

Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sewage sludge from wastewater treatment plants of Kunming City

Xiaoming Li, Shimin Zhao, Shigang Li
Kunming Environmental Monitoring Center
Kunming, Yunnan, China
lixiaoming.km@163.com

Shimin Zhao, Xiaoxia Yang, Daowei Wang, Shigang Li,
Xuejun Pan
Faculty of Environmental Science and Engineering, Kunming
University of Science and Technology
Kunming, Yunnan, China
xjpan@kmust.edu.cn

Abstract- In this study, the concentrations, distribution and sources of 16 polycyclic aromatic hydrocarbons (PAHs) and 28 polychlorinated biphenyls (PCBs) in sewage sludge samples from wastewater treatment plants of Kunming city were investigated. The total PAHs concentration (Σ PAHs) varied from 1941 to 3635 ng/g, and the total PCBs concentration (Σ PCBs) ranged from 7.55 to 21.66 ng/g. The results of sources identification suggested that PAHs in sewage sludge were mostly produced from biomass and petroleum combustion. PCBs composition and congener ratios indicated that the less chlorinated were the dominant source.

Keywords- Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls; Sewage sludge; Wastewater treatment plants

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two kinds of typical persistent organic pollutants (POPs) for their toxicity, bioaccumulation, persistence, and impact on both ecosystems and human health. Generally, PAHs and PCBs are widely distributed in the environment and can be found in every corner of our lives^[1-2].

For their lipophilic and hydrophobic properties, sediments are the primary environmental repository of PAHs and PCBs^[3-4]. So they notably adsorb onto particulate after entering the treatment works. And then, they will be removed during the primary and secondary sedimentation of the wastewaters and subsequently transferred to the sludge^[5-7]. However, when sludge is used as fertilizer or disposed of in landfills, PAHs and PCBs will contaminate soil. Therefore, sludge should be monitored to prevent pollution^[8]. In this study, the concentrations, distribution and source of PAHs and PCBs were discussed in sewage sludge samples collected from wastewater treatment plants (WWTPs) of Kunming city. Operational conditions of the WWTPs are shown in Table I.

II. MATERIALS AND METHODS

A. Materials

In this study, 16 PAHs (mixture standard solution: 2000 μ g/mL, Supelco, USA) and 28 PCBs (mixture standard solution: 100 μ g/mL, Accustandard, USA) were analyzed. For PAHs, they included 2-ring PAHs (naphthalene, Na), 3-ring

PAHs (acenaphthylene, Acy; acenaphthene, Ace; fluorine, Flu; anthracene, An; phenanthrene, Ph), 4-ring PAHs (fluoranthene, Fl; pyrene, Pyr; benzo[a]anthracene, BaA; chrysene, Chrys), 5-ring PAHs (benzo[b]fluoranthene, BbF; benzo[k]fluoranthene, BkF; benzo[a]pyrene, BaP; dibenzo[a,h]anthracene, dBanA) and 6-ring PAHs (indeno[1,2,3-c,d]pyrene, IP; benzo[g,h,i]perylene, BghiP). For PCBs, there are di-chlorinated homologs (CB8), tri-chlorinated homologs (CB18, CB28), tetra-chlorinated homologs (CB44, CB52, CB66, CB77, CB81), penta-chlorinated homologs (CB101, CB105, CB114, CB118, CB123, CB126), hexa-chlorinated homologs (CB128, CB138, CB153, CB156, CB157, CB167, CB169), hepta-chlorinated homologs (CB170, CB180, CB187, CB189), octa-chlorinated homologs (CB195), nona-chlorinated homologs (CB206), deca-chlorinated homologs (CB209).

B. Sampling and Sampling Treatment

Sampling campaign of the sewage sludge was carried out in June 2012. Samples from each sampling site were well mixed and stored in 1L brown bottles that were heated at 400°C for 6 h in a muffle furnace before sampling. Each sample was frozen at -20°C on the day of collection. Before analysis, all samples were dried in vacuum freeze drier at less than -40°C for 48h. Then all freeze-dried samples were passed through a 100 mesh sieve and put into 100 mL brown bottles for analysis.

C. Analytical Methods

The procedures of sample extraction and analysis were performed according to previously reported methods by Wang^[9].

Samples were extracted by accelerated solvent extraction (ASE). A weighed sample (10.0 g) was mixed with 2.0 g diatomite (pyrolyzed at 600 °C for 4 h) and 2.0 g anhydrous sodium sulfate (pyrolyzed at 400 °C for 6 h) before being moved into a 22 mL extraction cell. After that, the samples were statically extracted with a mixture of hexane/acetone (1:1 v/v) using an accelerated solvent extractor (ASE-200, Dionex, USA) at 1500 psi, 90 °C for 6 min. Elution volume is 60% of the extraction cell. The extraction was carried out in one cycle. After removing water

TABLE I . OPERATIONAL CONDITIONS OF WASTEWATER TREATMENT PLANTS

Sites	WWTP ^a	Location ^a	Type of treatment	Sites area (×10 ³ m ²)	Population (×10 ³)	Flow (×10 ³ m ³ /d)	Received wastewater area (Km ²)
S1	The first WWTP	Urban southern	Oxidation ditch	114	30	12	24
S2	The second WWTP	Urban southeast	Improved A ² /O	117	56	10	50
S3	The third WWTP	Urban western	ICEAS	121	55	21	42
S4	The fourth WWTP	Urban northern	3AMBR	30	30	6	11.9
S5	The fifth WWTP	Urban northern	Improved A ² /O	81	25.6	18.5	28.5
S6	The sixth WWTP	Urban eastern	Improved A ² /O	66	18	13	42.4
S7	The seventh and eighth WWTPs	Urban southern, eastern and southeast	Improved A ² /O	210	57.9	30	42.3

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by adding 5.0 g anhydrous sodium sulfate, the extracts were concentrated to 2.0 mL by nitrogen evaporator (Turbo Vap II, Caliper, USA). For elimination of impurities, the concentrated extracts were passed through the Silica gel-Florisil composite columns activated with 7.0 mL hexane and flow rate 0.6 mL/min, and the target compounds were eluted with 17.0 mL mixture of hexane/acetone (19:1 v/v). As stated previously, the eluent was concentrated to 1.0 mL under a gentle stream of nitrogen for determination.

The identification and quantification of PAHs and PCBs were performed on an Agilent 7890 Gas Chromatograph coupled with Agilent 7000 GC/MS Triple Quad, Agilent 7693 Auto Sampler and DB-5 fused silica capillary column (30 m × 0.25 mm × 0.25 μm) operating in electron ionization (EI) mode. The samples were injected automatically (1.0 μL) in splitless with an injection temperature of 280 °C. And high-purity helium was used as a carrier gas (1.0 mL/min). The oven temperature program was as follows: initial temperature of 50 °C for 3 min, raised at 25 °C/min to 150 °C, held for 3 min, then increased to 240 °C at 6 °C/min, held for 5 min, finally to 280 °C at the rate of 16 °C/min, and held for 10 min. Ion source temperature was kept at 280 °C and ions were formed under electro-ionization at 70 eV. The acquisition mode was multiple reaction monitor (MRM) with 2 parent/product ion transitions being monitored for quantification and quality analysis. Quantification of individual compounds was based on the comparison of peak areas with surrogate standards.

D. Quality Control and Quality Assurance

Strict quality control and assurance measures were maintained in the monitoring process. For each analytical batch of samples, reagent blanks, procedural blanks, matrix spikes, and duplicate samples were analyzed for quality control and quality assurance. None of the target compounds were detected in the reagents, the procedural blank values was always below the detection limit.

In order to monitor the target compounds lost and defiled in the process of pretreatment and analysis, the surrogates 1,4-dichlorobenzene (1,4-Dcb, Supelco, USA) and decafluorobiphenyl (Dfb, Supelco, USA) were added to the samples before extraction. The recoveries of 1,4-Dcb varied from 80.8% to 103.4% and the recoveries of Dfb varied from 92.4% to 110.8%. The relative standard deviation (RSD) of

sample duplicates (n=3) was less than 14%. The detection limits ranged from 0.001 to 0.08 ng/g.

Five internal standard of PAHs (naphthalene-d₈, acenaphthylene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, pyrene-d₁₂) (Supelco, USA) and an internal standard of PCBs (2,4,5,6-Tetrachloro-m-xylene, Tc-m-x) (Supelco, USA) were added to all samples to monitor matrix effects. The average recoveries of internal standards of PAHs varied from 76.3% to 119.6%, and the average recoveries of internal standards of PCBs varied from 94.1% to 122.9%.

III. RESULTS AND DISCUSSION

A. Concentrations of PAHs and PCBs in Sludge Samples

The concentrations of PAHs with different ring numbers and ΣCOM/ΣPAHs in the sludge samples are listed in Table II. The total PAH concentrations (ΣPAHs) in the sludge samples ranged from 1942 (S4) to 3635 (S3) (mean 2956) ng/g. In order of the concentrations of ΣPAHs, the sequence was: S3 (3635 ng/g) > S5 (3456 ng/g) > S6 (3342 ng/g) > S1 (3069 ng/g) > S2 (2855 ng/g) > S7 (2395 ng/g) > S4 (1942 ng/g). The total PAH concentrations of municipal sludges are investigated in other studies. For example, Zeng found that the total 15 PAHs varied from 682.6 to 6926.6 ng/g in sludge from 6 WWTPs in Guangdong^[8]. Fang found that the total 16 PAHs ranged from 1156 to 6803 ng g⁻¹ in sludge from 14 WWTPs in Shanghai^[10]. Dai detected 2467.31-25923.79 ng/g PAHs in six sewage sludges collected in Beijing from 2004 to 2005^[11]. Perez found 3940 and 5520 ng/g PAHs in sludge from a WWTP in Spain^[12].

TABLE II . CONCENTRATIONS OF PAHs WITH DIFFERENT RING NUMBERS IN SLUDGE SAMPLES (ng/g)

	Samples						
	S1	S2	S3	S4	S5	S6	S7
2-ring	52	80	78	22	66	66	50
3-ring	352	386	554	259	433	618	315
4-ring	1436	1199	1682	985	1706	891	917
5-ring	928	847	941	528	914	1046	749
6-ring	301	344	380	148	337	721	363
ΣPAHs	3069	2855	3635	1942	3456	3342	2395
ΣCOM/ΣPAHs	0.87	0.84	0.83	0.86	0.86	0.80	0.85

The concentrations of individual congeners, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-chlorinated homologs, total PCB concentrations (ΣPCBs), CB170/CB28 and CB170/CB52 are presented in Table III. The ΣPCBs in

sludge samples varied from 7.55 to 21.66 ng/g, with a mean concentration of 12.22 ng/g, and the order was: S6 (21.66 ng/g) > S5 (14.68 ng/g) > S3 (11.40 ng/g) > S2 (11.23 ng/g) > S7 (9.58ng/g) > S1(9.42 ng/g) > S4 (7.55ng/g). Berset and Holzer (1996) observed PCB levels ranging from 43 to 550 ng/g (as $\Sigma 7$) in sewage sludge in Switzerland^[13]. Blanchard observed PCBs levels ranging from 120 to 1930 ng/g (as $\Sigma 7$) in sewage sludge in France^[14].

Compared with other cities, the concentrations of Σ PAHs and Σ PCBs in sludge samples from WWTPs of Kunming City were relatively low. The relatively higher concentration of Σ PAHs and Σ PCBs was found at S3, S5 and S6, because they had a relatively higher flow value than other sites, and all of them run at full load status. The lowest concentration of Σ PAHs and Σ PCBs was detected at S4, which had smallest site area and the least flow value with minimum pollutant. Blanchard investigated PAHs and PCBs in five sewers entering the Seine Aval treatment plant in the Paris area (France). The Clichy Argenteuil sewer displayed the highest PAHs concentration in relation to its high flow value 10kg/year, whose contamination level is higher than Clichy Bezons (8.6 kg/year), Reueil (3.9 kg/year), Saint Denis (2 kg for 8 months) and Nanterre (2.2 kg/year). It is also found that biodegradation process and adsorption to particles are the main elimination pathways of PAHs and PCBs^[14]. Even though S7 had the highest flow value, S7 run at normal operation with good biodegradation process, which led to the pollution level of S7 was relatively lighter than other sites.

TABLE III. CONCENTRATIONS OF PCBs IN SLUDGE SAMPLES (ng/g)

	Samples						
	S1	S2	S3	S4	S5	S6	S7
Di-PCBs	0.16	0.17	0.14	0.11	0.2	0.21	0.15
Tri-PCBs	1.82	2.13	2.27	1.06	4.44	1.72	1.19
Tetra-PCBs	4.03	5.15	4.89	3.99	7.15	10.06	4.94
Penta-PCBs	0.86	0.79	0.67	0.65	0.69	0.71	0.77
Hexa-PCBs	2.16	2.1	2.01	1.37	1.49	1.69	1.85
Hepta-PCBs	0.39	0.32	0.23	0.29	0.25	0.39	0.37
Octa-PCBs	ND	ND	ND	ND	ND	ND	ND
Nona-PCBs	ND	ND	0.03	ND	ND	0.09	ND
Deca-PCBs	ND	0.57	1.16	0.08	0.46	6.79	0.31
Σ PCBs	9.42	11.23	11.4	7.55	14.68	21.66	9.58
CB170/CB28	0.09	0.06	0.06	0.19	0.02	0.11	0.14
CB170/CB52	0.11	0.07	0.06	0.12	0.04	0.05	0.09

ND: not detected

B. PAHs Composition and Sources

The composition of PAHs in sludge is presented in Fig.1. The 4-ring PAHs were dominant in sludge ranging from 38.31% to 50.74%, except the sample from S6 where the 5-ring PAHs were dominant at 31.31%. The high molecular weight PAHs (≥ 4 -ring) were the dominant compounds in sludge, accounting for 79.54%-83.84% of the Σ PAHs, and 13.16%-20.46% of the Σ PAHs were the low molecular weight PAHs (2,3-ring). The compositional pattern of PAHs by ring size in the sludge confirmed that the PAHs were dominated by combustion process. The higher ratios of combustion PAH species (Σ COMB; Fl, Pyr, BaA, Chrys, BbF, BkF, BaP, BghiP and IP) and Σ PAHs indicated more combustion activities. In this study, the ratios of Σ COMB/ Σ PAHs varied from 0.78 to 0.86,

which indicated that extensive combustion activities affected the PAHs in sludge samples.

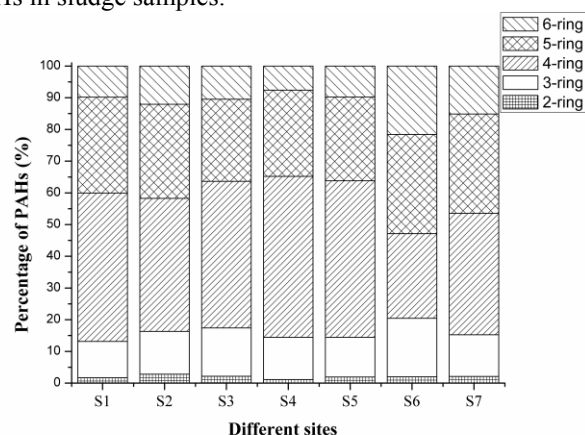


Fig.1. The distribution of PAHs with different ring numbers in different sites.

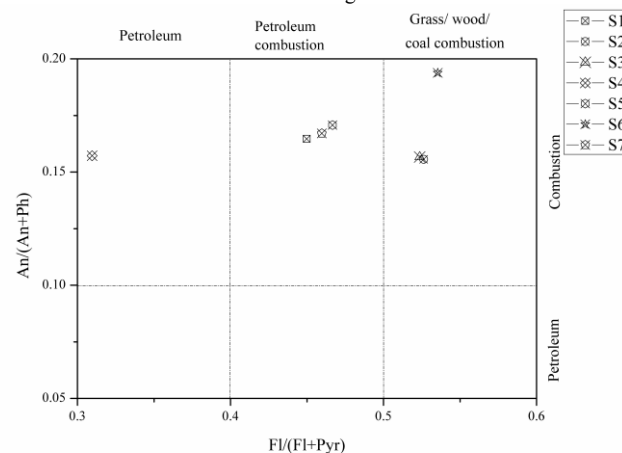


Fig.2. Plots of isomeric ratios An/(An + Ph) vs. Fl/(Fl+Pyr)

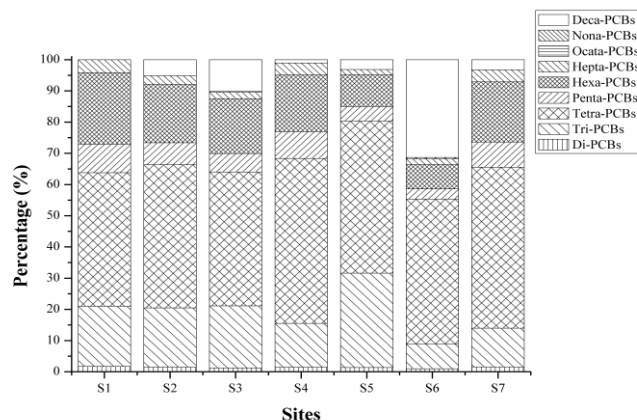


Fig. 3. Percent compositions of PCB congeners in different sites.

The Fl/(Fl+Pyr) versus An/(Ph+An) ratios were plotted in Fig.2. In this paper, ratios of An/(An+Ph) for all the sites were >0.1, and this means that PAHs were caused by combustion. For Fl/(Fl+Pyr), the ratios of some sites (S6, S3 and S2) >0.5 suggested that PAHs of these sites were mainly from biomass (grass, wood and coal) combustion, while the

radios of S4 <0.4 indicated that PAHs come from petroleum products. And the radios of the rest of sites (S1, S7 and S5) suggested that PAHs were mainly created by petroleum (vehicle, gasoline, fuel oil, crude oil et al.) combustion. It was similar with the primary sources of PAHs in Dianchi Lake which is the discharge area of WWTPs effluents^[15].

C. PCBs Composition and Sources Identification

According to the number of substituted chlorine atoms, the homologue percentages of PCBs in all samples were calculated, and are showed in Fig.3. The tetra-PCBs were dominant congeners in all samples, followed by tri-PCBs, and hexa-PCBs (mean 47.30%, 17.55%, and 16.38%, respectively). And the average proportions of the deca-, penta-, hepta-, di-, and nona-PCBs were 7.72%, 6.67%, 2.89%, 1.40% and 0.1%, respectively. Octa-PCBs were not detected in any of the samples. Their distribution is partly indicative of the less chlorinated Aroclor mixtures such as Aroclor 1016, 1232, 1242 and 1248, which was consistent with previous researches on PCBs contamination in Dianchi Lake^[1, 16].

CB28, 52 and 170 belong to *Tri-*, *Tetra-* and *Hepta-*chlorine compound, respectively. Therefore, the ratio of CB170/28 and CB170/52 are usually used to assess possible sources because they are not observed in the same Aroclor mixture^[17]. For all of the sites, the ratios of CB170/28 and CB170/52 varied from 0.02 to 0.19 and 0.04 to 0.12, respectively, which suggested that the inputs were largely dominated by the less chlorinated Aroclor mixtures.

IV. CONCLUSIONS

PAHs and PCBs in sludge from WWTPs of Kunming city were investigated and analyzed. Compared with other cities, the concentrations of ΣPAHs and ΣPCBs in sludge from WWTPs of Kunming city were relatively low. The relatively high PAHs and PCBs concentration were observed in the WWTPs of large flow value (S3, S4 and S5), while the lowest concentration of ΣPAHs and ΣPCBs was detected at S4 due to the least flow value. Based on the PAH composition and isomer ratios, the possible sources of PAHs were grass, wood, coal and petroleum combustion. According to the homologue percentages of PCBs and the congener ratios, the less chlorinated were the dominant source.

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