W4: Marine environment emergencies: Detection, monitoring, response and impacts

Spatial and temporal distribution, sources and ecological risk analysis of PAHs in the sediment from Yellow River estuary reach, China

Chuanyuan Wang

Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences

cywang@yic.ac.cn

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Content

1.1 Research background

As the 2nd largest river in China and 6th largest river in the world, the Yellow River carries a huge amount of sediments (1×10^9 t/a) to the Bohai Sea.

Estuaries and coastal zones are the main channels between lands and oceans, which trap significant quantities of natural and anthropogenic organic matter under the interactions of a series of physical, chemical and biological processes.

1.2 Research background

- *Polycyclic aromatic hydrocarbons* (PAHs) are ubiquitous contaminants in the environment, which mainly originate from *fossil fuel combustion and release of petroleum and petroleum products*.
- This is especially true for many coastal regions where the high anthropogenic influence and various contamination sources exist.

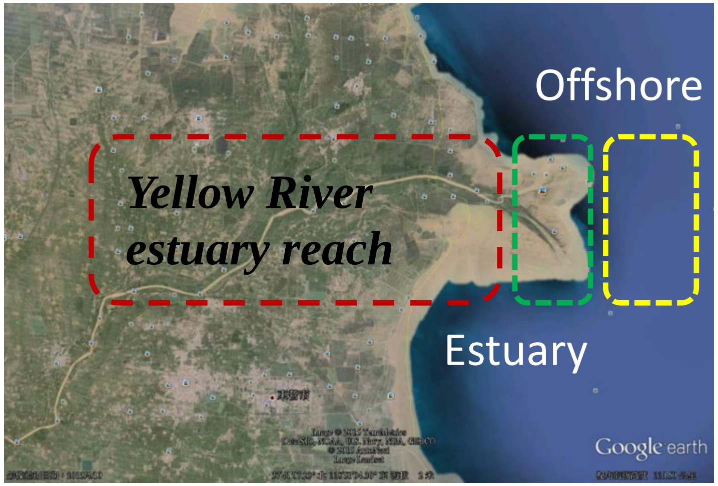
- Rapid economic growth in Bohai Bay raises concerns of significant pollution to aquatic environment.
- Shengli Oilfield, the second largest oilfield of China, is located here, which threats to the ecosystem of *Yellow River Delta* (YRD).

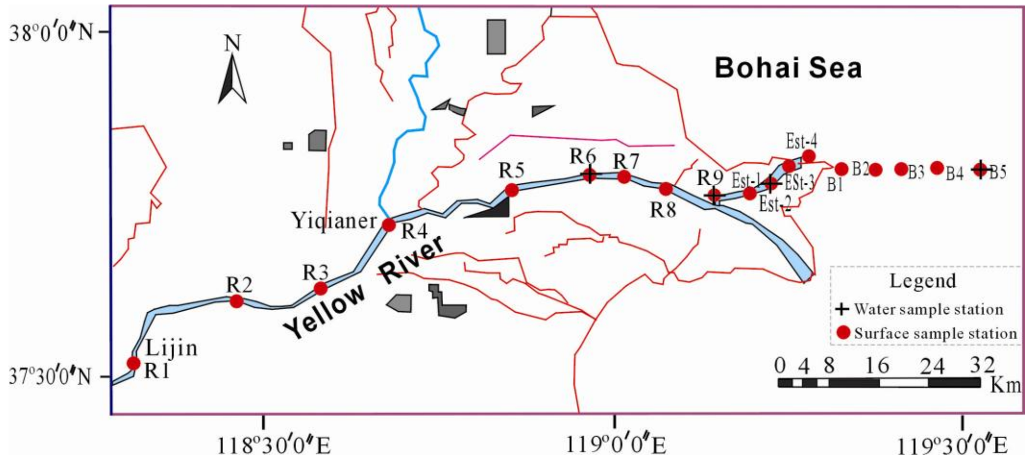
1.2 Aims of this study

- ***Distribution***: Determine spatial–temporal distributions of PAHs in sediment from Yellow River covering the riverine, estuary and offshore areas;

- ***Source***: Identify the possible sources of PAHs;
- ***Assessment:*** Assess the ecological risk of PAHs in this region.

2. Materials and methods





- ***Samples Collection:*** The sampling stations extending from the ***Yellow River estuary reach*** (YRER) (R1~R12) to ***estuary*** (Est-1~Est-4) and the ***offshore area*** of Bohai Sea with the transect (TT-B).

- Extraction and fractionation
- Gas Chromatography-Mass Spectrometer (GC-MS) analysis

3、Results and discussion

3.1 PAHs concentrations in sediment

Total 16 PAH concentrations ranged from 56.69 ng/g to 227.96 ng/g, with a mean of 111.14 ± 59.70 ng/g dry weights (dw).

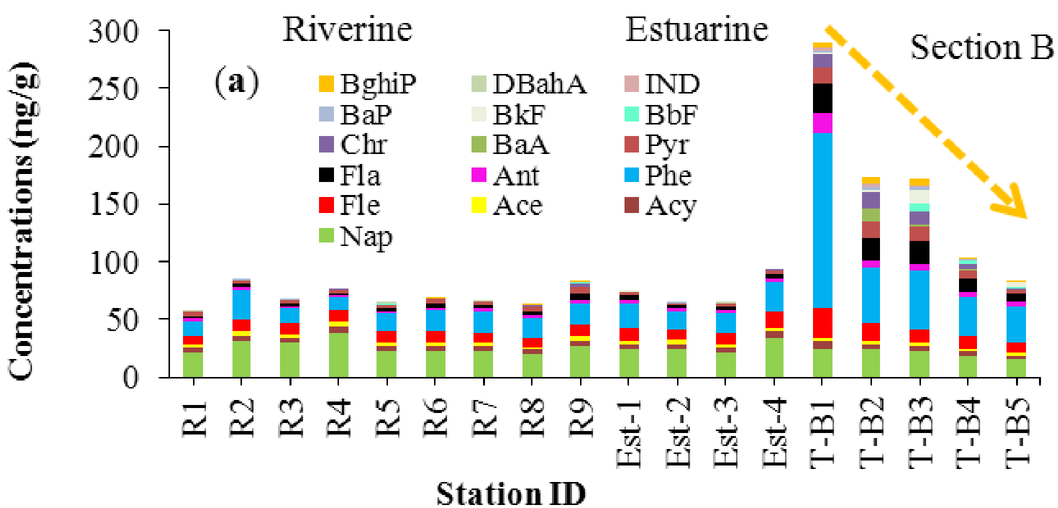
Compared with the other areas in the world, the contamination by PAHs in this study was：

- *Close to Yangze River Estuary, China (90.14–502.12 ng/g dw);*
- *Lower than Pearl River Delta, China (217–2680 ng/g dw), Mediterranean coast, Egypt (3.5–14100 ng/g dw), Elizabeth River wetland, USA (1200–22200 ng/g dw) and Masan Bay, Korea (9.1–1400 ng/g dw).*
- *Higher than Chongming wetlands near Shanghai, China (38.7–136.2 ng/g dw).*

3.2 Spatial and temporal distribution of PAHs

- The total concentrations of 16 ΣPAHs of sediments in transect of offshore area is 151.08±62.14%, being obviously higher than that of the riverine sediments of YRER (69.84±9.37%) and estuary (74.28±13.42%), which may be due to the *accumulation action* of organic matter in coastal zone of Bohai sea.
- Section: an overall pattern of seaward decrease

Input mainly from the Yellow River and land-sourced pollutant.



3.2 Spatial and temporal distribution of PAHs

- Sediments in the riverine and estuary area collected mainly consisted of fine particles with the grain size >4 μm (silt+sand); while the marine sediments mainly consisted of fine particles with the grain size <63 μm (silt+clay).

The content of the sediment appear to influence the PAHs distribution.

More clay? More PAHs

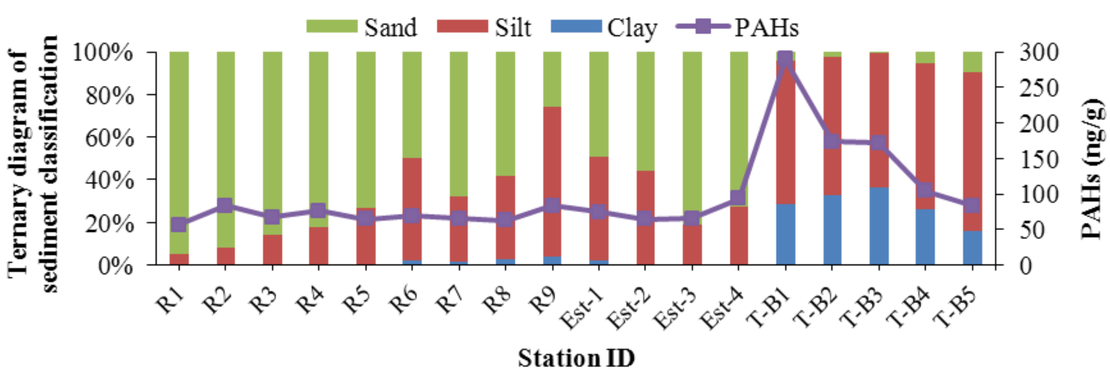
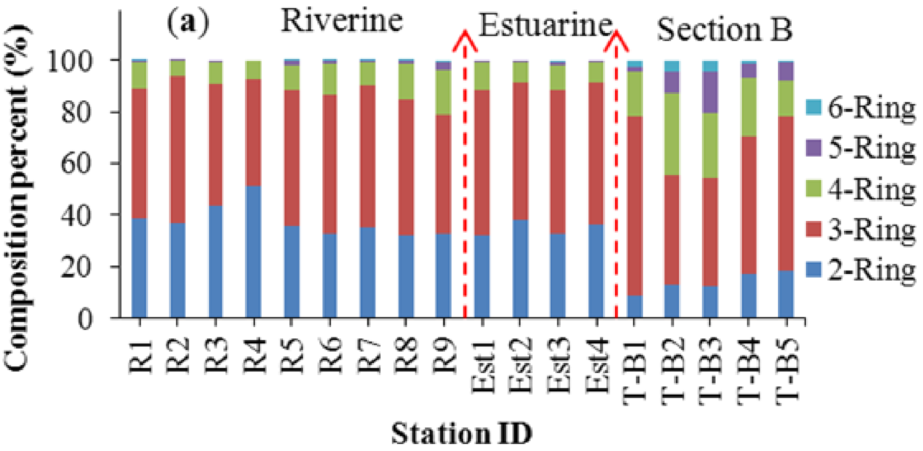


Fig.3 Distribution of ΣPAHs concentrations in sediment and ternary diagram showing the sediment classification and deposition patterns in Yellow River estuary reach

3. 3 PAHs sources identification

In general, ***low molecular weight*** PAHs (two- to three-ring) originate from ***petroleum products, natural digenesis***, while ***pyrolytic procedures*** mainly generate high molecular weight PAH components with four or more rings at high temperature.

Petroleum was the predominate source.



3.3 PAHs sources identification-- isomer pair ratio

Based on the PAHs isomer pair ratio

PAHs isomer ratios have also been used as distinct chemical tracers to infer possible sources of PAHs.

Flu/(Flu+Pyr) < 0.4 implies petroleum, 0.4–0.5 implies petroleum combustion, and > 0.5 implies combustion of coal and biomass;

Ant/(Ant+Phe) ratio < 0.10 are seen in petroleum input or diagenetic sources, whereas values > 0.1 are characteristic of combustion processes;

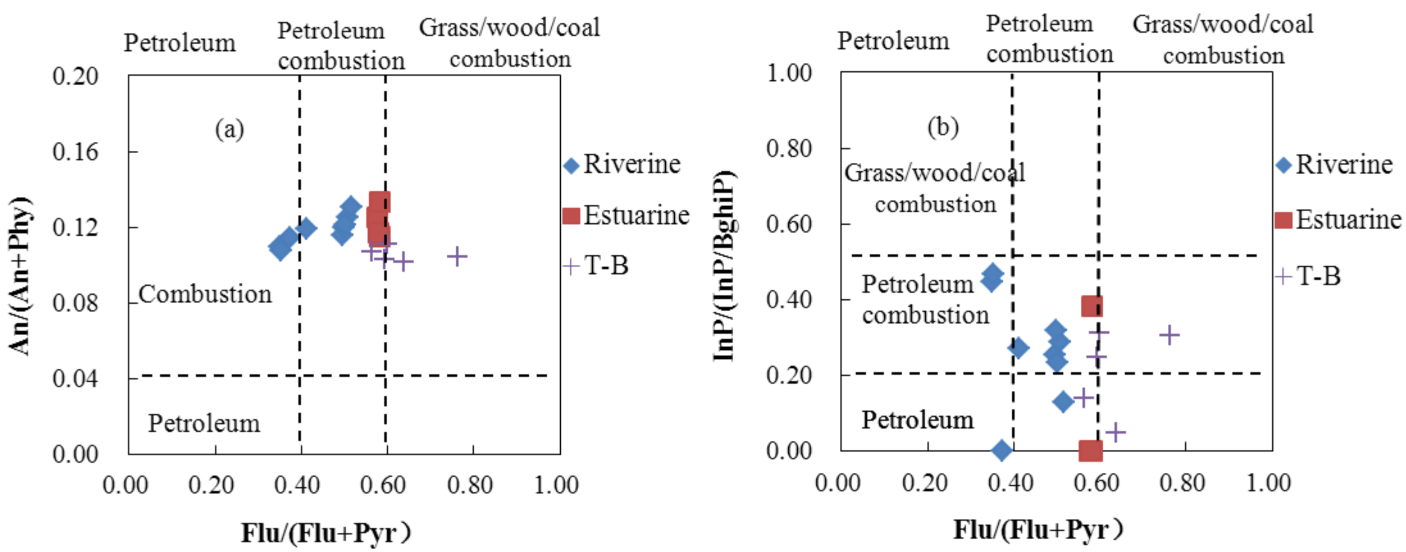
InP/(InP + BghiP) of <0.20 indicates a petroleum source; of >0.50 indicates combustion contribution of biomass and coal sources and between 0.20 and 0.50 indicates liquid fossil fuel combustion.

3.3 PAHs sources identification--isomer pair ratio

It can be seen that the riverine samples exhibited more evidence of petroleum pollution, while other samples from estuary and marine area may be derived primarily from biomass and coal combustion.

Moreover, pyrogenic sources are the major origins of PAHs in the Bohai sediments.

Except pyrolytic input as a major source, petrogenic may be also a source for PAHs because the oil platform of Shengli Oilfield could also contribute some PAHs.



3.4 Ecological risk assessment of PAHs

PAHs pollution levels (*Baumard et al. , 1998*):

- Low： 0-100 ng/g;
- Moderate: 100-1000 ng/g;
- High: 1000-5000 ng/g;
- Very high: >5000 ng/g.

Based on this classification, sediments from Yellow River Delta estuary (56.69 -290.04 ng/g drw) could be considered as **low to moderately polluted** with PAHs.

3.4 Ecological risk assessment of PAHs

- Sediment quality guidelines (SQGs,) are also an important tool for the assessment of contamination in marine and estuarine sediments (Long et al., 1995, 2006; Qiao et al., 2006; Quiroz et al., 2010).

ERL: effects range-low; ERM: effects range-median; TELs: threshold effects levels; PELs: probable effects levels;

- In the three ranges of chemical concentrations, *adverse biological effects* were expected rarely (<ERL/TEL), *occasionally* (≥ERL/TEL and <ERM/PEL), and *frequently* (≥ERM/PEL) .

3.4 Ecological risk assessment of PAHs

PAHs	Guideline				YRER		
	ER-L	ER-M	TEL	PEL	Riverine	Estuarine	Marine
Nap	160	2100	34.6	391	20.28-39.07	21.39-34.32	**15.58-24.96**
Ace	16	500	6.71	88.9	2.67-4.14	2.71-3.54	**2.46-3.11**
Acy	44	640	5.87	128	3.46-4.61	4.2-5.56	**3.38-6.69**
Flu	19	540	21.2	144	6.71-10.22	9.30-13.04	**7.94-24.82**
Phe	240	1500	86.7	544	11.08-25.02	15.22-25.57	**32.26-152.25**
Ant	85.3	1100	46.9	245	1.70-3.39	2.17-3.94	**3.75-17.15**
Fla	600	5100	113	1494	1.95-3.97	2.79-4.38	**7.31-24.79**
Pyr	665	2600	153	1398	2.82-5.81	2.05-3.13	**2.26-24.76**
BaA	261	1600	74.8	693	0.00-0.02	0.00	**0.01-10.57**
Chr	384	2800	108	846	0.00-2.82	0.19-0.27	**1.76-14.19**
BaP	430	1600	88.8	763	0.00-0.87	0.00-0.01	**0.17-2.95**
DBahA	**63.4**	**260**	**6.22**	**135**	**0.00-0.09**	**0.00-0.73**	**0.00-0.62**

PAHs will not cause *immediately adverse biological effects* in studied environment.

Conclusion

- Due to the accumulation action of organic matter in coastal zone of Bohai sea, the total concentrations of 16 ΣPAHs in transect of offshore area is obviously higher than those of the riverine and estuary.
- The ΣPAHs in the section show an overall pattern of seaward decrease, suggesting an input mainly from the Yellow River and land-sourced pollutant.

- ✓ The riverine samples exhibited more evidence of petroleum pollution, while other samples from estuary and marine area may be derived primarily from biomass and coal combustion.
- ✓ Pyrogenic sources are the major origins of PAHs in the Bohai sediments. Except pyrolytic input as a major source, petrogenic may be also a source for PAHs because the oil platform of Shengli Oilfield could also contribute some PAHs.

- ☐ Yellow River Delta estuary could be considered as low to moderately polluted with PAHs, and PAHs will not cause immediately adverse biological effects in studied environment.

Acknowledgements

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Thank you for your attention！