Removal of Organic Pollutants by a River Water Purification Demonstration Project

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Abstract. The efficiency of organic pollutants removed by an integrated river water purification demonstration project built in the Danshui River was investigated. Preferable removal results were obtained in the operation process of this project. More than 40% of polycyclic aromatic hydrocarbons (PAHs) were removed from river water by the demonstration project, and the removal rates for five kinds of homologues for Naphthalene, fluorene, phenanthrene, pyrene and fluoranthene were 44.13%-59.23%, 44.1%-54.61%, 50.90%-54.70%, 61.88%-80.61% and 44.83%-56.64%, respectively. Decabromodiphenyl ether(BDE-209) and bisphenol A(BPA) could be fully removed by this project. The results suggested that demonstration project could effectively remove the organic pollutants from river water and could be widely applicable in river water purification.

1. Introduction
As a result of rapid economic development of the Pearl River Delta (PRD) in recent decades, the pollution of organic pollutants in the water environment of the Pearl River was becoming more serious, thus threatening human health and ecological security in this area[1, 2]. Some kinds of organic pollutants, such as brominated flame retardants(BFRs)-Polybrominated diphenyl ethers (PBDEs), Polycyclic aromatic hydrocarbons(PAHs), Bisphenol A (BPA) and other pollutants, have been detected in water of East river, which was the one of upstream rivers of the Pearl River[3, 4]. For example, The 16 kinds of PAEs concentrations in riverine sediments in the PRD region ranged from 0.567 to 47.3µg/g dry weight (dw), with the mean and median concentrations of 5.34µg/g dw and 2.15µg/g dw, respectively[1].The concentrations of BDE-209 in sediments of Pearl River in china ranged from 30 to 7340 ng/g[5]. Therefore, elimination of organic pollutants from river water environment becomes an urgent task.

In general, chemical, physical and biological methods could be applied for removal of organic pollutants from polluted water[6]. However, the integrated technology with several kinds of treatment process was more effective for in-situ treatment of river water. In this research, we designed an integrated river water purification demonstration project in danshui river, which was the branche of East river. The river water purification demonstration project was composed of the different treatment process of oxidation, sedimentation, constructed wetland and Plant oxidation. The efficacy of three types of organic pollutants (on behalf of PAHs, BPA and PBDEs) in the river water removed by the
demonstration project were monitored and analyzed. The research results are beneficial for providing basic data for in-situ treatment of river water in practical application by integrated technology.

2. Materials and methods

2.1. Chemicals

Standard samples and experimental reagent of five kinds of polycyclic aromatic hydrocarbons (Naphthalene, fluorene, phenanthrene, pyrene and fluoranthene), Bisphenol A (BPA) and Decabromodiphenyl ether (BDE-209) used in this research were purchased from standard material center in China.

2.2. Water sample collection

The river water purification demonstration project of Danshui River located in huizhou, Guangdong province in China, and was operated from April to November in 2011. The water samples were collected below the 20 cm surface of the water and 1000 mL of each water sample was collected. To eliminate the effects of organic pollutants photolysis and microbial degradation in water samples, the collected water samples were placed in the glass bottles ultrasonic cleaned with dichloromethane, Glass bottles was covered with aluminum foil to prevent photodegradation. Bacteriostatic agent-sodium azide (NaN₃, 0.1%, v: v) was added in the water samples, and preserved at 4°C for analysis. Water quality of Danshui River was displayed in the Table 1.

| Parameter               | Unit | Value (Mean ± SD) |
|-------------------------|------|-------------------|
| CODcr                   | mg/L | 27.86±9.08        |
| BOD₅                    | mg/L | 4.48±1.23         |
| Total nitrogen (TN)     | mg/L | 12.26±4.77        |
| NH₃-N                   | mg/L | 9.97±4.97         |
| Total phosphorus (TP)   | mg/L | 1.48±1.09         |

2.3. Chemical analysis

2.3.1. Analysis of polycyclic aromatic hydrocarbons by HPLC. Water samples of 2 L were extracted with volumetric dichloromethane in batches for 40 min by ultrasonic extraction. This extraction was repeated two times and concentrated to 5 mL by rotary evaporation at 40 °C, then dried by N₂. Finally, diluted with 0.5 mL of Methanol for analysis. PAHs concentrations were quantified by HPLC using a C₁₈ column (4.6×150mm, 5μm, Agilent, USA). The chromatographic condition was: methanol: water = 87:13 (v: v), Flow rate 1.0ml/min, the detection wavelength was 254nm. The external standard method calculates the contents of naphthalene, fluorene, phenanthrene, pyrene and fluoranthene.

2.3.2. Analysis of BDE-209 by GC. Water samples of 2L were extracted with volumetric n-hexane/dichloromethane (1:1, v: v) for 40 min by ultrasonic extraction. This extraction was performed for two times and then organic phase was concentrated to 5 mL by rotary evaporation at 40 °C. The extracts were then purified by concentrated H₂SO₄ and dried by N₂ and finally diluted with 1 mL of n-hexane. The 1 mL extract was deeply filtrated by glass microfiber Filters (GF/C, whatman).

Quantitative analysis of BDE-209 was performed by an Agilent 6890 gas chromatograph (GC) equipped with a ⁶⁷Ni-electron capture detector (GC-µECD). DB-5 HT column (15 m Length × 0.25 mm I.D. × 0.10 μm Film, J & W Scientific, Folsom, CA) was selected as the analytical column. The GC-ECD was operated as follows: injection port, 280°C with splitless mode; Ultrahigh nitrogen (99.999%) at a constant flow rate of 1.5 mL min⁻¹ was used as carrier gas. Detector temperature was 320 °C. The oven program was set for: 2 min at 110 °C, ramp at 15 °C/min to 315°C (15min hold). The extracted sample (1 μL) was injected into the DB-5 HT column.
2.3.3. Analysis of BPA by HPLC. 20 mL of BPA in water was filtered with 0.45μm membrane and extracted by 22.5μL chlorobenzene and 0.5 mL of acetone, the extract was centrifuged for 8 min at 4000-5000rpm, the organic phase was used in HPLC analysis. The Chromatographic condition for BPA determination was: A C18 column (4.6 mm × 150 mm I.D.; 5-μm particle size) was used. The flow rate was 1.0 mL/min and the mobile phase was methanol: water = 80:20 (v: v), the detection wavelength was 220nm, and the column temperature was 30°C.

2.4. Parameters of river water purification demonstration project
The treatment capacity of river water purification demonstration project in Danshui River was 100m³/d, the river water was lifted to the demonstration project pretreatment pool by the pump. And the design parameters of demonstration project was shown in Table 2.

Table 2. Parameters of river water purification demonstration project in Danshui River.

| Treatment process                  | Daily treatment capacity(m³) | Design parameter (L×B) | Hydraulic retention time(h) | Surface load(m³/m²·h) |
|-----------------------------------|-----------------------------|------------------------|----------------------------|----------------------|
| Pre-treatment tank                | 360                         | Upper base,8.0m×4.0m;  | 1.5                        |                      |
|                                   |                             | Lower base,5.0m×1.0m;  |                           |                      |
|                                   |                             | H=1.5 m                 |                           |                      |
| Contact oxidation tank            | 180                         | 3.0m×3.0m H=1.4 m       | 2.2                        | 250g BOD5/m³·d       |
| Sedimentation tank                | 180                         | 3.3m×1.0m H=1.4 m       | 1.25                       |                      |
| Vertical flow artificial wetland   | 180                         | Upper base,8.0m×6m     | 4                          | 4.3                  |
|                                   |                             | Lower base,5.5m×3.5m    |                           |                      |
|                                   |                             | H=1.0 m                 |                           |                      |
| Horizontal subsurface flow constructed wetland | 180 | Upper base,8m×6m; Lower base, 5.5m×3.5m; H=1.0 m | 4.5 | 3.0 |
| Plant oxidation pond              | 360                         | 180 m²                  | 12                         |                      |

3. Results and discussions
From table 3, we can see that PAHs could be efficiently removed by the integrated river water purification demonstration project, more than 40% of PAHs was removed in the whole operation period of this project stably. The removal rates of five kinds of PAHs homologues for naphthalene, fluorene, phenanthrene, pyrene and fluoranthene were 44.13%-59.23%, 44.1%-54.61%, 50.90%-54.70%, 61.88%–80.61% and 44.83%-56.64%, respectively. For BPA, the concentrations of BPA in the Danshui river water are higher, which indicates the BPA pollution was more serious. The integrated river water purification demonstration project could completely eliminate BPA from the river water, no BPA was detected in the effluent of the project, and the removal rate was 100%. Meanwhile, BDE-209 was fully removed by this project.

The technology of remove toxic organic pollutants from water reported mainly include chemical oxidation(ozone oxidation, UV photolysis, advanced Fenton oxidation method, metal reduction, high-energy radiation, etc.), ultrasonic decomposition, adsorption and bioremediation(plant and microbial remediation)[7]. Chemical and physical methods are expensive, disruptive to the environment and also
involve high energy consumption. Therefore, Chemical and physical methods are not suitable for large-scale engineering application. Biodegradation is one of the most effective ways to eliminate organic pollution in natural environments with low cost, wide scope, long duration and higher removal rate[8]. Whether physical, chemical or biological method, it is often difficult to treat the polluted water to the ideal level by a single method, so the integrated treatment method is very important.

The integrated river water purification demonstration project in Danshui River was a combination of various treatment processes. Pre-treatment tank, contact oxidation tank and sedimentation could intercept the suspended particulate matter to remove toxic organic pollutants. Oxidation also could remove some of organic pollutants that were easily degraded. Construct wetland as a kind of water treatment method of low cost, low energy consumption and has the advantages of convenient maintenance and management, and could deeply purified the organic pollutants[9]. The result demonstrated that preferable removal results were obtained in the operation process and this project has the potential for popularization.

Table 3. Organic pollutants removed by water purification project in Danshui River.

| Pollutants  | Sampling date | 4.15 | 4.18 | 6.30 | 7.2 |
|-------------|---------------|------|------|------|-----|
|             | Inflow (ng/L) | Effluent (ng/L) | Removal rate (%) | Inflow (ng/L) | Effluent (ng/L) | Removal rate (%) | Inflow (ng/L) | Effluent (ng/L) | Removal rate (%) | Inflow (ng/L) | Effluent (ng/L) | Removal rate (%) |
| PAHs        |               |      |      |      |     |
| Naphthalene | 651.7         | 314.6 | 51.73 | 605  | 338 | 44.13 | 381.4 | 179.3 | 52.99 | 347.6 | 141.7 | 59.23 |
| Fluorene    | 80.5          | 45   | 44.10 | 86.8 | 49.8 | 42.63 | 43.4 | 19.7 | 54.61 | 44.8 | 22.4 | 50.00 |
| Phenanthrene| 197.8         | 89.6 | 54.70 | 199.1| 93.6 | 52.99 | 97.1 | 44.5 | 54.17 | 99.6 | 48.9 | 50.90 |
| Pyrene      | 16.7          | 4.2  | 74.85 | 18.1 | 6.9  | 61.88 | 18.4 | 5.9  | 67.93 | 16.5 | 3.2  | 80.61 |
| Fluoranthene| 14.3          | 6.2  | 56.64 | 14.9 | 6.5  | 56.38 | 8.7  | 4.8  | 44.83 | 8.1  | 4.2  | 48.15 |
| PBDEs       | BDE-209       | 16.5 | nd   | 100.00 | nd | 12.7 | nd | 100.00 | 3.2 | nd | 100.00 | 1.7 | nd | 100 |
| BPA         | BPA           | 11.59 (µg/L) | nd | 100 | 13.56 (µg/L) | nd | 100 | 29.52 (µg/L) | nd | 100 | 24.18 (µg/L) | nd | 100 |

Note: the concentration unit of BPA is µg/L, and the rest are ng/L. nd, not detected.

4. Conclusion
An integrated river water purification demonstration project was built in the Danshui River for removing the organic pollutants from river water. The removal efficiency for PAHs were over 40%. Decabromodiphenyl ether (BDE-209) and Bisphenol A (BPA) was fully removed by this project. The results suggested that demonstration project in Danshui river could effectively remove the toxic organic pollutants from water, demonstrating its popularization value for purification of toxic organic pollutants.

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