

# PICES 2015

## Distinguishing Crude Oils from Heavy Fuel Oils by Polycyclic Aromatic Hydrocarbon (PAHs) Fingerprints

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# Oil spills

To date, oil spills in the marine environments has become a global problem.

To characterize, identify, categorize, and quantify their sources and types is very important for environmental damage assessment.



# Spilled oil identification

## Spilled oil identification

attempts to answer the questions of:

### *Where, When, What, and Who (the 4 W's)?*

- **Where** and **when** did the oil spill occur?
- **What** was the spilled oil?
  - Contaminant identification and extent of impact?
  - What happens after the spill – sometime decades after?
  - Impact on sediments, soil, water and organisms?
  - Weathering degree and age-constraints on release of contaminants?
- **Who** is responsible for the spill?

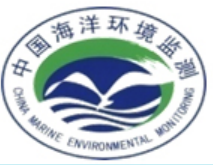
# Major Source-specific Target Analytes in oil



- ▶ oil is a complex mixture
- ▶ **Hydrocarbon groups**: TSEM, TPH, UCM, total saturates, total aromatics
- ▶ **n-Alkanes**: C8-C40 plus pristane and phytane
- ▶ **Polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs**
- ▶ **Biomarker terpanes and steranes**
- ▶ **Stable carbon isotopes**
- ▶ Other **heterocyclic hydrocarbons, heavy metals** and their chelates

# Diagnostic Ratios of Source-Specific PAHs

- ▶ • A number of diagnostic ratios of PAHs have been successfully used for source identification and differentiation:
- ▶ • *Double ratio plots:  $C2D/C2P : C2D/C2P$  and  $C3D/C3P : C3D/C3C$ ;*
- ▶ • *Ratios of 3 m-DBT isomers and ratios of 2 pairs of m-phenanthrenes;*
- ▶ •  *$\Sigma naphs / \Sigma \text{ total PAHs}$ ,  $\Sigma naphs / \Sigma chrys$ ,  $\Sigma phens / \Sigma chrys$ , and  $\Sigma dibens / \Sigma chrys$ ;*
- ▶ •  *$C0C : C1C : C2C : C3C$  and relative distribution of target PAHs in each homologous family;*
- ▶ • *Pyrogenic Index.*



# Differentiate the crude and heavy fuel oil

——In most case, the most spilled oil in marine are crude oil and refined oil products.

——It is important to differentiate the crude oil and refined oil products, especially for heavy fuel oil.

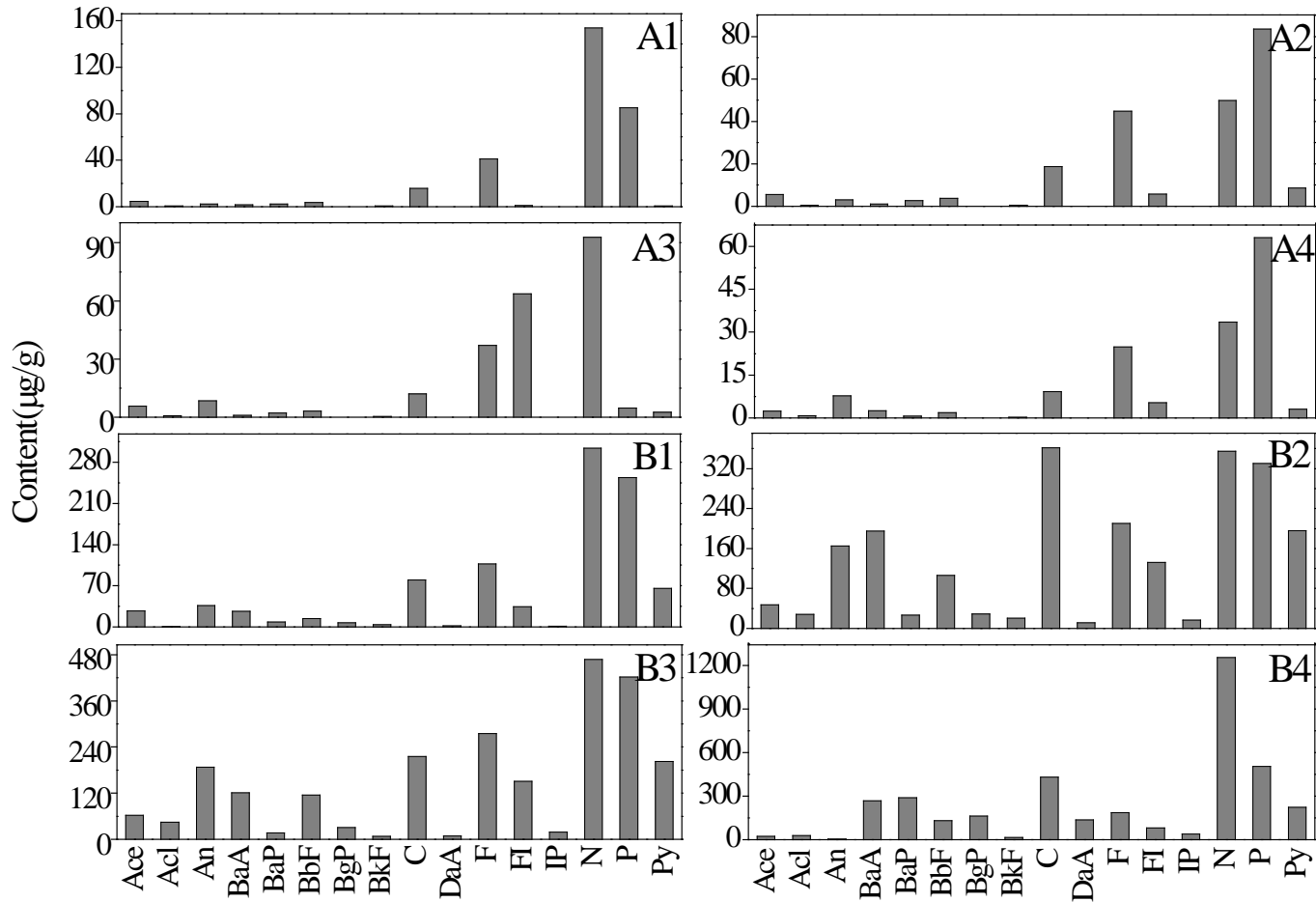
——The purpose of the study is to find a useful indicator to differentiate the crude oil and heavy fuel oil.



# Information of the eight oils

Number	Place	Type
A1	Russia	Crude oil
A2	Iran	Crude oil
A3	Saudi Arabia	Crude oil
A4	India	Crude oil
B1	Korea	Heavy fuel oil
B2	Korea	Heavy fuel oil
B3	Korea	Heavy fuel oil
B4	China	Heavy fuel oil

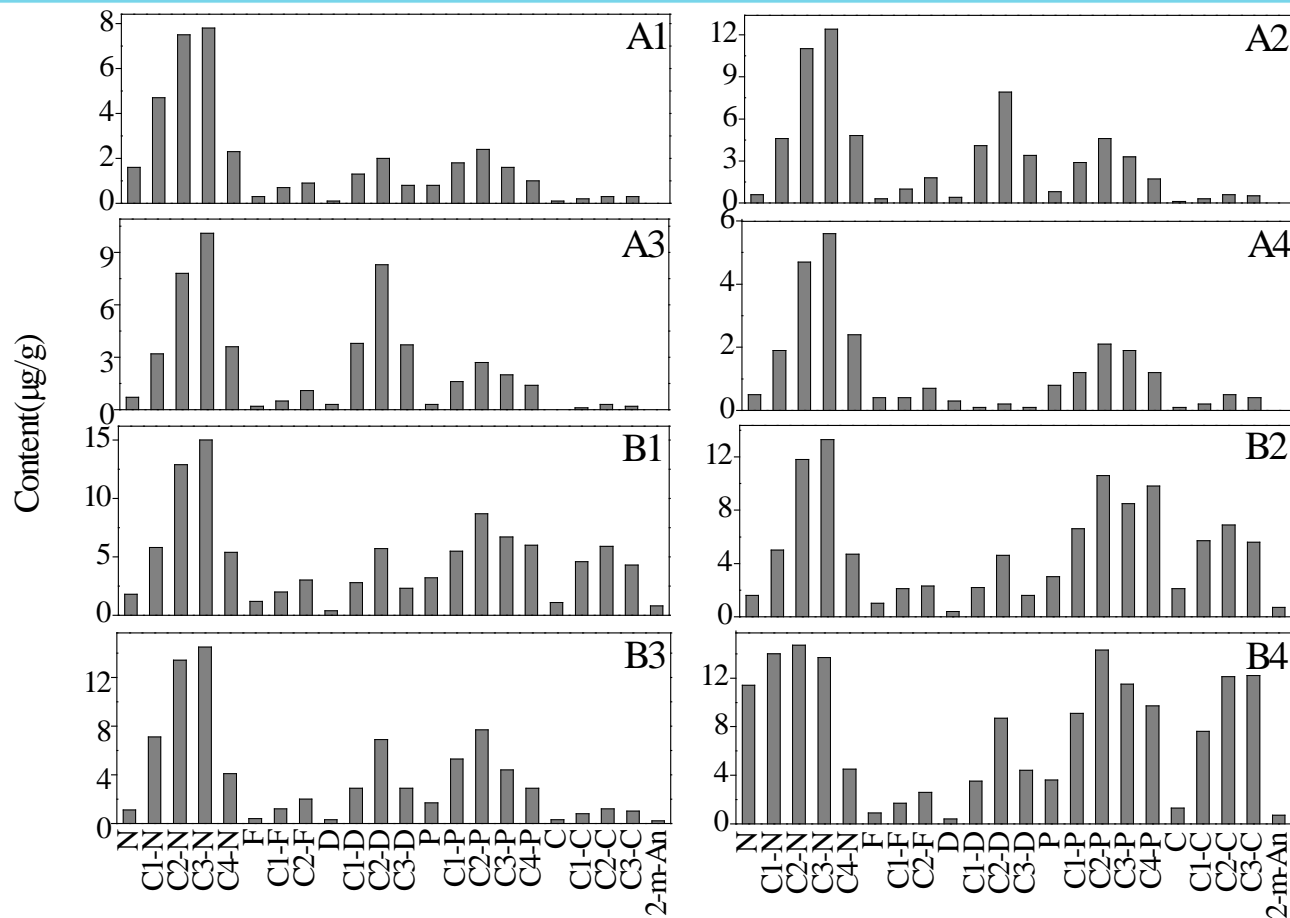
# Distributions of PAHs



Distributions of PAHs of EPA priority in the eight oils



# Alkylated PAHs homologues



Distributions of alkylated PAHs homologues in the eight oils

# Diagnostic ratios

Diagnostic ratio	Definition
$\Sigma N/\Sigma C$	(Naphthalene+C1-Naphthalenes+C2-Naphthalenes+C3-Naphthalenes+C4-Naphthales)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma P/\Sigma C$	(Phenanthrene+C1-Phenanthrene+C2-Phenanthrene+C3-Phenanthrene+C4-Phenanthrene)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma D/\Sigma C$	(Dibenzothiophenes+C1-Dibenzothiophenes+C2-Dibenzothiophenes+C3-Dibenzothiophenes+C4-Dibenzothiophenes)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma F/\Sigma C$	(Fluorene+C1-Fluorene+C2-Fluorene+C3-Fluorene+C4-Fluorene)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
An/P	Anthracene/Phenanthrene
BaA/C	Benzo[a]anthracene/Chrysene
2-m-An/total of MP	2-methylantracene/C1-Phenanthrenes
Fl/Py	Fluoranthene/Pyrene
PI	$\Sigma(\text{other 3-6-ring PAHs})/\Sigma(\text{5-alkylated PAHs})$
BeP/BaP	Benzo[e]pyrene/Benzo[a]pyrene



# Diagnostic ratios

## Different diagnostic ratios of PAHs of eight oils

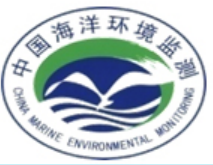
Diagnostic ratio	A1	A2	A3	A4	B1	B2	B3	B4
(C2-D/C2-P):(C3-D/C3-P)	1.667	1.667	1.662	1.810	1.909	2.305	1.360	1.590
(C3-D/C3-P):(C3-D/C3-C)	0.188	0.152	0.100	0.211	0.642	0.659	0.227	1.061
C2-D/C2-P	0.833	1.717	3.074	0.095	0.655	0.434	0.896	0.608
C3-D/C3-P	0.500	1.030	1.850	0.053	0.343	0.188	0.659	0.383
$\Sigma P/\Sigma D$	1.810	0.842	0.497	10.286	2.688	4.375	1.692	2.835
$\Sigma N/\Sigma C$	26.556	22.267	42.333	12.583	2.572	1.793	12.182	1.756
$\Sigma P/\Sigma C$	8.444	8.867	13.333	6.000	1.893	1.897	6.667	1.452
$\Sigma D/\Sigma C$	4.667	10.533	26.833	0.583	0.704	0.433	3.939	0.512
4-MD/1-MD	2.065	2.055	1.856	4.648	3.341	3.143	2.756	1.748
2-MN/1-MN	1.723	1.505	1.472	1.324	1.811	1.806	1.906	1.619
2-MP/1-MP	1.059	1.152	0.805	0.828	2.040	1.928	2.032	1.413
An/P	0.026	0.036	1.787	0.124	0.144	0.499	0.444	0.008
BaA/C	0.113	0.053	0.075	0.272	0.336	0.538	0.561	0.621
<b>2-m-An/total of MP</b>	<b>0.003</b>	<b>0.003</b>	<b>0.003</b>	<b>0.005</b>	<b>0.141</b>	<b>0.110</b>	<b>0.034</b>	<b>0.077</b>

MD:methyldibenzothiophene; MN:methylnaphthalene; MP:methylphenanthrene

## 2-m-An/total of MP

Diagnostic ratio	A1	A2	A3	A4	B1	B2	B3	B4
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- ◆ Ratios of 2-m-An/total of MP are different significantly between crude oil and heavy fuel oil samples. The ratios for crude oil are lower than 0.01, and all the ratios of heavy fuel oil are higher than 0.01.
- ◆ Compare with other ratios, the ratio of “2-m-An/total of MP” is an important indicator to differentiate the crude oil and heavy fuel oil.
- ◆ Reason: crude oil can generate or degrade to 2-m-An due to pyrolysis during the production of heavy fuel oil.



# Test the available of the ratio

15 heavy fuel oils (B1 to B15)

32 crude oils (C1 to C32)

produced in Turkmenistan, Korea, China, Vietnam, Morocco, Algeria, Sultan, Yemen, Saudi Arabia, Argentina, Russia, Indonesia, Brazil, Equatorial Guinea, Angola, and Mauritania.

◆ Based on the results of GC-MS analysis, **10 PAH diagnostic ratios** from 47 oils were calculated.

# Diagnostic ratios

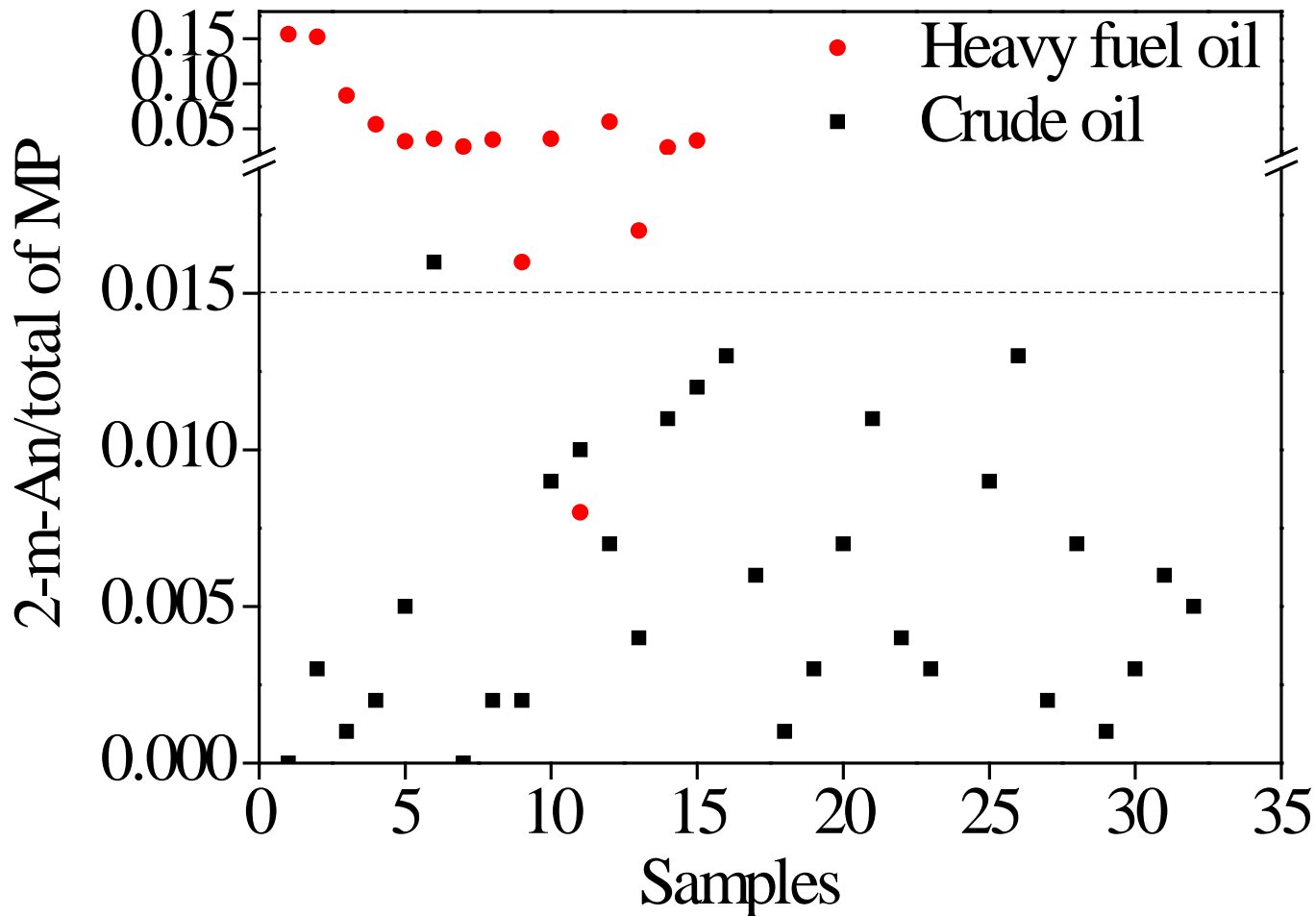
Diagnostic ratio	Definition
$\Sigma N/\Sigma C$	(Naphthalene+C1-Naphthalenes+C2-Naphthalenes+C3-Naphthalenes+C4-Naphthalenes)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma P/\Sigma C$	(Phenanthrene+C1-Phenanthrene+C2-Phenanthrene+C3-Phenanthrene+C4-Phenanthrene)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma D/\Sigma C$	(Dibenzothiophenes+C1-Dibenzothiophenes+C2-Dibenzothiophenes+C3-Dibenzothiophenes+C4-Dibenzothiophenes)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
$\Sigma F/\Sigma C$	(Fluorene+C1-Fluorene+C2-Fluorene+C3-Fluorene+C4-Fluorene)/(Chrysene+C1-Chrysenes+C2-Chrysenes+C3-Chrysenes)
An/P	Anthracene/Phenanthrene
BaA/C	Benzo[a]anthracene/Chrysene
<b>2-m-An/total of MP</b>	<b>2-methylanthracene/C1-Phenanthrenes</b>
Fl/Py	Fluoranthene/Pyrene
PI	$\Sigma(\text{other 3-6-ring PAHs})/\Sigma(\text{5-alkylated PAHs})$
BeP/BaP	Benzo[e]pyrene/Benzo[a]pyrene

# Diagnostic ratios

Table 3. Diagnostic ratios of polycyclic aromatic hydrocarbons (PAHs) from 47 oils

Diagnostic ratio	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	C1
$\Sigma N/\Sigma C$	3.136	1.808	1.810	6.805	3.585	2.470	3.315	3.319	1.820	9.144	4.076	1.888	3.150	3.695	2.928	10.771
$\Sigma P/\Sigma C$	2.343	1.512	1.272	5.340	4.787	3.455	4.386	4.471	3.035	3.714	4.634	2.685	4.837	4.371	4.582	5.700
$\Sigma D/\Sigma C$	0.880	0.493	0.579	1.320	1.518	0.919	3.930	0.909	1.032	0.900	2.836	0.664	1.376	1.184	1.942	0.603
$\Sigma F/\Sigma C$	0.939	0.576	0.510	2.610	1.496	0.856	1.574	1.079	0.799	1.685	1.545	0.680	1.511	1.660	2.153	1.935
An/P	0.403	0.427	0.193	0.108	0.067	0.087	0.090	0.094	0.032	0.095	0.026	0.134	0.037	0.054	0.155	0.003
BaA/C	0.724	0.695	0.453	0.484	0.336	0.312	0.178	0.335	0.135	0.305	0.061	0.378	0.167	0.203	0.491	0.019
2-m-An/total of MP	0.155	0.152	0.087	0.055	0.036	0.039	0.030	0.038	0.016	0.039	0.008	0.058	0.017	0.029	0.037	0.000
Fl/Py	0.677	0.571	0.369	0.176	0.436	0.487	0.571	0.458	0.997	0.176	0.625	0.415	0.720	0.643	0.313	0.669
PI	0.060	0.060	0.042	0.017	0.026	0.036	0.014	0.032	0.024	0.017	0.007	0.043	0.018	0.020	0.025	0.011
BeP/BaP	1.455	2.398	2.110	2.136	2.647	2.216	4.546	2.011	2.782	4.421	6.932	1.898	2.819	2.657	3.337	28.463
Diagnostic ratio	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
$\Sigma N/\Sigma C$	5.008	41.123	33.136	17.037	3.782	35.380	51.954	6.244	30.108	15.255	7.412	139.668	18.371	19.684	49.648	31.878
$\Sigma P/\Sigma C$	2.125	11.186	9.360	5.985	2.553	12.610	13.515	3.878	7.189	5.773	4.415	37.714	5.633	6.304	9.858	8.419
$\Sigma D/\Sigma C$	0.077	22.507	1.894	0.385	0.224	0.427	33.164	0.300	1.622	0.574	0.928	26.217	0.833	0.975	1.112	1.992
$\Sigma F/\Sigma C$	0.809	11.369	5.208	2.671	1.084	2.617	16.462	1.376	4.528	2.146	1.949	28.894	2.262	2.567	10.228	4.936
An/P	0.007	0.032	0.016	0.009	0.038	0.004	0.017	0.012	0.028	0.012	0.014	0.006	0.026	0.026	0.045	0.030
BaA/C	0.043	0.020	0.028	0.107	0.090	0.065	0.029	0.049	0.068	0.100	0.061	0.083	0.117	0.087	0.275	0.117
2-m-An/total of MP	0.003	0.001	0.002	0.005	0.016	0.000	0.002	0.002	0.009	0.010	0.007	0.004	0.011	0.012	0.013	0.006
Fl/Py	0.283	0.798	1.470	0.203	0.678	0.827	0.791	0.539	0.529	0.288	0.628	0.759	0.727	1.033	1.516	0.988
PI	0.006	0.002	0.003	0.007	0.024	0.001	0.002	0.012	0.003	0.010	0.013	0.005	0.008	0.006	0.005	0.003
BeP/BaP	30.408	27.000	22.159	27.195	14.705	14.909	5.451	49.200	9.007	9.780	13.378	5.033	7.252	10.810	1.264	4.259
Diagnostic ratio	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	
$\Sigma N/\Sigma C$	17.410	14.947	13.473	16.346	42.058	42.270	18.145	21.938	6.092	7.124	30.084	36.184	27.642	30.646	17.824	
$\Sigma P/\Sigma C$	6.545	6.434	7.109	5.955	12.154	10.860	6.174	6.166	4.017	3.039	9.178	11.077	7.620	7.848	4.814	
$\Sigma D/\Sigma C$	2.286	1.582	3.435	0.469	19.006	29.881	0.927	1.612	0.364	0.256	2.083	26.510	1.861	1.985	1.490	
$\Sigma F/\Sigma C$	4.768	2.333	2.782	2.628	14.372	16.828	2.241	3.391	1.823	1.013	5.906	15.659	3.661	5.046	4.157	
An/P	0.030	0.015	0.033	0.024	0.018	0.016	0.042	0.033	0.034	0.010	0.018	0.011	0.008	0.023	0.011	
BaA/C	0.044	0.075	0.099	0.107	0.010	0.018	0.191	0.100	0.071	0.062	0.114	0.030	0.098	0.121	0.091	
2-m-An/total of MP	0.001	0.003	0.007	0.011	0.004	0.003	0.020	0.009	0.013	0.002	0.007	0.001	0.003	0.006	0.005	
Fl/Py	0.693	0.570	0.807	1.073	0.657	0.758	1.509	0.761	0.730	0.525	1.267	1.128	0.850	1.073	1.583	
PI	0.005	0.006	0.008	0.008	0.003	0.002	0.007	0.004	0.018	0.005	0.003	0.002	0.003	0.004	0.003	
BeP/BaP	6.274	12.410	4.143	13.892	5.323	4.147	9.082	3.673	26.163	23.193	3.250	8.352	5.846	2.115	2.077	

# Diagnostic ratios



Difference of 2-m-An/total of MP between heavy fuel oil and crude oil.



# Conclusions

- ◆ The ratio of “2-m-An/total of MP” is a useful indicator to differentiate the crude oil and heavy fuel oil.
- ◆ In general, the ratio of “2-m-An/total of MP” **bigger than 0.015** indicates that the oil **is heavy fuel oil**, and the ratio **lower than 0.015** indicates that the oil is **crude oil**.



**Thanks!**

**谢 谢!**

