OSA as an unknown route of exposure to filter feeding bivalve in the turbid environment

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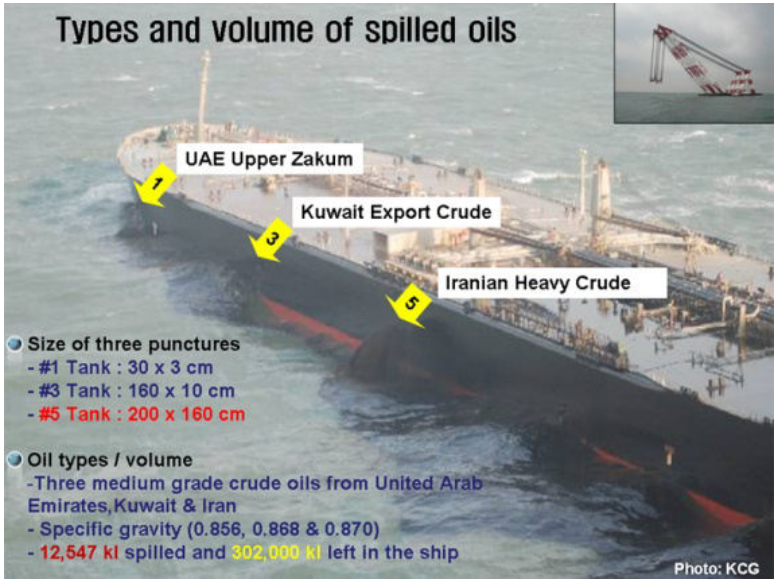
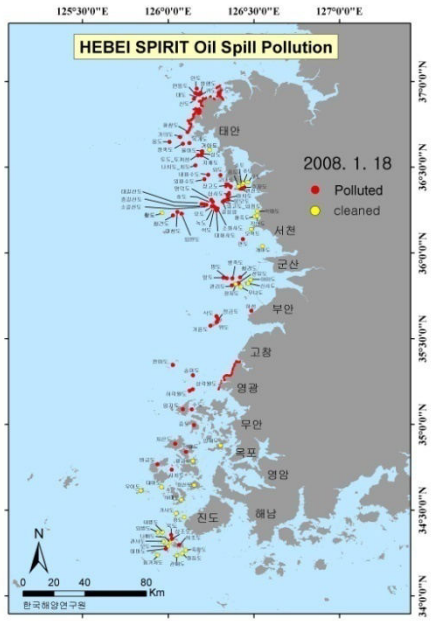
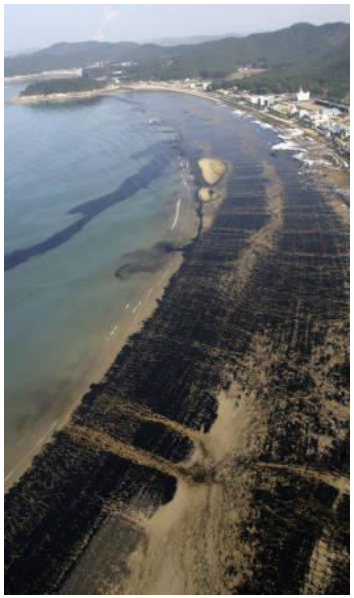
Introduction



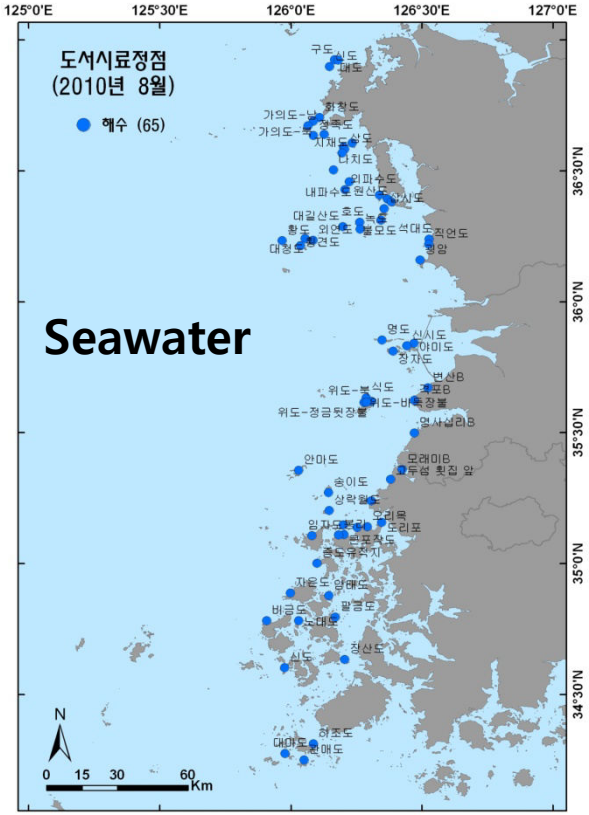


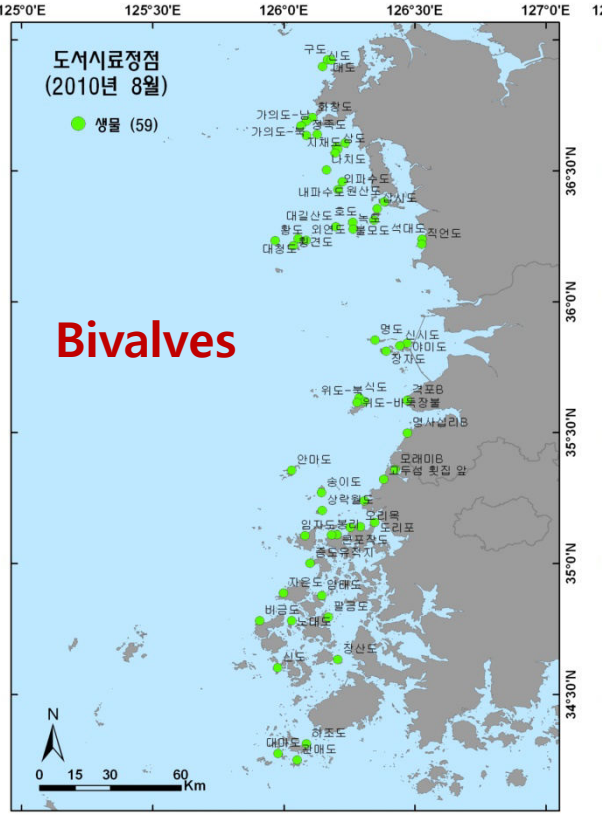


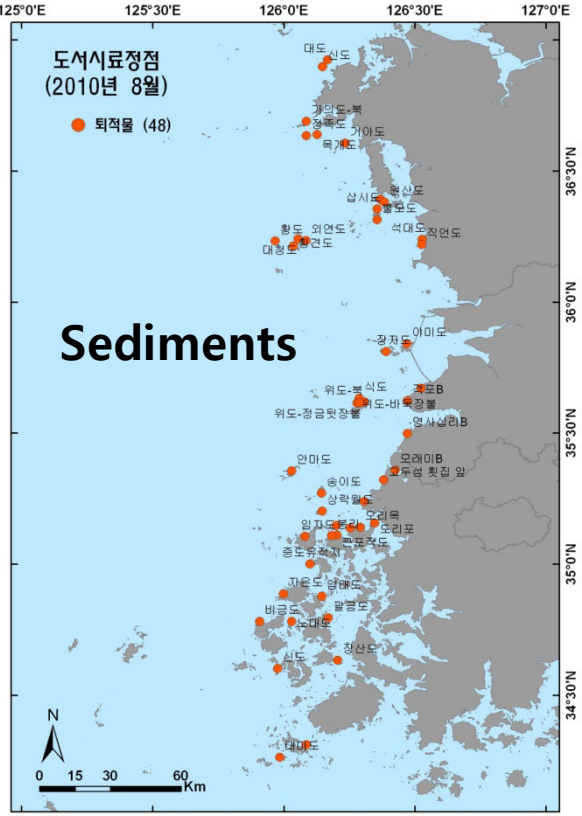
- **The Hebei Spirit Oil Spill: The Largest Oil Spill in Korea**

- Collision of MV Hebei Spirit with a barge on 7th December 2007 released approximately 12,547 kL (10,900 M/T) of crude oil.
- The MV Hebei Spirit was carrying three kinds of crude oil, namely UAE Upper Zakum (UZC), Kuwait export crude (KEC) and Iranian heavy crude (IHC).
- Due to the strong westerly wind, spilled oil polluted most of west coast of Korea, 375 km coastlines.
- More than one million of volunteers joined for initial oil cleanup.
- Oil spill compensation process is still under way.

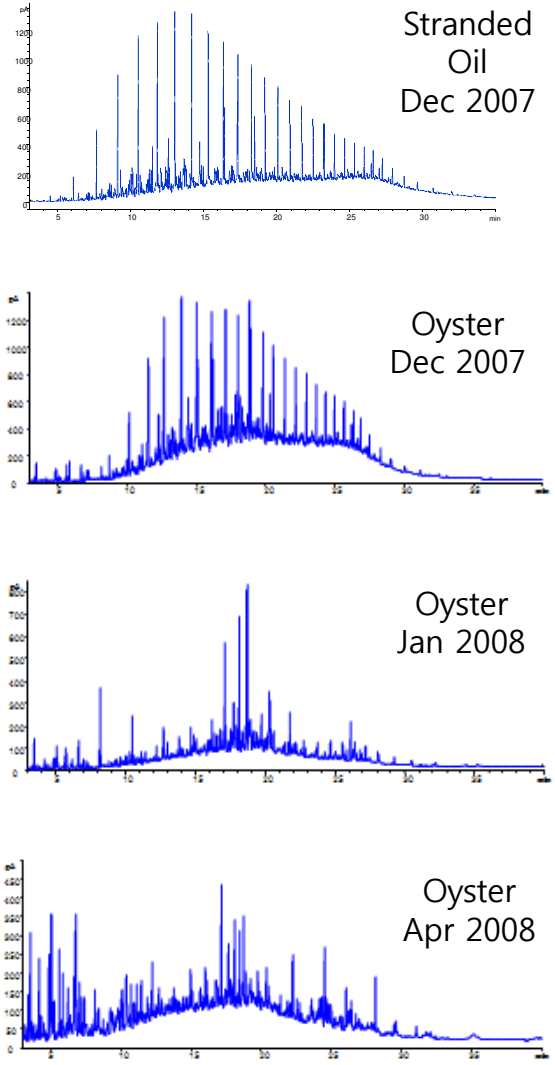
Multi-media monitoring for oil contamination





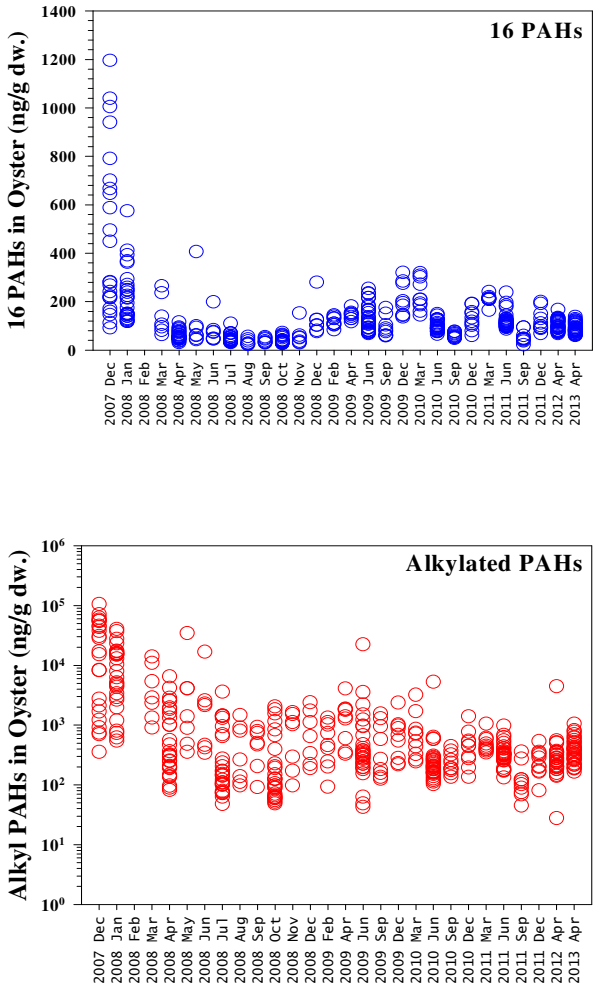


GC/FID Chromatogram



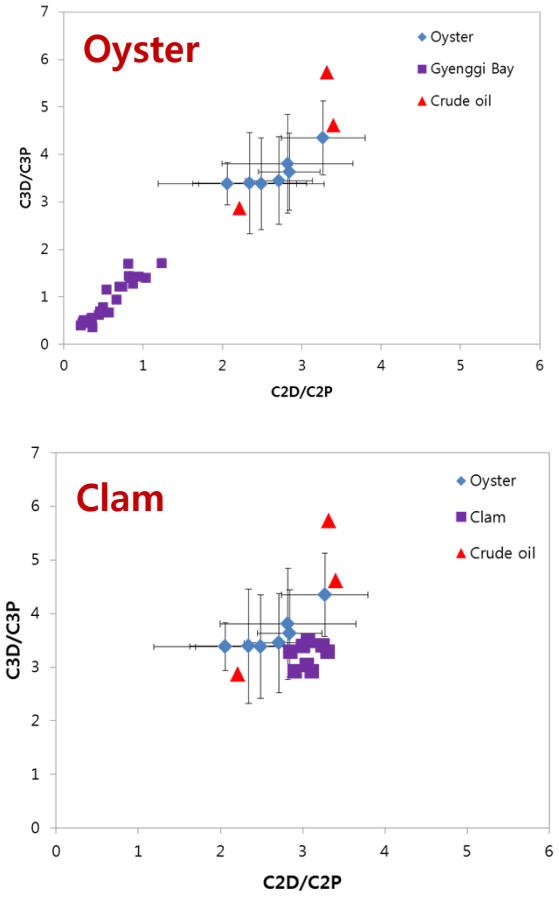
- Initial: oil droplet
- Persistent source

Long-Term Monitoring



- 16 PAHs decreased rapidly
- Alkyl PAHs persisted

Oil Fingerprinting



- PAH double ratio
- Manila clam: same with oyster

Route of exposure using exposure media

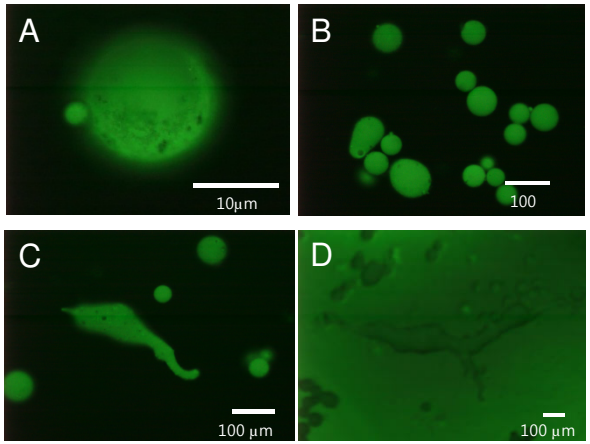
- Traditional route of exposures; Water Accommodated Fractions (WAF) and Mechanically Dissolved Oil (MDO).
- Traditional methods could not match the Petroleum Derived Hydrocarbon distributions in oysters from spill site.
- Tests of unknown mode of exposure; Oil SPM Aggregates (OSA)

OSA formation as the output of oil and particle interactions

- When oil and suspended particles interact, OSA is formed.
- OSA formation has been observed in several large spills; Exxon Valdez (1989), Sea Empress (1996) and Deep Water Horizon (2010).
- OSA is formed in 2 main steps;

  (1) Breaking of surface oil by wave actions

  (2) Interaction of oil and particles



Research objectives

- To compare the fate of oil in the traditionally used exposure methods.
- To identify the continuous source of oil contamination to bivalves in the HSOS.
- To identify the fate of spilled oil in high turbidity environments such as intertidal areas.

Materials and Method

- Formation of **WAF**

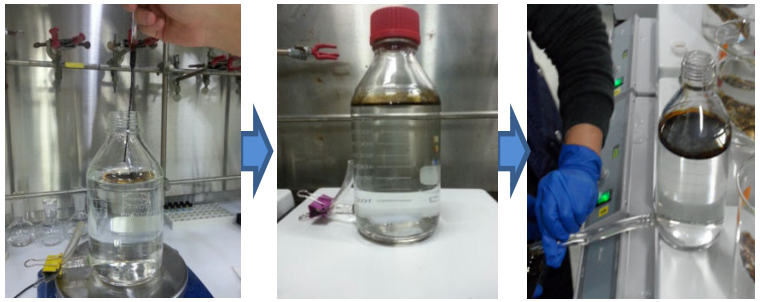
➢ Method following CROSERF with slight modification

(1) 1 L filtered seawater + magnetic stirrer

(2) Addition of **25 g** of Iranian Heavy Crude Oil

(3) Magnetic stirred at 120 rpm for 24 hours

(4) 900 ml of solution excluding surface oil was collected



- Formation of **MDO**

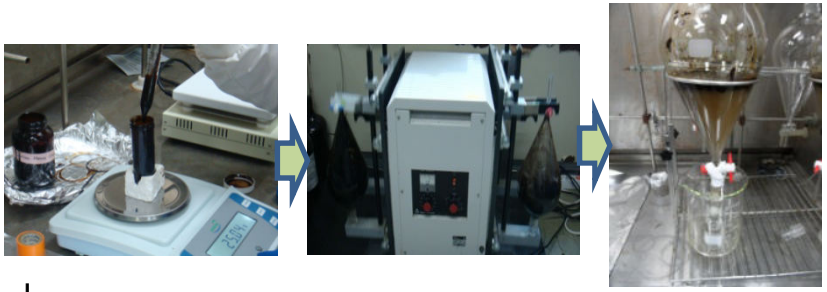
(1) 1 L filtered seawater placed in separatory funnel

(2) Addition of **25 g** of Iranian Heavy Crude Oil

(3) Vertical shaking at 50 rpm for 15 minutes

(4) Settled for 1 hour

(5) 900 ml of solution excluding surface oil was collected



- Formation of **OSA**

➢ Method following Khelifa et a., 2002 with slight modification.

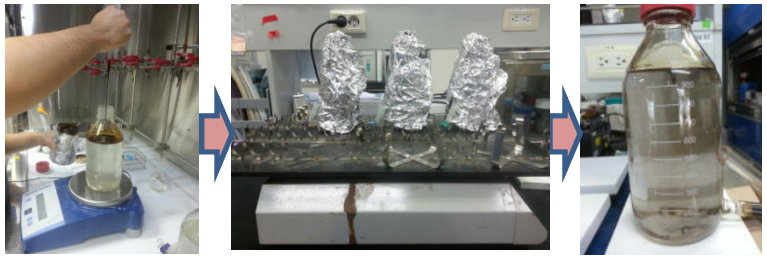
(1) 1 L filtered seawater + 200 mg of particle

(2) Solution + **600 mg** of Iranian Heavy Crude oil
(Approxi. 1/40 of MDO and WAF)

(3) Reciprocal shaking for 24 hours

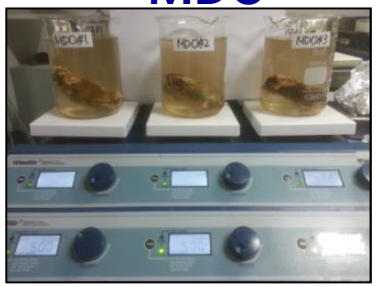
(4) Solution settled for 24 hours

(5) 900 ml of solution excluding surface oil was collected



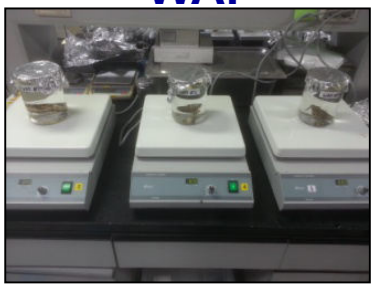
Acclimation

MDO



OSA

WAF



● Exposure of media to oysters

- Prior to exposure, oysters were acclimated in filtered seawater for 3 days.
- Oysters are placed into the beaker filled with 700 ml of exposure media and a small magnetic stirrer.
- 10-AU fluorometer equipped with oil kit was used to quantify total petroleum hydrocarbons before and after exposure.
- After 24 hours of exposure, exposure media was replaced with newly prepared exposure media.
- After 48 hours of exposure, oysters were collected and prepared for chemical analysis using GC/FID and GC/MS.

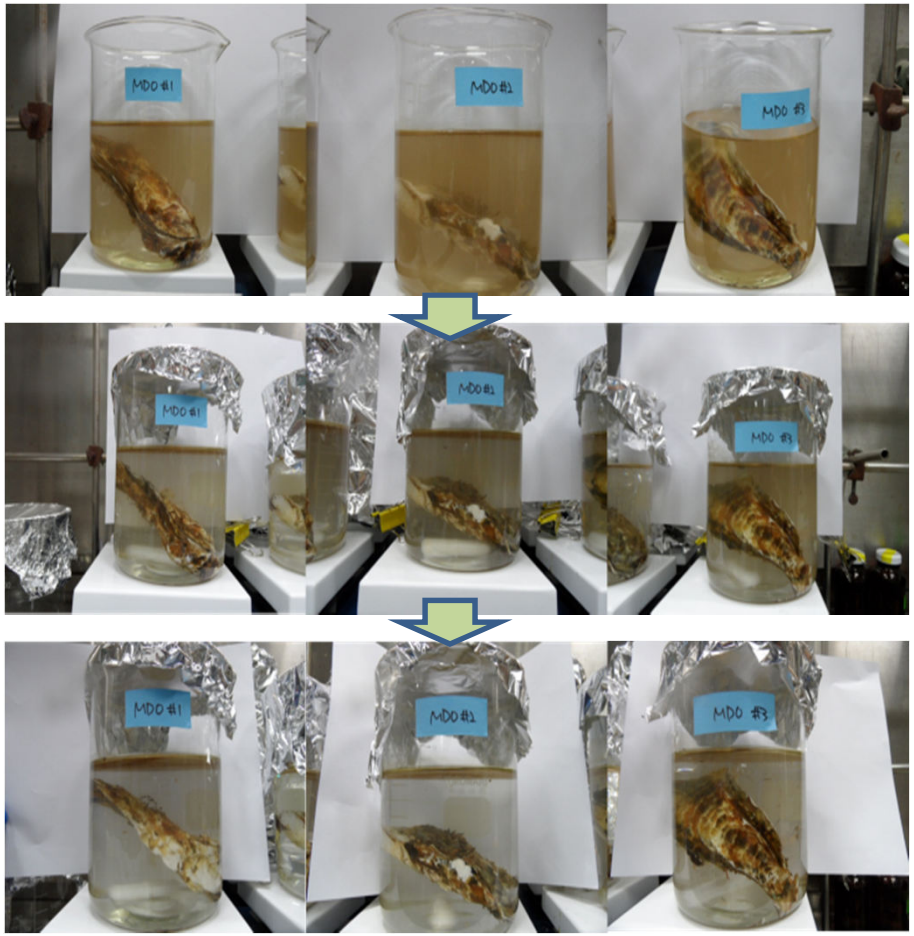
10-AU Fluorometer

GC-MS

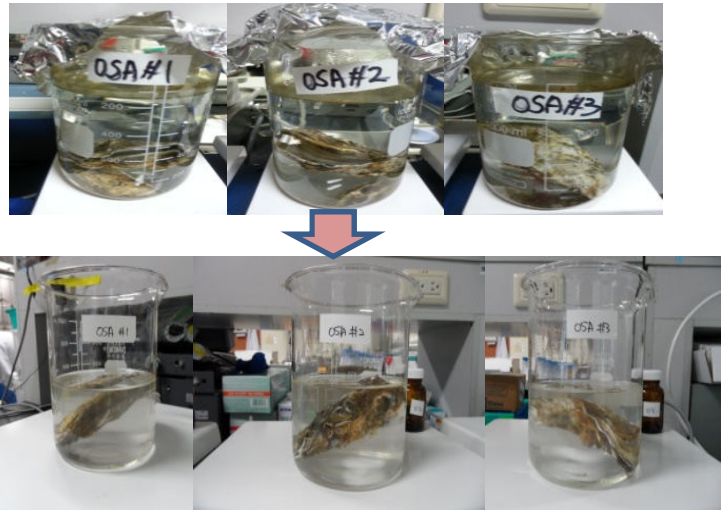
GC-FID

Visual observation of oyster uptake

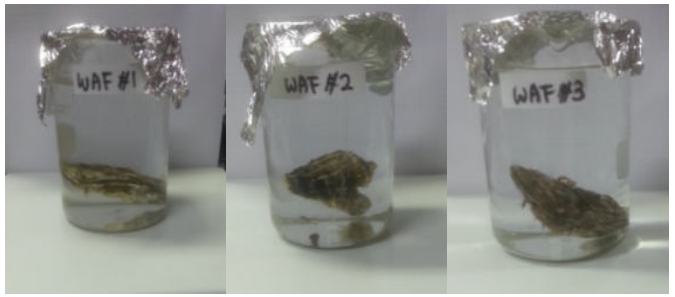
MDO



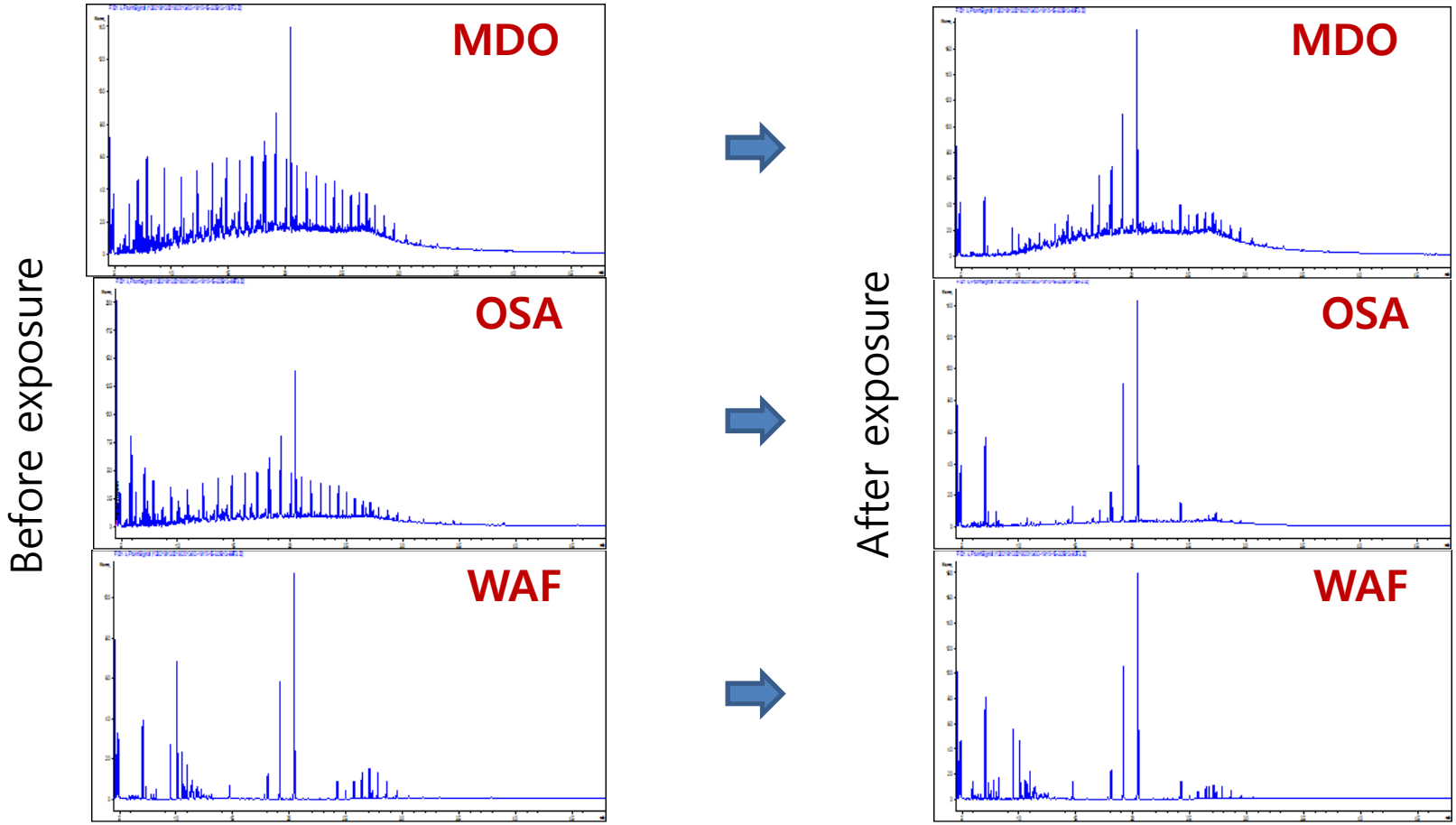
OSA



WAF

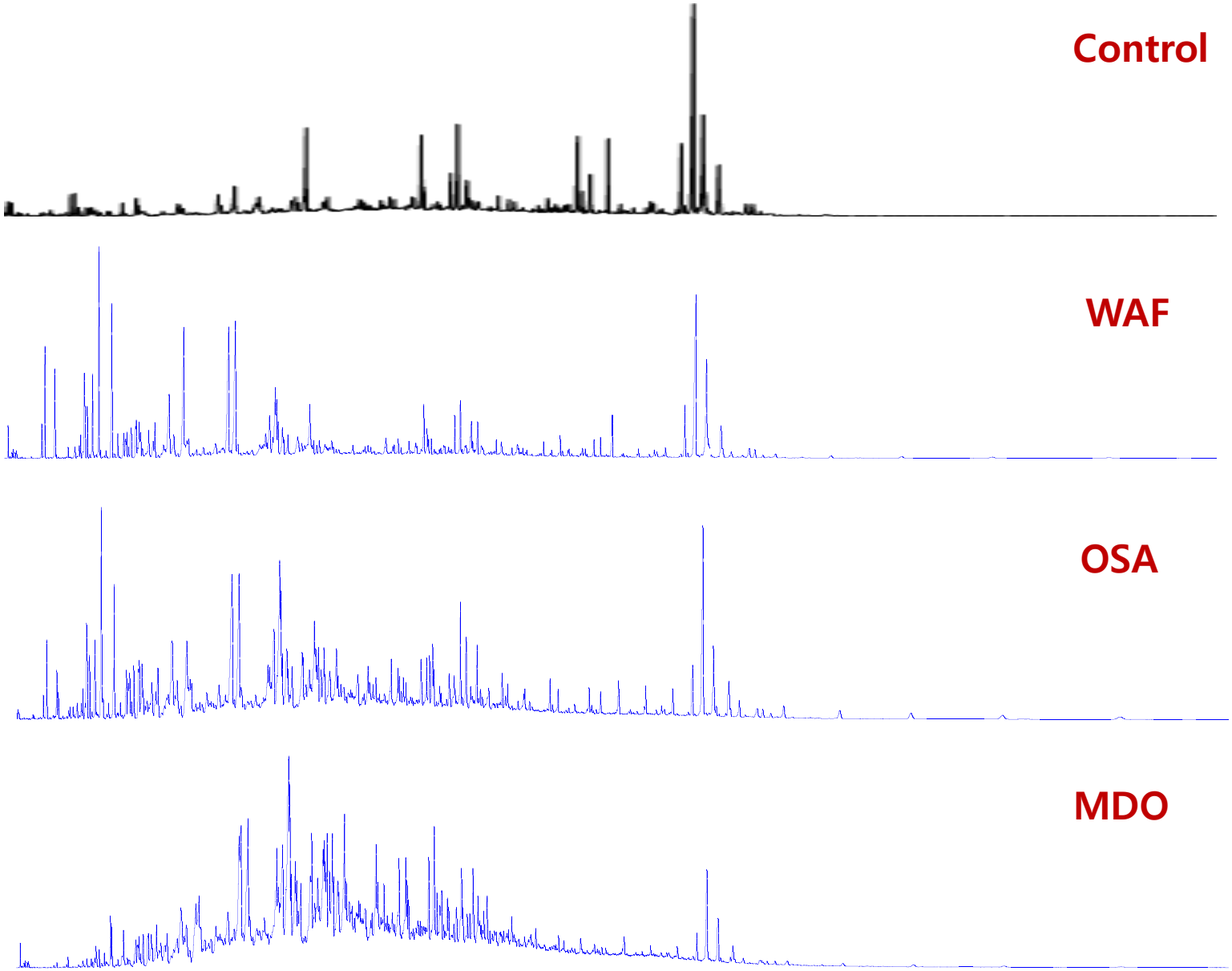


TPH Changes of Exposure Media



Exposure media	Before exposure (ppm)	After 24 hrs exposure (ppm)	Total loss (ppm)
MDO	**238.0**	**109.0**	**129.0 (highest)**
OSA	**48.0**	**44.4**	**4.4 (middle)**
WAF	**0.92**	**0.67**	**0.25 (lowest)**

GC/FID chromatograms of petroleum hydrocarbons in oysters



Accumulation of Petroleum Derived Hydrocarbons in oysters

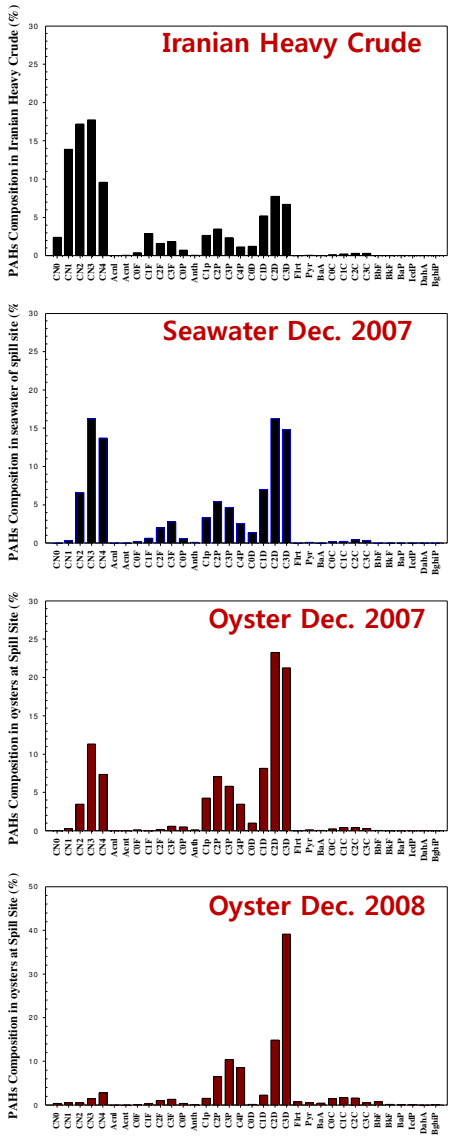
	Control	MDO (highest)	OSA (middle)	WAF (lowest)
TPH	18.5	113.0 ± 52.0	66.2 ± 15.9	35.8 ± 6.9
UCM	8.7	66.9 ± 39.9	28.1 ± 10.6	12.7 ± 0.6
n-Alkane	0.5	7.1 ± 6.3	1.1 ± 0.6	0.3 ± 0.0
16 PAHs	0.1	3.0 ± 0.5	2.8 ± 0.6	2.4 ± 0.9
Alkyl PAHs	0.3	60.2 ± 19.9	35.2 ± 6.1	13.8 ± 1.8

MDO>OSA>WAF.

- But n-alkane for WAF exposed oyster was similar with control oyster.
- 16 PAHs have similar concentrations for all oysters, however, the concentration of Alkylated PAHs was highest from MDO>OSA>WAF.
- This shows that, monitoring 16 PAHs alone is not suitable.
- Monitoring Alkylated PAHs could provide more accurate evaluation.

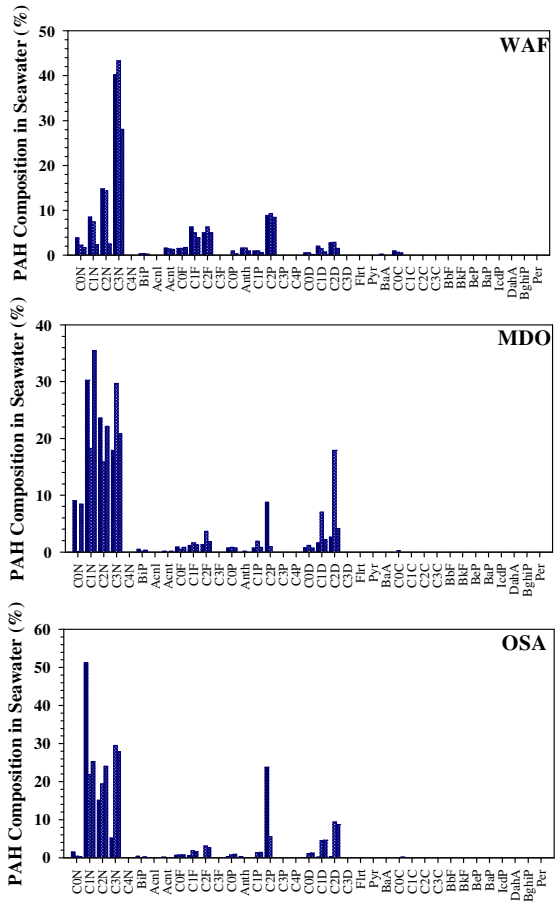
Comparison of PAH profiles

Field Samples

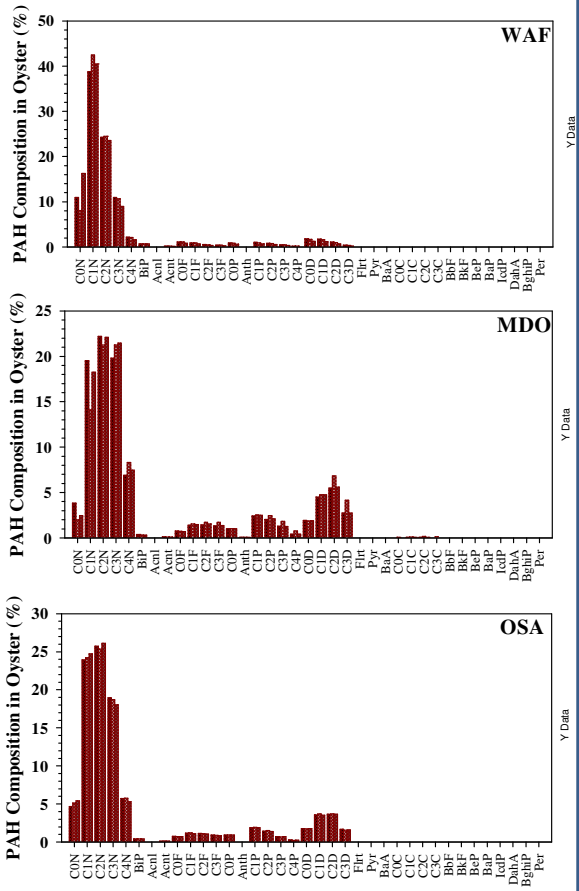


Route of Exposure Tests

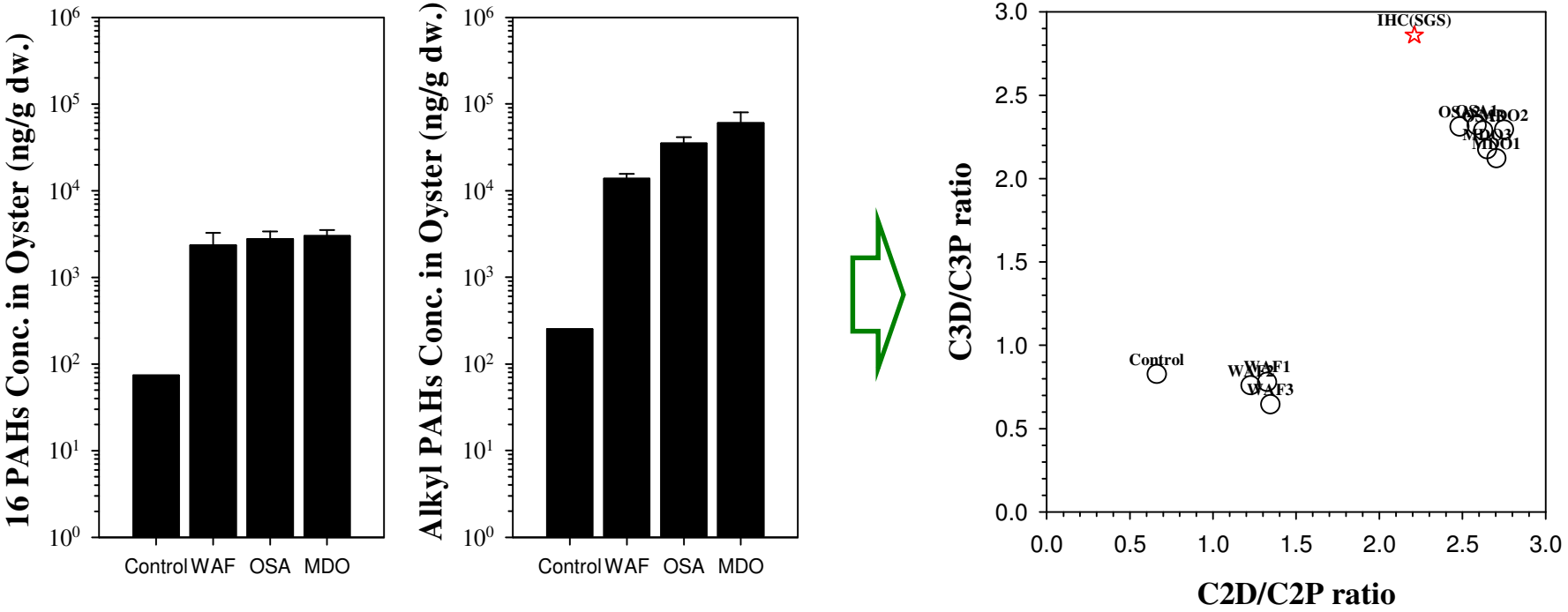
Exposure Media



Oysters

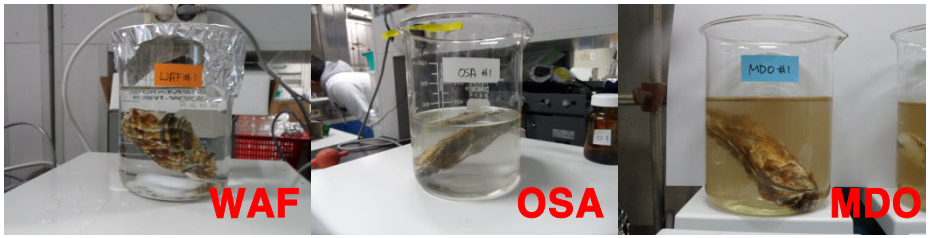


PAH double ratio plots



- 16 PAHs concentrations could not distinguish their route of exposure but alkyl PAHs could.
- Alkyl PAHs could be used in double ratio plots to identify their relativity with source oil.
- Double ratios using alkylated Phenanthrene and alkylated Dibenzothiophene has been widely used for oil fingerprinting.
- Double ratios of MDO and OSA matched more with the source oil but WAF did not match.
- Double ratio plots are very useful fingerprinting tool.

Conclusion



- To explain persistency of PAHs in oysters after the Hebei Spirit oil spill, available exposure method including WAF, MDO, and OSA were tested.
- Among three exposure media, OSA showed higher accumulation efficiency than others.
- Alkylated PAHs in oyster well exhibited accumulation of petroleum derived hydrocarbons.
- PAHs double ratio in oyster was proved to be useful for oil fingerprinting.
- OSA could be used as a new route of exposure to study the bioaccumulation of oil.

End of Presentation