Preliminary Analysis on Polycyclic Aromatic Hydrocarbons (PAHs) of Surface Sediment within Eastern Route of China's South-to-North Water Diversion Project_Case of NanSi Lake

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Abstract. With the implementation of the South-to-North water diversion project in china, water quality problems have become increasingly prominent along the Eastern Route of South-to-North Water Diversion Project, China. As an important water-transfer channel and storage lake for the Eastern Route, the water quality of Nansi Lake has a direct impact on the water quality security of The Eastern Route project. On the basis of measured data and previous research results, this paper has preliminarily analyzed the distribution, content, and changing trend of Polycyclic Aromatic Hydrocarbons (PAHs) of Nansi lake basin in China under the climate change. The analysis results show that the pollution control of Nansi lake basin has achieved significant results in recent years and the water quality is continuously improving, however, there are still some kinds of PAHs which are potentially threatening the diverting water quality of the Eastern Route project. Further effective measures for controlling pollution should be taken in the future along the Eastern Route project to reduce the adverse impact of these PAHs on water quality security.

Introduction

Polycyclic Aromatic Hydrocarbons(PAHs)usually mean the fused ring compounds which contain two or more benzene rings in linear, angular, or cluster-like arrangement. They are a series of persistent organic pollutants (POPs) that exist widely in the environment. These pollutants mainly come from human activities and energy utilization, such as the incomplete combustion of hydrocarbons, waste discharges in the petroleum refining, spills in offshore oil development and petroleum transportation, etc. Polycyclic aromatic persistent organic pollutants have characteristics of hydrophobicity, fat-solubility, semi-volatility, long-range migratory aptitude, high toxicity and high perniciousness, etc. Wang[1]suggests that these pollutants, which are hard to be decomposed for their specific and stable cyclic structure, can remain in the environmental media for several years or even decades or even longer, such as water body[2], soil[3] and substrate sludge, and can also accumulate in plants, animals and human body. Most POPs are carcinogenic, mutagenic and teratogenic, and can cause acute or chronic poisoning. Since 1980s, PAHs in the environmental media have drawn more and more attention[4], and some countries have made a great deal of detailed investigation and assessment on PAHs in sediments of lakes, estuaries, bays, and coastal zones in recent years[5]. In china, researches about the distribution of PAHs and pollution-tracking in some rivers and thalassic sediments have been also reported, such as the South China Sea, Yangtze River estuary and so on[6].

Nansi Lake, which is located in the border region between Jiangsu and Shandong province in the east part of China, is an essential part of Eastern Route of South-to-North Water Diversion Project, and it is also one of the important storage lakes of Eastern Route project, whose water quality has a direct impact on the water quality security of Eastern Route project. Of all the lakes along the Eastern Route of South-to-North Water Diversion Project, Nansi Lake has the worst water quality and the most difficult problem of sewage treatment. Over the past few years, more efforts have been made to prevent pollution in Nansi lake drainage area where water quality is continuously becoming better. However, persistent organic pollutants are quite chemically stable and difficult to decompose and degrade, which means they may remain in water, soil and lake sediment for long time. Thus, it is a threat to water quality security of the Eastern Route project. Therefore, the impact of PAHs on water quality in the diversion project should be fully taken into account in the pollution control of the Eastern Route. Based on the previous research, in October 2012, we made a chemical analysis again and preliminarily obtained some information of the distribution, content and changing trend of 16 kinds of EPA-PAHs in Nansi Lake sediments, which is new exploration to the further conduct of water pollution control in Nansi Lake Basin and the safety guarantee of water quality in the Eastern Route project.

Water Environment in Nansi Lake

Nansi Lake is the biggest freshwater lake in Shandong Province, including four connected lakes, Nanyang Lake, Dushan Lake, Zhaoyang Lake and Weishan Lake, and is divided into superior lake and lower lake by a 2nd level lake hydro Project. It stretches about 120 km from north to south and 5-25 km from west to east, and the total catchment is 31700 km^2, which includes 8580km^2 of eastern area, 21854km^2 of western area and 1266km^2 of water area. There are 53 rivers flowing into Nansi Lake, including 22 comparatively large rivers, and floods of all the rivers will flow into the sea through Hanzhuang Canal, Zhong requirements of South-to-North Water Diversion Project. Statistics of those key pollution sources along the project route suggest that papermaking, food and beverage sectors and chemical industry take top three positions in COD emission and they account for 62.40%, 9.80% and 8.20% of the total emission respectively[7]. Test of the treated waste water discharged by three typical industries, papermaking, textile printing and dyeing, shows that POPs which are hard to degrade still exist and they'll enter the water and surface sediments to affect the water quality of Nansi Lake to a certain degree.

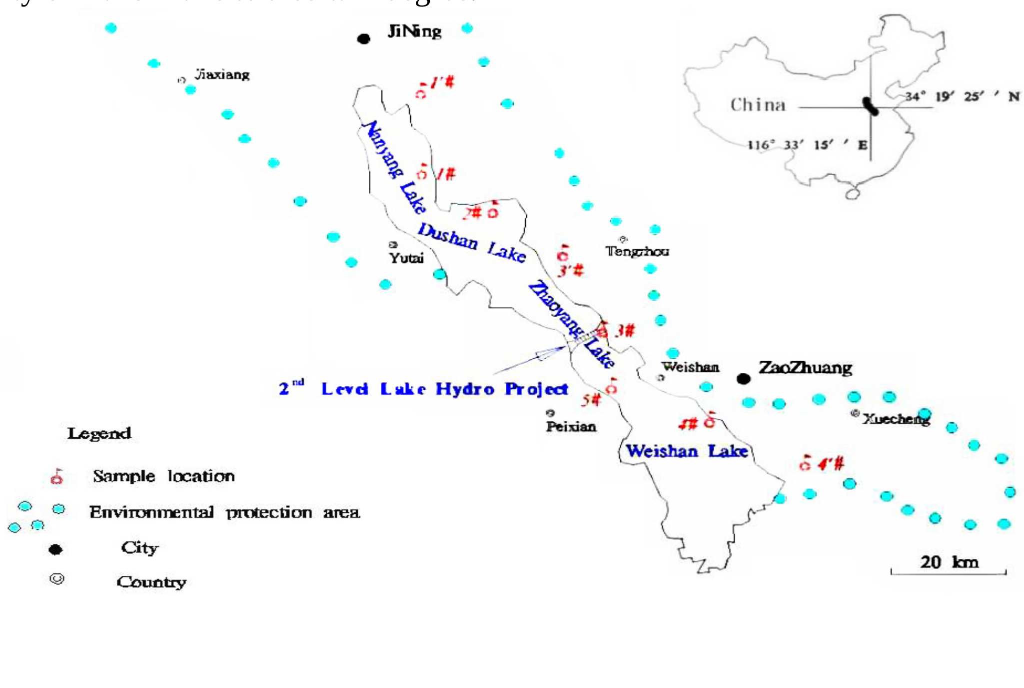

Fig1. Schematic research region and Sampling Location

Sampling and Testing of PAHs in Nansi Lake

Sampling Stations Layout and Sample Collection

According to the "Report on the State of the Environment in China from 2004 to 2008" issued by Chinese Environmental Protection Bureau, the water quality of Nansi Lake has always belonged to

Grade V or been worse than Grade V, which is far from the water quality requirements of South-to-North Water Diversion Project. There are 9 representative Sampling stations in Nansi lake, including five of them from 1# to 5# in the Lake District, and four of them from 1'# to 4'# in nearby typical rivers flowing into lakes. Fig 1 shows the schematic research region and Sampling locations . In October 2012, we carried out 7 effective samples in 9 sampling stations .The detailed Canal and Xinyi river after regulated.

Table 1 Sampling stations and sample descriptions

No.	Station location	North latitude	East longitude	Depth of water(m)	Sample description	Document number
1#	Nanyang Lake	35°7'17.7"N	116°39'52.3"E	5.0	Cinereous and slants yellow larger water content	1#
1'#	Baima river	35°11'48.6"N	116°42'46.5"E	2.0	Dark grey, viscous, larger water content, nearly no granular silt	--
2#	Dushan Lake	35°4'35.6"N	116°45'6.1"E	3.0	Dark, viscous	2#
2'#	Beisha river	35°2'24.0"N	116°56'44.5"E	0.5	shallow water, no-clay; only hard sands, sewage ditch	
3#	Zhaoyang Lake	34°52'38.3"N	116°59'36.3"E	2.0	charcoal grey, thicker, finely ground particle	2nd level lake Dam
3'#	Chengguo river	34°56'20.0"N	116° 57'40.2"E	6.0	charcoal grey, thicker, rough mud pellet, similar to3#	--
4#	Weishan Lake	34°38'23.5"N	117°16'43.5"E	2.5	close to black, viscous	4#
4'#	Hanzhuang Canal	34°35'44.1"N	117°21'38.4"E	4.0	no-clay,(river cleaned up Recently)	--
5#	Weishan Lake	34°41'53.4"N	117° 4'15.4"E	5.0	Yellow-dark colloidal mud, viscous	Gaolou Scenic
Notes	: 2 '#and 4'# are invalid samples					

Sample Testing

Instruments and Reagents

Instruments: MARSXPRESS microwave extraction instrument of Ampex U.S.; Agilent 6890-5973 gas chromatograph - mass spectrometer. Reagents: chromatography pure reagents n-hexane of Fisher, U.S., methylene dichloride and acetone, analytical pure reagents anhydrous sodium sulfate, activated silica gel (80-100 mesh), neutral alumina (80-100 mesh); standard samples of PAHs recovery rate indicator: naphthalene-D8 (purchased from American Accustandard company); The PAHs standard materials purchased from American Supelco Corporation.

Extraction

Sample pretreatment: water content of the samples can be calculated after lyophilization and milled by 2 mm sieve; Weigh 10g of soil, and then add 25 μL of 0.02mg/mL standard sample of PAHs recovery rate indicator-naphthalene -D8.Extraction procedure: Put the prepared sample into the extraction tin, and then add 25mL solvent to do the extraction in microwave extraction instrument. Extraction conditions: the solvent is acetone/ n-hexane (1:1, V/V) , 25 mL, and the temperature should be 105 °C, then warm for 10 mins, maintain for 10 mins , and cool for 30 mins to room temperature; then conduct rotary evaporation after extraction, concentrating the sample to about 1 mL.

Sample Purification

Purification reagent pretreatment: anhydrous Na_2SO_4: dipping into methanol and cleaning with ultrasonic washer for half an hour, Soxhlet extraction in dichloromethane for 72h, burning for 4 hours at 450 °C. Activating silica gel: dipping into methanol and cleaning with ultrasonic washer for half an hour, Soxhlet extraction in dichloromethane for 72 hours, activating for 12 hours at 180°C and preserved in bottle after getting dry naturally under room temperature. Activating alumina: dipping into methanol and cleaning with ultrasonic washer for half an hour, using Soxhlet extraction in dichloromethane for 72 hours, activating for 12 hours at 250°C and preserved in bottle after getting dry naturally under room temperature. Select the glass column with a knob at diameter 1.5cm, adding absorbent cotton at the bottom, then packing dry column. Firstly, wet with n-hexane 30mL, then choose the sample, and clean with 30mL of n-hexane, remove impurities. Secondly, clean with 150mL of dichloromethane, then collect the eluent. Finally concentrate to 5 mL by rotary evaporation, blow by pressured gas, bring to volume 1mL by n-hexane, and put it in the GC-MS sample bottle.

Sample Testing

DB - 5ms Silica capillary column (30m×0.25mm×0.25um). Chromatographic column temperature program: maintain at 60 °C, heating up to 300 °C by 5 °C per minute, then maintaining 10 min; Inlet temperature at 250 °C; temperament transfer line temperature at 290 °C; flow rate of carrier gas: 1ml/min; injection mode: splitless (0.75 min) ; injection volume: l uL; mass spectrometry ion source is Electron Impact (EI); electron multiplier voltage is 2893ev; scan mass range (m / z) is 50-350amu; selecting ion monitoring mode.

Quality Assurance and Control

In order to reduce testing error, we carried out two parallel samples at each station and tested twice in parallel for each sample. Take 3'# sample as example (shown in Table 2), it adopts deuterated naphthalene as the indicator of recovery rate to control the quality. The result shows that recovery coefficient is between 50.7% and 68.9%, and relative standard deviation of each parallel sample is between 1.5% and 5.9% and all of them meet the requirements.

Table 2 QA/QC report of sample 3'#

PAHs	testing result (ng/g)				average (ng/g)	RSD (%)
	1	2	3	4		
Nap	35.8	36.3	31.8	33.9	34.45	5.9
Any	108.9	105.9	107.4	112.7	108.725	2.7
Ane	45.3	47.2	46.6	48.1	46.8	2.5
Fle	35.8	38.4	35.8	36.8	36.7	3.3
Phe	28.4	26.8	27.6	28.9	27.925	3.3
Ant	27.5	28.1	26.9	25.3	26.95	4.5
Fla	152.3	154.8	157.3	157.2	155.4	1.5
Pyr	14.8	14.9	15.1	16.2	15.25	4.2
Baa	70.3	68.5	71.1	72.5	70.6	2.4
Chr	15.4	16.9	15.2	14.3	15.45	7.0
Bbf/Bkf	140.6	138.7	142.3	144.2	141.45	1.7
Bap	28.9	28.4	30.8	31.6	29.925	5.1
Daa	31.4	30.2	32.5	31.7	31.45	3.0
I1p/Bgp	8.9	8.7	9.3	9.5	9.1	4.0

Testing Result

For the 7 effective samples, we tested all the target materials (16 kinds of PAHs-EPA) and the result is illustrated in Table 3.

Table 3 Testing results of each site sample PAHs (ng/g)

PAHs	1#	1'#	2#	3#	3'#	4#	5#
Nap	ND	ND	ND	ND	34.5	ND	ND
Any	ND	101.2	ND	ND	108.7	ND	ND
Ane	ND	44.5	ND	ND	46.8	ND	ND
Fle	ND	ND	ND	ND	36.7	ND	ND
Phe	ND	ND	ND	ND	27.9	ND	ND
Ant	ND	ND	ND	ND	26.9	ND	ND
Fla	ND	155.0	ND	ND	155.4	9.4	ND
Pyr	5.8	112.7	10.3	5.4	15.3	9.0	9.5
Baa	ND	93.5	5.2	ND	70.6	ND	ND
Chr	5.3	ND	3.1	6.7	15.5	4.2	21.2
Bbf /Bkf	33.2	61.3	ND	ND	141.5	ND	13.7
Bap	41.4	65.3	ND	ND	29.9	4.2	7.0
Daa	103.7	ND	ND	897.1	31.5	154.1	ND
I1p/ Bgp	68.2	ND	ND	ND	34.5	136.9	ND
total	257.6	633.5	18.6	909.2	755.5	307.2	45.4
Note	ND means not detected, the same below.						

As shown in Table 3, we can come to the primary conclusion or suggestions that: Firstly, the total content of PAHs in each station is between 18.6 to 909.2 ng/g in Nansi Lake, and the content of PAHs in the 2^{nd} level lake dam region(3# . 3'# stations) which is located in the middle of the lake is highest , While the southern and northern regions of lake is comparatively low. It means the pollution in central part of Nansi Lake is even worse and we should pay more attention to pollution control in this area. Secondly, the total amount of PAHs in other stations in 2012 is less than that in 2002 in Nansi Lake except 3# station(the 2^{nd} level dam). On the whole, in recent years, the content of PAHs shows a decreasing trend in Nansi Lake. At the same time, it should also be noted that the total contents of PAHs are still high in some stations (such as 1 #, 3 # and 4 #), and continue to show an upward trend in certain station. (such as 3 #). Thirdly, the content of PAHs of simple structure is very little in Nansi Lake while in recent years there are some complex polycyclic Aromatic Hydrocarbons coming into existence in some areas and accumulating, and they're still increasing, such as Naphthophenanthrene(a, h), indeno (1,2,3-cd) pyrene and benzo (ghi) perylene. These complex PAHs are more easily accumulated in the surface sediments of lake-bottom due to their high boiling points, and they deserve more attention in pollution control in the future[8].

Conclusion

On the basis of measured data and previous research results, this paper preliminarily analyzed the distribution, content, and changing trend of PAHs in Nansi lake basin. The current test results show that the pollution control has achieved significant results and the water quality is continuously improving in recent years. But, some PAHs of complex structure still exist which are potentially threatening the water quality of Eastern Route of South-to-North Diversion project. Further effective measures should be taken in the future pollution control work of Eastern Route project to reduce the adverse impact of these kinds of PAHs on water quality security. In addition, this paper measured and analyzed only 7 samples from 9 stations in Nansi Lake, which means the samples are insufficient and we should increase the number of sampling sites, and then thoroughly analyze the distribution, content, and changing trend of PAHs of Nansi lake basin, which will help to conduct pollution control in Nansi Lake basin in future.

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