

Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyl Contamination in DaTong City, China

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In recent decades, there has been a worldwide increase in interest in the fate and behavior of such persistent pollutants as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the environment (Alcock et al. 1996; Baek et al. 1991; Schnoor 1996). The persistence of these pollutants is due to their chemically stable nature, hydrophobicity, resistance to degradation, affinity for living systems, bioaccumulative capacity and general toxicity. (Bobovnikova et al. 1993; Tuominen et al. 1988). Reports on the status of PAHs and PCBs contamination are increasing in many areas (Galassi et al. 1997; Iwata et al. 1995; Jeremiason et al. 1994; Sanders et al. 1996).

China is the largest coal consuming country in the world. Three fourth of China's total energy comes, either directly or indirectly, from the burning of coal. As a result, PAH contamination in China is certainly one of the main environment problems.

DaTong City is located in northern ShanXi province, China. ShanXi province is the heavy chemical industry base of China. Recoverable coal reserves are 27% of the nation's total. ShanXi province contributes most of its coal to the other provinces. In recent years, with the development of industry, ShanXi province provides more secondary energy such as coke and electric power. Contamination becomes more and more serious. The Yu and Shili Rivers, the main rivers in DaTong City, have both become avenues of disposal for industrial and municipal wastes.

The purpose of this work is to determine the amount and distribution of PAHs and PCBs in water and crops from DaTong City, and examine the influence of organic contamination.

MATERIALS AND METHODS

Water samples were taken near the drainage mouth of several important industrial plants and along the Yu River and Shili River of DaTong City in May 1998. The sampling locations are shown in Figure 1, in which Sample A was the river

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A-E: River section along flow direction
 F-I: effluent point of industrial plant
 Flowing into Yu River:
 F: chemical plant
 H: chemical fabric plant
 I: pharmaceutical factory
 Flowing into Shili River:
 G: coking plant

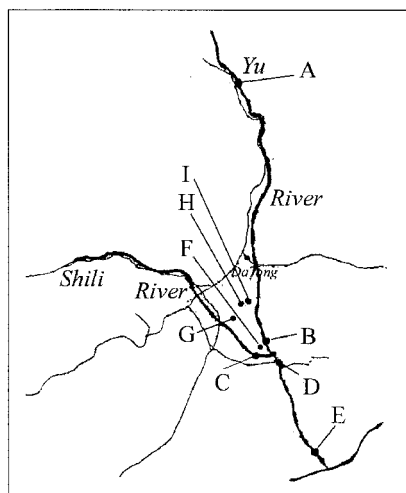


Figure 1. Map showing the sampling locations in DaTong City

upstream control site. Samples A-E were surface water, while Samples F-I were wastewater. Crop samples were taken near the first two sampling locations.

All reagents utilized were redistilled in all-glass appliances. Silica gel (100-200 mesh) from the Sea Chemical Plant of Qingdao, China and Florisil (60-100mesh) from the Yizhong Chemical Plant of Beijing were activated for 16h at 130°C before use.

For the determination of PAHs in water, 1 L water was liquid-liquid extracted with 60 mL hexane 3 times, then dried by anhydrous sodium sulfate. The extract was concentrated to about 1mL and cleaned using a silica gel column. The column was eluted with 25mL hexane and 50mL dichloromethane (DCM)/hexane (2/3,v/v) successively. A 35-65mL fraction was collected for PAHs analysis.

For determination of PAHs in crops, 200g ground samples were extracted for 2h in acetone. The extract was concentrated and transferred to a separator funnel with 25mL cyclohexane. Then, 50mL N, N-dimethylformamide/distilled water (9:1,v/v) was added to the funnel. After mixing and layering, the upper cyclohexane layer was discarded. The lower layer was extracted again with 100mL water/cyclohexane (1/1, v/v). The upper organic phase was washed with distilled water and concentrated to about 1mL. The concentrated sample was cleaned with a silica gel column to remove interfering compounds. After the eluent was concentrated again, the sample was transferred to a Sephadex LH-20 gel column (300 × 19mm I.D.) and eluted with cyclohexane-methanol-dichloromethane (5:4:3). The PAH was collected in a 60-100ml fraction. The fraction was concentrated to *ca.*, 1mL and the solvent was exchanged with hexane for GC analysis.

For the determination of PCBs in water, 1L was extracted with 60mL hexane three times. Then the extract was dried with an anhydrous Na₂SO₄ column and K.D. concentrated to about 3mL. To eliminate interfering organic co-extractants and macromolecules, 2mL concentrated sulfuric acid was added to the sample and vigorously shaken. After centrifugation, the sulfuric acid layer was discarded. The procedure was repeated several times until the acid layer remained colorless. The extract was then washed with 2% NaCl solution and dried with anhydrous Na₂SO₄. Further clean up was done by chromatography on the Florisil column. PCBs were eluted from the column in the first 30mL fraction using 6% ether/petroleum ether. After being concentrated to a proper volume, the sample was analyzed by Gas Chromatograph for PCBs.

GC analysis for PAHs was performed with a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with a flame-ionization detector and fused silica capillary column, coated with SE-52 (12m × 0.25mm). The chromatographic parameters were as follows: Temperature was 300°C for the injector and detector. The oven temperature was: 40°C(2.0min) to 280°C(20min) at a rate of 4°C/min. Highly pure nitrogen was the carrier gas. 1 μ L sample was injected with splitless model.

Congener-specific PCBs analysis was performed on a Varian 3740A gas chromatograph equipped with ⁶³Ni electronic capture detector and a SE-54 column (0.25mm × 18m). The carrier gas was highly pure nitrogen. The injector temperature was 300°C and detector temperature was 350°C. The temperature program was: 50°C(2.0min) to 280°C(20min) at a rate of 4°C/min.

Recovery tests were carried out by spiking a standard mixture of several PAHs or PCBs, into water. The recoveries were 84.0%, 90.4%, 96.0%, 91.6% for naphthalene, phenanthrene, chrysene, and benzo[a]pyrene respectively. The relative deviation was less than 10%. For PCBs, the recoveries of Aroclor 1254 averaged 68%; the relative deviation was less than 15%. Concentrations reported here were not corrected for recovery. A solvent blank was prepared by the same procedure as the samples and did not reveal any PAHs/PCBs contamination. The method detection limit was defined as the amount that gave a signal-to-noise ratio of 3. The analytical performance was regularly controlled with the standard samples. The total concentration was calculated from the sum of concentrations of identified PAH and PCB individual congeners.

RESULTS AND DISCUSSION

PAHs were detected in all samples. Table 1 records the concentrations of PAHs in industrial wastewater and subsurface water. Σ PAHs was the sum of 22 PAH

Table 1. PAHs concentrations determined in DaTong water samples (unit: $\mu\text{g/L}$)

PAHs NAME	A	B	C	D	E	F	G	H	I
Nap	0.03	0.59	1.62	0.43	0.69	16.31	89.89	ND	0.20
2-Mnap	ND	0.51	1.64	0.29	0.67	22.21	27.01	ND	0.15
1-Mnap	ND	0.29	1.47	0.37	0.85	39.73	17.10	ND	0.08
Bip	ND	0.22	0.12	0.04	0.16	0.56	3.78	ND	0.03
Acy	0.03	0.28	1.02	0.20	9.09	ND	5.77	ND	ND
Ace	ND	0.18	1.13	0.73	0.82	4.01	5.46	0.13	0.04
Flu	ND	0.29	1.78	0.80	1.36	0.24	9.69	0.25	0.09
Phe	ND	0.39	0.44	0.11	0.68	0.14	5.06	0.34	0.22
Ant	ND	0.28	0.30	0.06	0.24	0.11	1.89	0.05	0.02
Fla	ND	0.20	0.18	0.16	0.26	0.03	1.27	0.09	0.14
Pyr	0.03	0.12	0.22	0.14	0.26	0.03	0.96	0.09	0.11
Bf	ND	0.10	0.11	0.03	0.05	0.07	1.52	0.03	0.03
Baa	ND	ND	ND	ND	ND	ND	0.38	ND	0.62
Cry	ND	ND	ND	ND	ND	ND	0.39	ND	0.79
Bbf	ND	ND	ND	ND	0.04	ND	0.78	0.13	1.07
Bkf	ND	0.85	ND	ND	ND	ND	2.70	0.06	0.37
Bap	0.08	0.19	ND	0.05	0.09	0.07	0.39	0.14	0.76
Per	ND	ND	ND	ND	ND	0.04	0.25	0.04	ND
Dphan	ND	ND	ND	ND	ND	ND	0.23	0.18	0.03
Dban	ND	ND	ND	ND	ND	ND	0.24	0.06	0.05
Bghi	ND	ND	ND	ND	ND	ND	0.25	0.05	0.25
Dmnap	ND	0.96	3.71	0.99	1.16	2.21	27.20	0.23	0.05
Σ PAHs	0.16	5.43	13.75	4.40	16.41	85.78	202.30	1.87	5.10

ND: not detectable ($<0.006 \mu\text{g/L}$)

Nap=naphthalene, 2-Mnap=2-methylnaphthalene, 1-Mnap=1-methylnaphthalene, Bip=biphenyl, Acy=acenaphthylene, Ace=acenaphthene, Flu=fluorene, Phe=phenanthrene, Ant=anthracene, Fla=fluoranthene, Pyr=pyrene, Bf=benzo(b)fluorene+benzo(a)fluorene, Baa=benzo(a)anthracene, Cry=chrysene, Bbf=benzo(b)fluoranthene, Bkf=benzo(k)fluoranthene, Bap=benzo(a)pyrene, Per=perylene, Dphan=diphenylanthracene, Dban=dibenzo(ah)anthracene, Bghi=benzo(ghi)perylene, Dmnap=dimethylnaphthaleneconcentrations

homologues. Concentrations of Σ PAHs varied from 1.87 to 202 $\mu\text{g/L}$ in the wastewater samples. Among four sampling sites, the highest levels of PAHs were detected in the coking plant wastewater sample G, in which all of the 22 PAHs were detected. The second highest level was the chemical plant wastewater sample F. PAHs contamination of the two other industrial wastewaters, chemical fabric plant sample H and pharmaceutical factory sample I, was not significant. In the surface water, Σ PAH ranged from 0.16-16.41 $\mu\text{g/L}$. The upstream control site A, showed the lowest level of PAH contamination (0.16 $\mu\text{g/L}$). Total PAHs concentrations along the Yu River roughly showed an increasing tendency in the direction of flow, which indicated that the intense industrial activities along its shores and domestic sewage discharge have contributed to the deterioration of water quality in the Yu River.

Compared the investigation result with other data, the total PAHs levels were close to those in several rivers of the Pearl River Delta Region, China (5-15 $\mu\text{g/L}$) (Yang, 1997), but 2-3 orders of magnitude higher than those in the St. Lawrence River (3.55 to 45.4ng/L) and its tributaries (3.55 to 87.3ng/L) (Pham et al.1993). Martens et al. (1997) determined the concentration and distribution of PAHs in the surface

Table 2. PAHs concentrations determined in DaTong plant samples (unit:µg/kg)

Sampling location PAHs name	IM [#] DT [*]	Chinese cabbage			corn			millet
		A river	B well	B river	A river	B well	B river	A river
Bkf	<0.01	2.24	ND	1.09	0.38	1.61	7.40	4.56
Bap	0.37	1.76	2.10	1.32	ND	0.55	ND	0.62
Per	<0.01	ND	0.67	ND	ND	ND	ND	0.04
Dphan	0.44	1.78	0.66	1.30	ND	ND	ND	0.52
Bghi	0.03	0.87	1.66	0.83	ND	0.33	0.25	0.33
Phe	<0.01	0.39	0.64	0.32	3.21	2.33	4.00	5.31
Ant	0.54	1.44	ND	ND	ND	ND	ND	0.57
Fla	0.40	ND [*]	1.88	ND	1.25	3.05	2.19	6.54
Pyr	0.35	ND	1.00	1.04	1.20	2.53	2.78	3.78
Bbf	<0.01	ND	0.10	0.09	0.25	0.55	0.68	0.44
Baa	<0.01	ND	1.52	0.09	0.41	0.65	0.37	0.56
Cry	<0.01	ND	3.24	0.74	0.40	0.95	1.17	3.43
Bkf	1.00	1.80	7.21	1.12	ND	ND	ND	ND
∑PAHs		10.3	21.1	7.94	7.10	12.5	18.9	26.7

IM: irrigation mode

* DT: detection limit

ND: not detectable

water and groundwater of the experimental farm of a rural region in Bavaria, Germany (0.5-10ng/l). The PAHs in Siskiwit Lake, which is located on a wilderness island in Northern Lake Superior, were also in the level (McVeaty and Hites 1988). From this, we can conclude that the rivers in DaTong City have been seriously polluted by PAHs.

The PAH patterns at each site were similar. The most abundant hydrocarbons in the water samples were two- to four-ring polycyclic aromatic hydrocarbons such as naphthalene, methyl naphthalene, acenaphthene, fluorine, phenanthrene, and benzofluorene. Some compounds, such as pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene, were present only in industrial wastewater samples.

Data on the PAHs contents of crop samples are presented in Table 2. The ∑ PAHs in three crop samples ranged from 7.1 to 26.7 µ g/kg in which benzofluoranthene, benzo(a)pyrene, diphenylanthracene, phenanthrene, fluoranthene and pyrene were most abundant compounds. Average PAHs content was 13.11, and 12.83 µ g/kg, in Chinese cabbage and corn respectively. The PAHs contamination in the three crop samples was only slightly different, though they were irrigated by different water quality. The results indicate that the ecological influence of PAHs contamination on the three crops sampled is not significant. Edwards (1983) and Schwab et al. (1998) concluded that the uptake of PAHs was dependent on a number of factors, including PAHs concentration and plant species. Uptake and translocation of PAHs via the plant root system have been reported by some workers (Suzuki et al. 1977; Yang et al. 1997). However, various lines of evidence indicated that concentrations in the aboveground portions of plants by PAHs normally may be dominated by

Table 3. PCBs concentrations determined in DaTong waste water samples (unit:ng/L)

IUPAC No.	Detection Limit	Sampling Location								
		A	B	C	D	E	F	G	H	I
101	0.09	1.50	1.68	0.70	ND	ND	2.74	2.26	ND	ND
110	0.08	3.33	3.33	1.12	0.91	ND	ND	1.98	ND	ND
118/108	0.08	3.97	4.37	0.88	1.02	0.71	ND	1.97	ND	ND
128	0.09	0.67	ND	ND	ND	ND	ND	ND	ND	ND
138	0.10	3.75	ND	1.43	1.09	1.05	ND	4.13	ND	ND
153	0.05	1.20	ND	ND	0.49	ND	0.83	0.64	ND	ND
16/32	0.03	0.87	ND	ND	0.94	ND	2.87	ND	1.11	ND
31/28	0.02	0.70	ND	ND	ND	ND	ND	2.98	ND	ND
41/64	0.02	0.46	0.98	0.63	0.17	ND	0.62	ND	ND	0.32
44	0.02	0.91	1.65	ND	ND	1.72	ND	ND	ND	1.16
45	0.03	ND	ND	ND	0.42	ND	2.19	ND	0.61	ND
52	0.04	0.51	0.50	0.64	0.48	0.79	0.76	ND	0.58	1.61
60/56	0.07	1.78	3.06	1.91	1.10	2.88	0.63	2.49	0.40	1.46
66	0.99	6.18	4.92	3.35	2.54	5.09	2.85	3.57	ND	2.62
7	0.03	ND	0.59	1.51	0.86	0.93	0.42	ND	0.49	2.32
70	0.10	ND	ND	2.27	ND	ND	0.66	ND	ND	ND
8	0.06	4.31	9.08	5.84	14.50	8.00	2.09	6.48	5.45	18.76
82	0.10	ND	ND	ND	ND	ND	1.78	1.45	ND	ND
85	0.07	ND	ND	2.71	ND	1.82	ND	5.07	ND	2.37
87	0.05	1.66	ND	ND	0.90	0.58	0.61	ND	0.66	ND
97	0.11	0.72	1.08	ND	ND	ND	0.80	ND	ND	ND
99	0.08	1.13	2.31	ND	ND	1.97	ND	1.12	ND	ND
ΣPCBs		33.66	33.55	22.99	25.42	25.54	19.85	34.14	9.29	30.61

ND : not detectable

atmospheric deposition, with the pollutants originating from automobile exhaust and industrial emissions (Schwab et al. 1998).

Total PCB concentrations of each sampling site were also studied by summing contributions of individual congeners. Total PCBs ranged from 9.29-33.66ng/L. Concentration at site H was significantly lower when compared to the other eight samples. The total PCB concentrations averaged 28.22 ± 5.68 ng/L if sample H was excluded. Compared with representative marine and lake areas, such as San Francisco Bay and the Hudson River (Jarman et al., 1997; WHO, 1993), it seems that PCBs pollution in DaTong City was not yet serious.

The concentrations of individual congeners in the sample are listed in Table 3. The patterns of PCB congeners in water samples were similar, and were dominated by di- pentachlorobiphenyl. The congeners with more than six chlorine substitutes were not detected in water samples. It was reported atmospheric deposition was thought to be responsible for 58-90% of Lake Superior and Lake Michigan's PCB burden (Eisenreich et al. 1981). Volatilization was a major loss process for PCBs from the water column (Xi et al 1998). Fluxes in air-water exchange of polychlorinated biphenyl congeners were different. Di-pentachlorobiphenyls represented 70-90% of the total flux in Lake Superior (Hornbuckle et al. 1994). From the sampling locations of DaTong City, it is possible that atmospheric deposition is the source of PCBs in DaTong City.

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