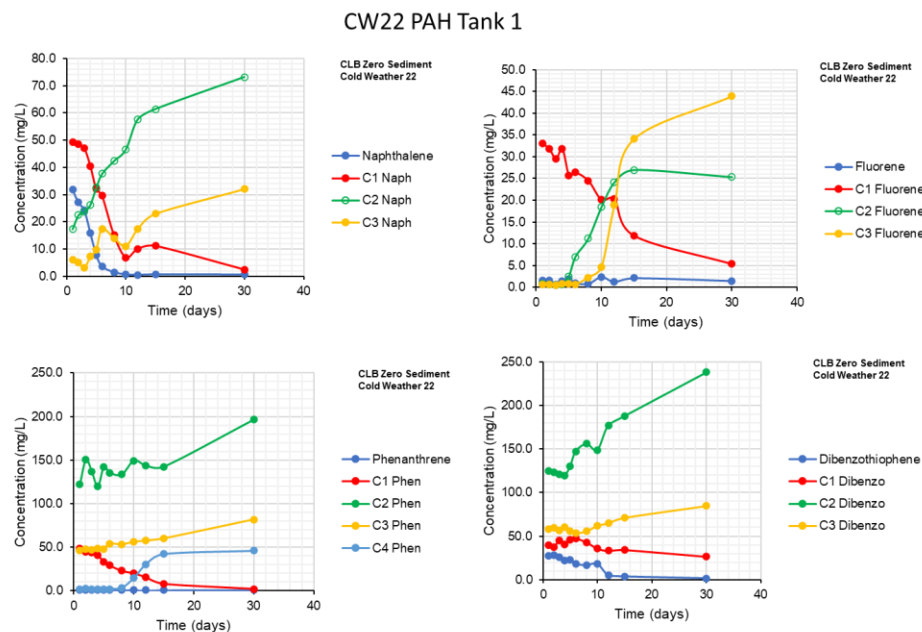


Figure C-26. CW22 PAH tank 1 – CLB zero sediment.

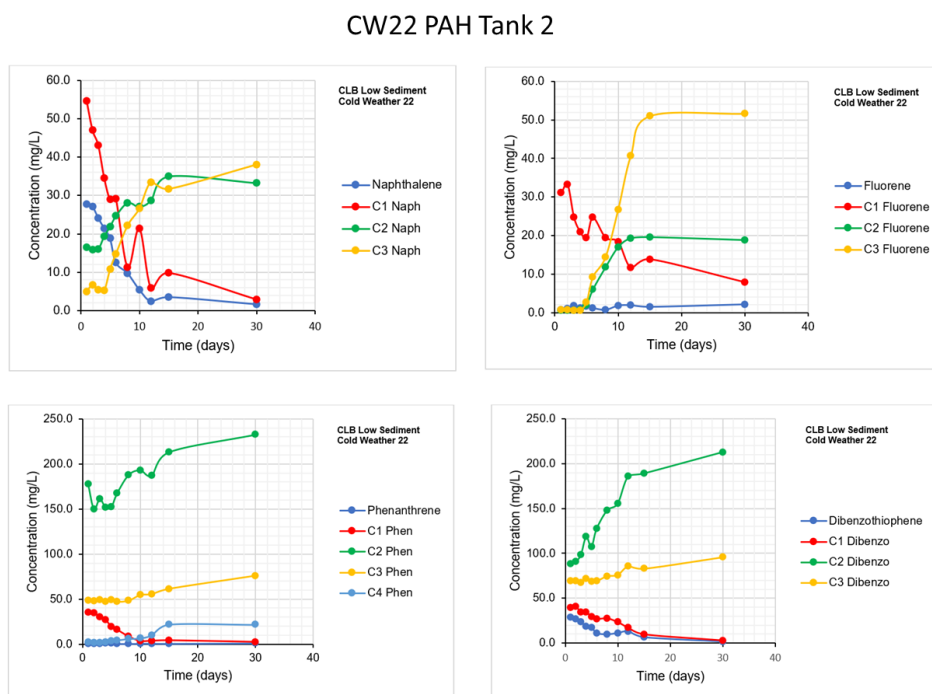


Figure C-27. CW22 PAH tank 2 – CLB low sediment.

CW22 PAH Tank 3

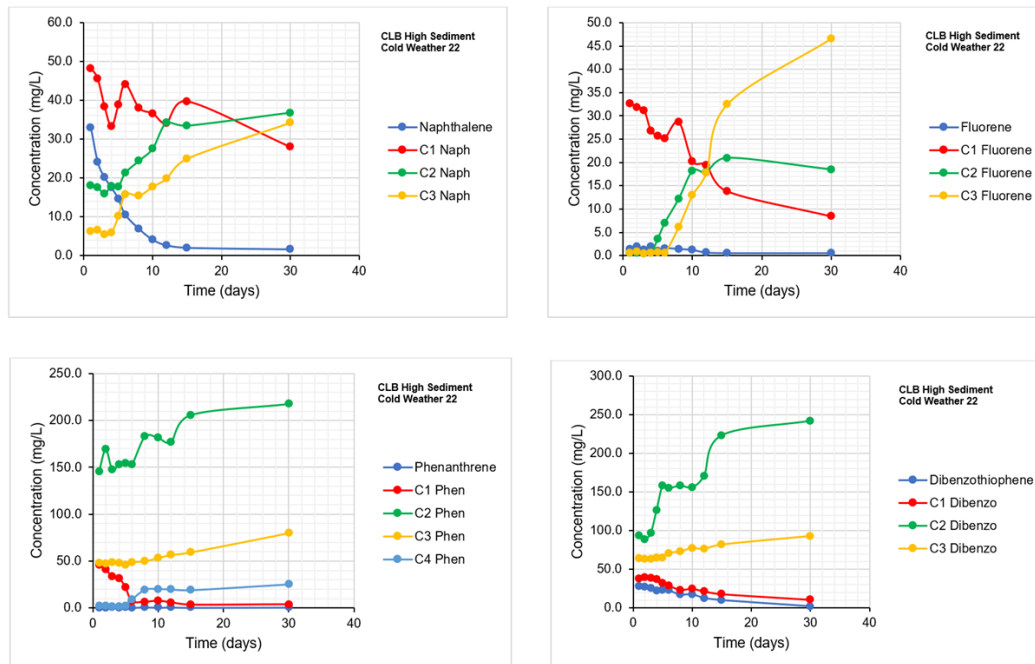


Figure C-28. CW22 PAH tank 3 – CLB high sediment.

CW22 PAH Tank 4

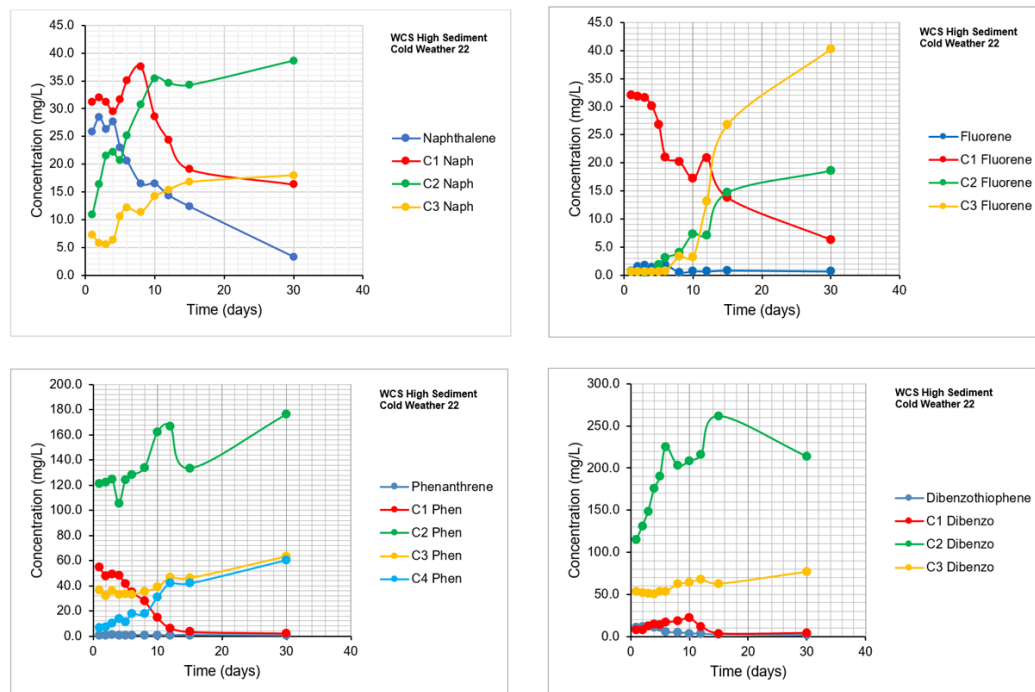


Figure C-29. CW22 PAH tank 4 – WCS high sediment.



CW22 PAH Tank 5

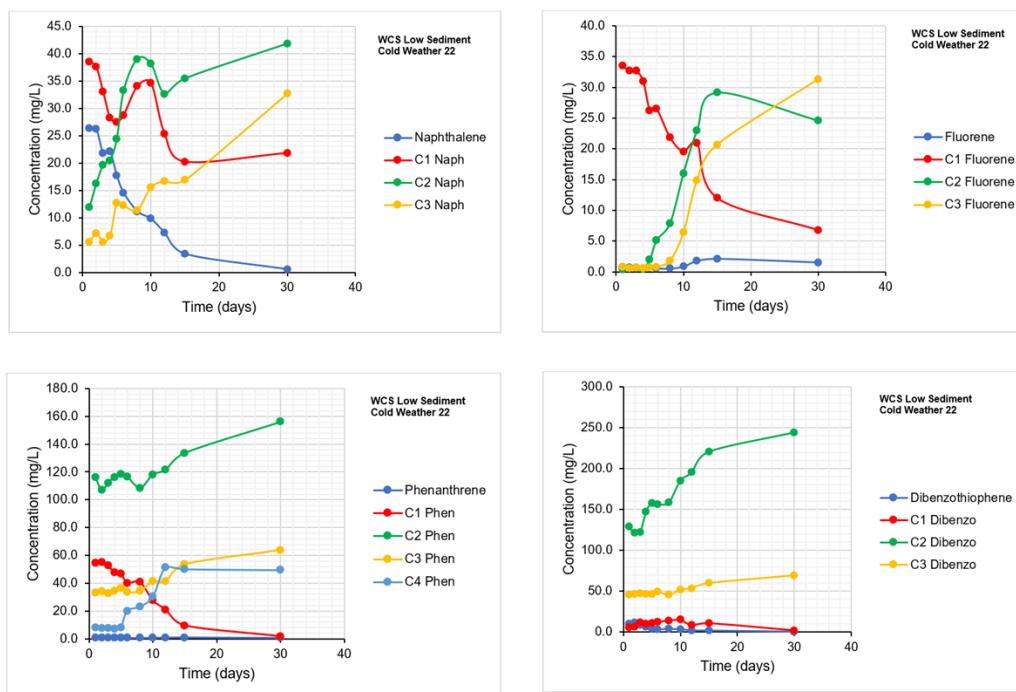


Figure C-30. CW22 PAH tank 5 – WCS low sediment.

CW22 PAH Tank 6

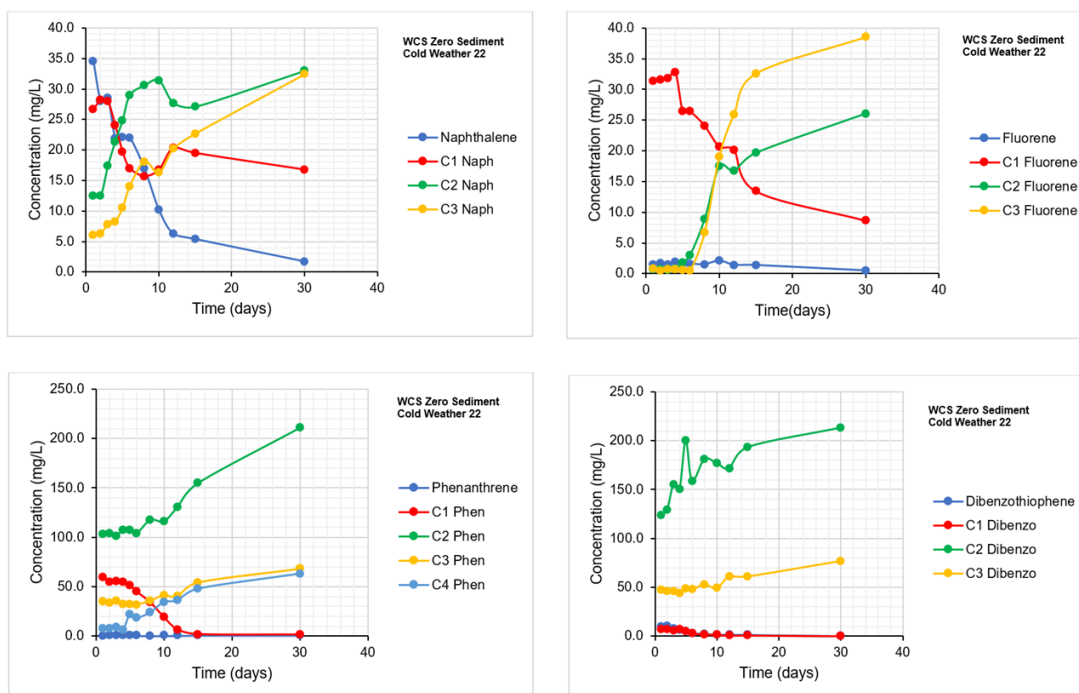


Figure C-31. CW22 PAH tank 6 – WCS zero sediment.

In CW22 only, researchers used an independent lab to provide additional PAH analysis. This section provides results and discussion of CW22 PAH contents based on that analysis. The oil components change with time, and GCMS was used to characterize the changes of the alkanes and aromatics when sampled on day 8, day 15 and day 30 in each tank. Figure C-32 shows the mass loss (normalized to hopane) of Cold Lake Blend (CLB) for alkanes from 13 to 34 carbons (1a) and aromatics including naphthalenes, fluoranthenes, phenanthrenes, dibenzothiophenes, benz[a]anthracenes and chrysenes (1b) in tank 1 (0 mg/L of sediment). The GC-MS results were normalized to hopane to track evaporation and degradation since hopane does not evaporate significantly and does not degrade over the time scale of investigation. The results indicate that the loss of every alkane increased with time especially at 30 days. Meanwhile, the mass loss of light fractions ($C \leq 17$) was relatively higher (mostly > 60 percent) compared with those heavier fractions (mostly around 25 percent) after 8 days and 15 days. However, after 30 days, approximately 75 percent of the alkanes were lost.

The mass loss of the aromatics in the same tank showed a similar trend, as most of them were lost in as little as 15 days, but loss increased significantly to around 75 percent after 30 days. The dispersibility of the low-molecular-weight hydrocarbons is reduced for the highly viscous dilbit, which delays the onset of biodegradation as well (Venosa and Zhu, 2003). Therefore, regardless of the sediment concentration in the tank, the oil fractions of the dilbit products changed slowly within 15 days.

The oil mass data for the samples taken from Tank # 2 (100 mg/L of sediment) and Tank #3 (1,000 mg/L of sediment) are shown in Figures C-33 and C-34. Generally, the mass loss results were similar to the results from Tank #1. As the oil concentration was 3 g/L, the mass ratio of sediment to oil was 1:30 for the 100 mg/L and 1:3 for the 1,000 mg/L.

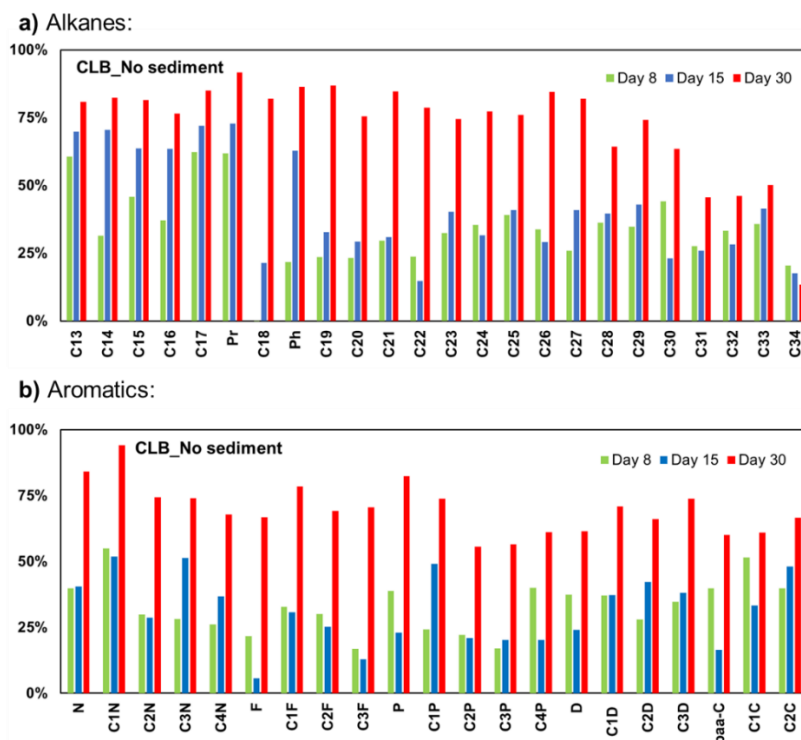


Figure C-32. CW22 PAH tank 1 – CLB zero sediment.

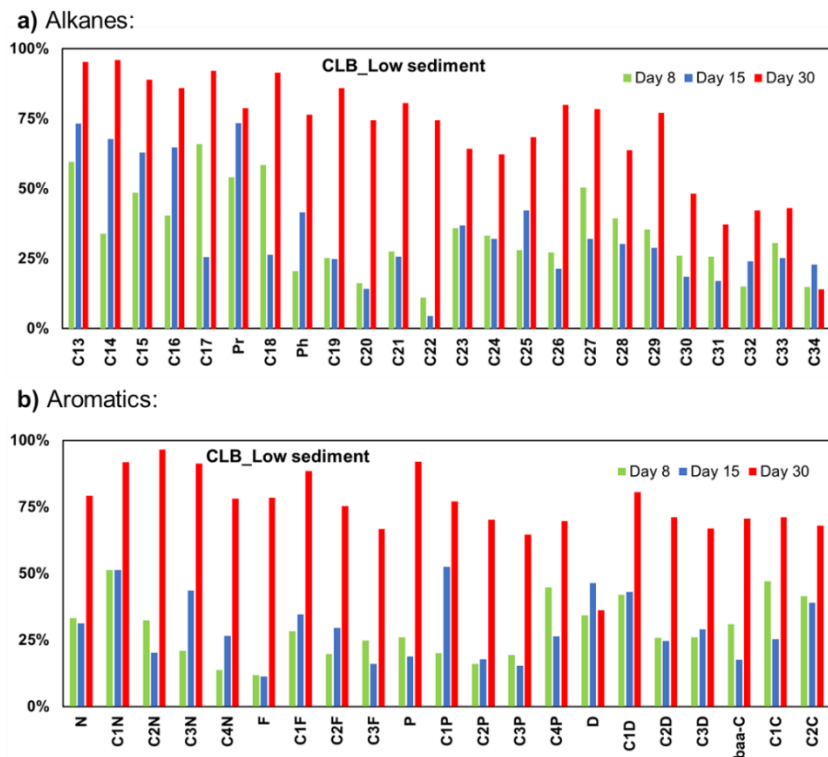


Figure C-33. CW22 PAH tank 2 – CLB low sediment.

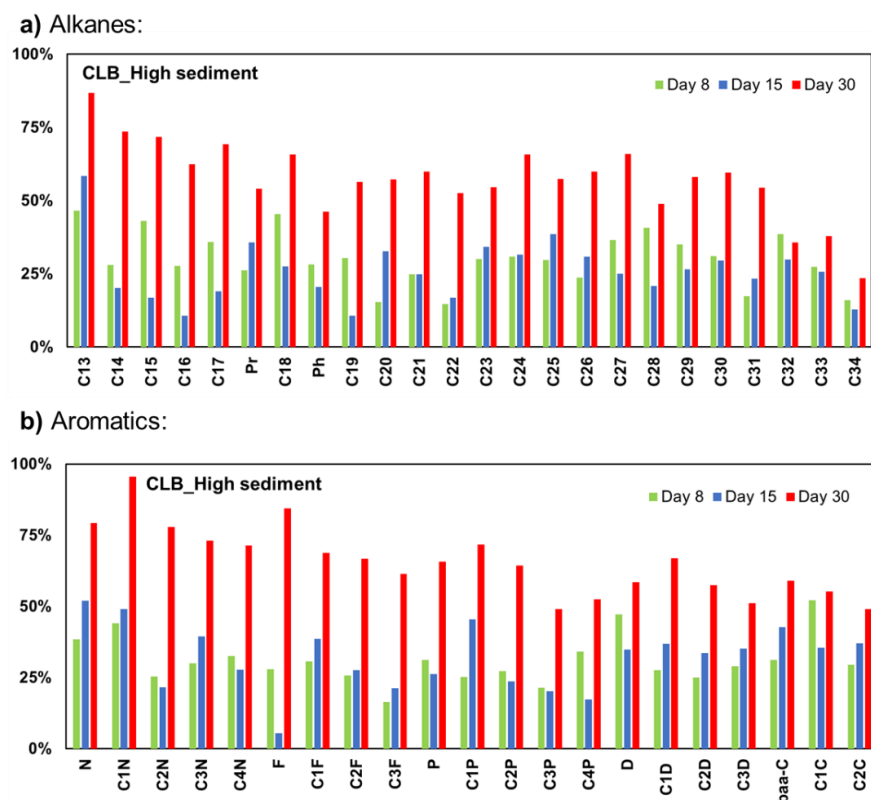


Figure C-34. CW22 PAH tank 3 – CLB high sediment.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

Figure C-35 shows the GCMS results of the WCS (Western Canadian Select) oil after 8 days, 15 days and 30 days mixing without sediment. One may conclude that the mass loss of alkanes from 13 to 34 carbons and that of the aromatics did not change with the time. The WCS did not exhibit a huge degradation going from day 15 to day 30, as noted for the CLB. This was also confirmed for the 100 mg/L and 1,000 mg/L sediment concentrations, Figures C-36 and C-37, respectively.

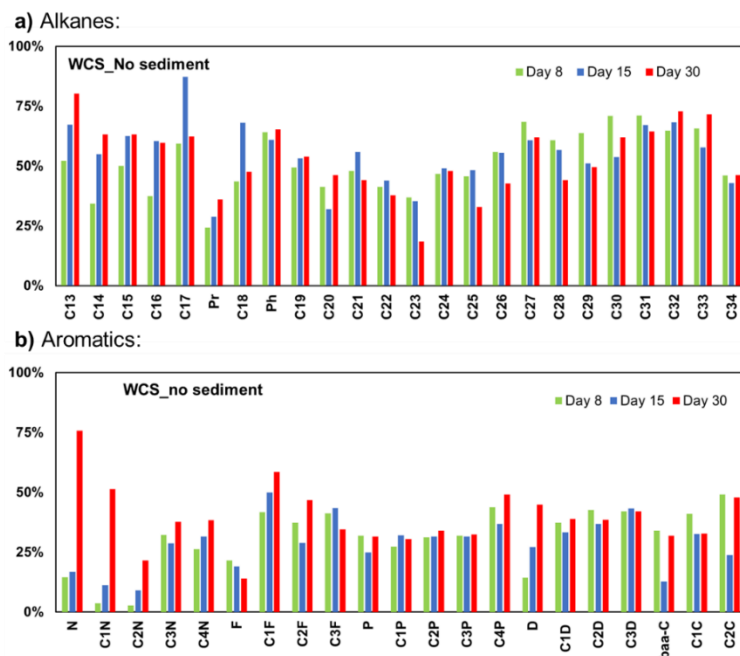


Figure C-35. CW22 PAH tank 6 – WCS zero sediment.

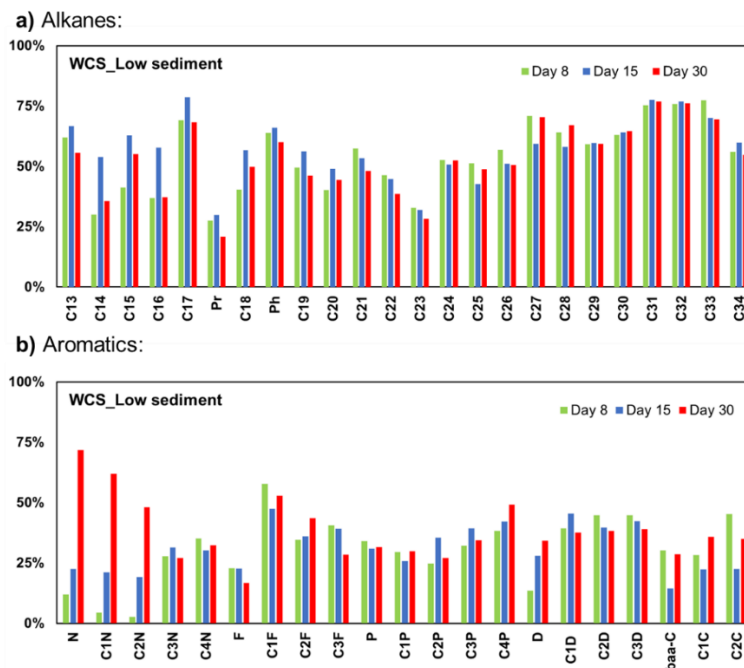


Figure C-36. CW22 PAH tank 5 – WCS low sediment.



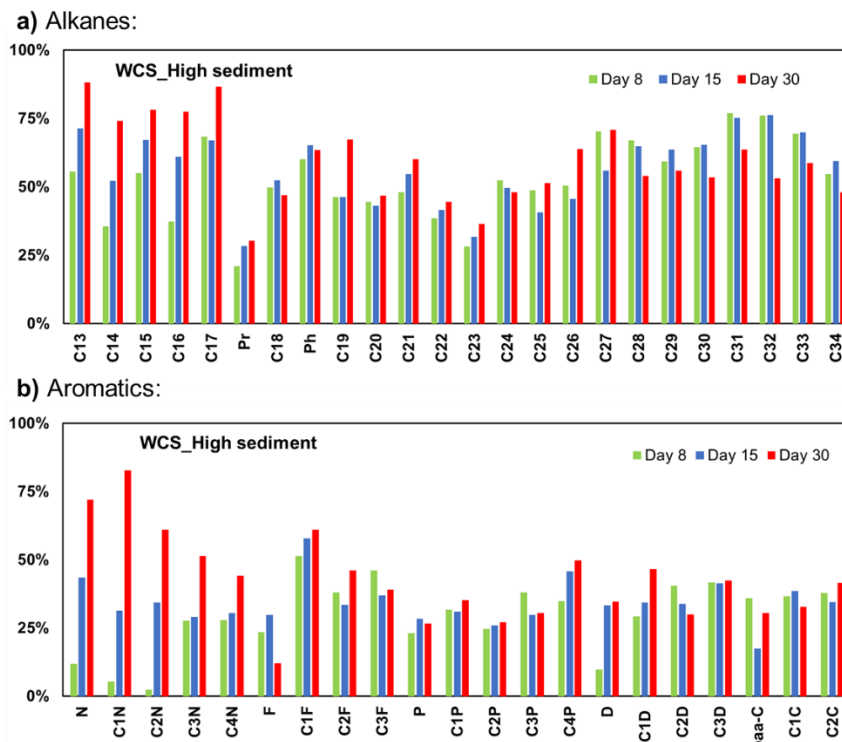


Figure C-37. CW22 PAH tank 4 – WCS high sediment.

Assuming the mass loss for alkanes should be the same despite the carbon numbers, the one-way ANOVA tests show that the differences between various sediment concentrations were statistically insignificant for CLB oil collected from the tanks on day 8, as shown in Figure C-38(a). Similarly, the p-values of aromatics at various sediment concentrations (Figure C-38(b)) also indicate statistically insignificant differences. This further confirmed the insufficient oil-particle aggregate (OPA) formation in these tanks.

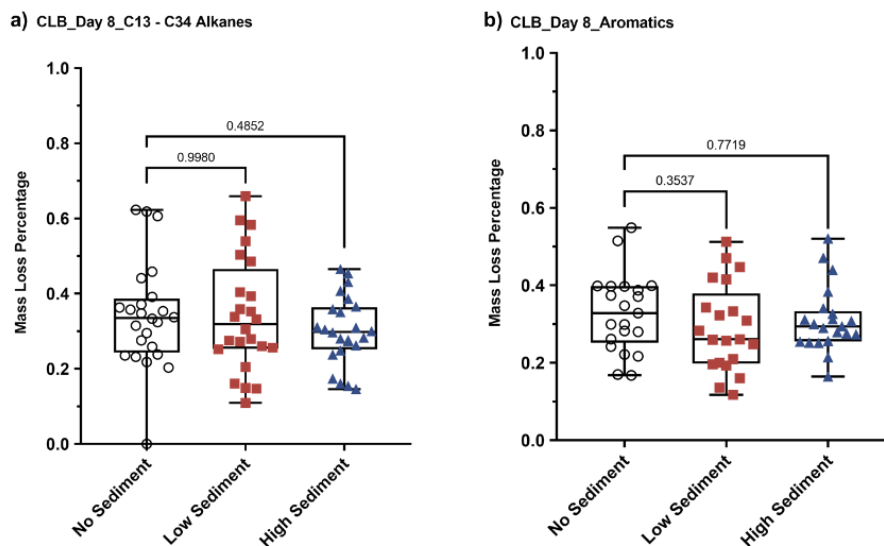


Figure C-38. CW22 CLB ANOVA day 8.

For CLB oil collected from the tanks on day 15, the p-values of alkanes and aromatics from the various sediment concentrations are shown in Figure C-39(a) and C-39(b), respectively. Only the mass loss of alkanes for the samples from the high sediment tanks shows a significant difference compared to the samples from the control tank. This indicates that after a longer mixing time, in the presence of a high sediment concentration, the average mass loss of alkanes decreases from 40 percent to around 25 percent.

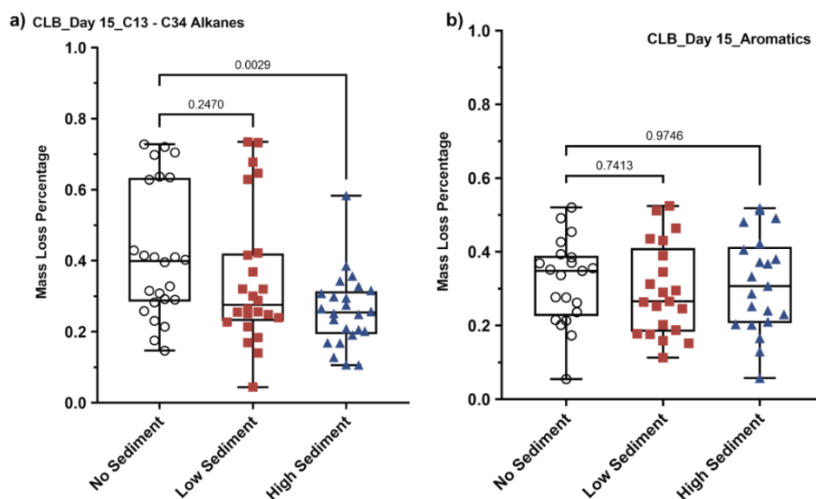


Figure C-39. CW22 CLB ANOVA day 15.

For CLB oil collected from the tanks on day 30, the p-value in Figure C-40(a) indicates that the alkanes in the high sediment tank exhibited a statistically significant mass loss compared to the loss of alkanes in the samples from the control tank. This indicates that after a longer mixing time, in the presence of a high sediment concentration, the average mass loss of alkanes decreases from approximately 80 percent to less than 60 percent. Figure C-40(b) shows that the aromatics in the low sediment tank had a statistically significant mass loss compared to the control tank.

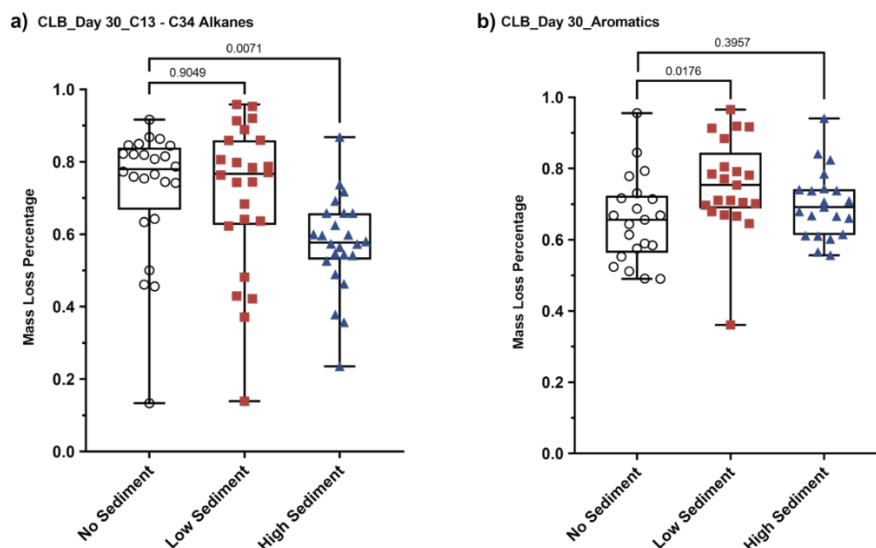


Figure C-40. CW22 CLB ANOVA day 30.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

The one-way ANOVA tests of the mass loss of alkanes and aromatics for WCS oils are shown in Figures C-41 to C-43. However, there were no statistically significant differences were found for any cases. The oil components seemed to have very limited changes in these tanks.

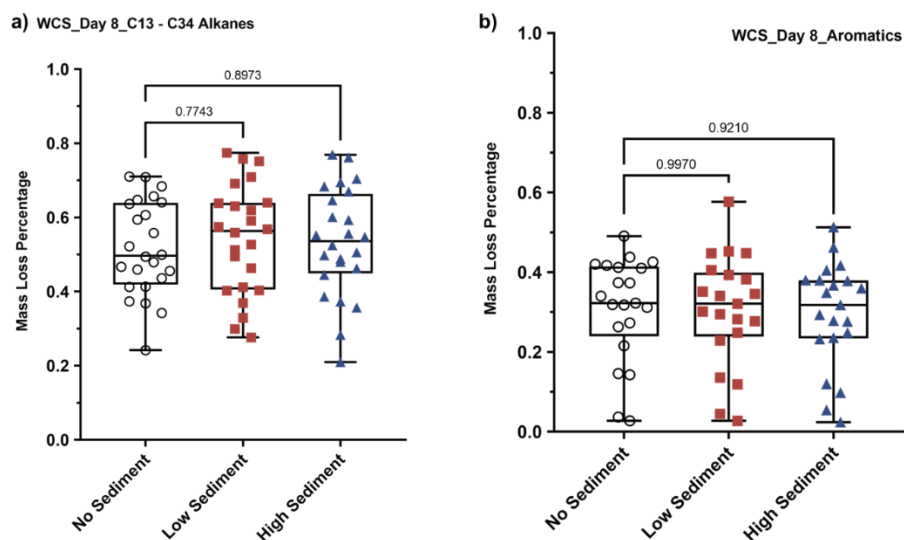


Figure C-41. CW22 WCS ANOVA day 8.

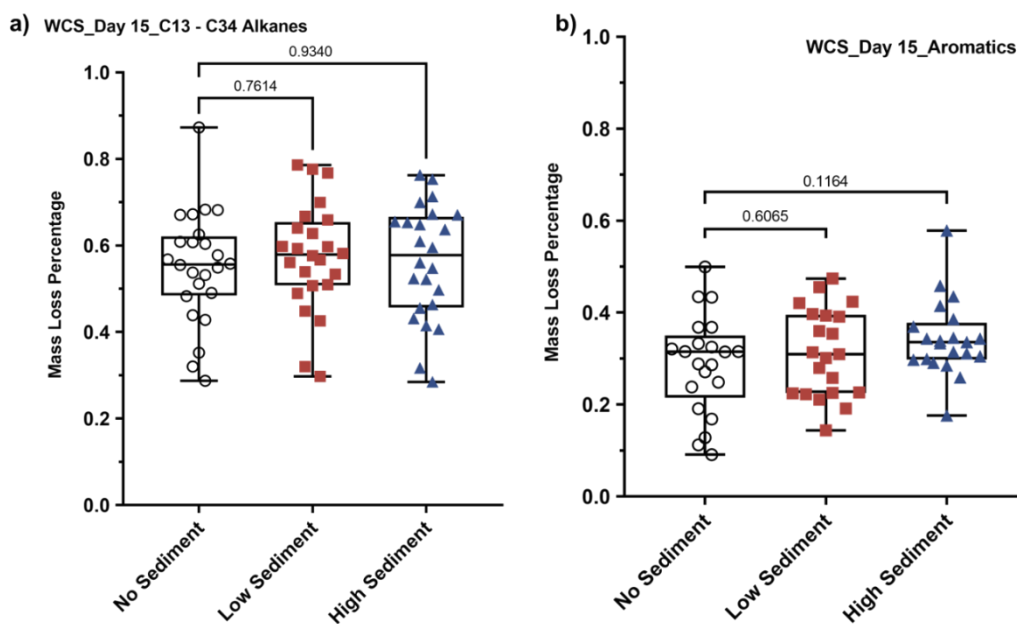


Figure C-42. CW22 WCS ANOVA day 15.



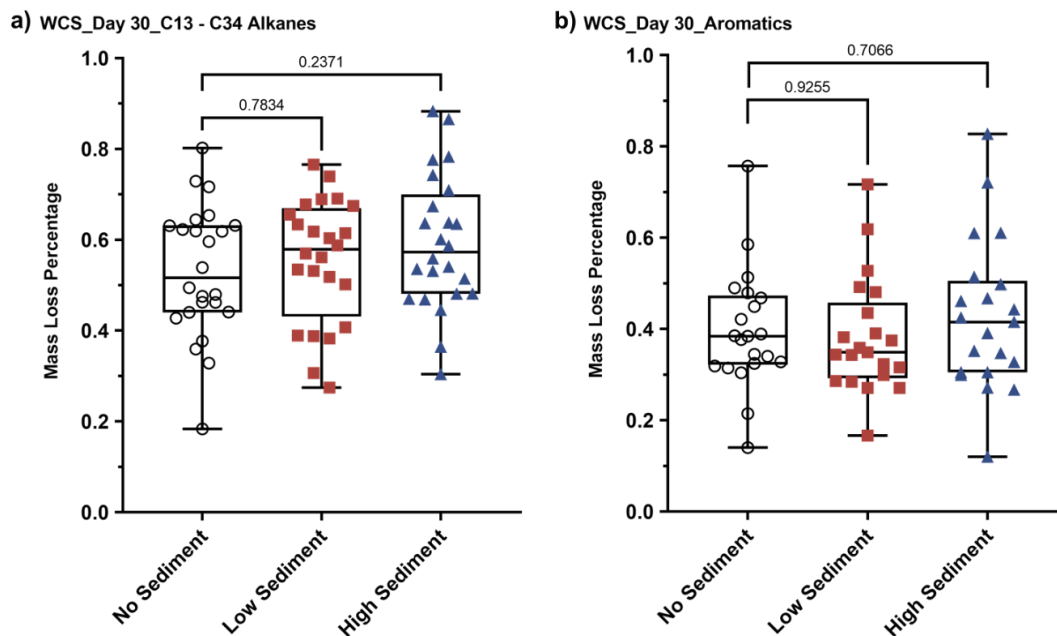


Figure C-43. CW22 WCS ANOVA day 30.

C.7.3 PAH results from the Lab Scale Jars

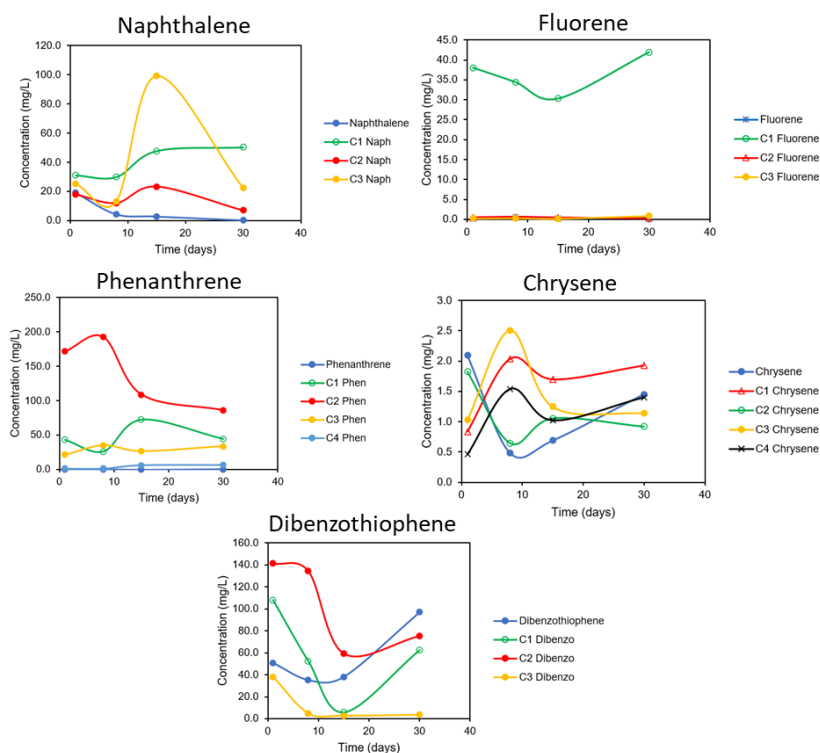


Figure C-44. WW22 PAH CLB evaporation.

Guidance Document – Behavior of Dilbit in the Freshwater Environment

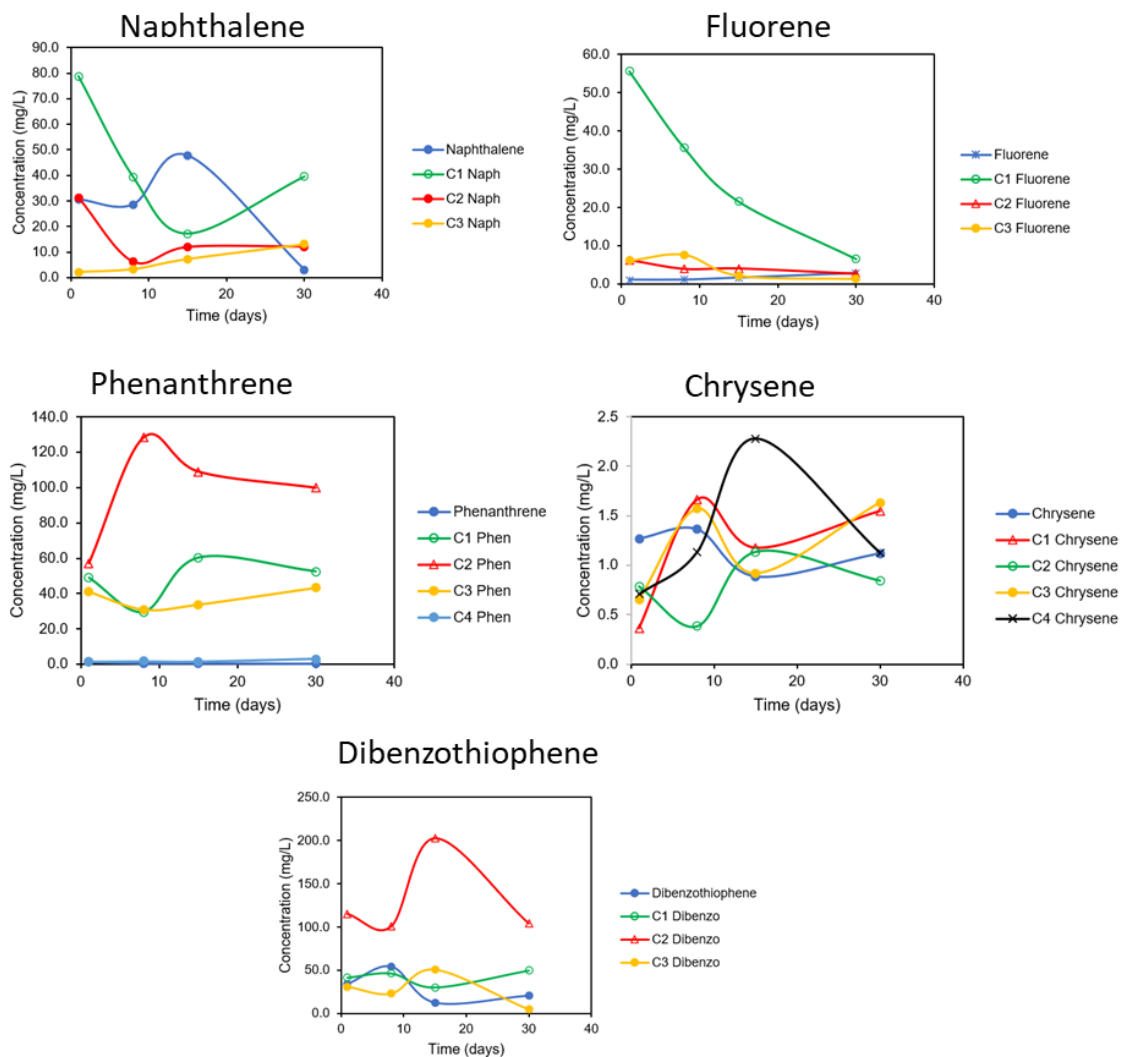


Figure C-45. WW22 PAH CLB photo-oxidation.



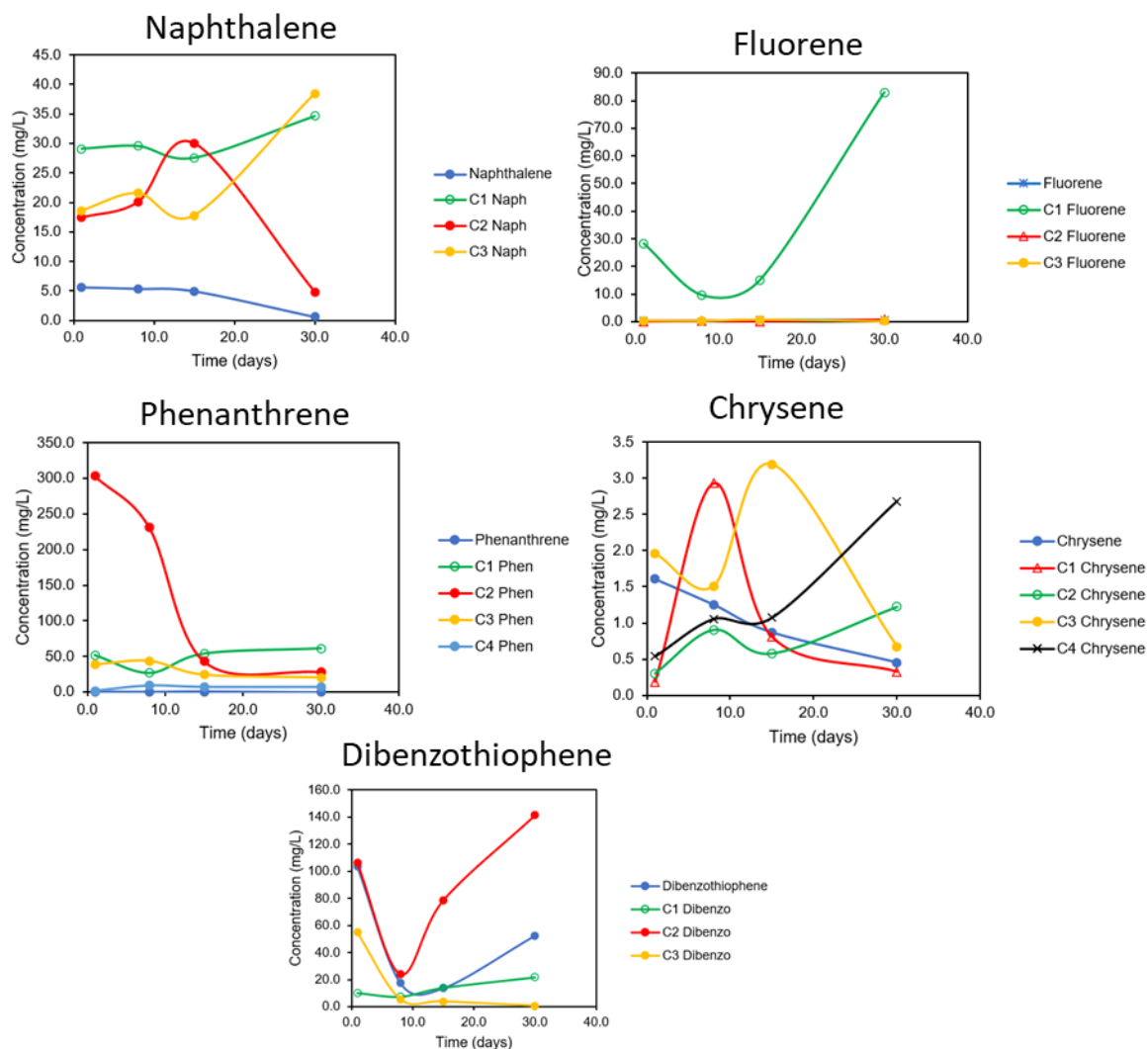


Figure C-46. WW22 PAH WCS evaporation.

Guidance Document – Behavior of Dilbit in the Freshwater Environment

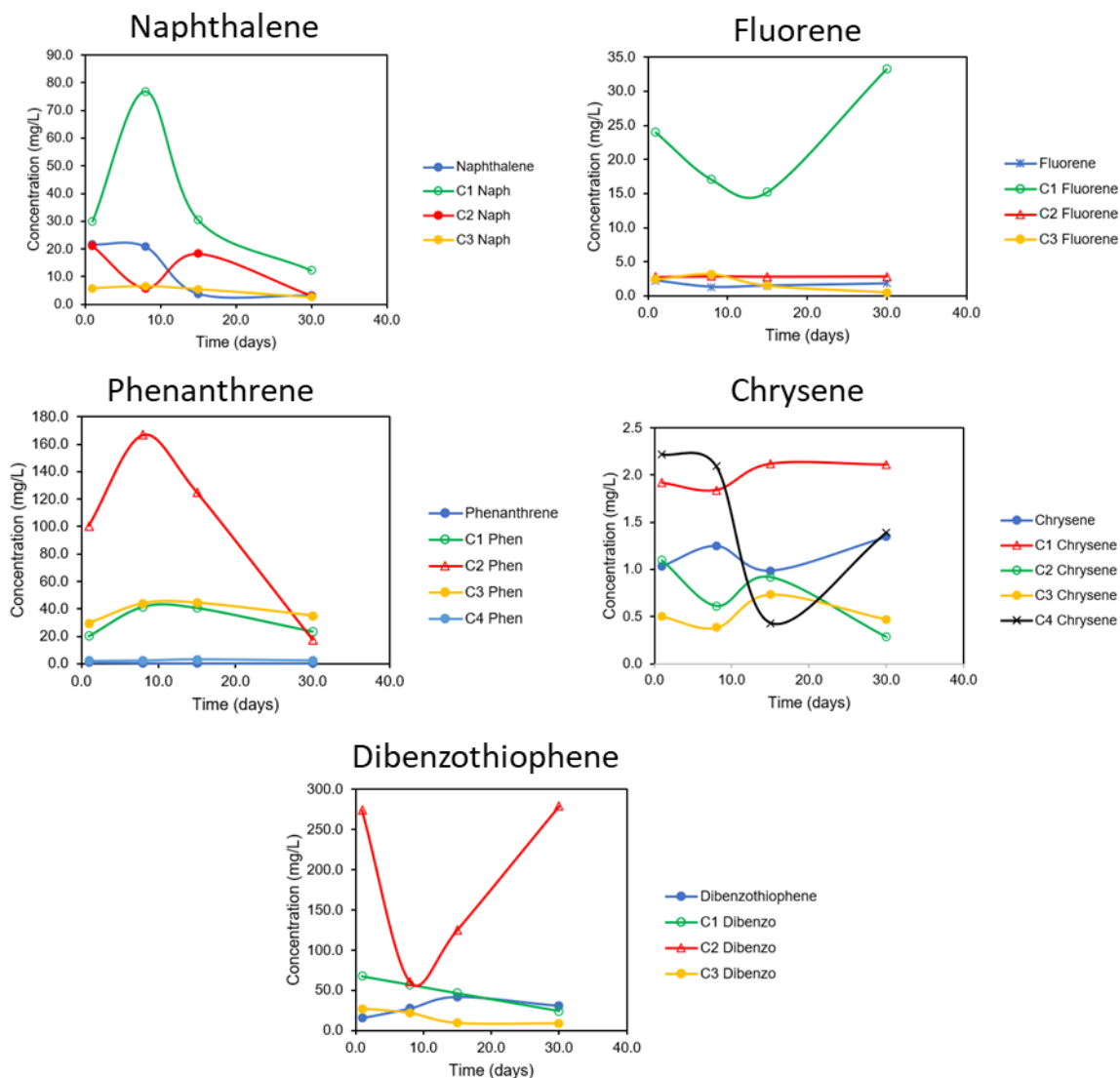


Figure C-47. WW22 PAH WCS photo-oxidation.



Guidance Document – Behavior of Dilbit in the Freshwater Environment

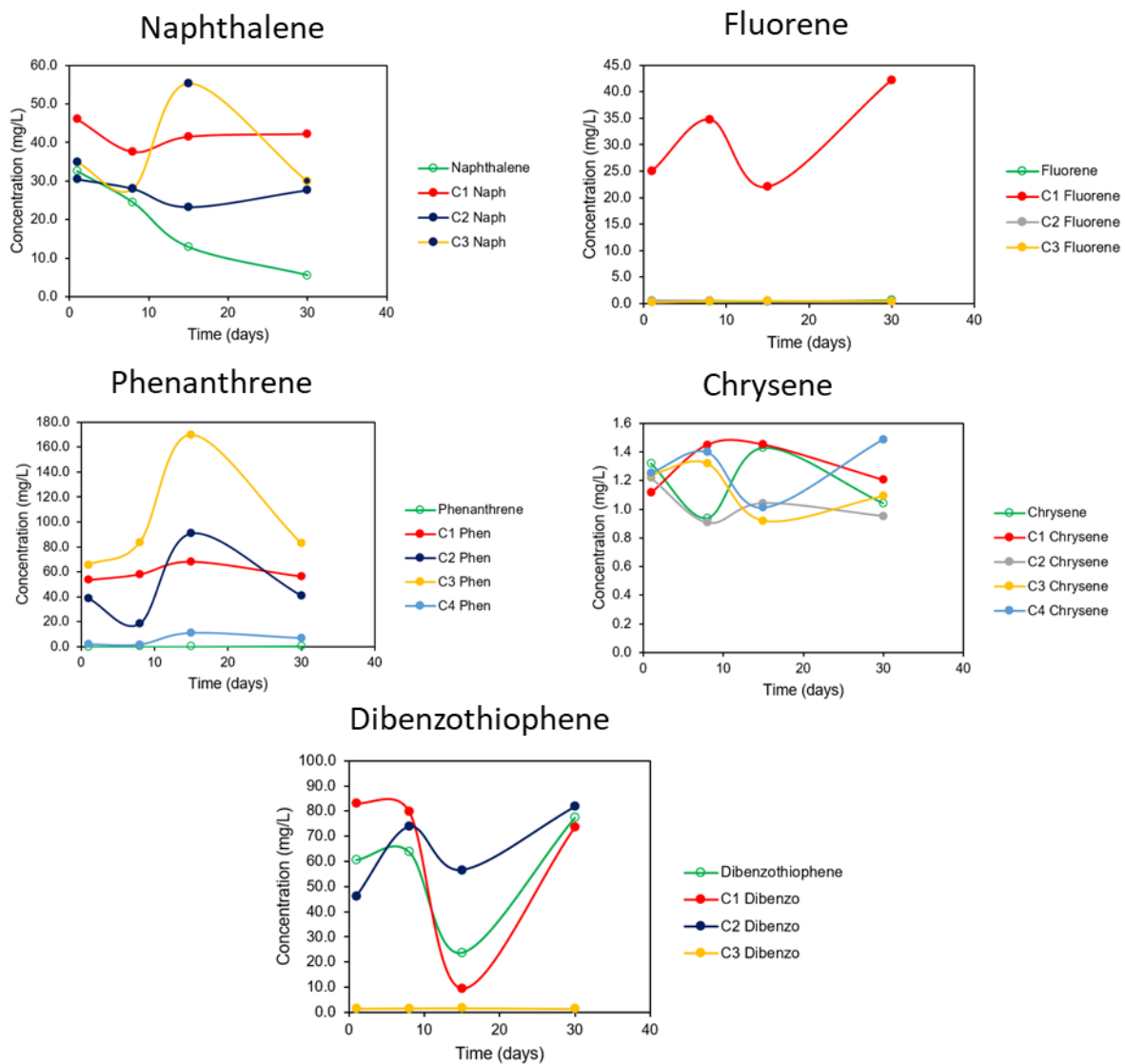


Figure C-48. CW22 PAH CLB evaporation.



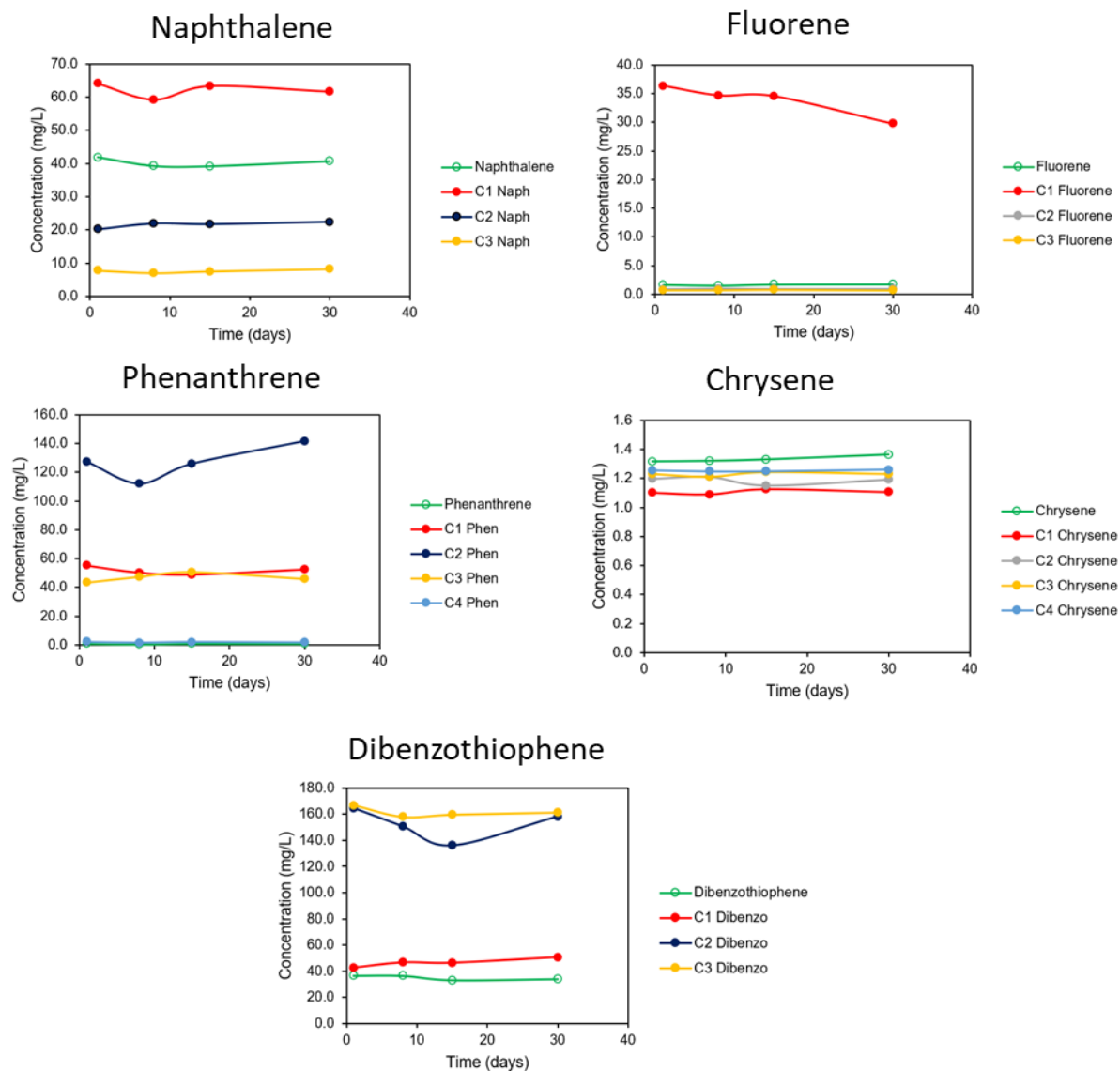


Figure C-49. CW22 PAH CLB photo-oxidation.

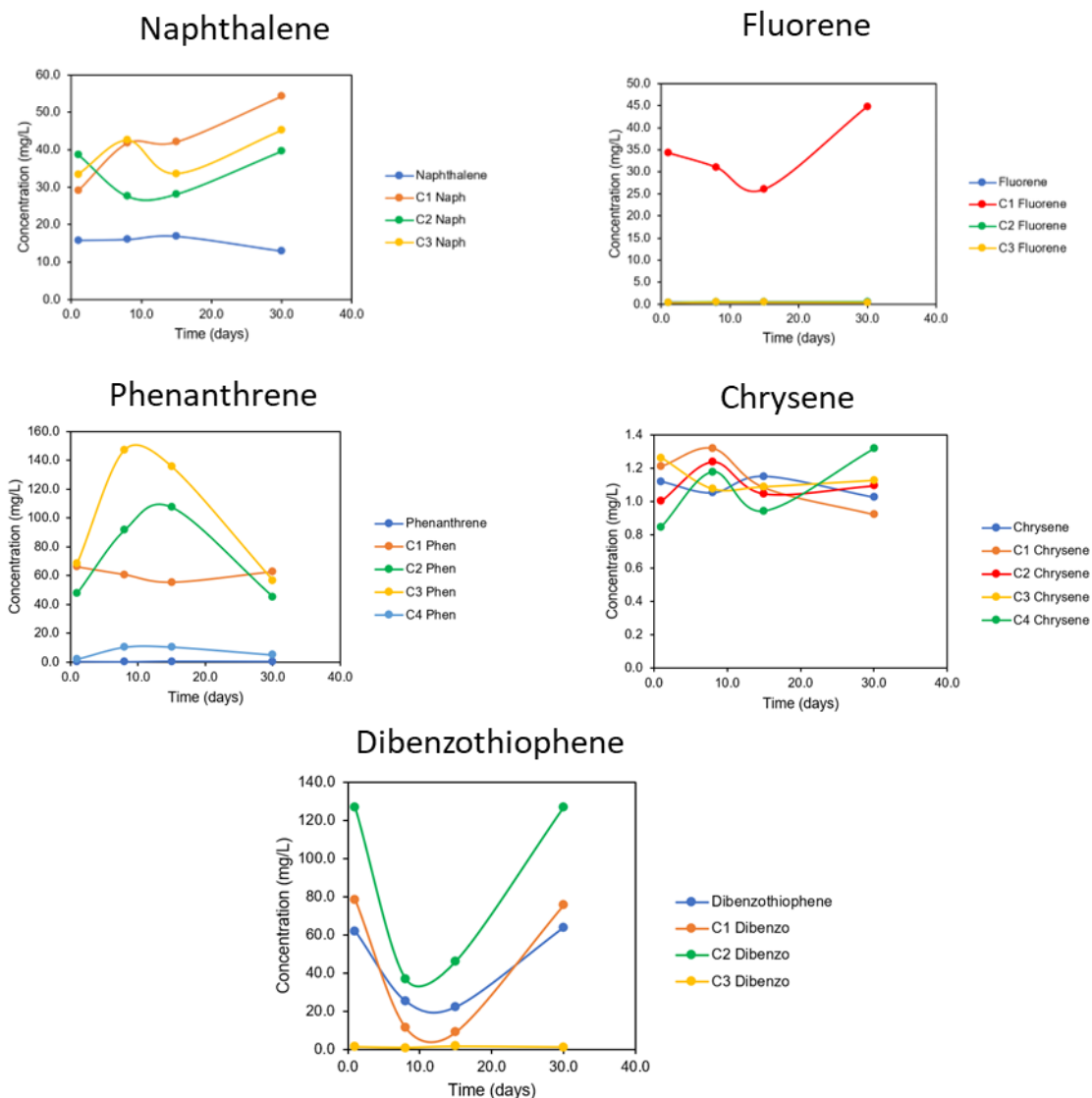


Figure C-50. CW22 PAH WCS evaporation.

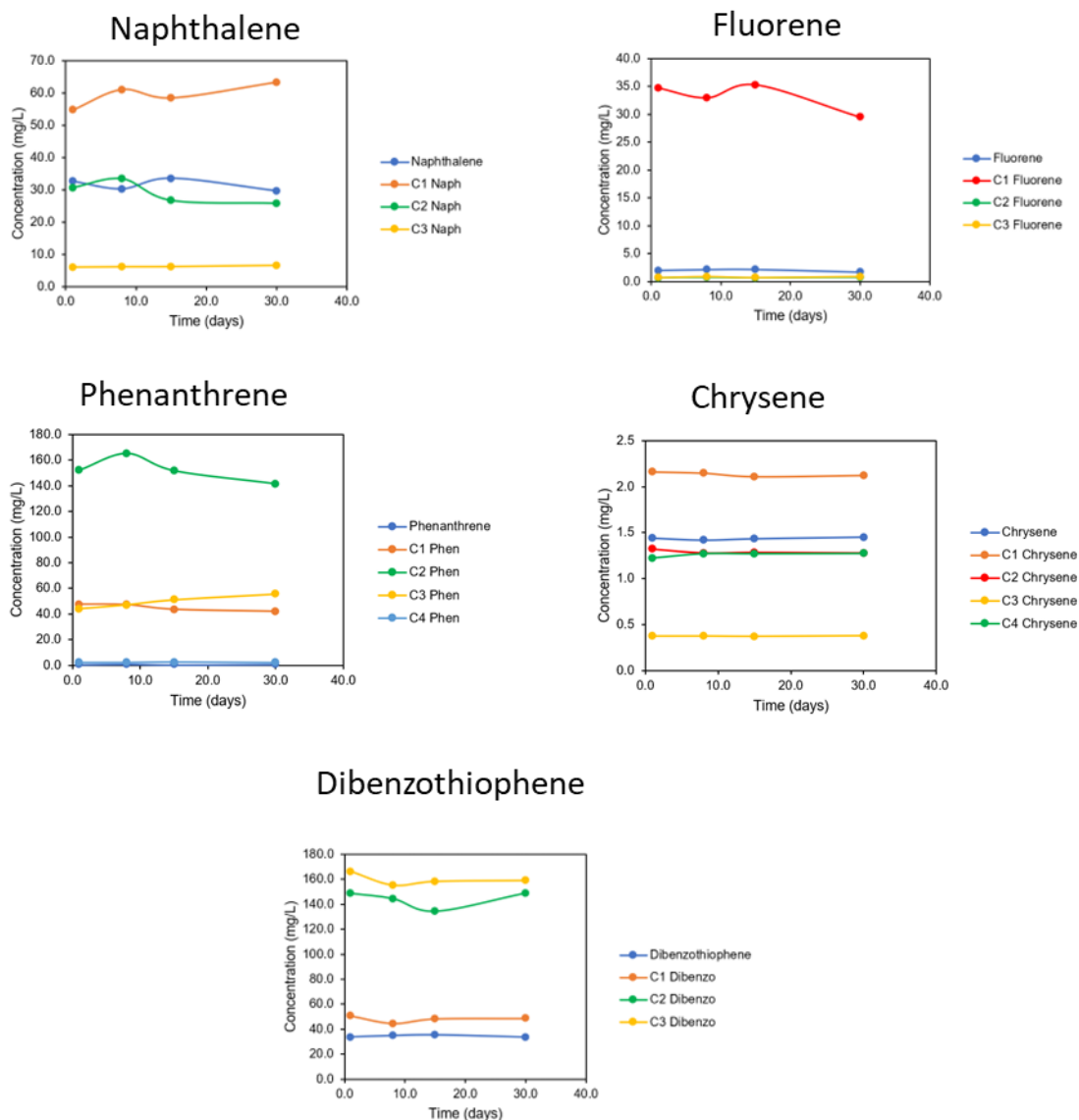


Figure C-51. CW22 PAH WCS photo-oxidation.

(This page intentionally left blank.)

