

Occurrence, composition and ecological restoration of organic pollutants in water environment of South Canal, China

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Abstract. Ecological restoration of polluted river water was carried out in South Canal by adding microbial water purifying agents and biological compound enzymes. The objective of present study was to investigate the ecological restoration effect of organic pollutants by this efficient immobilized microbial technologies, analysis the occurrence and composition of organic pollutants including fifteen persistent organochlorine pesticides (OCPs), seventeen polycyclic aromatic hydrocarbons (PAHs) and eighteen organophosphorus pesticides (OPPs) both in natural water environment and ecological restoration area of South Canal, China. Results showed that the total concentrations of OCPs ranged from 1.11 to 1.78 ng·L⁻¹, PAHs from 52.76 to 60.28 ng·L⁻¹, and OPPs from 6.51 to 17.50 ng·L⁻¹. Microbial water purifying agents and biological compound enzymes essentially had no effects on biological degradation of OCPs and PAHs in the river, but could remove OPPs with degradation rates ranging from 19.6% to 62.8% (35.2% in average). Degradation mechanisms of microbial water purifying agents and biological compound enzymes on OCPs, PAHs and OPPs remained to be further studied. This technology has a certain value in practical ecological restoration of organic pollutants in rivers and lakes.

1. Introduction

With the rapid development of social economy, a large number of domestic sewage and industrial wastewater were discharged into river directly without treatment, which caused serious water pollutions and destroyed the ecological environment of the river, and finally weakened the purification capacity of the river. Highly effective microorganism technologies are a new kind of environmental biotechnologies combined by bioecological remediation and water restoration [1]. It can effectively improve concentrations and activities of microorganisms in water environment by adding exogenous microbial strains and biological enzymes [2]. Organic materials, nitrogen, phosphorus and other pollutants are degraded, transformed and absorbed through the assimilation and dissimilation by microorganisms. At present, conditions of water environment had been improved apparently using high efficient microbial technology by a large number of researchers, while they carried out indoor water purification experiments or practical applications by adding high efficient microbial agents into the water [3-6]. However, previous studies mainly focused on conventional indicators concentrations of water environment including ammonia nitrogen, chemical oxygen demand, total nitrogen and total phosphorus degraded effectively by adding microbial agents to pollutants. Practical applications of



microbial technology for organic pollutants restoration in polluted river water were relatively less, and more experiments for specific organic pollutants degradation were carried out in the stage of laboratory research through screening microbial strains by single or multiple strains [7-10]. Faced with complex system of organic pollution in the river, little literature had been reported organic pollutants treatment using high efficient microbial technology, such as persistent organic pollutants (POPs), organophosphorus pesticides (OPPs).

Owing to the characteristics of stable physical and chemical properties, POPs have been detected in various environmental media such as atmosphere, plants, water, sediments and soils. POPs have strong toxicity, can translate with long chain migration, accumulate along the food chain and cause serious harm to human health. Organochlorine Pesticides (OCPs) such as Hexachlorocyclohexanes (HCHs) and Dichlorodiphenyltrichloroethanes (DDTs) were still widely existed in various environmental media because of its persistence, bioaccumulation and toxicity even though it had been banned since 1980s. Polycyclic aromatic hydrocarbons (PAHs) are a wide group of organic contaminants composed of fused aromatic rings, known to be ubiquitous in environment and of great concern due to their toxic, mutagenic and carcinogenic potentials to the ecosystem and human beings. PAHs are widely distributed in the river water through atmospheric deposition, surface runoff, municipal and industrial effluents, oil spillage or leakage [11, 12]. Its main sources are divided into two categories including fuel combustion and petrochemical products [13]. OPPs are kinds of pesticides occupied the largest pesticide market share in China and especially widely used in agricultural activities. A large number of OPPs pesticides applied in the agricultural production period could enter rivers, lakes and other water bodies through rainfall, runoff and other means, causing surface water pollution and toxic effects on microorganisms, fish, human and other mammals [14]. Although OPPs are thought to be easily degraded and low residues in environment, some studies have shown that it can be transformed into some kinds of persistent pollutants [15]. Pollution status, composition and distribution characteristics of OCPs, PAHs and OPPs have been extensive reported in multi medium environment such as surface water [16-19], soil [20, 21], sediment [22], and estuary [23, 24] in Haihe River Basin. However, little attention has been paid attention to the pollution characteristics of OCPs, PAHs and other persistent organic pollutants in surface water of Zhangweinan subwatershed, except Cao *et al* [25] studied the pollution characteristics and risk assessment of dissolved PAHs. In addition, OPPs have not been reported in various environmental media related to the Zhangweinan subwatershed. The widespread existences of persistent OCPs and PAHs, as well as the extensive use of OPPs in agricultural activities, posed a potential risk and threat to the ecological environment and human health.

As a part of the Grand Canal from Beijing to Hangzhou, South canal is one of the main flood discharge channel in Zhangweinan River, Haihe River Basin. South Canal carried a large number of domestic sewage and industrial sewage from upstream and surrounding without treatment, and immediately created extremely serious water pollution. Contaminated river water have threatened human health through drinking water and ingesting food around South Canal basin, which showed that comprehensive management and restoration of water pollution become essential. In order to deal with the water pollution situation of the South Canal, efficient immobilized microbial technologies coupled with efficient microbial purifying agents and biological compound enzymes were used in ecological restoration experiment carried out in South Canal water. Pollution loads including concentrations of COD, ammonia and other pollution indicators in South canal were gradually reduced, and also the water ecosystems were reconstructed and gradually recovered in South canal. The objective of present study was to investigate compositions, distributions and concentrations of fifteen persistent OCPs, seventeen PAHs and eighteen OPPs in surface water of South Canal, Zhangweinan River Basin, obtain the pollution characteristics of organic pollutants in ecological restoration water environment of the South Canal and discuss the ecological restoration effect of organic pollutants coupled by efficient microbial water purifying agents and biological compound enzymes.

2. Materials and methods

2.1. Study area

The study area was located in the Dezhou section of the South Canal, Dezhou city, Shandong province, China. The distance from Sinvsi Gate to the lower reaches of the South Canal were 665 meters and this sections were selected as the experimental area (as shown in figure 1). Dam with 1 meters height was built in the downstream to maintain the river water level at an average depth of 2.5 m and ensure river water stability overflows. The average width of water surface was 60 m and storage capacity of this area was about $10 \times 10^4 \text{ m}^3$. Velocity of the inflow river water from Sinvsi Gate was about $1 \times 10^4 \text{ m}^3$ every day and water quantity was in stable.

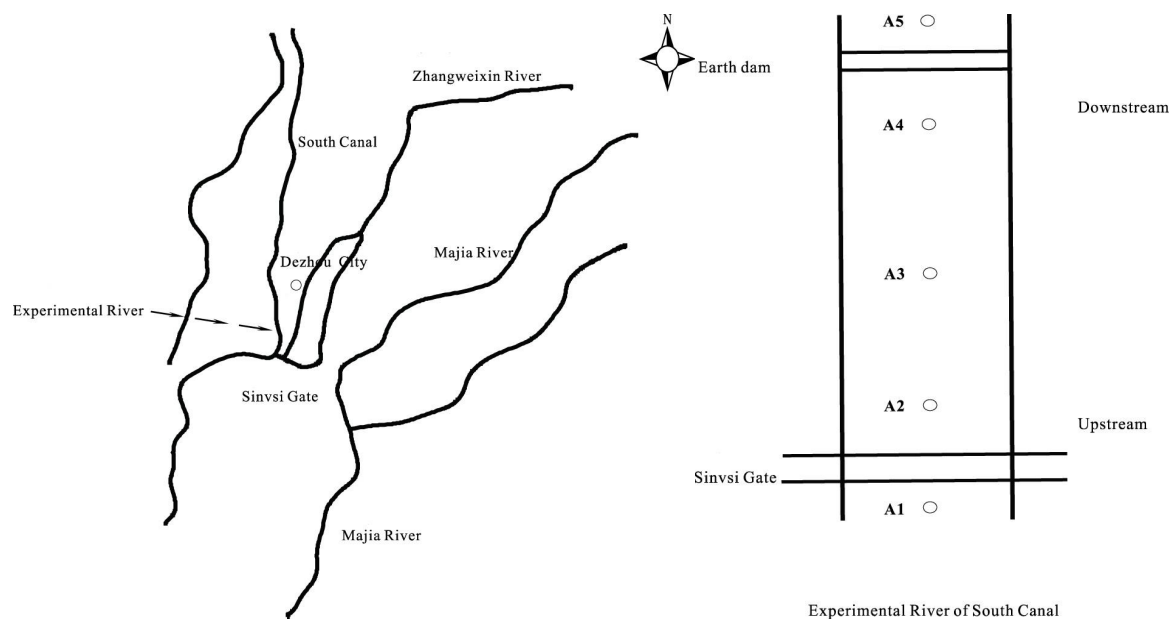


Figure 1. Experimental sites of South Canal and sampling sections.

2.2. Chemicals and instruments

Agilent 7890A/7000B (Agilent, USA), Automatic solid phase extraction instrument (GL Science, Japan); Bond Elut C18 Solid phase extraction column (500 mg/6 mL, Agilent).

Standard mixture solution for OCPs contained fifteen components, including α -HCH, β -HCH, γ -HCH, δ -HCH, p , p' -DDE, p , p' -DDD, o , p' -DDT and p , p' -DDT from research institute of standard sample, ministry of environmental protection. Heptachlor, Heptachlor epoxide, Aldrin, Dieldrin, Isodrin, α -Endosulfan and β -Endosulfan were obtained from research Institute of environmental protection, Ministry of Agriculture.

Standard mixture solution for PAHs contained seventeen components, including Naphthalene (Nap), Acenaphthene (AcP), Acenaphthylene (AcPy), Fluorene (FL), Phenanthrene (Phe), Anthracene (Ant), Carbazole (Car), Fluoranthene (Flu), Pyrene (Pyr), Benz(a)anthracene (BaA), Chrysene (Chr), Benz(b)fluoranthene (BbFL), Benz(k)fluoranthene (BkFL), Benzo(a)pyrene (BaP), Indeno (1,2,3-cd)pyrene (InP), Benzo(g,h,i)pyrene (BghiP) and Drbenz(a,h)anthracene (DBA) were obtained from accustandard company, USA.

Standard mixture solution for OPPs contained eighteen components, including Methamidophos (MTP), (Dichlorvos, DDVP), Acephate (ACP), Omethoate (OMT), Ethoprophos (ETP), Monocrotophos (MOP), Phorate (PHO), Dimethoate (DIT), Isazophos (ISP), Diammonium phosphate (DAP), Methyl parathion (MEP), Malathion (MAT), Chlorpyrifos (CHP), Parathion (PAT), Bromophos (BRP), Isufenphos-methyl (IPM), Methidathion (MED) and Triazophos (TZP) were obtained from research institute of standard sample, ministry of environmental protection.

Ethyl acetate and dichloromethane were chromatography pure and from Duksan, Korea. Methanol was HPLC grade and from Baker company, USA.

Bpa-1017 series microbial water purifying agents and Bacto-Zyme 1011 series of biological enzymes were purchased from Beijing Bangyuan environmental protection technology Co., Ltd.

2.3. Experiment methods

2.3.1. Field experiments design

Experiments were carried out from April to July in 2014. A certain proportion of the microbial water purifying agents (Bpa-1017 series) and biological compound enzymes (Bacto-Zyme 1011 series) were added to water body of the experimental rivers. One aerator was installed in upstream of experiment section to provide sufficient oxygen for the water body and increase the flow of river water. Several artificial floating beds were built in surface water of the experimental area and a large number of artificial forests were fixed at the bottom of the water as efficient microbial carriers, which provided attachment and growth conditions for microorganisms, protozoa, small pelagic animal that participated in water purification.

2.3.2. Sample collection

As shown in figure 1, five sampling sections were set up, include one background section above Sinvsi Gate (A1) to reflect the pollution status of organic pollutants in the South Canal, and four sections in experimental area of South Canal to reflect ecological restoration effect of organic pollutants, which located in upstream (A2), midstream (A3), downstream (A4) of the river and under the river dam (A5) of the south canal respectively. Glass bottles were used to collect the surface water (0.5 m) samples of 1 L for laboratory analysis after ecological restoration experiments finished. Concentrations of dissolved oxygen in surface water were measured by portable multi parameter detector (YSI EXO2).

2.4. Analysis of organic materials

2.4.1. Sample extraction. Water samples were filtered and enriched by Bond Elut C18 solid-phase extraction cartridges. Volume of the samples were 500 mL and methanol was added according to the rate of V (water samples): V (methanol) = 100:1. Solid-phase extraction columns were placed in automatic solid-phase extraction apparatus, washed and purified by 5 mL dichloromethane and ethyl acetate at a flow rate of $3 \text{ mL} \cdot \text{min}^{-1}$ respectively, and then activated by 10 mL methanol and ultra water at a flow rate of $5 \text{ mL} \cdot \text{min}^{-1}$. Water samples were passed through the cartridges at about the rate of $15 \text{ mL} \cdot \text{min}^{-1}$ under vacuum. After extraction, the cartridges were dried and then eluted three times by 2 mL ethyl acetate, 2 mL dichloromethane and 2 mL dichloromethane with the rate of $1 \text{ mL} \cdot \text{min}^{-1}$, $1 \text{ mL} \cdot \text{min}^{-1}$ and $2 \text{ mL} \cdot \text{min}^{-1}$ respectively. Elutes were collected and concentrated to 1 mL by dichloromethane for GC/MS/MS analysis.

2.4.2. Gas chromatograph and tandem mass spectrometry analysis. HP-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Agilent) was used to detect the concentrations of OCPs in water samples. High purity nitrogen was used as carrier gas at 1.2 mL/min with the pressure of 11.681 psi under a constant flow mode. Transmission line temperature was maintained at 280°C . Injection volume was $1.0 \mu\text{L}$ with splitless inject mode.

Oven program for OCPs was programmed to keep the initial temperature at 80°C for 1 minute, then raised to 230°C at the rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ and held for 6 minutes. The total analysis time was 14.5 minute. Injector temperature was 270°C . For PAHs was programmed to keep the initial temperature at 80°C for 1 minute, then raised to 250°C at the rate of $20^\circ\text{C} \cdot \text{min}^{-1}$, and then raised to 300°C at the rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ and held for 5.5 minute. The total analysis time was 20.0 minute. Injector temperature was 270°C . And for OPPs was programmed to keep the initial temperature at 80°C for 1 minute, then raised to 200°C at the rate of $15^\circ\text{C} \cdot \text{min}^{-1}$ and held for 3 minute, and then raised to 250°C at the rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ and held for 2 minute. The total analysis time was 17.5 minute. Injector temperature was

240°C.

Mass spectrometer conditions were selected as ionization mode: EI, electron energy 70 eV, interface temperature 280 °C, ion source temperature 230 °C, quadropole temperature 150 °C, solvent delay 7.5 min. The parameters of chromatography and mass spectrometry were optimized by SCAN and productor mode and detection mode were in multiple reaction monitoring (MRM).

2.4.3. Quality control and quality assurance. Quality control and quality assurance in sample analysis refer to the requirements of USEPA and QA/QC in water environment standard of China (SL 219-2013). The quality of the monitoring results can be guaranteed by blank, standard added recovery and parallel sampling. In this study, recoveries of OCPs in water samples ranged from 70.3% to 115.1%, and the relative standard deviations (RSD) ranged from 0.6% to 12.2%, and the detection limits from 0.08 to 0.38 ng·L⁻¹. Recoveries of PAHs ranged from 69.8% to 111.6%, relative standard deviations (RSD) from 4.9% to 12.6%, and detection limits from 0.11% to 0.40 ng·L⁻¹. Recoveries of OPPs ranged from 86.1% to 117.2%, relative standard deviations (RSD) from 1.1% to 15.8%, and detection limits from 0.09% to 0.82 ng·L⁻¹. Fifteen OCPs, seventeen PAHs and eighteen OPPs were quantitatively analyzed by Mass Hunter data acquisition software of Agilent 7890A/7000B gas chromatography-tandem mass spectrometry instrument.

2.5. Statistical analysis

SPSS17.0 statistical software was used for data analysis.

3. Results and discussion

3.1. Occurrence and compositions of organic pollutants in natural water environment of South Canal

Several components of OCPs, PAHs and OPPs were detected in natural water environment of South Canal reflected by A1 sampling sites. As shown in table 1, total concentrations of OCPs were 1.45 ng·L⁻¹, which stands for three OCPs including α -HCH, β -HCH and γ -HCH examined in this study. Eleven categories of PAHs including Nap, AcP, AcPy, FL, Phe, Ant, Car, Flu, Pyr, BaA and Chr were detected and total concentrations were 54.70 ng·L⁻¹. Two kinds of OPPs including DDVP and IPM were detected and total concentrations were 17.50 ng·L⁻¹.

Pollutions of OCPs and PAHs in this study were lower than that of the other rivers and lakes in China. According to literatures, surface water were polluted by OCPs with varying degrees, such as HCHs, DDTs, Heptachlor, Heptachlor epoxide, Aldrin in China's seven river basin including Yellow River, Yangtze River, Pearl River, Hai River, Liao River, Songhua River and Huai River [26, 27]. For example, concentrations of HCHs ranged from 9.27 to 10.51 ng·L⁻¹ in water environment of Nanjing section of Yangtze River, and DDTs from 1.57 to 1.79 ng·L⁻¹ [28], while HCHs in Haihe River ranged from 3.95 to 20.15 ng·L⁻¹, and DDTs from 6.88 to 35.23 ng·L⁻¹ [29]. For the concentrations of PAHs, they were 321.80 to 6234.90 ng·L⁻¹ in Yangtze River [30], 987.13 to 2878.50 ng·L⁻¹ in Pearl River [31], as well as 1800 to 35000 ng·L⁻¹ in Hai River [32]. In addition, total concentrations of dissolved PAHs in surface water of Sinvisi Gate ranged from 74.50 to 99.00 ng·L⁻¹ in the year of 2008 in South Canal according to the survey of pollution characteristics by Cao Zhiguo [25]. Results of this study indicated that low pollution levels of PAHs currently relative to that of in history.

Most parts of OPPs in agricultural production activities could not be efficiently used by crops, and conversely entered into rivers, lakes and other water bodies through rain, sedimentation and runoff. Total concentrations of OPPs in the Pearl River estuary area ranged from 4.44 to 635 ng·L⁻¹ [33]. Eight kinds of OPPs were found in three lakes of Beijing, with total concentration ranged from 0.18 to 0.63 ng·L⁻¹ [34], among them four categories including dichlorvos, methamidophos, dimethoate and methyl parathion were detected. It can be seen that the concentrations of OPPs in rivers and lakes in some areas of China were much higher than that of in South canal.

Table 1. Occurrence and compositions of organic pollutants in natural water environment of South Canal/ng·L⁻¹.

Pollutants	Concentrations	Pollutants	Concentrations	Pollutants	Concentrations
α -HCH	0.30	Nap	9.50	MTP	ND
β -HCH	0.78	AcP	4.94	DDVP	15.31
γ -HCH	0.37	AcPy	0.68	ACP	ND
δ -HCH	ND	FL	2.09	OMT	ND
<i>p,p'</i> -DDE	ND	Phe	10.29	ETP	ND
<i>p,p'</i> -DDD	ND	Ant	23.00	MOP	ND
<i>o,p'</i> -DDT	ND	Car	0.52	PHO	ND
<i>p,p'</i> -DDT	ND	Flu	1.80	DIT	ND
Heptachlor	ND	Pyr	1.44	ISP	ND
Heptachlor epoxide	ND	BaA	0.32	DAP	ND
Aldrin	ND	Chr	0.11	MEP	ND
Dieldrin	ND	BbFL	ND	MAT	ND
Isodrin	ND	BkFL	ND	CHP	ND
α -Endosulfan	ND	BaP	ND	PAT	ND
β -Endosulfan	ND	InP	ND	BRP	ND
—	—	BghiP	ND	IPM	2.19
—	—	DBA	ND	MED	ND
—	—	—	—	TZP	ND
Σ OCPs	1.45	Σ PAHs	54.70	Σ OPPs	17.50

Note: ND stands for not detected. "—"stands for no data.

Table 2. Human health ambient water quality criteria and aquatic life criteria by EPA/ μ g·L⁻¹.

OCPs	Water quality criteria for human health		Water quality criteria for aquatic organisms (fresh water)	
	Consumption of water and organism	Consumption of organism only	Acute toxicity	Chronic toxicity
α -HCH	0.00036	0.00039	—	—
β -HCH	0.0080	0.014	—	—
γ -HCH	4.2	4.4	0.95	—
<i>p,p'</i> -DDD	0.00012	0.00012	—	—
<i>p,p'</i> -DDE	0.000018	0.000018	—	—
<i>p,p'</i> -DDT	0.000030	0.000030	1.1	0.001
Heptachlor	0.0000059	0.0000059	0.52	0.0038
Heptachlor epoxide	0.000032	0.000032	0.52	0.0038
Aldrin	0.00000077	0.00000077	3.0	—
Dieldrin	0.0000012	0.0000012	0.24	0.056
Isodrin	0.03	0.03	0.086	0.036
α -Endosulfan	20	30	0.22	0.056
β -Endosulfan	20	40	0.22	0.056

Note: "—"stands for no data.

Environmental water quality criteria is the basis for establishing the limits of water quality standards, which is of great significance for the prediction, evaluation, control and treatment of pollutants, maintain rivers or lakes in a good ecological environment. As shown in table 2, according to the toxicological data and numerical calculation, EPA formulated OCPs water quality criteria for human health and aquatic organisms. Human health quality criteria represent the maximum acceptable concentrations of pollutants that do not produce harmful effects on the human health through drinking water or by eating aquatic organisms. This criterion indicates that the lowest concentration of specific pollutants in water will not pose a significant risk for most aquatic species, including the values of acute toxicity and chronic toxicity. According to human health standard of OCPs for water quality and aquatic water quality criteria, the south canal water OCPs concentration was less than water quality criteria for human health and freshwater aquatic organisms.

Because of high hydrophobic and lip solubility, PAHs could be enriched and enlarged in the organism through food chain, and then entered into the human body by fish and shellfish intake. Some countries and international organizations have established the safety standards for aquatic organisms exposed to PAHs contaminated water through a large number of available toxicological data and a series of extrapolation methods [35] (as shown in table 3). Data in safety standard indicated the concentration of PAHs that could constitute threat to human health by bioaccumulation of aquatic organisms through food chain, especially mussels and oysters filter feeding animal. As reflected in table 3, single components of PAHs in surface water of the South Canal did not exceed the safety standards of each countries or organizations referring to the international safety standards, but the total concentration of PAHs exceeded the quality standard of the United States and environmental maximum allowable concentration limits in European Union.

Table 3. Safety guidelines for aquatic organisms exposed to PAHs in water/ $\mu\text{g}\cdot\text{L}^{-1}$.

PAHs	Maximum allowable concentration limits in Ireland	Water quality standards draft in Canada	Ecotoxicological evaluation criteria by Khosrow and Paris Committee	Water quality assessment criteria in Denmark	Environmental quality standards in United State	maximum allowable concentration limits in European Union
Nap	—	11.0	1.0~10.0	1.0	—	—
Phe	2.0	0.8	—	—	4.6	—
Ant	—	0.12	0.005~0.05	0.01	—	—
Flu	0.5	—	0.05~0.5	—	—	—
BaA	0.2	—	—	—	—	—
BkFL	0.1	—	—	—	—	—
BaP	0.1	0.008	0.01~0.1	—	—	—
BghiP	0.02	—	—	—	—	—
Σ PAHs	—	—	—	—	0.03	0.2

Note: "—"stands for no data.

For the safety standards for aquatic organisms exposed to OPPs shown in table 4, some information could be collected from different countries and organizations except from water quality standards draft in Canada, water environmental quality standards in China and Environmental quality standards in United State. According to existed safety guidelines, it was obvious that each component of OPPs in surface water of the South Canal did not exceed the safety standards of Canada, China and United State.

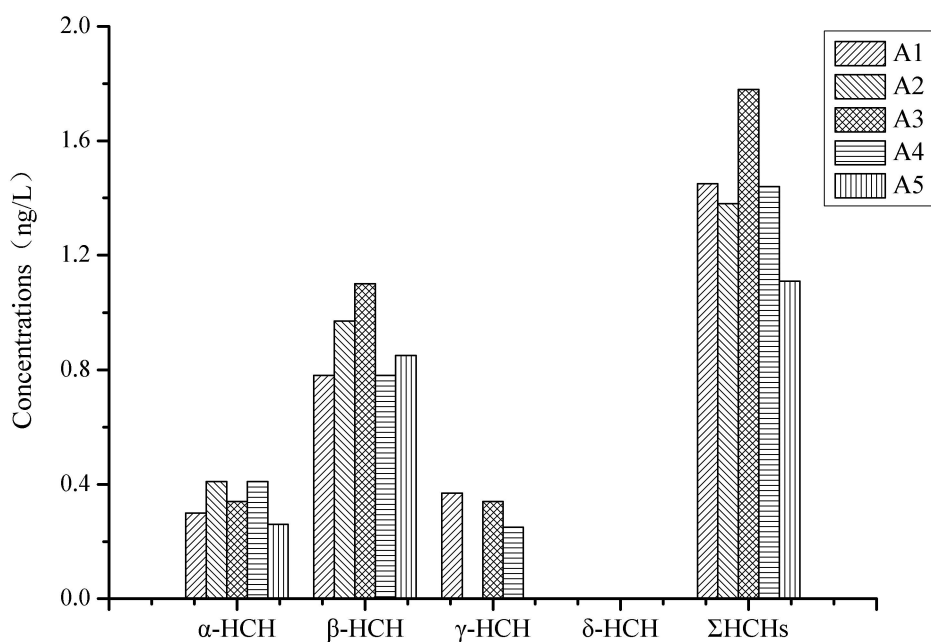
Table 4. Safety guidelines for aquatic organisms exposed to OPPs in water/ $\mu\text{g}\cdot\text{L}^{-1}$.

PAHs	Water standards draft in Canada	Water quality standards in China	Water environmental quality standards in United State
DDVP	—	50	—
DIT	6.20	80	—
MEP	—	2	—
MAT	—	50	0.10
CHP	0.02	—	—
PAT	—	3	0.013

Note: "—"stands for no data.

3.2. Occurrence and compositions of OCPs in experimental area

Water quality of South Canal had been greatly improved from worse than grade V to grade IV by adding high efficient microbial water purifying agents and biological compound enzymes. As shown in figure 2, α -HCH, β -HCH and γ -HCH in fifteen OCPs were detected in surface water sampling sites of A1, A2, A3, A4 and A5, and the other twelve OCPs were not detected. α -HCH and β -HCH were detected in each sampling sites and the detection rate was 100%, and γ -HCH was only detected in sites of A1, A3 and A4 with detection rate 60%. Total concentrations of HCHs ranged from 1.11 to 1.78 $\text{ng}\cdot\text{L}^{-1}$ (1.43 $\text{ng}\cdot\text{L}^{-1}$ in average), and β -HCH was the highest concentrations of HCHs in each sampling sites.

**Figure 2.** Concentrations of organochlorine pesticides in experimental water body of South Canal.

In this study, concentrations of organic pollutants in A1 sampling sites were used to reflect the background organic pollution status of water environment in South Canal, and microbial water purifying agents and biological enzymes were not added into this area. Concentrations of organic pollutants in A2-A5 sampling sites were considered as ecological restoration area and degradation efficiency could be observed when concentrations of organic pollutants in which were compared with A1 sampling sites. Total concentrations of OCPs and its isomers showed no significant difference in different sampling sites between background and ecological restoration area ($P>0.05$), which could

explain that the microbial water purifying agents and biological compound enzymes used in our research could not degrade OCPs in river water environment obviously. Studies have shown that microorganisms could degrade OCPs, and microbial coupled with the enzyme morphology on the degradation of OCPs are closely related to dehydrochlorinase, hydrolase and dehydrogenase. Degradation processes of OCPs were completed by the ways of co-metabolism, metabolism or mineralization synergism during different species [36]. At present preliminary microorganisms proved to degrade OCPs were pseudomonas that contained sphingomonas UT26 [37], B90 [38, 39] and brown rot fungi [40], and also including serial genres such as clostridium, bacillus, corynebacterium, micrococcus and hydrogenomonas. Meanwhile, persistent OCPs degradation in river water environment was affected by many environmental factors, such as organic carbon source [41], pH [42], humic acid [42], and so on.

In addition, according to the existing literature, degradations of chlorinated organic contaminants by microorganisms were carried out in the laboratory conditions with high initial concentration. While as organochlorine pollutants reached to a certain low concentrations, the degradation rates changed slowly and degradation process became time consuming, because extremely low concentrations of chlorinated aromatic compounds could not be used by microorganisms [43]. Currently, pollutions of organochlorine pollutants in surface water environments such as rivers and lakes are relatively in a low level, and the concentration of pollutants is oligotrophic for degrading bacteria. How to improve the degradation efficiencies of chlorinated organic contaminants by microorganisms in oligotrophic environment was the key to solve water pollution problems [43]. OCPs were not degraded by microorganisms and enzyme technology in South Canal, and how to use this technology to treat organochlorine pollutants in actual water ecological restoration process need to be further studied.

3.3. Occurrence and compositions of PAHs in experimental area

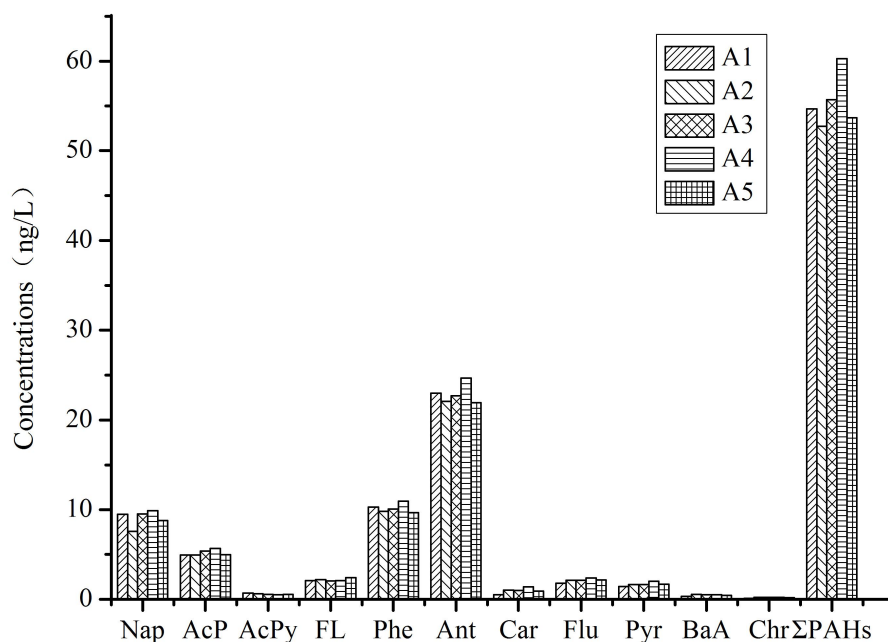


Figure 3. Concentrations of PAHs in experimental water body of South Canal.

As shown in figure 3, eleven kinds of PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benz(a)anthracene and chrysene were detected in experimental area in South Canal. Other six kinds of PAHs including benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, benzo(g,h,i)pyrene and drbenz(a,h)anbhracene were not detected. Concentrations of anthracene is the

highest in all PAHs components with $22.87 \text{ ng}\cdot\text{L}^{-1}$ in average, and followed by phenanthrene and naphthalene, the average concentrations were $10.18 \text{ ng}\cdot\text{L}^{-1}$ and $9.07 \text{ ng}\cdot\text{L}^{-1}$ especially. Total concentrations of PAHs ranged from 52.76 to $60.28 \text{ ng}\cdot\text{L}^{-1}$ with $55.44 \text{ ng}\cdot\text{L}^{-1}$ in average. While for the composition of PAHs in surface water of South Canal, 2 to 4-rings PAHs were in dominant and compositions above the 5-rings were not detected. Among them, concentrations of 3-rings PAHs accounted for the largest proportion in each sampling sites with the range from 72.8% to 75.1%, and followed by the 2-rings PAHs, the proportion of which ranged from 16.3% to 18.9%. 4-rings PAHs were occupied the least proportion and ranged from 3.7% to 5.1%.

Comparison of PAHs concentrations in surface waters in A1 sampling sites and ecological restoration experiment sections from A2 to A5 sampling sites, concentrations of eleven PAHs showed no significant differences ($P>0.05$). Microbial water purifying agents and biological compound enzymes had no obvious effect on the degradation of PAHs, which showed similar degradation effects of OCPs. Studies had shown that treatments of PAHs in water environment were mainly contributed by microbial degradations. Naphthalene and other low molecular weight of PAHs were relatively easy to be degraded, but for the high molecular weight PAHs above 4-rings or 4 rings, the characteristics of hydrophobicity and stability increased with increasing molecular weight, such as the components of chrysene, benzo[a]pyrene were persistent in environment and were difficult to be degraded by microorganisms [44]. It was generally believed that monooxygenase and dioxygenase were key enzymes for microbial degradation of PAHs [45]. The main reason that PAHs were not easy to be degraded by microorganisms was that no suitable efficient catalytic enzymes existed to improve degradation efficiency of microbial [46]. In our study, low molecular weight components accounted for most of the PAHs, and microbial water purifying agents and biological compound enzymes showed no degradation effect, which indicated that the added microbial water purifying agents and biological compound enzymes were not suitable for PAHs degradations. According to the pollution conditions of PAHs in natural river water, it was necessary to find a highly effective degradation enzyme to improve the biodegradation efficiency.

3.4. Occurrence and compositions of OPPs in experimental area

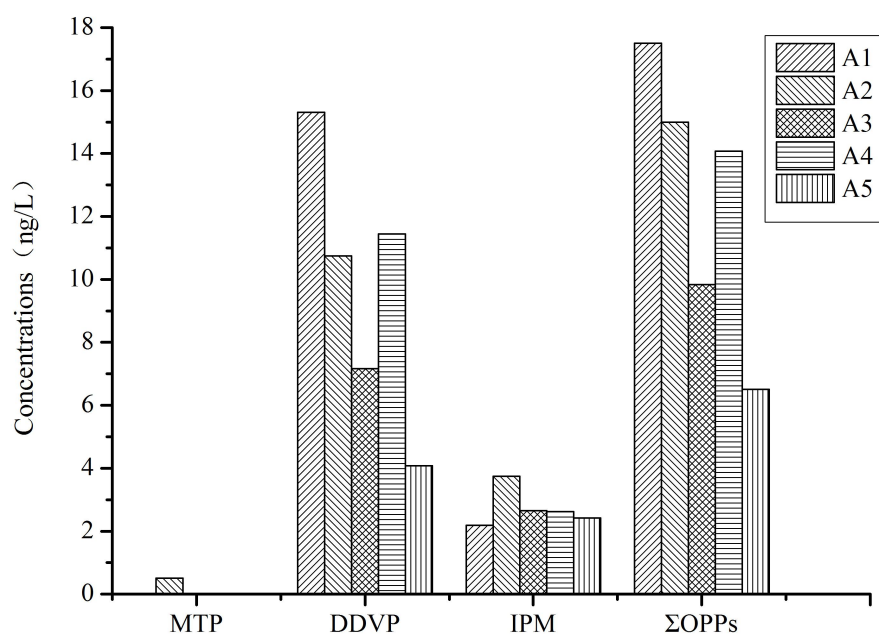


Figure 4. Concentrations of organophosphorus pesticides in experimental water body of South Canal.

As shown in figure 4, methamidophos, dichlorvos and isofenphos methyl were detected in surface

water South Canal respectively, and other fifteen kinds of OPPs were not detected. Among them, dichlorvos and isofenphos-methyl were detected in each sampling sites and the detection rates were 100%; methamidophos was only detected in A2 sites and the detection rate was 20%. It can be also seen from figure 4 that concentration of dichlorvos was highest among three kinds of OPPs. Total concentrations of OPPs in experimental area ranged from 6.51 to 17.50 ng·L⁻¹, and the average value was 12.58 ng·L⁻¹.

As shown in figure 4, total concentrations of OPPs in A1 sites were higher than that of in A2-A5 sites and showed significant difference ($P < 0.05$), which indicated that microbial water purifying agents and biological compound enzymes had a certain effect on the degradation of OPPs in water environment of South Canal. According to the analysis of monitoring data, the degradation rate of OPPs ranged from 19.6% to 62.8% with 35.2% in average. Water in experimental area was in an aerobic environment with sufficient dissolved oxygen under the action of aeration device. Concentrations of dissolved oxygen ranged from 10.80 to 14.00 mg·L⁻¹ in each sampling sites. Adequate concentrations of oxygen ensured that aerobic microorganisms had sufficient activity to promote the degradation of organic pollutants. Mechanisms of microbial degradation of OPPs were similar to that of OCPs, and mainly comprised three types including co-metabolism, communal synergistic metabolisms and mineralization [47]. A variety of microorganisms were separated to degrade OPPs residues including bacteria, actinomycetes, fungi and algae, especially bacteria and fungi were studied thoroughly [47, 48]. P-N, P-O and P-S chemical bonds of OPPs were broken in different degrees and conducted its degradation [49]. Many kinds of enzymes could degrade OPPs including oxygenase, dehydrogenase, azo reductase and peroxidase, and microbial degradations of OPPs were accomplished by the synergistic action of multiple enzymes in many cases. Factors affecting microbial to degrade OPPs mainly included pH, temperature, water types and properties, physical and chemical factors such as oxidation-reduction potential, substrate type and its chemical structure, substrate concentration, biochemical factors such as activity and types of microbial, factors of substrate concentration [50]. A variety of bacteria, fungi and algae were probably existed in the water environment of South Canal and influencing factors of OPPs degradation consisted of the degradation reasons in a certain extent. According to the situations of generally relatively high concentrations of OPPs in water bodies of actual ecological restoration demonstration project, application this ecological restoration technology coupled with microorganisms and enzymes to degrade OPPs have a future prospect. Next steps of the research should consider how to improve degradation efficiency of OPPs in actual ecological restoration process.

4. Conclusion

Occurrence, composition and ecological restoration of organic pollutants in water environment of South Canal were studied by monitoring thirty-two persistent organic pollutants including fifteen OCPs and seventeen PAHs. Results showed that microbial water purifying agents and biological compound enzymes had not obvious effects on degradation of OCPs and PAHs in water body, while provided a certain effect on OPPs. The degradation rate of microbial water purifying agents and biological compound enzymes to total OPPs ranged from 19.6% to 62.8% with 35.2% in average. Degradation mechanisms of OCPs, PAHs and OPPs by high efficient microbial water purifying agents and biological enzymes in the river water environment remains to be further studied. Ecological restoration technologies coupled with microorganisms and enzymes to treat organic pollutants used in our study had a certain reference to practical application on the rivers and lakes.

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