

8-1-2014

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## Recommended Citation

Jijun, Gao, "The Typical Organic Pollutants Health Risk Research Of The Main Source Water In Yellow River Basin" (2014). *CUNY Academic Works*.  
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## **THE TYPICAL ORGANIC POLLUTANTS HEALTH RISK RESEARCH OF THE MAIN SOURCE WATER IN YELLOW RIVER BASIN**

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### **ABSTRACT**

The benzene, toluene, nitrobenzene, p-nitrochlorobenzene, 2,4-dinitrotoluene and 2,4-dinitrochlorobenzene, dichlorvos, demeton, dimethoate methyl parathion, malathion and parathion were more frequently detected in the main source water of Yellow River basin, especially the organophosphorous pesticides, the detection rates of dichlorvos, demeton, methyl parathion, malathion and parathion are all much higher than 90% in the fifty source water points. The health risk assessment results suggested that the noncarcinogenic risk HQ values of the target compounds were less than one, and the cancer risk values of most source water sites were much less than the  $1 \times 10^{-6}$ , only the sites 23,24,25,26 cancer risk values were much higher than the  $1 \times 10^{-6}$ , which indicated that the health risk produced by the target compounds in the most source water was in an acceptable level.

Keywords Yellow River basin, benzene, organic pollution, source water

### **1. INTRODUCTION**

With an area of 752443 km<sup>2</sup> and flowing through 11 provinces from Tibet to Shandong Province, entering into Bohai Sea. The Yellow River basin is the second largest water system in China. Because of the rapid development of economy and explosion of city population, water pollution and shortage have become a stupendous obstacle to the sustainable development of social economy in this area [1]. Organic pollutants have been of great concern because of the large production and usage, their deleterious effect on non-target organism, ubiquity, bioaccumulation and persistence in the environment[2]. Especially the organophosphorous pesticides (OPPs), Nitrobenzene compounds, chlorobenzene compounds and benzene homology were the most extensively used chemicals in China, resulting in widespread contamination in various environmental compartments[3-5]. To understand the contamination status and potential affection to drinking water safety of the representative organic pollutants in the main source water of Yellow River basin, according to the Chinese surface water quality standard, samples collected from fifty source water of Yellow River basin were analyzed for benzene homology, chlorobenzene compounds, nitrobenzene compounds, organophosphorous pesticides(OPPs).

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## 2. MATERIALS AND METHODS

### 2.1 Sampling and Sample Pretreatments

Samples were collected from the fifty source water points, the global positioning system (GPS) was used to locate the sampling positions, the sites map distribution was shown in Fig 1.

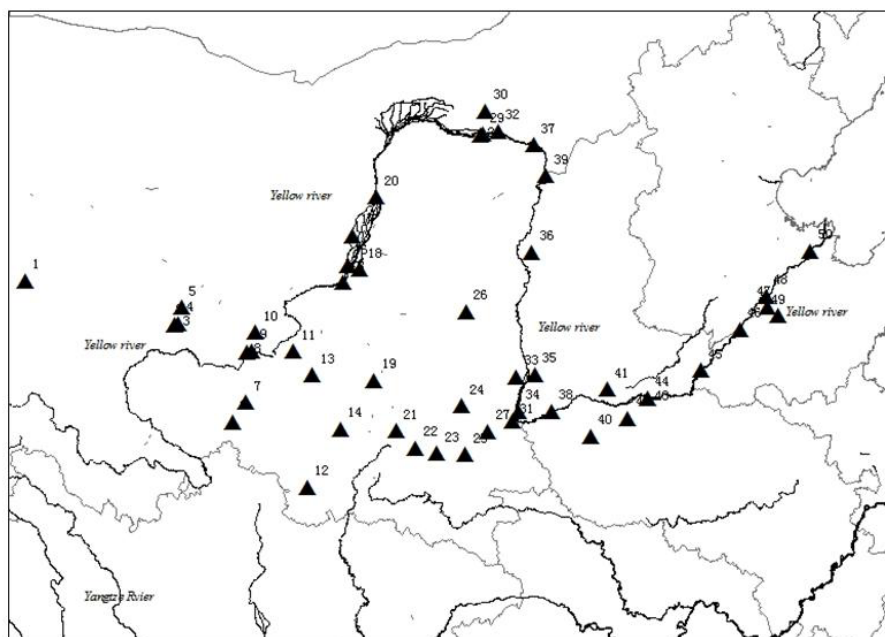


Fig.1. The sample points distribution map

Samples for benzene homology and chlorobenzene compounds analysis were collected in 2010 and should be put in amber glass sampling bottles, all the samples should be refrigerated and shipped to the laboratory, and maintain at the temperature 4°C, the analysis of all samples must be finished in 7 days. Samples for nitrobenzene compounds and OPPs analysis were collected in glass sampling bottles, all the samples must be extracted in field immediately and should be analyzed in two weeks. Aliquots of the sample (5.0 l) were filtered through a 0.45 µm glass fiber membrane under vacuum and then surrogate standards (1,3-dimethyl-2-nitrobenzene, perylene-D12) were added[6]. Water samples were extracted by solid phase extraction (SPE) following published procedures [7-9]. All the samples were collected in duplicate. Samples for nitrobenzene compounds and OPPs analysis were collected in glass sampling bottles.

### 2.2. Chemical Analysis

#### 2.2.1 Benzene homology and chlorobenzene compounds analysis

All solvents used for sample processing and analysis were HPLC grade. Deionized water was prepared using a Milli-Q system (Millipore, Watford). Chemical standards of all the compounds were obtained from Supelco. To all samples, blanks, and calibration standards, add internal standard (fluorobenzene) and the surrogates (1,2-dichlorobenzene-d4, BFB). Standards and samples must be analyzed in exactly the same way and room temperature should be reasonably constant.

## 2.2.2 Nitrobenzene compounds and OPPs analysis

Working standards were prepared in methylene chloride, the internal standards (acenaphthene-D10, phenanthrene-D10, and chrysene-D12) and the surrogates (1,3-dimethyl-2-nitrobenzene, perylene-D12) were added to each working standard. These solutions were further diluted with methylene chloride to prepare calibration solutions.

An agilent 6890 GC coupled to a model 5973N MS detector in selected ion mode was used for nitrobenzene compounds and OPPs analysis. The capillary columns were HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The carrier gas was helium for MS. The inlet was heated to 200°C. The GC column temperature was programmed as follows: initially at 60°C (equilibrium time 1 min), increased to 140°C at the rate of 10°C min<sup>-1</sup>, then to 230°C at 5°C min<sup>-1</sup> before reaching 260°C at 10°C min<sup>-1</sup> and held for 5 min. The MS temperature was set at 280°C and the electron impact energy was 70eV.

## 2.3. Risk Analysis

In order to estimate the daily exposure of an individual, U.S EPA[10] suggests the Lifetime Average Daily Dose (LADD) as the exposure metric. The following equation is a similar representation of daily exposure for ingestion route modified from U.S EPA[11] and Chrostowski[12]:

$$CDI = \frac{C \times DI}{BW} \quad (1)$$

Where CDI is the chronic exposure dose (mg/kg.d), DI is the average daily intake rate of drinking water (2.2l/d), C is the drinking water contaminant concentration (mg/l), and the BW is average body weight (70kg). Values of these three input variables, specific to each subject, were used to estimate the subject individual's chronic daily exposure level. Deterministic exposure assessment involved using Eq.(1) to estimate individual exposures. Lifetime cancer risk associated with ingestion exposures is calculated using the following equation[10,11]:

$$R = CDI \times SF \quad (2)$$

where R is the probability of excess lifetime cancer, and SF was the cancer slope factor of the chemical(mg/kg.d). To estimate noncarcinogenic risk, the hazard quotient(HQ) was calculated using the following equation[13]:

$$HQ = \frac{CDI}{RfD} \quad (3)$$

Where RfD is the reference dose (mg/kg.d). SF and RfD values employed in this study were obtained from USEPA[14]. The RfD and SF values of the target compounds were shown in the table 1.

Table 1. The list of chosen target compounds and data from the Integrated Risk Information System (IRIS) of USEPA

compounds	Reference dose(RfD) (mg/kg.day)	Slope factor(SF) (mg/kg.day)
Benzene homology		
benzene	$4 \times 10^{-3}$	$5.5 \times 10^{-2}$
toluene	$8 \times 10^{-2}$	--
ethylbenzene	$1 \times 10^{-1}$	--
isopropylbenzene	--	--
Chlorobenzene compounds		
1,4-dichlorobenzene	--	--
1,2-dichlorobenzene	$9 \times 10^{-2}$	--
chlorobenzene	$2 \times 10^{-2}$	--
Organophosphorous		
pesticides		
dichlorvos	$5 \times 10^{-4}$	$2.9 \times 10^{-1}$
demeton	$4 \times 10^{-5}$	--
dimethoate	$2 \times 10^{-4}$	--
methyl parathion	$2.5 \times 10^{-4}$	--
malathion	$2 \times 10^{-2}$	--
parathion	--	--
Nitrobenzene compounds		
nitrobenzene	$2 \times 10^{-3}$	--
p-nitrochlorobenzene	--	--
2,4-dinitrotoluene	$2 \times 10^{-3}$	--
2,4-dinitrochlorobenzene	--	--

#### 2.4. QA/QC Procedures

The residue levels of the target compounds were quantitatively determined by the internal standard method using peak area. The method detection limits (MDLs) of the target compounds were taken to be 3:1 signal versus noise value (S/N). For every set of 10 samples, a procedural blank and a spiked sample with standards were run to check for the interference and cross-contamination.

#### 2.5. Statistical analysis

Values for all the target compounds lower than MDL were substituted with zero prior to statistical analysis, software Excel was used in this study.

### 3. RESULTS AND DISCUSSION

#### 3.1. The concentrations results of the target compounds

##### 3.1.1 The concentrations of the benzene homology and chlorobenzene compounds

For all the samples, the detection rates of the four compounds were 100%, 98%, 54% and 52%, respectively. The concentrations for benzene ranged from 20.0 to 15200.0 ng l<sup>-1</sup>, with a mean level of 1049.0 ng l<sup>-1</sup>, and the 90% percentile value was 507.0 ng l<sup>-1</sup>. The concentration range of toluene was from <12.5 to 9540.0 ng l<sup>-1</sup>, with a mean value of 601.6 ng l<sup>-1</sup>, and the 90% percentile value was 989.0 ng l<sup>-1</sup>; the ethyl benzene concentration ranged from <14.3 to 280.0 ng l<sup>-1</sup>, and the 90% percentile value was 131.0 ng l<sup>-1</sup>. The concentration of isopropylbenzene was from <8.5 to 90.0 ng l<sup>-1</sup>, with a mean value of 7.2 ng l<sup>-1</sup>, and the 90% percentile value was 10.0 ng l<sup>-1</sup>.

### 3.1.2 The concentrations results of the nitrobenzene compounds and organophosphorous pesticides

For all the samples, the detection rates of the nitrobenzene, p-nitrochlorobenzene, 2,4-dinitrotoluene and 2,4-dinitrochlorobenzene were 80.0%, 86.0%, 78.0% and 90.0%, respectively. The detection rates of the four nitrobenzene compounds were similar. In addition, it was also known that the mean values of the nitrobenzene, p-nitrochlorobenzene and 2,4-dinitrochlorobenzene were 218.2 ng l<sup>-1</sup>, 278.4 ng l<sup>-1</sup> and 675.4 ng l<sup>-1</sup>, ranged from <6.2 to 8450.0 ng l<sup>-1</sup>, <10.5 to 12420 ng l<sup>-1</sup>, <14.2 to 32210.0 ng l<sup>-1</sup>, respectively. Relative to the nitrobenzene, p-nitrochlorobenzene and 2,4-dinitrochlorobenzene, the mean levels of the 2,4-dinitrotoluene were 62.6 ng l<sup>-1</sup>, with a concentration range from <10.8 to 840 ng l<sup>-1</sup>.

The detection rates of the dichlorvos, demeton, dimethoate, methyl parathion, malathion and parathion were 100%, 98%, 68%, 98%, 100% and 98%, respectively. Compared with the benzene homology, chlorobenzene compounds and nitrobenzene compounds, the detection rates of organophosphorous pesticides were much higher, which proved that the organophosphorous pesticides widely occurred in the Yellow River basin.

### 3.2 The health risk assessment results

The carcinogenic and noncarcinogenic risks attributable to nitrobenzne compounds, benzene homology, OPPs and chlorobenzene compounds were assessed using the deterministic approach. Carcinogenic risk values greater than 1 in a million (10<sup>-6</sup>) are generally considered unacceptable by the U.S EPA[15]. However, this acceptable level may change according to national standards and environmental policies and may be as high as 10<sup>-4</sup>[16,17]. HQ values of the noncarcinogenic risks greater than one indicated a potential for an adverse effect to occur or the need for the further study.

For this study, the noncarcinogenic risk of isopropylbenzene and 1,4-dichlorobenzene could not be calculated since the RfD were not available for them. According to the noncarcinogenic risk result, it should be seen that the calculated HQ values pointed out negligible noncarcinogenic risks, even the maximum total HQ value for the source water point 26 was almost 3 times less than one. For the cancer risk, the cancer risks of benzene and dichlorvos could be calculated, while the other compounds could not be calculated since SFs of them were not available. A range was given for the SF of benzene [14]; the upper limit of the given range was used in calculations. In the Table 2, the statistics of carcinogenic risk were presented. According to the Table 3, it should be concluded that the cancer risk values of benzene and dichlorvos in the most source water sites were all less than the 1×10<sup>-6</sup>, only the sites 23,24,25,26 cancer risk values were higher than the 1×10<sup>-6</sup>, the maximum total cancer risk value (2.64×10<sup>-5</sup>) occurred in the source water point 26, followed by the 25, 24, 23, the cancer risk values were 2.338×10<sup>-5</sup>, 1.711×10<sup>-5</sup> and 1.367×10<sup>-5</sup>, respectively. So the cancer risks produced by the benzene and dichlorvos of the sites 23,24,25,26 were in the unacceptable level and should be given more attention.

Table 2. The statistical results of cancer risk for benzene and dichlorvos ×10<sup>-6</sup>

Source water number	Benzene cancer risk level	Dichlorvos cancer risk level	Total cancer risk level
1	0.1	0.0	0.1
2	0.1	0.1	0.2
3	0.1	0.1	0.1
4	1.9	0.1	2.0
5	0.1	0.0	0.1
6	0.1	0.0	0.1

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7	0.1	0.0	0.1
8	0.1	0.0	0.2
9	0.2	0.0	0.2
10	0.2	0.0	0.2
11	0.0	0.0	0.1
12	0.1	0.0	0.1
13	0.1	0.1	0.2
14	0.1	0.0	0.1
15	0.1	0.0	0.1
16	0.2	0.0	0.2
17	0.1	0.0	0.1
18	0.2	0.0	0.3
19	0.2	0.0	0.2
20	0.2	0.0	0.2
21	0.2	0.0	0.3
22	0.6	0.1	0.7
23	13.7	0.0	13.7
24	17.1	0.0	17.1
25	23.4	0.0	23.4
26	26.3	0.1	26.4
27	0.3	0.0	0.3
28	0.1	0.0	0.1
29	0.2	0.0	0.2
30	0.2	0.0	0.2
31	0.1	0.0	0.1
32	0.2	0.0	0.2
33	0.2	0.0	0.2
34	0.2	0.0	0.2
35	0.2	0.0	0.3
36	0.1	0.1	0.2
37	0.1	0.0	0.1
38	0.8	0.0	0.8
39	0.4	0.0	0.4
40	0.3	0.0	0.3
41	0.2	0.1	0.3
42	0.1	0.0	0.1
43	0.1	0.0	0.1
44	0.1	0.0	0.2
45	0.1	0.0	0.1
46	0.2	0.1	0.3
47	0.4	0.0	0.4
48	0.6	0.0	0.6
49	0.1	0.0	0.1
50	0.3	0.1	0.4

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#### 4. CONCLUSIONS

The levels of the 17 compounds in the fifty source water sites were all below the corresponding standard limits of the environmental quality for surface water (chinese), and the benzene, toluene, nitrobenzene, p-nitrochlorobenzene, 2,4-dinitrochlorobenzene, dichlorvos, demeton, methyl parathion, malathion and parathion were more frequently detected in the fifty source water sites, which indicated that they were the main organic pollutants in the main source water of the Yellow River basin. The health risk assessment results suggested that the noncarcinogenic risk HQ values of the target compounds were less than one, and the cancer risk values of most source water sites were all less than the  $1 \times 10^{-6}$ , only the sites 23,24,25,26 cancer risk values were higher than the  $1 \times 10^{-6}$ , which indicated that the cancer risks produced by the benzene and dichlorvos of the sites 23,24,25,26 were in the unacceptable level and should be given more attention.

#### ACKNOWLEDGEMENTS

This work was supported by Non-profit Industry Financial Program of MWR (201201032) and Major Science and Technology Program for Water Pollution Control and Treatment(2012ZX07104-001).

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