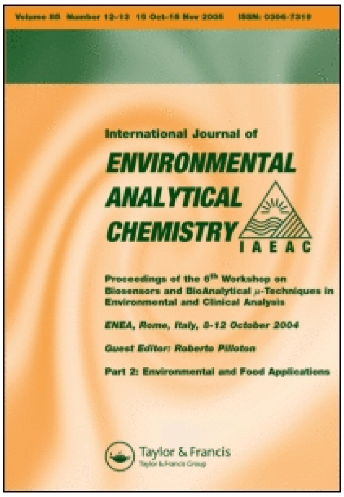

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Chemical Analysis and Toxicity Tests of Organic Pollutants in Xi River Water and Suspended Sediment of Shenyang City

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CHEMICAL ANALYSIS AND TOXICITY TESTS OF ORGANIC POLLUTANTS IN XI RIVER WATER AND SUSPENDED SEDIMENT OF SHENYANG CITY

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In 1987, in a 10-day investigation, two kinds of raw water and their suspended sediment samples were successively collected from the upper and middle reaches of the Xi River. The water and the suspended sediment samples were prepared by filtration of the raw water through a 0.45 μm membrane. The pH values of the water samples were adjusted to neutral (pH 6.5), basic (pH 11.0) and acid (pH 2.0) and passed through three adsorption columns filled with GDX macroreticular resin (MRR). The organic pollutants were subsequently eluted from the columns with CH_2Cl_2. Suspended sediment samples were extracted with CH_2Cl_2 by Soxhlet extraction. Organic pollutants were separated on silica gel columns and analyzed by GC and GC-MS and assayed for acute toxicity, Ames test response, and micronucleus test response. Over 200 organic pollutants in the river water and the suspended sediments were determined. More than 60 main pollutants were identified according to the results of the chemical analysis and toxicity tests.

KEY WORDS: Organic pollutants, suspended sediment, macroreticular resin (MRR), acute toxicity test, Ames test, micronucleus test.

INTRODUCTION

The Xi River is a major canal into which more than 4.2 x 10^5 tonnes of wastewater flow daily from the west industrial area of the city of Shenyang in Northeast China. Being polluted, the raw water of Xi River is black, muddy, and malodorous, and cannot be directly used for irrigation. Shenyang is located in an area which is short of water. In order to keep the release of pollutants under control, to set up engineering project for wastewater treatment, and to render the Xi River containing the treated wastewater suitable for irrigation, it is very important to identify the major pollutants in the water system using chemical analysis and toxicity tests, and minimize their entry into the Xi River.

The use of macroreticular resins (MRR) for the adsorptive extraction of organic pollutants from water is a common concentration technique[1-3]. Recent studies have indicated that the acidic, basic, and neutral organic chemicals in water can be adsorbed separately on a MRR column by adjusting the pH value of water sample.

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MATERIALS AND METHODS

Chemicals and materials

Acetone, dichloromethane (DCM), hexane, and methanol were AR purity and were redistilled in glass at our laboratory. NaOH, Na_2CO_3, H_2SO_4, acetic anhydride and other chemicals were AR or GR purity. Anhydrous Na_2SO_4 (AR) was heated at 400°C for 4 h. The chromatography silica gel was 60–100 mesh. GDX-301 (less polar) and GDX-502 (polar) macroreticular resin (MRR), 40–60 mesh, were obtained from the Second Chemical Agent Factory of Tianjin, China. The MRR were Soxhlet-extracted respectively with acetone and DCM for 8 h, and then stored under CH_3OH.

The *Daphnia carinata* King used for the acute toxicity tests were 0–16 h old. The mice for the bone marrow micronucleus tests were male and 18–22 g each. The *Salmonella typhimurium* histidine auxotrophic strains TA98 and TA100 for the Ames tests were obtained from the Tumor Institute of Shanghai, China.

Sampling

In order to understand the nature of the pollution of the Xi River, and to provide sufficient organic pollutant fractions for toxicity tests, 800 L of raw water were collected at each sampling point over a period of 10 days (March 6–15, 1987) from the headwaters channel (the upper reaches, sampling as UW) and from the Ganguan bridge (the middle reaches, sampling as MW) of the Xi River near the western area of the Shenyang city, China. The depth of water was < 1 m.

At the each sampling point, ca. 80 L raw water collected daily contained a considerable amount of suspended sediment. The water was opaque and had pH 6.5 and temperature 10–15°C.

The raw water samples were filtered immediately through 0.45 μm filter membranes. The particulate matter remaining on the filter membrane was considered to represent suspended sediment from the water samples. In this manner, 2.0 kg (wet weight) of upper reaches suspended sediment (USS) and 2.6 kg (wet weight) of middle suspended sediment (MSS) were obtained.

Enrichment and classification

The treated GDX-301 and GDX-502 MRR were mixed 1:3 (V/V) and formed the packing (13 g) of the first column. The second and third columns were packed with 13 g GDX 502 MRR. The columns were 20 mm i.d. x 250 mm.

The enrichment and classification procedure are shown in Figure 1. The flow rate of water through the MRR columns was 20 mL/min. The MRR columns could be used to sample up to ca. 50 L of water. The acidic(A), basic(B), neutral(N) and other components of organic pollutants were subsequently separated.

Wet suspended sediment samples obtained daily were stored at 4°C. Raw water samples were composited before extraction. Sediment samples were dried by admixture with anhydrous Na_2SO_4, screened (< 36 mesh), and Soxhlet extracted with CH_2Cl_2 for 10 h. The extract was cleaned up on a silica gel column and the pollutants separately eluted in *n*-hexane, *n*-hexane/CH_2Cl_2 (1:1, v/v), CH_2Cl_2, and CH_2Cl_2/CH_3OH (1:1, v/v).

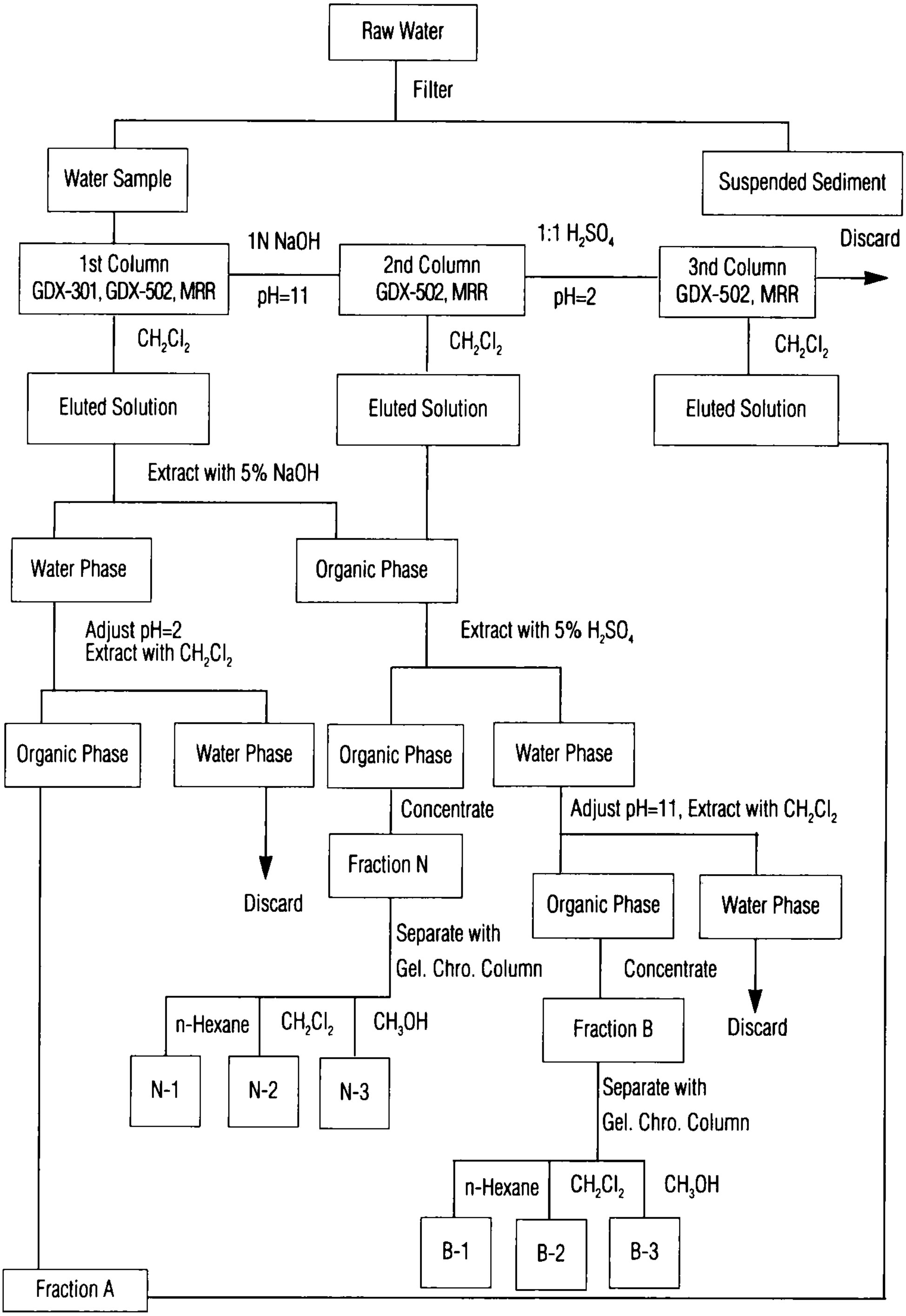

Figure 1 Classification system for organic pollutants in water samples.

From the 2 suspended sediment samples (USS and MSS), 8 component pollutants were separated: USS-1, USS-2, USS-3, USS-4; MSS-1, MSS-2, MSS-3, and MSS-4. The fractions were dried by passage through anhydrous Na_2SO_4, concentrated on a rotary vacuum evaporator, and analyzed using both chemical and toxicity tests.

Analysis

Where possible, fractions were analyzed directly by GC and GC-MS. Polar fractions were acylated as follows: 10 mL 5% Na_2SO_4 was added with stirring and, following centrifugal separation, 5 mL acetic anhydride was added to the aqueous layer and allowed to stand for 20 min. The solution was extracted with hexane and concentrated to 0.2 mL for analysis.

. GC analyses was performed on a Chinese gas chromatograph, SC-7 GC, equipped with an OV-101 capillary column and a flame ionization detector. The injector and detector were maintained at 240°C and 280°C respectively. Column temperature: 50°C for 4 min, 4°C/min to 240°C. Nitrogen was used as the carrier gas. Injection volumes were 1–2 μL.

GC-MS analyses were performed on a Finnigan-MAT 4510 GC-MS. GC conditions: OV-101 capillary column (0.22 mm i.d. x 50 m); column temperature: 80°C or 5 min, 4°C/min to 290°C. Injector temperature was 280°C. MS conditions: ionizing voltage, 70 ev; filament current, 0.23 mA; electron multiplier, 1400 volts; mass range, 30–500 amu; scan time, 1 sec. A NBS library was used in the identification of the pollutants present in the extracts.

HPLC analyses were performed on a Varian 5000 HPLC. HPLC conditions: CH-10 column (4 mm i.d. x 30 cm); column temperature, 30°C; mobile phase, CH_3OH/water (75:25, v/v); flow rate, 1.0 mL/min; UV detector at 254 nm.

UV quantification of benzoic acid as performed on a 751 model UV/vis spectrophotometer of Chinese manufacture.

The major organic pollutants in water samples were quantitatively determined using the Analytical Methods of Organic Pollutants of the U.S.A. EPA[4]. To enable the organic pollutants to be qualitatively identified in the samples, the weighting factors for 13 typical chemicals were determined by GC. To quantitatively calculate the main organic pollutants in the suspended sediments, extraction recovery for 7 typical chemicals were added to sediment samples and determined by Soxhlet extraction. The sediment samples used for recovery studies for these compounds were preextracted with CH_2Cl_2 in a Soxhlet extractor for 16 h.

Toxicity testing

The biotoxicity tests for the above organic pollutant fractions, i.e., the acute toxicity tests using *Daphnia carinata* King, the bone marrow micronucleus tests using the mice, and the Ames tests were carried out using literature methods[5–7].

RESULTS AND DISCUSSION

An enrichment method was designed by adjusting the pH value of the water samples and using 3 columns filled with different polarity MRRs to separately adsorb the acid, basic, and neutral organic chemicals. The recovery rates using simulated water samples are given in Table 1. Higher recoveries were consistently obtained using the 3-column technique.

The qualitative analysis results of organic pollutants in water and suspended sediment samples are given in Table 2. As the determined chemicals are too many, their categories are only listed.

The EPA Priority Organic Pollutants identified in the samples are given in Table 3. The results show that more than 200 organic pollutants including 17 EPA priority pollutants were identified in the MW, UW, MSS and USS samples. The main categories of organic pollutants identified in the classified compositions are briefly given in Table 4, indicating the organic pollutants identified in different components are related to their chemical properties, to the polarity of MRR, to the acidity or basicity of water samples, and to the polarity of solvents eluting the silica gel chromatography cleanup columns.

Table 1 Percent recoveries of organic chemicals from water for one- and three-column techniques.

Chemicals	*Anal. method*	*Concn. (μg/L)*	*R (%) 1 column*	*R (%) 3 column*
1. Anthracene	HPLC	9.9	53	57
2. Naphthalene	HPLC	23.2	60	88
3. *p*-Dinitrophenylamine	HPLC	21.8	75	92
4. Nitrobenzene	HPLC	20	86	118
5. Quinoline	HPLC	50	62	80
6. Dibutyl phthalate	HPLC	100	71	94
7. Chlorobenzene	HPLC	100	58	100
8. *p*-Dimethylbenzene	HPLC	150	45	60
9. Benzoic acid	UV	1000	47	108

Table 2 Numbers of organic pollutants identified in the samples.

Organic pollutants	*MW*[a]	*UW*	*MSS*	*USS*
1. Aliphatic hydrocarbons	27	5	62	42
2. Aromatic hydrocarbons	12	19	9	11
3. Halogen hydrocarbons	8	4	5	6
4. Aldehydes and ketones	24	12	11	8
5. Ethers	8	3	4	2
6. Esters	18	13	13	8
7. Compounds containing nitro	6	5	2	1
8. Nitriles	2	2	4	2
9. Amines	2	4	5	1
10. Heterocyclic compounds	26	13	9	1
11. Alcohols	23	8	8	5
12. Phenols	11	11	3	2
13. Carboxylic acids	15	17	8	10
14. Others	–	–	3	–
Total	182	116	146	99

[a] MW and UW = water from the middle and upper reaches of the Xi River, respectively; MSS and USS = suspended sediments from the same sampling points.

Table 3 U.S. EPA priority organic pollutants identified in Xi River water and sediment.

Pollutants	*MW*	*UW*	*MSS*	*USS*
1. Acenaphthene	+[a]	+	+	−
2. α-BHC	+	+	+	+
3. β-BHC	−	+	+	−
4. γ-BHC	−	−	−	+
5. δ-BHC	−	−	−	+
6. Chlorobenzene	+	−	−	−
7. Di-*n*-butyl phthalate	−	+	+	+
8. Diethyl phthalate	−	+	−	−
9. 2,4-Dichlorobenzene	+	+	−	−
10. Di-*n*-octyl phthalate	+	−	+	+
11. Ethyl benzene	+	−	−	−
12. Isophorone	+	−	+	−
13. Naphthalene	+	+	+	−
14. Phenanthrene	−	+	+	+
15. Phenol	+	+	+	−
16. Pyrene	−	−	−	+
17. Toluene	+	−	−	−
Total (17)	10	9	9	7

[a] + = identified.

Table 4 Main categories of organic pollutants in the classified components.

Fractions	*Main categories of organic pollutants*
UW-B[a]	Amines, heterocyclic compounds
UW-N-1	Arenes, halogen hydrocarbons, aldehydes, ketones, ethers, nitriles, compounds containing nitro
UW-N-2	Nitriles, esters
UW-A	Alcohols, carboxylic acids, phenols
MW-B	Heterocyclic compound, amines
MW-N-1	Aliphatic hydrocarbons, arenes, esters
MW-N-2	Ketones, aldehydes, nitriles, ethers, compounds containing nitro
MW-N-3	Aliphatic hydrocarbons, ketones, esters, ethers
MW-A	Alcohols, carboxylic acids, phenols
MSS-1	Alkanes, alkenes
MSS-2	PAHs, HCBs(α-, β-, γ-), halogenated hydrocarbons
MSS-3	Ketones, phenols
MSS-4	Carboxylic acids, alcohols
USS-1	Alkanes, alkenes
USS-2	PAHs, heterocyclic compounds, HCBs(α-, β-, γ-)
USS-3	Phenols, ketones
USS-4	Carboxylic acids, alcohols

[a] B = basic extract, N = neutral extract (fractions, 1,2, and 3 where applicable), and A = acidic extract.

The results of toxicity tests are given in Table 5. Toxicities are related to the properties and amounts of organic pollutants and tested biospecies. Because they contained many hydrocarbons, the extracts such as MW, MSS-1, MSS-2, USS-1 have high acute toxicity to Daphnia carinata. The mutagenicity, however, mainly depend on carcinogenic chemicals (such as PAHs, aromatic amines, halogen hydrocarbons) and

Table 5 Results of toxicity tests for the pollutants present in water and suspended sediment samples from the Xi River.

Samples	*Mortality (Daphnia carinata) (in 48 h)*	*Mutagenicity micronuclei test*	*Mutagenicity Ames text (TA98)*	*(TA100)*
MW	100.0		+	+
MW-A	37.5	+	+	–
MW-B	34.4	–	+	–
MW-B-1	2.2			
MW-B-2	7.8			
MW-B-3	10.0			
MW-N	34.4	++	+	+
MW-N-1	21.0	+	–	–
MW-N-2	15.0	–	–	+
MW-N-3	16.1		+	+
UW	11.1		+	+
UW-A	2.0		+	–
UW-B	3.8		+	–
UW-N	4.4		+	+
MSS	48.0	–		
MSS-1	88.9	+		
MSS-2	66.8	–		
MSS-3	35.6	–		
MSS-4	4.4	–		
USS	43.8	–		
USS-1	60.0	–		
USS-2	16.7	–		
USS-3	14.4	–		
USS-4	14.4	–		

"+" Means positive, "++" Means more positive, "–" Means negative.

their concentrations. The sampes, MW, MW-N, UW, MSS-1, which contain such kinds of chemicals, had high mutagenicity.

The quantitative formula for water sample extracts is

$$C_i = (M_{is}/A_{is})\cdot A_i\cdot(V_o/V_w) \qquad (1)$$

where C_i is the concentration of i organic pollutant in the water, V_w is the sample volume, A_i and A_{is} are the peak areas separately produced by GC to analyze i organic chemical and the standard chemical of i category, M_{is} is the concentration of standard chemical of i category, V_o is the concentrated volume of sample. The ratio M_{is}/A_{is} is the weight correction factor (f). Some f values determined are given in Table 6. With f replacing M_{is}/A_{is}, the formula (1) becomes

$$C_i = f_i\cdot A_i\cdot(V_o/V_w) \qquad (2).$$

The quantitative formula for suspended sediment sample extracts is

$$M_i = f_i\cdot A_i\cdot V_o/W\cdot R_{is} \qquad (3)$$

where M_i is the content of i organic pollutants in sample, W is the weight of dry sample, f_i, A_i and V_o are the same as formula (1), R_{is} is the rate of recovery for typical chemicals added in the suspended sediment sample using Soxhlet extraction (Table 7).

Table 6 Values of weight correction factor (f) some typical standard chemicals.

Chemicals	*f* *($x10^{-4}$)*	*Chemicals*	*f* *($x10^{-4}$)*
Methylisobutylketone	3.91	Quinoline	1.28
Tetrahydrofuran	2.70	α-HBC	5.36
Pyridine	2.20	*n*-Heptadecane	1.82
Chlorobenzene	1.25	Methyl hexadecanoate	3.57
Nitrobenzene	0.63	Dimethylphthalate	4.79
n-Butanol	1.20	*o*-Methyl phenol	0.97
Naphthalene	1.95		

Table 7 Percent recovery for some pollutants by soxhlet extraction.

Chemicals	*R (%)*
Methylisobutylketone	50
n-Butanol	76.5
Naphthalene	88.0
n-Tridecane	85.1
α-HBC	115.3
Quinoline	78.9
Methyl hexadecanoate	87.9

Based on the amount and the toxicity of organic pollutants determined, the main pollutants in the samples of Xi River were identified (see Table 8 and 9). The results indicate that the water quality of the Xi River were seriously polluted, especially by hydrocarbons, pesticides, PAHs, and intermediates from pharmaceutical syntheses. Our investigation has provided scientific evidence to keep the release of pollutants under control, to set up engineering projects for wastewater treatment, and to render the Xi River containing the treated wastewater suitable for irrigation.

CONCLUSIONS

1. Organic pollutants can be effectively extracted from river water using macroreticular resins by adjusting the pH value of the water samples, by using 3 MRR columns separately to adsorb the neutral, basic and acid fractions from the corresponding pH value of water sample, and by using different polar MRR to concentrate the organic pollutants.

2. In the investigation, over 200 organic pollutants, including 17 U.S. EPA priority pollutants, were determined in water and suspended sediment from the Xi River. Among them, more than 60 main organic pollutants were qualitatively determined. The results indicate that the river water was seriously polluted, especially from the middle reaches of the river.

3. The results of toxicity tests indicate that the toxicity of organic pollutants is different for each test organism. The fractions mainly containing hydrocarbons are highly toxic for *Daphnia carinata*, but they are not mutagenic. On the other hand, the fractions

Table 8 Quantitative results of main organic pollutants in MW and UW samples.

Organic pollutants	*MW (mg/L)*	*UW (mg/L)*
1. Toluene	0.006	–
2. 1,2-Dimethylbenzene	0.011	–
3. 1-Ethyl-2-methylcyclopentane	0.006	–
4. Benzaldehyde	0.017	1.026
5. Phenyl isonitrile	0.018	–
6. Acetophenone	0.068	–
7. Chlorobenzene	0.081	–
8. 1,2,3-Trichlorobenzene	0.006	1.344
9. Quinoline	0.032	0.012
10. Naphthalene	0.070	0.039
11. 2-Methylnaphthalene	0.010	–
12. 1-Ethyl-4-nitrobenzene	0.115	0.025
13. 4-Nitrophenylethane-1-one	0.014	–
14. 3-Aminophenylethane-1-one	0.038	0.056
15. 2-Cyclohexylidenecyclohexanone	0.037	–
16. 5-Hexyldihydrofuranone	0.091	–
17. 1,3,7-Trimethyldihydropurine-2,6-dione	0.098	–
18. 2-(Dimethylamino)phenyl benzoic acid	0.028	–
19. Dihexyl ether	0.057	–
20. 9-Oxyloctadecen-2-ol	0.029	–
21. 2,4-Diphenyl-hydropyrrole	0.035	–
22. Diethyl phthalate	0.077	–
23. Di-*n*-butyl phthalate	0.260	0.115
24. Methyl tetradecanoate	0.422	0.032
25. Methyl hexadecanoate	0.059	0.078
26. 1,4-Dimethylbenzene	–	0.696
27. 1-Propynylbenzene	–	0.027
28. Benzylnitrile	–	0.076
29. 4-Nitrobenzaldehyde	–	0.028
30. 2-Methyl-5-ethylpyridine	–	0.013
31. N-Ethylaniline	–	0.004
32. 2,7-Dimethylnaphthalene	–	0.005
33. α-HBC	–	0.017
34. 1,2-Dihydroacenaphthylene	–	0.019
35. 9-Hydrofluorene	–	0.030
36. Phenanthrene	–	0.036
37. 2-(Dimethylamino)benzoic acid	–	0.006
38. Phenoxylacetic acid	–	0.027
39. 2-Phenylethyl acetate	–	1.561
40. Methyl 11-hexadecanoate	–	0.077
41. Methyl 10-octadecanoate	–	0.091

containing PAHs, aromatic amines, and halogenated hydrocarbons, showed mutagenicity by the Ames tests and micronucleus tests. The use of these toxicity tests can reflect the properties and amounts of organic chemicals in water and sediment samples from contaminated river systems.

4. The results from this investigation provide evidence that improvement of wastewater treatment systems within the watershed of the Xi River is required.

5. The nature and concentrations of contaminants in the water supply should be considered in regard to the use of wastewater for irrigation of the area of the Shenyang city.

Table 9 Contents of main organic pollutants in suspended sediment samples.

Organic pollutants	*MSS(mg/kg)*	*USS (mg/kg)*
1. *n*-Alkanes(C_{11}–C_{29})	832.05	482.42
2. 1,24-Trichlorobenzene	1.19	0.64
3. Biphenyl	–	0.17
4. Phenanthrene	18.75	–
5. Pyrene	2.00	1.30
6. α-HBC	19.34	11.20
7. β-HBC	8.05	–
8. γ-HBC	3.17	8.74
9. δ-HBC	–	2.10
10. hexadecanoic acid	70.83	31.62
11. Nonadecanoic acid	53.20	22.17
12. Hexadecanol	349.73	24.93
13. Diethyl phthalate	28.20	–
14. Di-*n*-butyl phthalate	33.60	10.20
15. Di-*n*-octhyl phthalate	51.12	19.56
16. Naphthalene	2.29	–
17. Acenaphthylene	0.60	–
18. Isophornone	3.69	–
19. *n*-Alkenes(C_{14},C_{15},C_{16},C_{17})	18.80	6.72
20. 4*H*-Cyclopenta[def]phenanthene	11.99	–
21. 8-Hydronaphthalene	1.06	–
22. Anthracene	14.82	1.08
23. 1-Chlorotetradecane	4.59	–
24. 1-Chlorooctadecane	12.12	–
25. Naphthalene-5,12-dione	24.81	–
26. Cyclopentane-1,3-dione	46.80	–
27. 3-Hexene-2,5-dione	2.60	–
28. 2-Methylnaphthalene	–	1.65
29. 9-Hydrofluoren	–	0.81
30. 1-Iodohexadecane	–	3.01
31. 2-Methylhexadecanal	–	5.87
32. Ethoxyoctadecane	–	2.87
33. Methylhexadecanoate	–	9.90
34. Methyltetradecanoate	–	2.98

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