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Primary research on distribution and source identification of PAHs in wetlands of the Yellow River Delta（2006）

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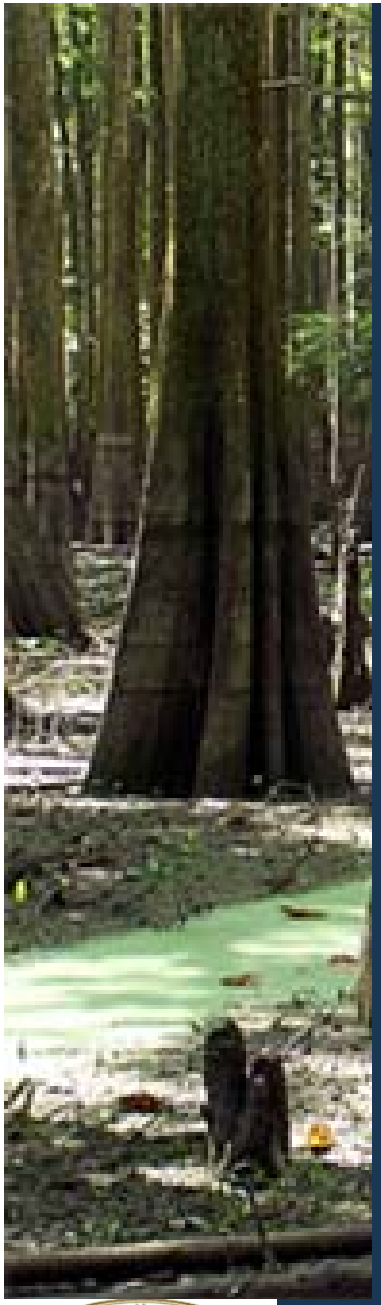

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1. Background

1). PAHs

Many contaminants accumulate in coastal environments and represent a significant risk to human and environmental health. As a group of nonionic hydrophobic organic contaminants, PAHs, polycyclic aromatic hydrocarbons, are ubiquitously present in coastal areas.

PAHs are of great concern because they distribute widely in the environment and many of them have toxic and carcinogenic properties. PAHs can bioaccumulate in the food web, which can cause both acute and chronic effects on fish birds and other mammals that feed on the aquatic organisms. So human health will also be affected.

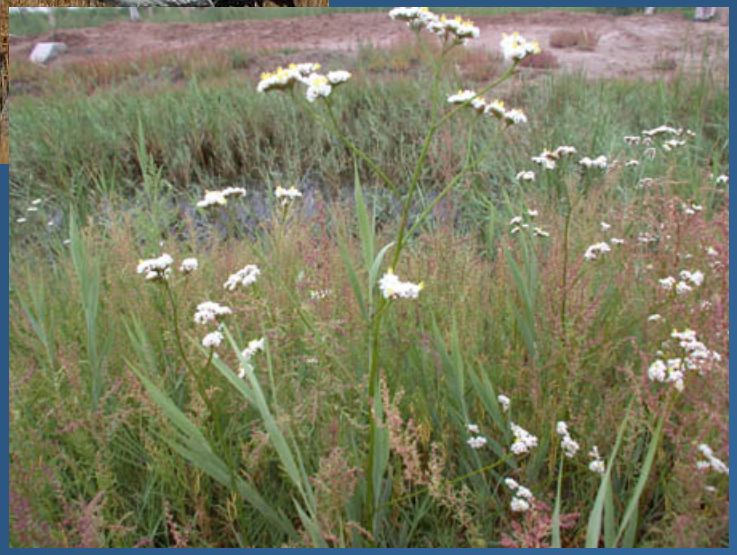
Due to the persistent and toxic of PAHs, U.S. EPA (Environmental Protection Agency) has listed 16 kinds of PAHs as the priority controlled pollutants, as follow:

Name	Abbr.	Name	Abbr.
Naphthalene	Nap	Benzo(a)anthracene	B(a)A
Acenaphthylene	Ace	Chrysene	Chr
Acenaphthene	Ace′	Benzo(b)fluoranthene	B(b)f
fluroene	Flu	Benzo(k)fluoranthene	B(k)f
Phenanthrene	Phe	Benzo(a)pyrene	B(a)p
Anthracene	Ant	Indeno(1,2,3-cd)pyrene	Ind
Fluoranthene	Fluoran	Dibenzo[a,h]anthracene	Dibenzo
Pyrene	Pyr	Benzo(ghi)pyrene	B(ghi)p

2). Wetland

Being the most biologically important and productive ecosystems on earth, Coastal wetlands are the issue of geological research in recent years. Coastal wetlands not only can provide food, habitats and spawning grounds to a wide variety of infauna but also act as important staging areas for migratory waterfowl and other birds. Coastal wetlands also possess high socioeconomic values. They play important roles in the protection of shorelines and banks from erosion and can be used to treat domestic and industrial wastewaters.

The Wetland of the Yellow River Delta is the youngest wetland in China.



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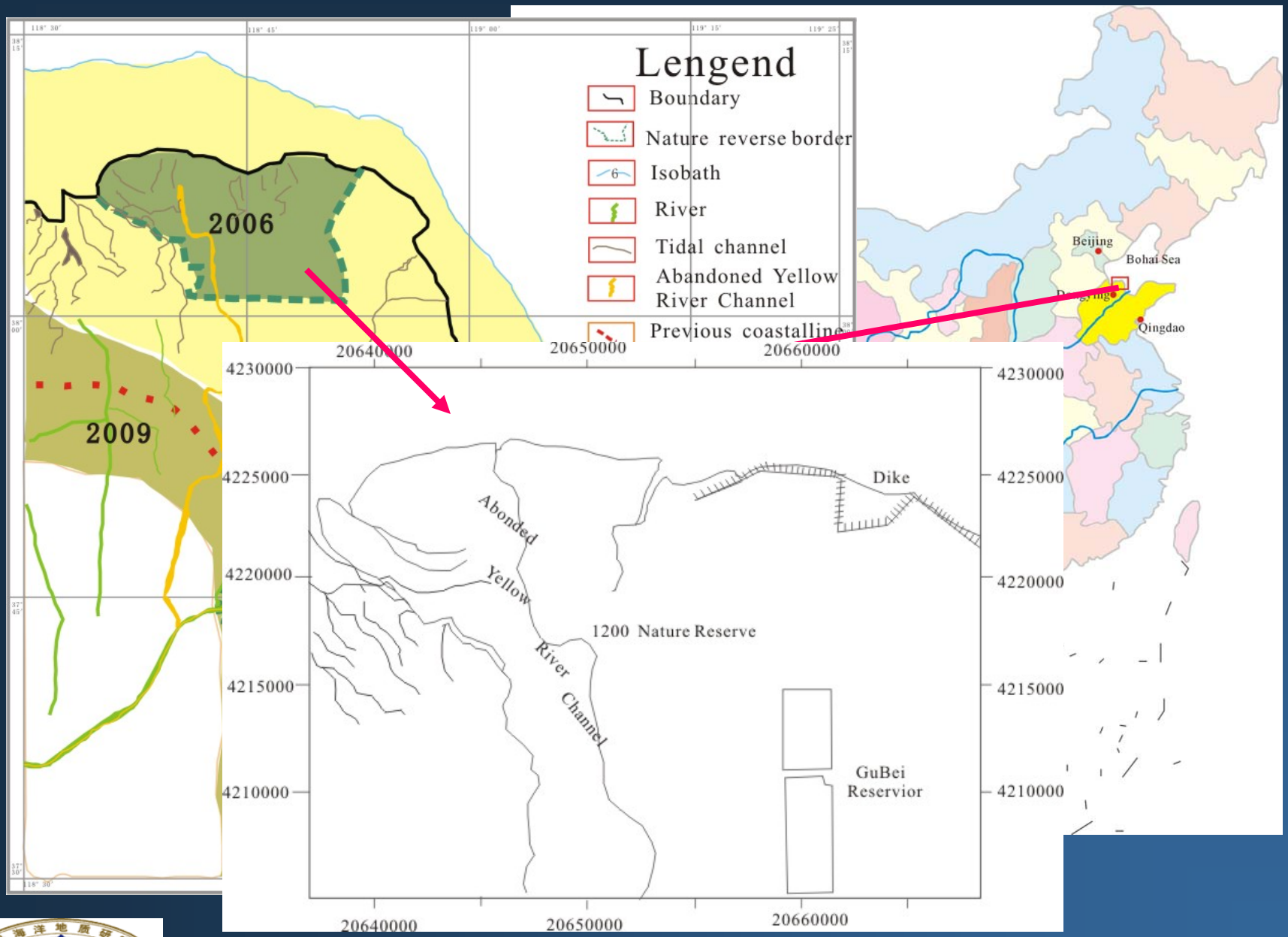
3). Our Project

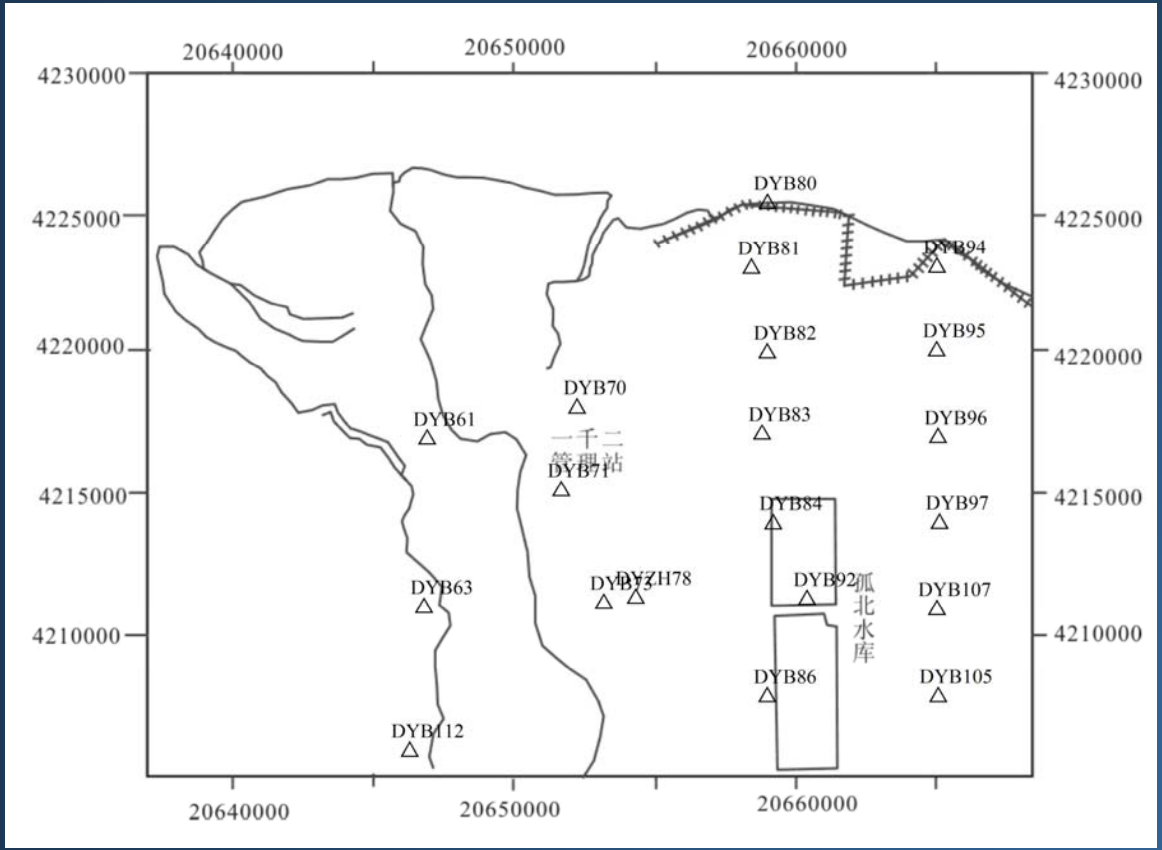
Our project, The Comprehensive Geological Assessment & Survey of Coastal Wetlands in the Yellow River Delta, began in 2006. It will last four years. The purpose of this project is to study the wetlands from geological and geochemical view. It also explains the evolution of wetland, predicts its developing trend and then makes bio-ecological assessment of it.


Lengend
Boundary
Nature reverse border
Isobath
River
Tidal channel
Abandoned Yellow River Channel
Previous coastalline
2006
2009
Beijing
Bohai Sea
Qingdao
20640000
20650000
20660000
4230000
4225000
4220000
4215000
4210000
Dike
Abonded
Yellow
River
Channel
1200 Nature Reserve
GuBei
Reservior

2. Sampling & analysis

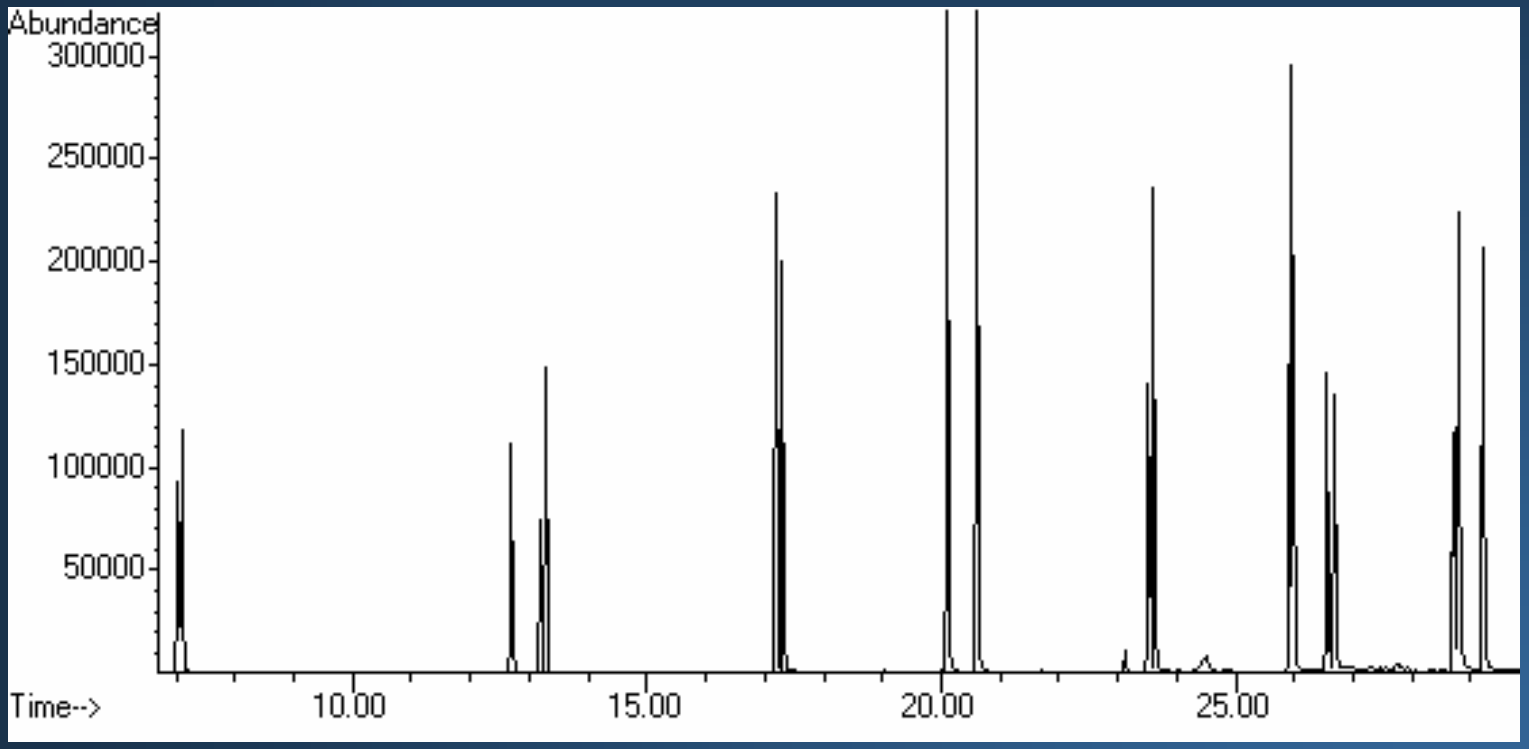
1). Sample station

20 stations were selected in research area of 2006 (Fig.). We sampled the surface soil and stored in frozen until to be analyzed.



2). Analysis method

After extraction, purifying, washing, concentration, soil samples are test by GC-MS in lab. The chromatogram and detection limit of PAHs standards are as follow:



Chromatogram of PAHs standards（GC-MS）

Detection limit and Correlative coefficient of GC-MS

PAHs	Correlative coefficient（R2）	Detection limit (ng/g)	PAHs	Correlative coefficient（R2）	Detection limit (ng/g)
Nap	0.9996	0.31	Chr	0.996	0.36
Ace	0.9953	0.26	B(b)f	0.9886	0.09
Ace′	0.999	0.44	B(k)f	0.9981	0.35
Flu	0.9925	0.1	B(a)p	0.9852	0.45
Phe	0.9947	0.14	Ind	0.9864	0.9
Fluran	0.9945	0.1	Dibenzo	0.9955	1.34
Pyr	0.9962	0.17	B [ghi] p	0.9962	0.93
B [a] A	0.9783	0.15			

3. Results & Discussion

1). Results

Test data are as follow :

Station	Nap	Flu	Phen	Pyr	B [a] A	Chr	B [k] f	Ind	Dibenzo	B [ghi] p	∑PAHs
	2-3rings			>4rings							
DYB61	2.903	2.156	nd	nd	25.034	nd	25.621	32.059	33.536	nd	121.308
DYB63	2.892	1.857	nd	nd	25.966	nd	nd	33.370	33.546	31.336	128.968
DYB70	3.734	2.727	nd	nd	25.253	nd	nd	32.626	33.608	nd	97.949
DYB71	2.590	nd	nd	nd	24.935	nd	nd	nd	nd	nd	27.525
DYB73	4.249	2.551	0.028	nd	25.020	nd	25.655	nd	nd	nd	57.504
DYZH78	2.771	2.854	nd	nd	25.002	nd	25.670	32.112	33.620	nd	122.030
DYB80	2.722	1.862	nd	nd	25.003	nd	nd	32.130	33.635	nd	95.353
DYB81	3.102	2.826	nd	nd	24.977	nd	25.701	nd	nd	nd	56.607
DYB82	2.545	nd	nd	nd	24.932	nd	nd	nd	nd	nd	27.477
DYB84	2.618	nd	nd	nd	24.990	nd	nd	32.029	nd	nd	59.637
DYB86	2.611	nd	nd	nd	24.971	nd	nd	nd	nd	nd	27.582
DYB83	2.482	nd	nd	nd	24.972	nd	nd	nd	nd	nd	27.454

continiued

Station	Nap	Flu	Phen	Pyr	B [a] A	Chr	B [k] f	Ind	Dibenzo	B [ghi] p	∑PAHs
	2-3rings			>4rings							
DYB92	3.171	2.109	nd	nd	24.953	nd	nd	32.055	33.550	nd	95.838
DYB94	2.773	2.189	nd	nd	24.940	nd	nd	32.172	nd	31.237	93.310
DYB95	2.638	nd	nd	nd	24.917	nd	nd	32.038	nd	nd	59.593
DYB96	5.481	2.716	nd	nd	24.900	nd	nd	nd	nd	nd	33.097
DYB97	2.670	nd	nd	nd	25.144	nd	nd	32.152	nd	nd	59.967
DYB105	3.587	2.196	0.057	0.039	25.689	nd	25.709	33.326	nd	nd	90.603
DYB107	3.835	2.107	0.037	0.029	25.095	nd	25.815	nd	nd	nd	56.917
DYB112	2.614	1.857	nd	nd	24.880	20.304	nd	nd	33.541	nd	83.196
Max	5.481	2.854	0.057	0.039	25.966	20.304	25.815	33.370	33.635	31.336	128.968
Min	2.482	nd	nd	nd	24.880	nd	nd	nd	nd	nd	27.454
Average	3.099	1.500	0.006	0.003	25.079	1.015	7.709	17.803	11.752	3.129	71.096

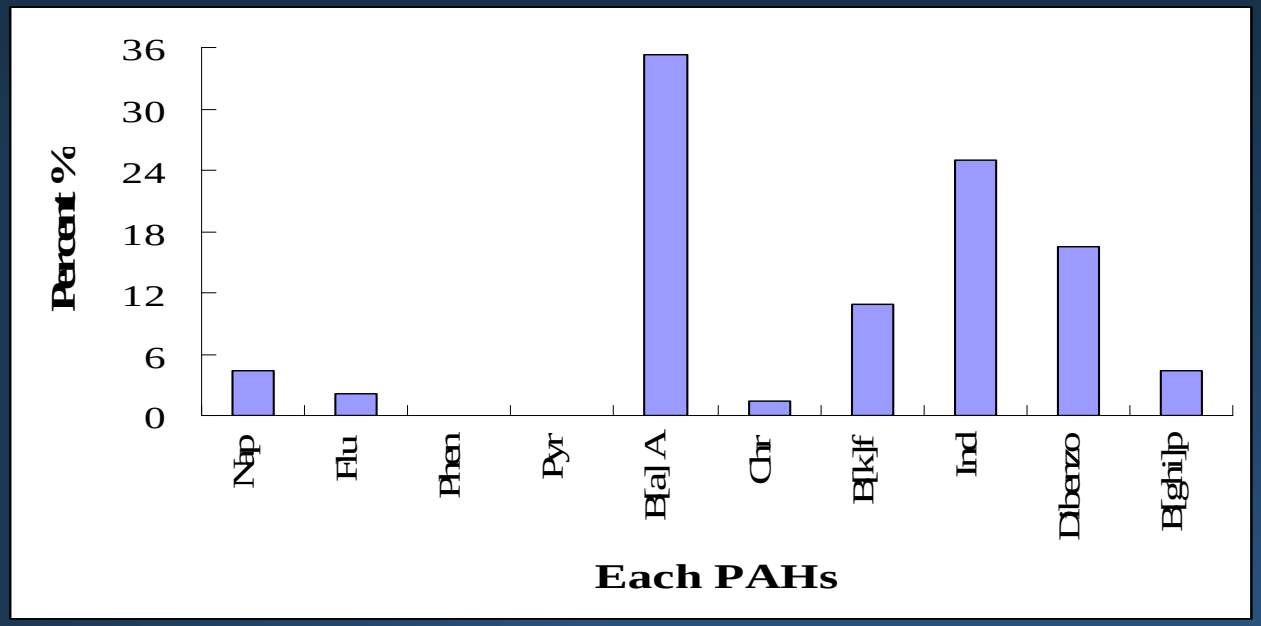
Unit: ng/g

nd means under detection limit;

The total PAHs concentration of some research areas in the world (ug/g)

Research Area	Min of ∑PAHs	Max of ∑PAHs
Iraq marsh	0.590	2.070
South Carolina marsh	0.069	37
Elizabeth River surface sediments	~1.40	~172
Baltimore Harbor	0.089	30
Elizabeth River wetland	1.2	22.2
Beijing city	0.366	27.825
Hangzhou city	0.0597	0.6158
Yalujiang Estuary	0.37	0.84
Tianjin vegetable lands	1.008	7.082
MaiPo marsh of Hong Kong	0.18	0.83
This research	0.0275	0.129

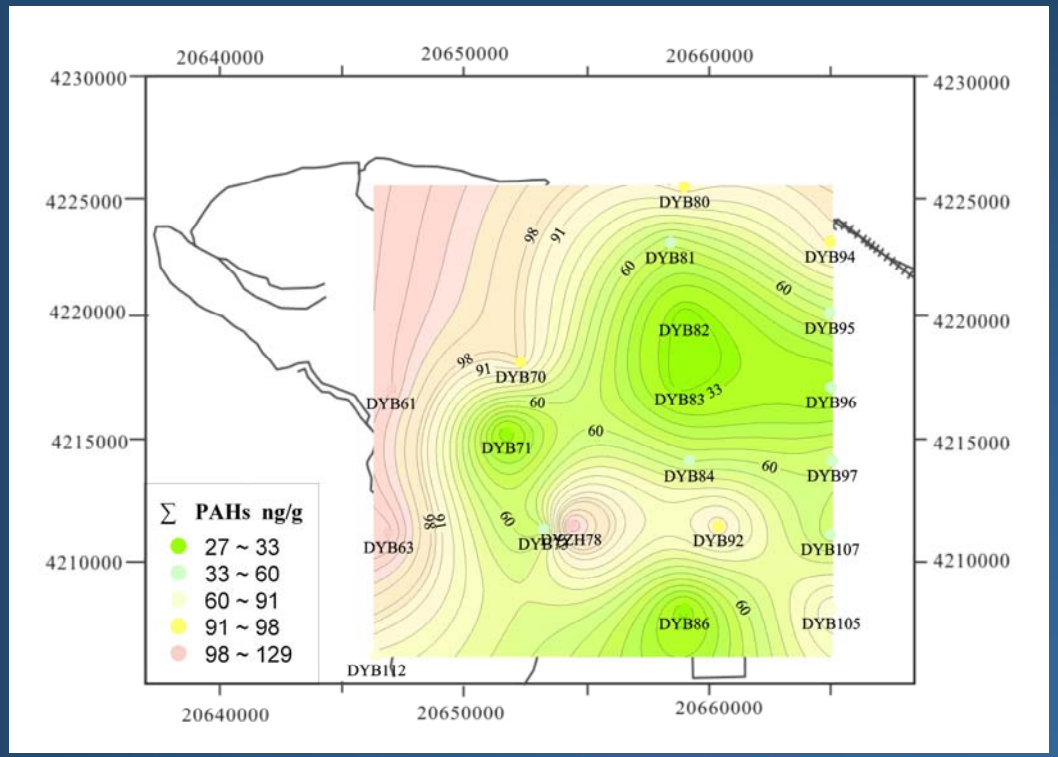
We can see from this two tables: in 16 EPA priority PAHs, only 10 of them were detected. The total PAHs concentration in surface soil of research area varied from 27.454 ~ 128.968ng/g and its average is 71.096ng/g, which is much lower than other research areas in the world.



The percentage of each PAHs

This Fig. shows the percentage of these 10 PAHs in the total concentration of PAHs. It indicates that B[a]A, B[k]f, Ind and Dibenzo are top four PAHs, which takes more than 80% of the total. In addition, the benzoic rings of them are all more than three or four rings. While other PAHs such as Nap, Chr, B[a]p etc. have very small percentage. So the PAHs pollution mainly caused by the top four PAHs .

It's obvious that in 2006 research area the relative high PAHs concentration area mainly distributes from the Abundant Yellow River Channel to 1200 Nature Reserve. While relative low concentration area locates in the western of research area. It shows the trend that the PAHs pollution gently decreases from the east to the west. There are only some individual stations with medium higher value distributing near the Dike in north and the Gubei Reservoir in middle of the research area. The total Distributing characteristics of PAHs here are not-point source pollution.

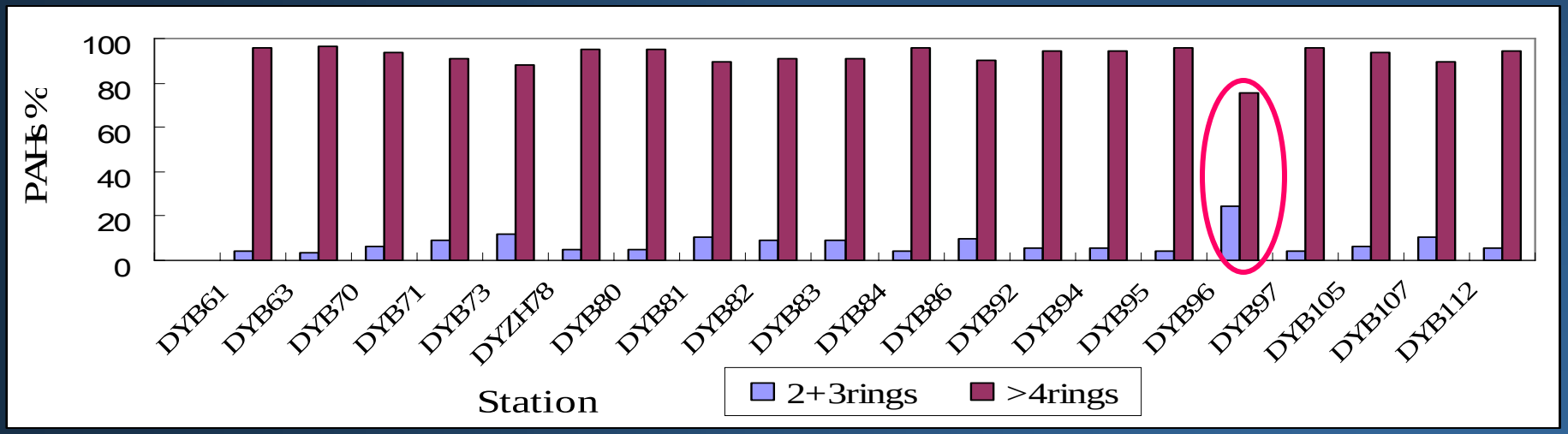


Contour map of ∑PAHs (ng/g)

2) Sources identification

The sources of PAHs in environments are very complicated. Different sources of PAHs have different structure and components. They also can keep relatively stable during transportation and deposition. So we could distinguish the source of PAHs according to component's characteristics. Usually the relative abundance of different ringed PAHs especially the 2~3ringed and the 4~6 ringed can be used to estimates the sources of PAHs. PAHs with 4 ~6 rings have high molecular weight (mol. wt.) and mainly come from fossil fuel bursting in high temperature, while lower molecular weight PAHs (2~3ringed) come from petroleum pollution.

Fig. shows the percentage of 2~3 ringed PAHs and 4~6 ringed PAHs of every station. It is obvious that 4~6 ringed PAHs almost dominated in every station comparing with the 2~3 ringed. Their mean percentage is over 80%, while the percentage of 2~3 ringed PAHs are very small. So PAHs here is mainly caused by high temperature pyrogenation. Petroleum source pollution is not very bad. There are only one special station DYB96. Its percentage of 2~3 ringed PAHs has reached 25%, which maybe caused by the leakage of crude oil. Because this station is just near the Dongying Crude Oil Port, oil transportation can cause oil pollution.



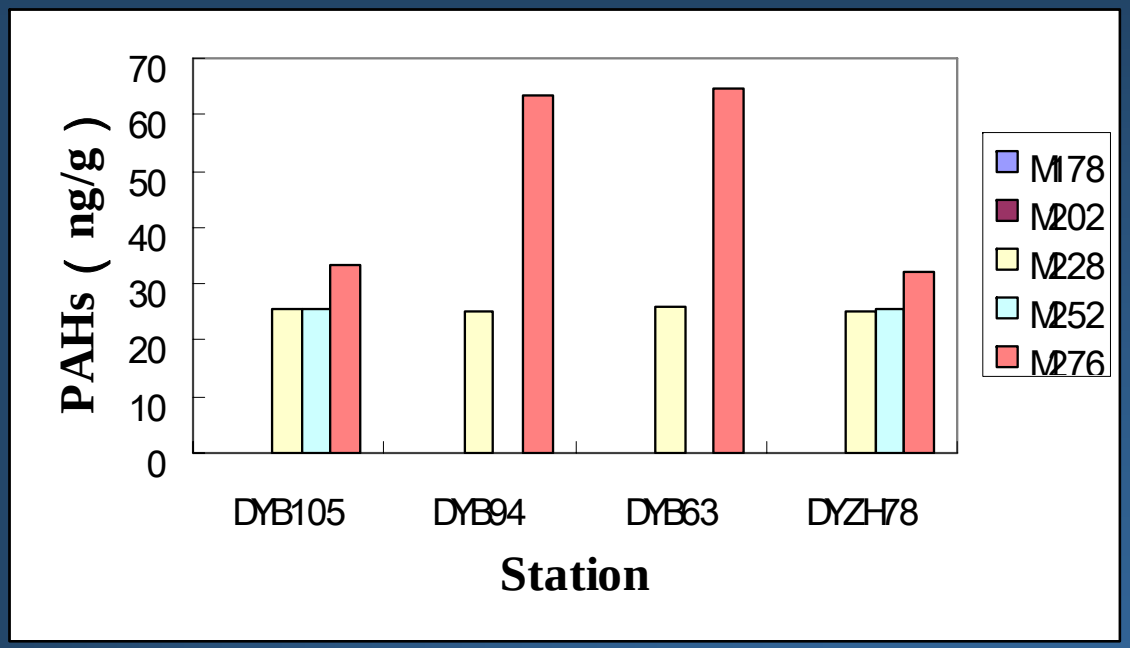
Distribution of different ringed PAHs in soil

Furthermore, the source identification of PAHs also can be distinguished by molecular weight of 3~5 ringed isomeric compounds. They can be divided into five groups according to molecular weight as follow:

Group number	Group name	PAHs
1	M178	Phe, Ant
2	M202	Fluran, Pyr
3	M228	B[a]a, Chr
4	M252	B[b]f, B[k]f, B[a]p,
5	M276	Ind, B[ghi]p

Some research has showed that M178 dominated in PAHs means source of fuel pollution; the combination of M202, M228, M252 dominated means source of gas burning and flue particles; and M252, M276 dominated means source of high temperature pyrogenation.

Four stations were selected to study the source of PAHs by this way. They are DYB105(Gubei Reservoir)、DYB94(Dike)、DYB63（1200 Nature Reserve）and DYZH78（Abundant Yellow River Channel）. The results show that M252, M276 dominated in this area and M178 has the small concentration. This indicates source of PAHs here mainly come from high temperature pyrogenation. M228 distributes in each station equally and with higher concentration means flue particles also a main source of PAHs here.



Distribution characteristics of five molecular weight groups in DYB105,DYB94,DYB63,DYZH78 stations

3) Potential ecological risk

Long and Morgan conducted an extensive review of publication that provided both concentrations of contaminants in sediment and observed biological effects .

They ranked the consensus values from low to high. Effects-range low (ERL) and effects-range median (ERM) sediment quality guidelines were derived from the lowest 10th percentile and 50th percentile of the biological effects data , separating concentrations of the contaminants into ranges that were rarely(< ERL) , occasionally(≥ERL ,< ERL) and frequently (≥ERM) associated with acute toxicological effects.

The ERL and ERM guidelines for PAHs were derived for 12 of the 16 PAHs compounds list as priority pollutants by the US EPA in Table.

ERL and ERM guideline values for PAHs (ng/g dw)

PAHs	ERL	ERM
Nap	160	2100
Ace	44	640
Ace′	16	500
Flu	19	540
Phe	240	1500
Ant	85	1100
Fluran	600	5100
Pyr	665	2600
B[a]A	261	1600
Chr	384	2800
B[a]p	430	1600
Dibenzo	63	260
ΣPAHs	4022	44792

We compared the measured concentration of PAHs compounds from the present study to the ERL and ERM values.
The total PAHs concentrations for all sites were all below the ERL.
No ERL for individual PAHs concentration were exceeded as well.
These finding indicated that surface soil in wetlands of research area is at low ecological risk, which might not exert significant potential damage to the organisms in this area.

4. Conclusion

- In this research, only 10 EPA priority PAHs were detected. The total concentration of PAHs in surface soil varied from 27.454 ~ 128.968ng/g and the average value is 71.096ng/g, which is much lower than other research areas in the world.
- B[a]A, B[k]f, Ind and Dibenzo are top four PAHs in every station.
- The PAHs pollution gently decreases from the east to the west. The total distributing characteristics of PAHs here are not-point source pollution.

- **The source of PAHs here mainly comes from high temperature pyrogenation. Petroleum source pollution is not very bad.**

- **The ecological risk in wetlands of research area is low, which might not exert significant potential damage to the organisms in this area.**

Thank you for your attention!