In situ formation of oil-suspended particulate matter aggregates (OSA) during mechanical cleanup activities

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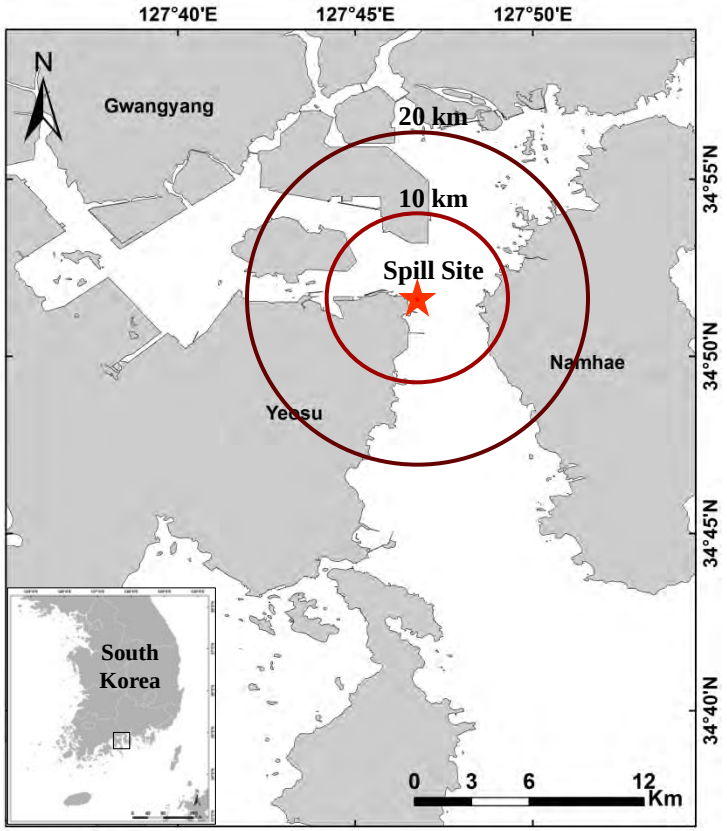
Introduction



- **The *Wu Yi San* Oil Spill: Significance?**

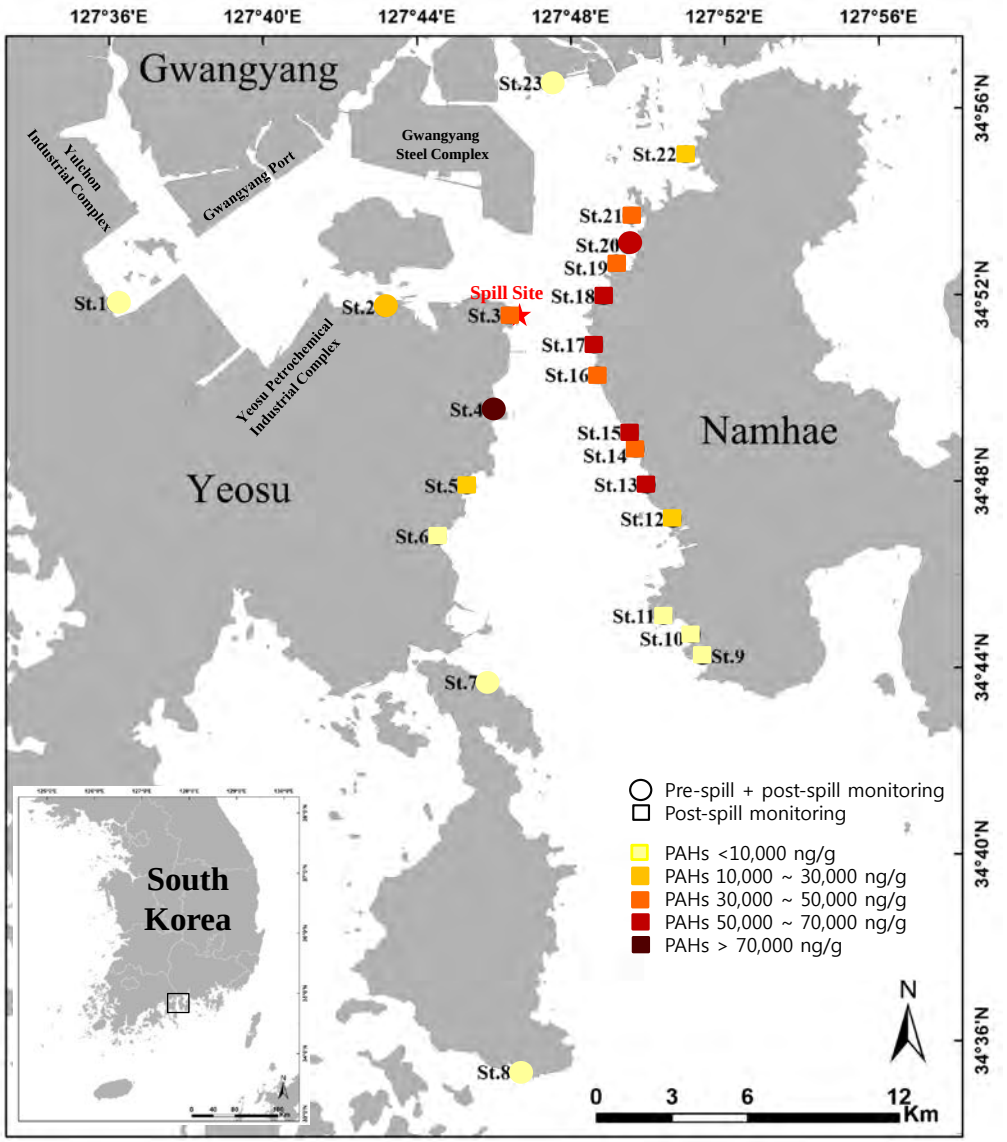
➢ Collision of VLCC *Wu Yi San* into the floating pipelines of petrochemical complex on 31st January 2014 released approximately 900 kL (800 M/T) of oil.

➢ The ruptured pipelines released three kinds of oil, namely Basrah Light, Naphtha, and oil-water mixture.

➢ Due to the tidal exchange influence by the South Sea, the spilled oil rapidly polluted over 20 km of coastlines along the Gwangyang Bay.

➢ Emergency responses were performed to remove and recover the spilled oil in a short time.

Introduction



Emergency environmental responses

- As part of the emergency oil spill response, multi-media environmental monitoring were performed.
- TPH in seawater exceeded their quality guidelines for over a week.
- PAHs in bivalves from 5 out of 23 stations exceeded the "Level of Concern", thus showing high toxic potentials.
- Of the 5 stations, only 1 (Station 4) was found to continuously exceed the "Level of Concern" even after 60 days.
- Detailed investigation was further performed on station 4 (Sindeok)

Introduction

Site Characterization

- **Boulder-armored beach**

➢ Sindeok beach is a typical boulder-armored beach, where tendency of residual oil persistence is high.

➢ Tiered approach from visual observation, TPH, SARA, GC, to GCxGC analysis were performed to reveal spatial distribution and weathering status of residual oil.

Introduction

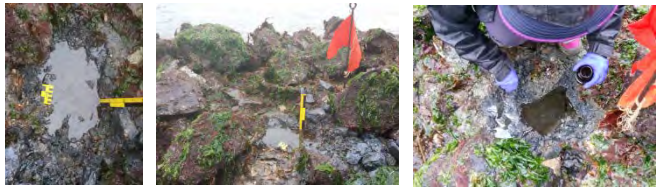
Scientific SCAT (shoreline cleanup assessment technique)

Upper intertidal

Middle intertidal

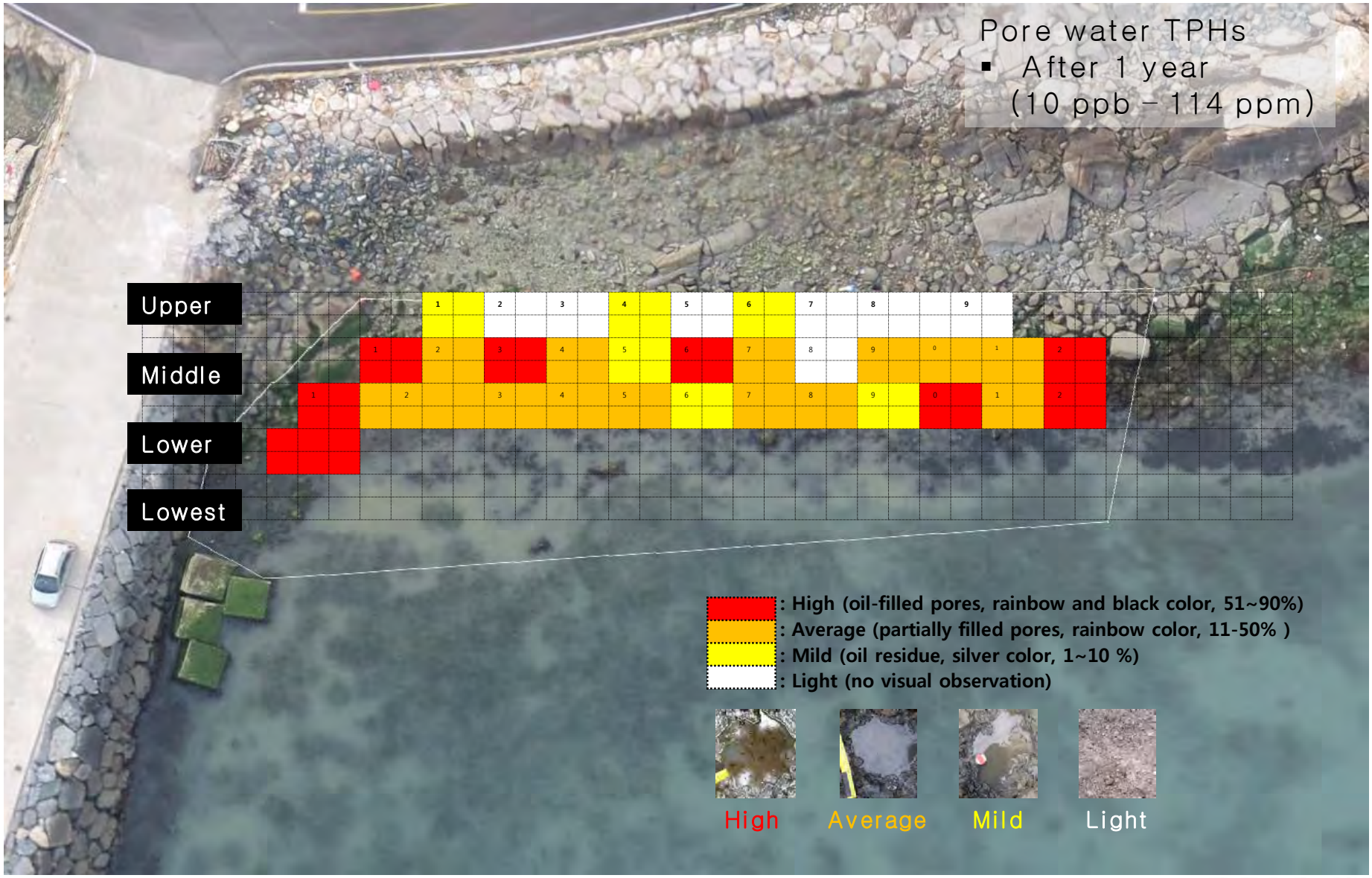
Lower intertidal

Lowest intertidal



Introduction

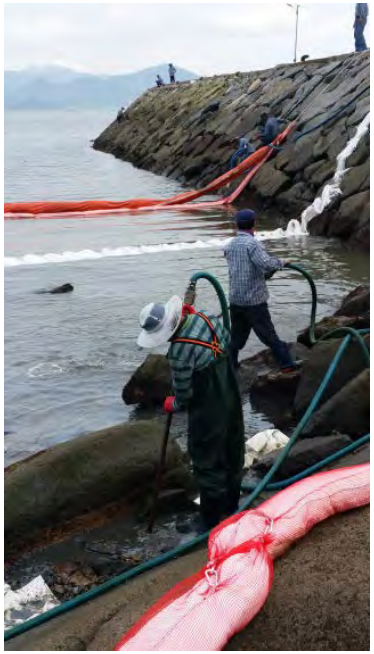
TPH Concentrations in Pore Water



Introduction

Further Remediation Processes

Flushing Process



Re-suspension of Oil

Flushing ➡ **Surface oil removal**

- Relocation of large boulders
- High pressure seawater

- Oil absorption pads
- Snares

Objectives

1. To identify the weathering status of residual oil.
2. To confirm *in situ* formations of OSA during mechanical cleanup processes.
3. To identify degradation enhancement of petroleum hydrocarbons in the form of OSA.
4. To calculate mass balance of OSA and dispersed oil in a lab-scale simulation.

Methods

Part 1

Analysis of Residual Oil	• Screening: SARA content and GC-FID • Detailed analysis: GC-MSD and GC x GC-FID

Part 2

Physical Properties and Counting of Particles	• UV epi-Fluorescence Microscope • ChemFlow Particle Analyze
Chemical Properties and Degradation of Oil in OSA	• Saturate Compounds (GC-FID) • Polycyclic Aromatic Hydrocarbons (GC-MSD)

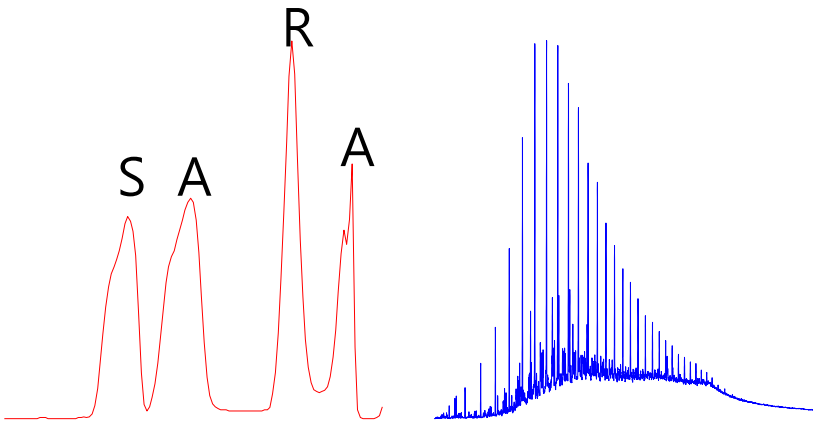
Part 3

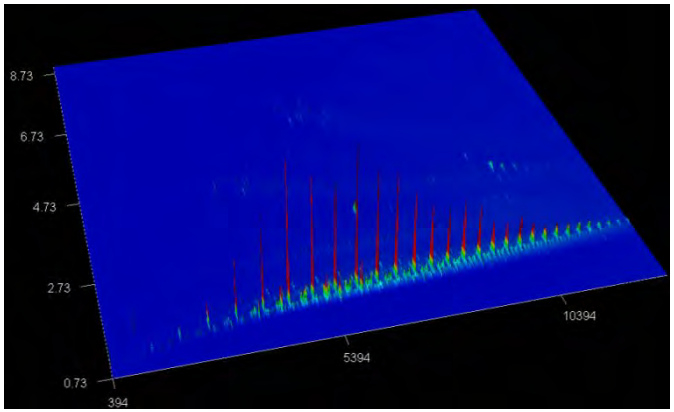
Laboratory Formation of OSA	• Natural Seawater • Artificially weathered oil
Calculation of OSA Mass Balance	• Relative distribution according to buoyancy

Results & Discussion_Weathering Status

2014/02/04
Stranded Oil

Slightly weathered

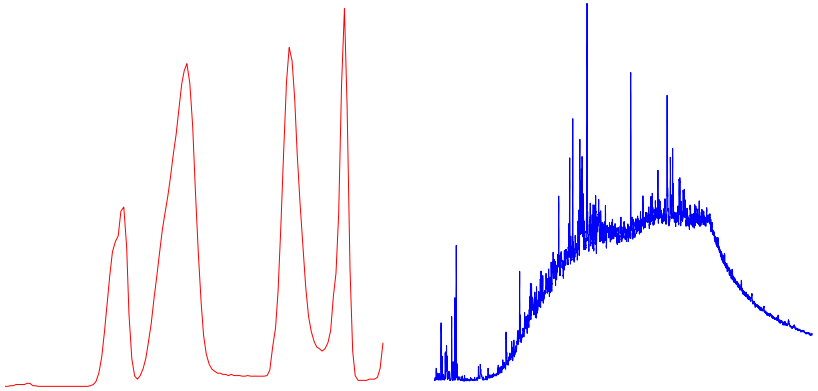


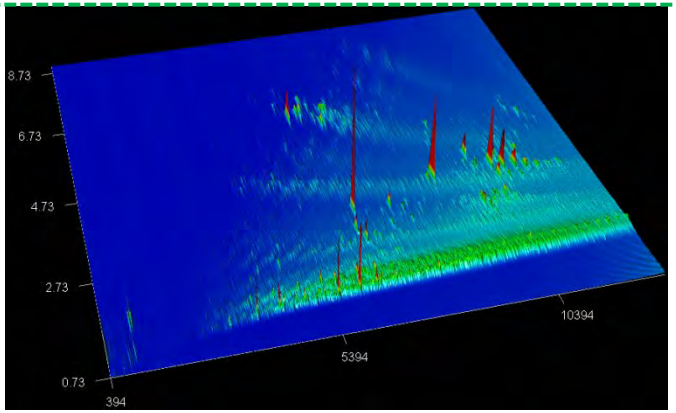


Residual oils

2015/03/05
Lower Intertidal

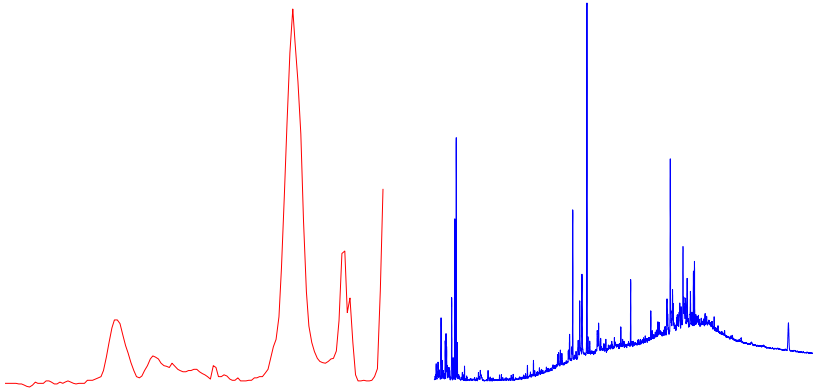
Highly weathered

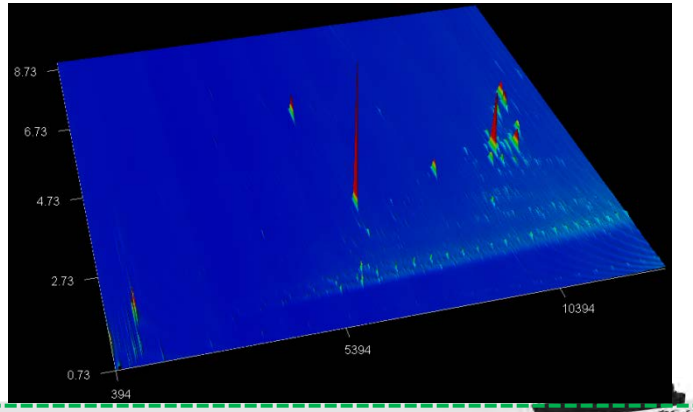




2015/03/05
Upper Intertidal

Extremely weathered





Results & Discussion_After math of Flushing Activity

Environmental Condition

- **Favorable condition for OSA**
  - Re-suspension of large amount of SPM and residual oil.
  - Turbulence energy generated by waves and mechanical movements promoted favorable conditions for OSA formation.

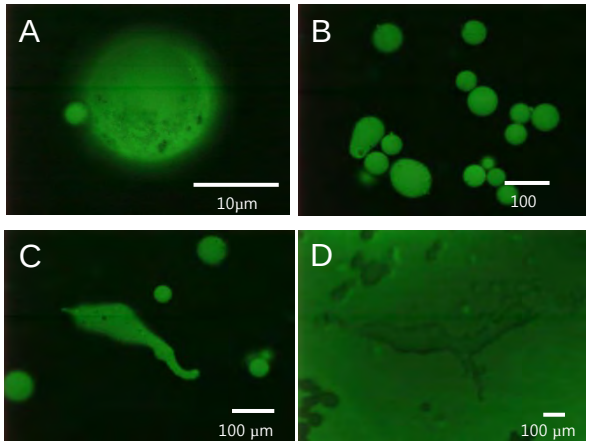
Results & Discussion_Confirmation of OSA formations

Formation Mechanism of Oil-SPM Aggregates (OSA)

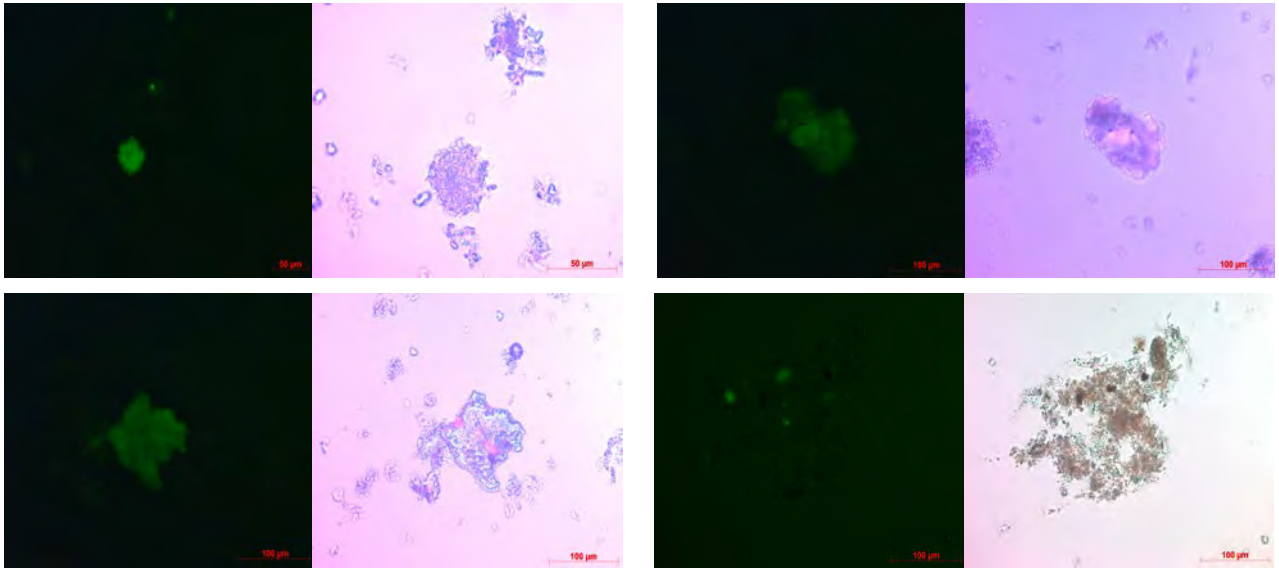
- When oil and suspended particles interact, OSA is formed.
- OSA formation in several large spills; Exxon Valdez (1989), Sea Empress (1996) and Deep Water Horizon (2010).
- Formed as 3 types; (i) Droplet, (ii) Solid, (iii) Flake
- OSA is formed in 2 main steps;

  (1) Breaking of surface oil by turbulence

  (2) Interaction of oil and particles



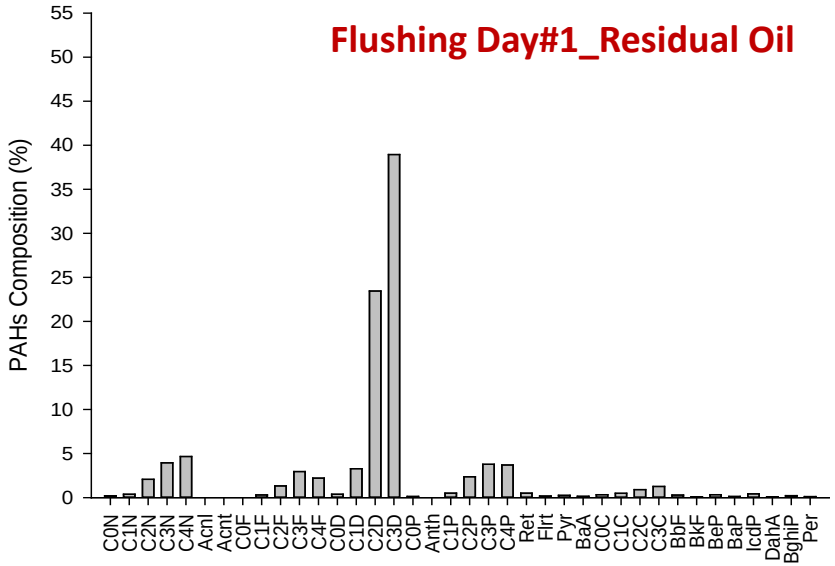
Microscopic observation of OSA

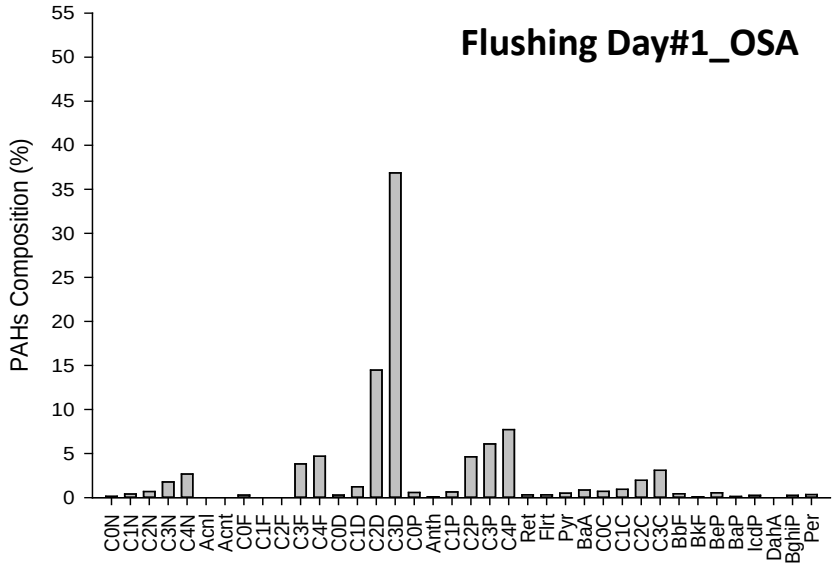


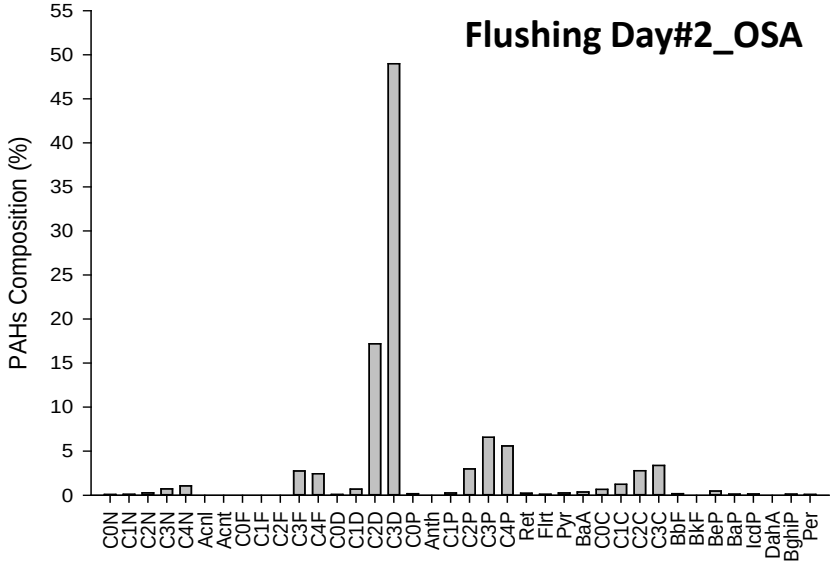
- Seawater samples collected after mechanical cleanup.
- OSA samples observed through visible and ultraviolet light microscope.
- Flake type OSA were mainly observed.

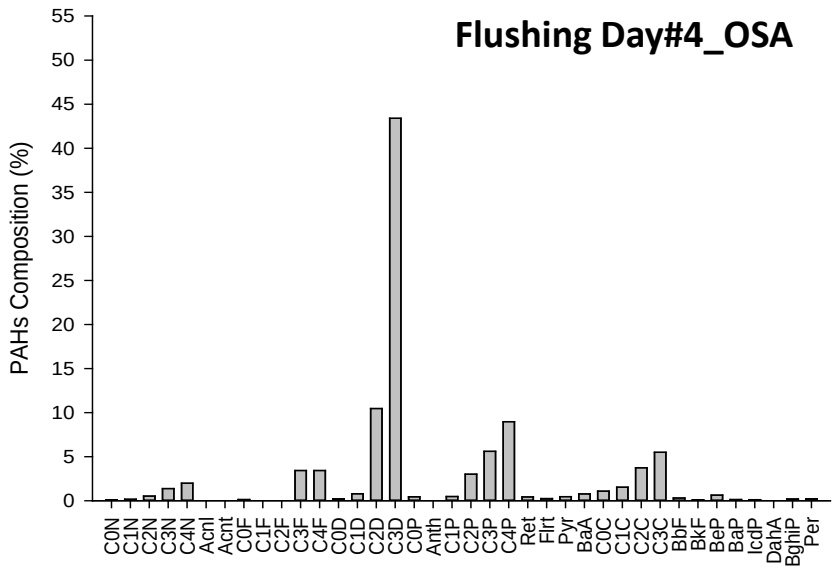
Results & Discussion_Degradation of oil in OSA

PAHs Composition Profiles of OSA

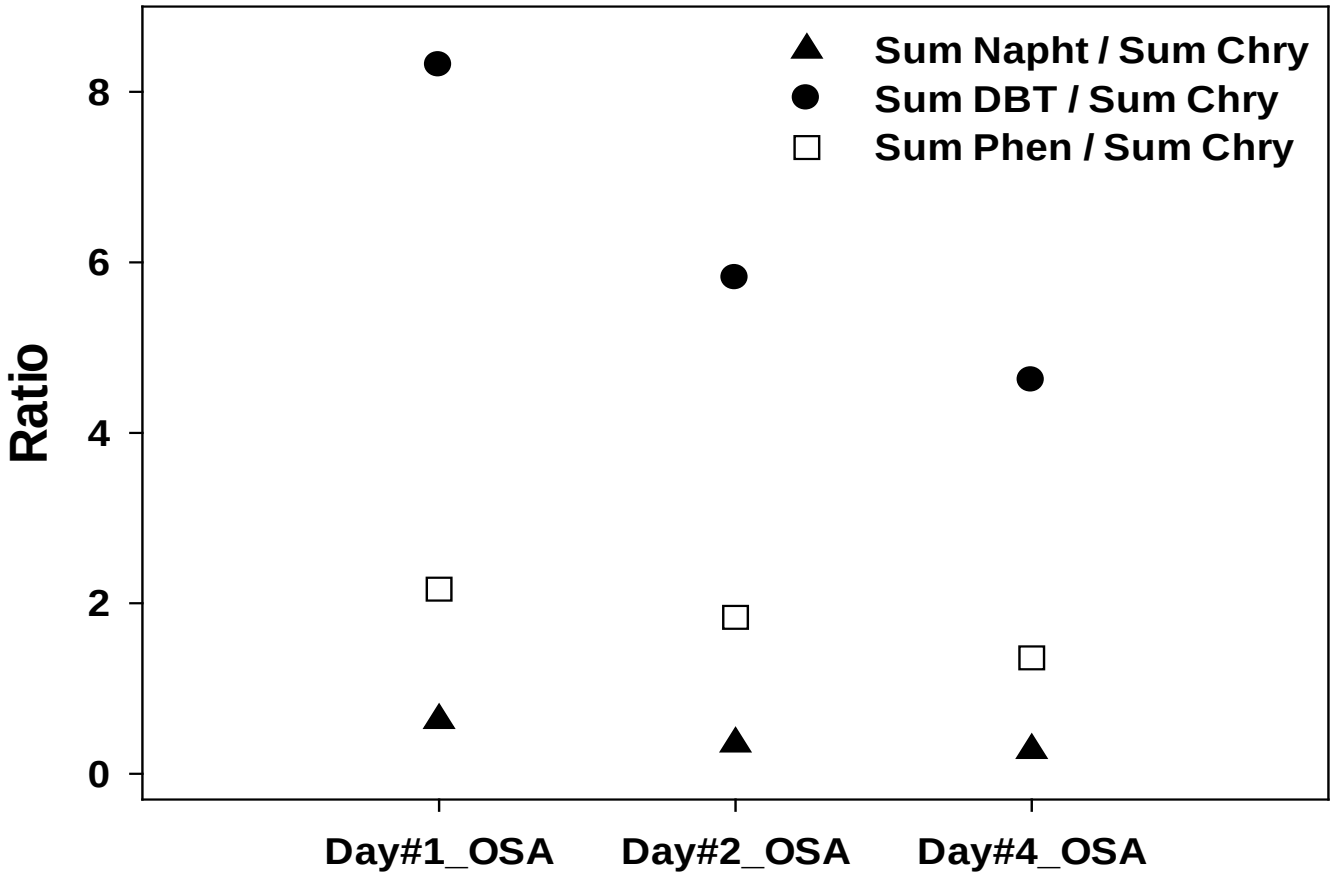








Results & Discussion_Degradation of oil in OSA



- **Degradation enhanced by OSA formation**
  - PAHs degrade at different rates based on molecular weight, ratios of PAHs can be used to identify levels of degradation.
  - These ratios showed degradation of PAHs through 1, 2, and 4 days.
  - Suggests enhancement of oil degradation in the form of OSA.

Results & Discussion_Physical Properties of Marine Particles

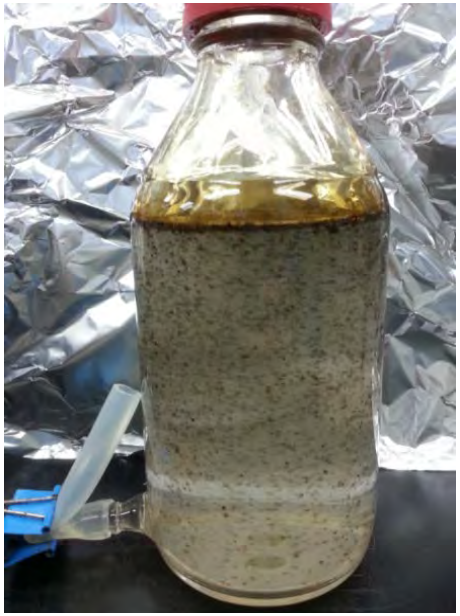
Environmental Parameters

Parameters	Salinity (PSU)	Temperature (°C)	Turbulence	Oil Type	Particle Type	Particle size (μm)	Total SPM (mg/ml)	Particle Count (counts/ml)	Mean Size (μm)	Min size (μm)	Max size (μm)
	24	25	Low	Basrah light + Naphta	Natural	16.8	1.98	60,096 ± 925	16.8 ± 0.09	<2	85.8 ± 1.10

Buoyancy Fraction of Natural OSA

Buoyancy	Positive	Neutral	Negative
Sample Fraction	Top 10%	Middle 80%	Bottom 10%
Estimated OSA %	<1%	~5%	>95%
OSA type	Inconsistent, particle coated and particle penetrated oil droplets with some fine water droplets entrapped in the large aggregate		
OSA size (Microscope)	100 ~ 300 um	100 ~ 300 um	100 ~ 300 um

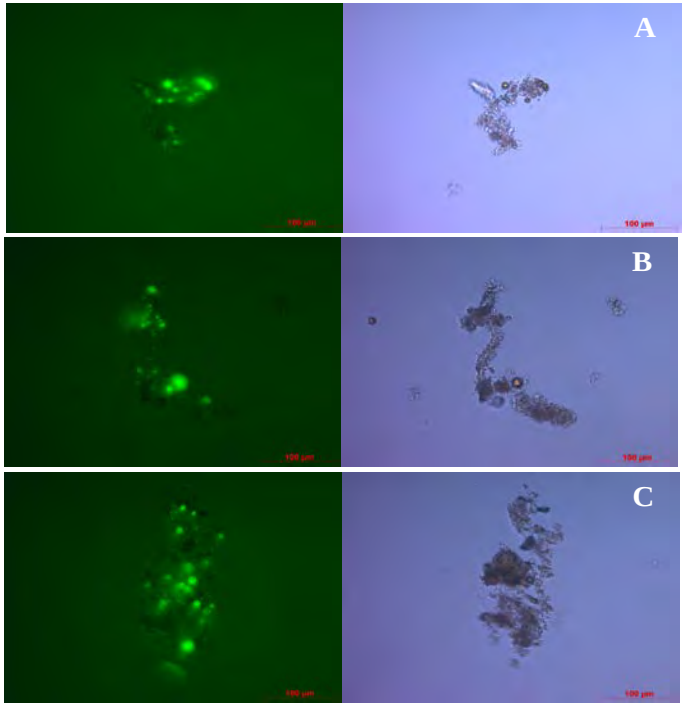
Results & Discussion_Laboratory Verification of OSA Formation

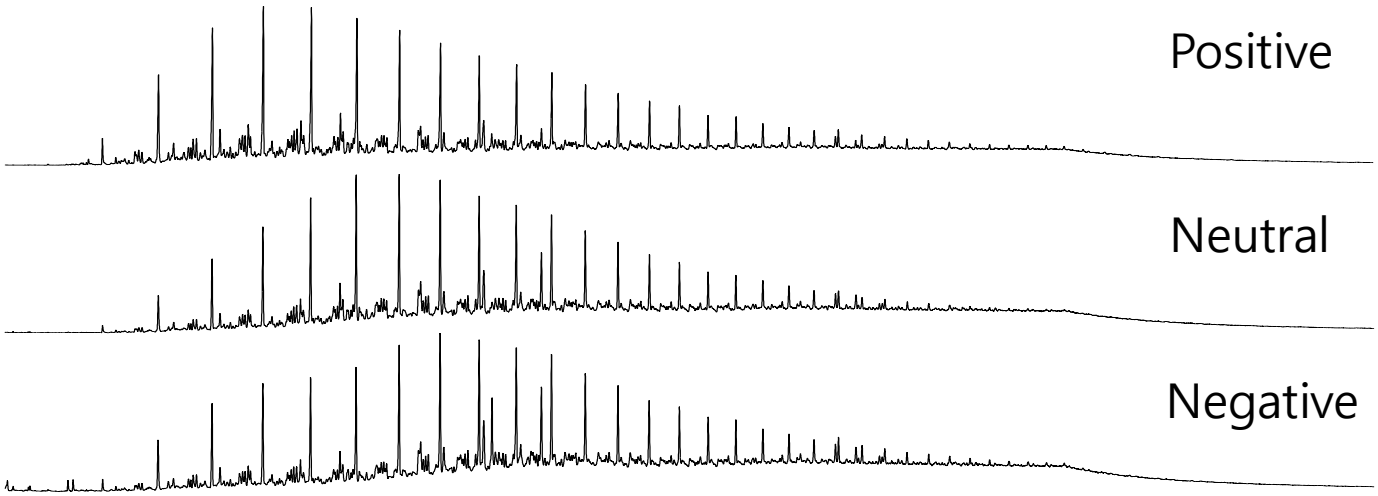


5% (Positive)

90% (Neutral)

5% (Negative)





Results & Discussion_Laboratory Verification of OSA Formation

Buoyancy Fraction	TPH by Fractions (%)	Form of Oil
Positive (Top 5%)	52.2 ± 10.7	Oil slick
Neutral (Middle 90%)	32.2 ± 9.8	Dissolved and OSA
Negative (Bottom 5%)	15.6 ± 3.5	OSA

- **Significance of OSA formation**

➢ Fraction is highest from Positive>Neutral>Negative buoyancy.

➢ Relatively represented as oil slick, dissolved and OSA, and OSA, respectively.

➢ Positive fraction; 52% is mostly removed by snares and absorption pads.

➢ Neutral fraction; 32% may degrade naturally.

➢ Negative fraction; 16% may settle down on the seafloor and persist for a longer period of time.

Conclusion

1. Formation of OSA was enhanced during mechanical cleanup.
2. OSA could form in the field even with highly weathered oil.
3. Formation of OSA enhanced degradation of petroleum hydrocarbons.
4. Fate of oil during cleanup process was demonstrated with mass balance calculation.


~Thank You~