Behavior, mass inventories and modeling evaluation of xenobiotic endocrine-disrupting chemicals along an urban receiving wastewater river in Henan Province, China

Yi-Zhang Zhang, Xian-Fang Song, Akihiko Kondoh, Jun Xia, Chang-Yuan Tang

Graduate School of Horticulture, Chiba University, Matsudo 271-8510, Japan
Key Laboratory of Water Cycle and Related Land Surface Process, Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Datun Rd. A11, Chaoyang District, Beijing 100101, China
The Center for Environmental Remote Rensing, Chiba University, Chiba 263-8522, Japan

A B S T R A C T

Historically, the locations of cities mainly depend on the available water source and the urban river not only supplies the fresh water to city but also receives its wastewaters. To analyze the influences of urban zone on its receiving water river, the Jialu River in Henan Province, China, a typical urban river was chosen. Water and sediment samples were collected along the river in 2007 to analyze the concentrations of xenobiotic endocrine-disrupting chemicals (XEDCs) including nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in surface water and sediment. The results showed that the concentrations of OP, NP and BPA in surface water were 20.9–63.2 ng L\(^{-1}\) (mean 39.8 ng L\(^{-1}\)), 75.2–1520 ng L\(^{-1}\) (mean 645 ng L\(^{-1}\)), 410–2990 ng L\(^{-1}\) (mean 1535 ng L\(^{-1}\)), respectively. The lowest and highest concentrations of XEDCs in surface water were found in the upper stream and downstream of Zhengzhou urban zone, which was regarded as the major discharge source of these chemicals to this river. The concentrations of OP, NP and BPA in the sediment were 15.9–31.1 ng g\(^{-1}\), 145–349 ng g\(^{-1}\), and 626–3584 ng g\(^{-1}\) with the average concentrations of 21.4 ng g\(^{-1}\), 257 ng g\(^{-1}\) and 2291 ng g\(^{-1}\), respectively. The results of in situ sediment-water partition of XEDCs showed that the partition coefficients (log\(K_{oc}\)) in the downstream were higher than that in the upstream, which was mainly caused by the retransfer of surface sediment from the upper stream to the downstream. Comparison of measured and theoretical inventories of XEDCs in sediment indicated that the residual time of XEDCs in sediment in the river was about 5 years, which was in the same order of magnitude with its big flood frequency. In order to predict concentration variances of XEDCs in surface water, a fugacity-hydrodynamic model was developed according to the concept of in series completely stirred tank reactors (CSTR). The model results showed that about 29–65% of XEDCs derived from the urban zone (about 2.0 t yr\(^{-1}\)) would finally dissipate from aqueous phase in the 170 km downstream of the river. Assuming the discharge amount of XEDCs from the urban zone remaining constant, the predicted concentrations of the total XEDCs in the over 90% river reach would be higher than 1.0 \(\mu\)g L\(^{-1}\) under all normal, high water and low water season in 2007.

© 2010 Elsevier Ltd. All rights reserved.
1. Introduction

Xenobiotic endocrine-disrupting chemicals (XEDCs) such as alkylphenols (APs) and bisphenol A (BPA) have attracted serious attention in environmental science research and policy due to their ubiquity and estrogenic activities (Sumpter and Johnson, 2005). APs, which mainly contain nonylphenol (NP) and octylphenol (OP), are the degradation products of the widely used non-ionic surfactants alkylphenol ethoxylates (APEs) (Sharma et al., 2009). Bisphenol A is an important intermediate used to synthesis polycarbonate plastic, epoxy resin and other plastic material such as polyvinyl chloride (PVC) (Staples et al., 1998; Klecka et al., 2001). In China, the production and consumption of BPA were estimated at 3.2 × 10^8 t and 1.05 × 10^8 t in 2001 (Zeng et al., 2006). Most APs and BPA are released from the sewage treatment plants (STPs) effluents, which led to a net accumulation in the aquatic ecosystem of urban rivers (Ying et al., 2002; Céspedes et al., 2008; Kang et al., 2007).

Once entering the aquatic environment, XEDCs would moderate partition to organic phases such as sediments, soils and aquatic organism in light of their relatively high log octanol–water partition coefficients of 3.4–4.48 (Cousins et al., 2002; Ahel and Giger, 1993). Although they are not considered to be persistent organic pollutants, XEDCs are regularly detected in a variety of environmental media including the surface water and groundwater (Cailléaud et al., 2007; Latorre et al., 2003), sediments (Fu et al., 2007), aquatic organism (Belfroid et al., 2002; Pojana et al., 2007) etc. Concern has increased on these XEDCs such as the 4-tertiary isomers of NP and OP, which was shown to be 10^3–10^4 times less estrogenic potent than 17β-oestradiol (Jobling and Sumpter, 1993; Johnson et al., 2005). Thus, these chemicals have already been designated as priority hazardous substances in Water Framework Directive of European Union and they are subject to an environmental risk assessment (ERA) (Soares et al., 2008; Oehlmann et al., 2008).

Monitoring of water quality on the concentrations of organic contaminants is costly and difficult to perform due to both temporal and spatial sampling restrictions (Gevaert et al., 2009). Mathematical model provides an efficient way to predict the behavior and fate of contaminants in the environment and has been applied to determine levels of organic microcontaminants in STPs effluent and river water such as steroidal estrogens (Johnson and Williams, 2004). Johnson et al. (2008) compared the advantages and weaknesses of modeling and chemical analysis for polar organic chemicals in rivers and indicated that combination of measurements and models would provide the greatest confidence in assessing the risk of organic microcontaminants to the wildlife. In the past, the fugacity models have been successfully applied in predicting the multimedia fate of organic chemicals in the environment (Huang et al., 2007). Although the fugacity model IV can be used for describing unsteady environmental conditions, the model still regards the environment media as a well-mixing box by regardless of the longitudinal, vertical and lateral variances (Deksissa et al., 2004). Kilic and Aral (2009) developed a continuous and dynamic model to simulate the behavior and fate of organic contaminants in all phases, but the model was considered complex due to several non-linear equations were involved. Thus, development of a simple mathematical model for assessing the water quality in an urban receiving river is important.

The Huaihe River, one of the five main rivers in China, has attracted national attentions due to its frequent flood disasters and degeneration of water quality. The river has been seriously polluted and becomes more and more vulnerable to water pollution since 1980s. With economic growth and urbanization development, increasing discharges of industrial and domestic wastewaters were observed in the Huaihe River basin (Chen et al., 2005). One of its tributary, the Jialu River, has been regarded as a typical polluted urban receiving river (Lu et al., 2008), where the levels of APs in surface water have also been reported in our previous study (Zhang et al., 2009). As a sequential part of an interdisciplinary research focusing on the assessment of water body quality and hydrological process of the contaminants, the objectives of this paper are 1) to make clear the distribution characterization of XEDCs in surface water and sediment along the river; 2) to estimate the sediment inventory of XEDCs and discuss their behavior and fate along the river; 3) to develop a fugacity-hydrodynamic model for predicting the concentrations of the organic pollutants in surface water.

2. Materials and methods

2.1. Site description and sample collection

Originating from Xinmi County, Henan Province, the Jialu River is 256-km long with its basin area of 5896 km². It flows via Zhengzhou, Zhongmou, Weishi and Xihua then down into the Shaying River near Zhoukou city. The Jialu River basin has been undergoing a rapid economic growth and urbanization, facing massive discharge of wastewater and declining surface water quality. Large numbers of treated and untreated sewage from the alongshore cities, towns and villages were estimated to be 25,124 × 10^4 tons per year from 1996 to 1999, 81% of which were discharged from Zhengzhou urban zone (Xiao et al., 1999). Zhengzhou city has a long history for textile and metallurgy industries, and has been listed as one of the six most important industrial cities by “the development of central zones” stratagem of Chinese Government. In 2006, the total population of the city was 7.20 millions, of this 3.06 millions was non-agricultural population (Statistical Bureau of Zhengzhou city, 2007). The concentrations of NH₄-N in surface water, which was observed at downstream of the urban zone, varied from 25.8 to 87.8 mg L⁻¹ with the average concentration of 63.9 mg L⁻¹ in the year 2007 (Li, 2009). Thus, it is reasonable to regard that the Zhengzhou urban zone has a strong impact on the surface water quality of the Jialu River.

Surface water samples were collected with pre-rinsed 2-L glass bottles at each site along the river in September 2007. The sampling locations were shown in the Fig. S1 in supplementary information section. After filtering through a pre-baked 0.45 µm glass fiber membrane by a portable vacuum pump in situ, the samples were subsequently refrigerated and the extraction was performed within 24 h. Top 5-cm surface sediments were taken using stainless steel small-volume grab sampler and placed in precleaned glass bottles. The samples
were stored in a refrigerator at −20 °C until analysis. Repeated measures of dissolved oxygen (DO) and electric conductivity (EC) were performed in situ by portable meters (D-55, Horiba, Japan). The global positioning system (GPS) was used to locate the sampling sites.

### 2.2. Analytical procedure

All solvents used for sampling and analysis were HPLC grade. 4-tert-octylphenol and bisphenol A were purchased from Wako Pure Chemical Industries (Japan), 4-nonylphenol (technical grade) corresponding to a mixture of different isomers was obtained from Tokyo Chemical Industry (Japan). Phenanthrene-d$_{10}$ was purchased from AccuStandard, Inc (USA). Sodium sulfate (analytical reagent grade, Wako Pure Chemical Industries Ltd., Japan) was rinsed with dichloromethane (DCM) and hexane for three times and completely dried in the fume hood. The dried sodium sulfate was baked at 450 °C for 4 h and stored in desiccator. The Florisil® (60–200 mesh, USA) was activated at 650 °C for 3 h and deactivated at 130 °C for 12 h, then the Florisil® was cooled in desiccators and after it, ultrapure water (5%, w:w) was added. To remove organic contaminants, all the glassware used for organic compounds analysis were baked for 4–5 h at 450 °C prior to use.

The method of pretreatment for water samples was described by our previous report (Zhang et al., 2009). Briefly, each filtrate was extracted by solid-phase extraction cartridge (InertSep RP-1, GL sciences). These cartridges had been previously washed with 5 mL each of DCM, methanol, and ultrapure water. The analyte was eluted from cartridges with 20 mL dichloromethane after 30 min dryness, and then the solution was concentrated to 0.2 mL under a gentle stream of high purity nitrogen. The extraction of target compounds from sediment was based on the method reported by Ardititsoglou and Voutsia (2008). Sediment samples (10.0 g) were ultrasonically extracted in triplicate with 20 ml of acetone: methanol (1:1) for 20 min. The appropriate volume of the internal standard (phenanthrene-d$_{10}$) was added into sample prior to GC-MS analysis. The instrumental conditions for analyzing OP, NP and BPA, and the quality assurance/quality control (QA/QC) were described in detailed in supplementary information section.

The method of determining organic carbon contents of sediment samples was also provided in supplementary information section. In addition, a non-parametric Spearman rank R correlation test was performed to assess relationships between XEDCs and environmental parameters with the SPSS 13.0 for windows.

### 3. Theories and models

To predict the dynamic transport and fate of organic pollutants in a natural river, the model developed in this study regarded the river as lots of completely stirred tank reactors (CSTR) connected in series. Due to the river has a small width length ratio (<0.3), one-dimensional advection-disperse St. Venant equation was introduced to solve the hydrodynamic conditions of natural river systems. Without consideration of lateral input along the river, the mass balance equation of XEDCs can be generally described:

\[
\frac{\partial C}{\partial t} + \frac{\partial (\rho_C C)}{\partial x} = \nabla \cdot (D_C \nabla C) + \sum \mathcal{R} C + \frac{\partial N}{\partial x}
\]

where $C$ (all symbols were listed in Table 1) are the concentrations of XEDCs in aqueous phase (µg L$^{-1}$); $\mu$ is the average velocity of the river water (m s$^{-1}$); $E$ denotes longitudinal dispersion coefficients (m$^{2}$ s$^{-1}$); $\sum \mathcal{R}$ present the sum of all reaction rate constants including biodegradation and photolysis, which are on the basis of assumption of these reaction are subject to first-order kinetics (s$^{-1}$); $N$ represents multimedia mass transfer flux (mg s$^{-1}$) such as air–water diffusion, which is a function of concentration ($C$) and varies with the distance $x$. $A$ is the area of the cross-section ($m^{2}$).

Multimedia fugacity model has been applied to describe the partitioning and transfer of organic pollutants from one phase to the other based on the approach of Mackay (2001). Briefly, the concentration ($C$) can be replaced by the product of fugacity ($f$, Pa) and fugacity capacity ($Z$, mol m$^{-3}$ Pa$^{-1}$). Fugacity ($f$) is identical to the partial pressure of ideal gases related with the chemical potential. Fugacity capacities ($Z$) for air, water and sediment can be calculated using the equations (Mackay and Paterson, 1991):

\[
Z_{A} = \frac{1}{RT} \\
Z_{W} = \frac{1}{H} = \frac{S_{W}}{F_{W}} \\
Z = \frac{\rho(\%OC)K_{oc}}{H}
\]

where R is the universal gas constant (=8.314 Pa m$^{3}$ mol$^{-1}$ K$^{-1}$); $T$ is the absolute temperature (K); $H$ is Henry’s law constant (Pa m$^{3}$ mol$^{-1}$); $S_{W}$ and $P_{A}$ are the aqueous solubility (mol m$^{-3}$) and vapor pressure (Pa), $K_{oc}$ is organic carbon-normalized partition coefficient (L kg$^{-1}$); $\rho$ is the density of sediment (kg L$^{-1}$); OC% is the fraction of total organic carbon.

Transfer flux $N$ (mol h$^{-1}$) of the compound between two phases can be calculated with transfer/transformation rate ($D$, mol h$^{-1}$ Pa$^{-1}$) and fugacity difference between two phases ($f_{1} - f_{2}$) based on the approach described by Mackay (2001):

\[
N = D(f_{1} - f_{2}) = \frac{B AZ}{\delta y}(f_{1} - f_{2})
\]

where $B$ is molecular diffusion coefficient (m$^{2}$ h$^{-1}$); $\delta y$ represents the diffusion path length (m); $\delta$ is the interfacial area (m$^{2}$). The detailed descriptions of parameterization for hydrodynamic and fugacity models were provided in the supplementary information section.

### 4. Results and discussion

#### 4.1. Occurrence of XEDCs in surface water and sediment along the river

Concentrations of BPA in the surface water of the Jialu River varied from 0.41 to 2.99 µg L$^{-1}$ with mean value of 1.54 µg L$^{-1}$.
Table 1 – Symbols used in the context.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>m²</td>
<td>Area of cross section</td>
</tr>
<tr>
<td>A_up</td>
<td>m² h⁻¹</td>
<td>Molecular diffusion coefficient in water</td>
</tr>
<tr>
<td>A_sed</td>
<td>m² h⁻¹</td>
<td>Molecular diffusion coefficient in sediment</td>
</tr>
<tr>
<td>C_w</td>
<td>µg L⁻¹</td>
<td>Concentrations of chemicals in aqueous phase</td>
</tr>
<tr>
<td>C_s</td>
<td>µg g⁻¹</td>
<td>Concentrations of chemicals in sediment</td>
</tr>
<tr>
<td>C_ua</td>
<td>ng m⁻³</td>
<td>Concentrations of chemicals in air</td>
</tr>
<tr>
<td>d</td>
<td>cm</td>
<td>Thickness of sediment sampled</td>
</tr>
<tr>
<td>D_w</td>
<td>mol h⁻¹ Pa⁻¹</td>
<td>Air–water transfer parameter</td>
</tr>
<tr>
<td>D_s</td>
<td>mol h⁻¹ Pa⁻¹</td>
<td>Sediment–water transfer parameter</td>
</tr>
<tr>
<td>E</td>
<td>m² s⁻¹</td>
<td>Longitudinal dispersion coefficient</td>
</tr>
<tr>
<td>f_a</td>
<td>Pa</td>
<td>Fugacity of air</td>
</tr>
<tr>
<td>f_s</td>
<td>Pa</td>
<td>Fugacity of sediment</td>
</tr>
<tr>
<td>g</td>
<td>m s⁻²</td>
<td>Gravitational acceleration</td>
</tr>
<tr>
<td>h</td>
<td>m</td>
<td>Depth of river</td>
</tr>
<tr>
<td>l</td>
<td>dimensionless</td>
<td>Hydraulic gradient</td>
</tr>
<tr>
<td>l_bio</td>
<td>d⁻¹</td>
<td>Air-side mass transfer coefficient over water</td>
</tr>
<tr>
<td>K_w</td>
<td>m⁻¹</td>
<td>Water-side mass transfer coefficient over water</td>
</tr>
<tr>
<td>K_s</td>
<td>m⁻¹</td>
<td>Water-side mass transfer coefficient over sediment</td>
</tr>
<tr>
<td>k_dil</td>
<td>m⁻¹</td>
<td>Dilution factor vs. distance</td>
</tr>
<tr>
<td>K_OC</td>
<td>L kg⁻¹</td>
<td>Organic carbon normalized partition coefficient</td>
</tr>
<tr>
<td>K_p</td>
<td>L kg⁻¹</td>
<td>Suspended particles/sediment and water partition coefficient</td>
</tr>
<tr>
<td>K_oaw</td>
<td>dimensionless</td>
<td>Octanol–water partition coefficient</td>
</tr>
<tr>
<td>N_tan</td>
<td>mol h⁻¹</td>
<td>Total mass transfer flux between phases</td>
</tr>
<tr>
<td>N_dif</td>
<td>mol h⁻¹</td>
<td>Air–diffusive flux</td>
</tr>
<tr>
<td>N_dif_s</td>
<td>mol h⁻¹</td>
<td>Sediment–water diffusive flux</td>
</tr>
<tr>
<td>P_s</td>
<td>Pa</td>
<td>Vapor pressure</td>
</tr>
<tr>
<td>Q</td>
<td>m³ s⁻¹</td>
<td>River water discharge</td>
</tr>
<tr>
<td>R</td>
<td>m₂ mol⁻¹ K</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>S_w</td>
<td>mol m⁻³</td>
<td>Solubility of chemicals in aqueous phase</td>
</tr>
<tr>
<td>T</td>
<td>K</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>OC%</td>
<td>dimensionless</td>
<td>Organic carbon content in sediment</td>
</tr>
<tr>
<td>µ</td>
<td>m s⁻¹</td>
<td>Flow velocity of river water</td>
</tr>
<tr>
<td>µ*</td>
<td>m s⁻¹</td>
<td>Friction velocity of river water</td>
</tr>
<tr>
<td>V_m</td>
<td>ml mol⁻¹</td>
<td>Molar volume of chemical at 20 °C</td>
</tr>
<tr>
<td>Z_f</td>
<td>mol m⁻³ h⁻¹</td>
<td>Fugacity capacity of air</td>
</tr>
<tr>
<td>Z_s</td>
<td>mol m⁻³ h⁻¹</td>
<td>Fugacity capacity of sediment</td>
</tr>
<tr>
<td>Z_w</td>
<td>mol m⁻³ h⁻¹</td>
<td>Fugacity capacity of water</td>
</tr>
<tr>
<td>x</td>
<td>m</td>
<td>Simulation distance step</td>
</tr>
<tr>
<td>ø</td>
<td>m</td>
<td>Unit river length</td>
</tr>
<tr>
<td>ρ</td>
<td>kg L⁻¹</td>
<td>Sediment density</td>
</tr>
<tr>
<td>θ</td>
<td>dimensionless</td>
<td>Porosity of sediment</td>
</tr>
<tr>
<td>γ</td>
<td>cp</td>
<td>Water viscosity coefficient at 20 °C</td>
</tr>
<tr>
<td>δ</td>
<td>dimensionless</td>
<td>Transfer factor</td>
</tr>
<tr>
<td>ξ</td>
<td>m²</td>
<td>Interfacial area</td>
</tr>
<tr>
<td>ω</td>
<td>m</td>
<td>Water surface width</td>
</tr>
<tr>
<td>ϕ</td>
<td>kg L⁻¹</td>
<td>Suspended particles concentration</td>
</tr>
</tbody>
</table>

S2 was allocated in the 2 km downstream of Zhengzhou urban zone, where EC value was the highest (1566 µS cm⁻¹). The mean concentration of DO in the surface water was 2.75 mg L⁻¹ with the lowest concentration of 0.53 mg L⁻¹ at S2, after this site, DO concentrations increased gradually to 3.80 mg L⁻¹ at S7 (Zhang et al., 2009). In contrary to DO variances, the concentrations of XEDCs in surface water decreased gradually along the river (S2–S7) and the concentration of BPA declined to 0.92 µg L⁻¹ at site S7 near the urban zone of Zhoukou. Several studies reported that high concentrations of XEDCs were detected in the industrial wastewaters such as textile effluents (Fürhacker et al., 2000; Hale et al., 2000; Solé et al., 2000). Zhengzhou is one of the important textile industries cities in China and according to Yang et al. (2008), there are at least 11 textile mills, 1 pesticide factory and 1 detergent factory locating in its urban zone with the discharged wastewater of 24-1300 t d⁻¹. All the treated/untreated industrial and domestic wastewaters were finally discharged into the Jialu River, the only wastewater receiver of the urban zone. Furthermore, no more big wastewater source was found along the river after it runs from S2 and therefore, the Zhengzhou urban zone can be regarded as the principal discharge source of XEDCs in the study area (Zhang et al., 2009).

The good positive correlations were found between BPA and OP/NP and the relationship coefficients (R) were 0.93 (p < 0.01) for OP and 0.89 (p < 0.01) for NP, respectively. The log (BPA/NP) ratio in surface water increased gradually from 0.29 (site S2) to 1.16 (site S6), whereas the log (BPA/OP) ratio remained in the range 1.54–1.72 along the river indicating the dissipation of NP from aqueous phase being faster than that of BPA and OP. The explanation for different behaviors of NP, OP and BPA in surface water might be due to their physical–chemical characteristics and biodegradation rates. The octanol-water partition coefficient (log K_oaw) of NP (4.48) is higher than that of OP (4.12) and BPA (3.40) indicating that compared with OP and BPA, NP should have higher affinity to...
SPM and is easier to be adsorbed to SPM or bed sediment (Ahel and Giger, 1993; Staples et al., 1998). Johnson et al. (2000) studied the biodegradation of OP in surface water samples from Calder River and indicated that the biodegradation rate of OP, calculated as half-lives, were ranged from 8 to 13 d in the urban/industrial river water. Compared with the result, the dissipation rates of XEDCs were found to be faster in the Jialu River and the estimated half-lives of OP, NP and BPA removed from aqueous phase were 2.4, 1.6 and 2.5 d, respectively. In addition to biodegradation, sorption to suspended particles and bed sediment will also be an important mechanism for removal of XEDCs from aqueous phase such as OP, which has a strong affinity for bed sediment with 

\[ K_p = 6 - 580 \text{ L kg}^{-1} \]  

(Johnson et al., 1998).

Sharma et al. (2009) summarized the concentrations of BPA in river water from different regions in the world and reported the concentration range of BPA was from 0.005 to 4.0 μg L⁻¹. Jin et al. (2004) reported the levels of XEDCs in surface water near Tianjin city, north China, and gave the highest concentration of BPA was 8.30 μg L⁻¹. Dong et al. (2009) found the highest concentration of BPA was 3.92 μg L⁻¹ in surface water of the Pearl River estuary with its average concentration of 2.06 μg L⁻¹. Thus, it is found that BPA concentration in Jialu River was similar to results of these investigations.

The sediment concentrations of XEDCs in the Jialu River were 15.9–31.1 ng g⁻¹ for OP, 145–349 ng g⁻¹ for NP and 626–3584 ng g⁻¹ for BPA and their average concentrations were 21.4, 257 and 2291 ng g⁻¹, respectively (Fig. 1). The average sediment concentration of XEDCs in middle and lower reaches (S4–S7) were higher than that in upper stream (S2–S4) with the ratios of 1.56 for OP, 1.22 for NP and 2.15 for BPA, respectively. The log(Kop), log(KNP) and log(KBPA) in all sediment samples were 1.32, 2.39 and 3.30 indicating the BPA and NP were the main contaminants compared with the OP. The correlation coefficients (R) of NP/BPA and OP in sediment were 0.54 (p < 0.05) for NP and 0.71 (p < 0.05) for BPA, respectively.

4.2 In situ sediment—water partition of XEDCs along the river

Understanding the degree of sediment—water partitioning of the organic pollutants is of importance in the risk assessment of river ecosystem, development of sediment quality criteria and modeling the environmental behavior and fate of contaminants (Gobas and Maclean, 2003). Some studies have reported that the adsorption of organic contaminants to sediment related with sediment’s organic carbon content (Xue et al., 2006). Organic carbon contents (OC%) in all sediment samples from the Jialu River varied from 2.44 to 3.06% with the mean value of 2.72%. The positive correlation between OC% and concentrations of XEDCs were found and correlation coefficients were 0.77 (P < 0.05) for OP, 0.71 (P > 0.05) for NP and 0.43 (P > 0.05) for BPA. The results indicated that sediment with the higher organic carbon was likely to adsorb the more XEDCs, and organic carbon plays an important role in controlling adsorption of XEDCs to sediment in the river.

Although the disequilibrium status between sediment and water always occur and organic contaminants always undergo dynamic sorption/desorption in river ecosystem, the distribution of organic contaminants between water and sediment is still good indicator for predicting their behavior and fate in the environment (Schwarzenbach et al., 2003). In situ organic carbon-normalized partition coefficient (Koc') between sediment and water is defined in eq. (4)

\[ K_{oc}' = \frac{K_p}{f_{oc}} \]  

where \( f_{oc} \) is organic carbon fraction in sediment; \( C_s \) presents the XEDCs concentration in the sediment (μg g⁻¹); \( C_{aq} \) denotes the concentration of XEDCs in aqueous phase (μg L⁻¹). The unit of partition coefficient (Kp) is L kg⁻¹.

Table 2 showed the values of equilibrium partition coefficients (log Koc), octanol—water partition coefficient (log Kow) and measured in situ sediment—water partition coefficients (log Koc') in the Jialu River. Means of measured in situ log Koc' of XEDCs along the Jialu River were in the range from 4.32 to 4.65 with their standard deviation (SD) of 0.23–0.58. As shown in Table 2, measured in situ log Koc' values of OP, NP and BPA in the downstream (S5–S7) were greater than that in the upper stream (S2–S4). In situ log Koc' values in the upstream varied from 4.04 to 4.19 for OP, which were in the range of equilibrium partition coefficients from the literature. And they varied from 3.81 to 3.98 for NP, which were lower than the equilibrium values. Although the values of measured in situ log Koc' of BPA in the Jialu River were similar with the results of that (4.05–4.23) in Tiber river, Central Italy (Patrolocco et al., 2006), they were one order of magnitude higher than the literature results (Staples et al., 1998; Ying et al., 2003). Some studies showed that comparing with the measured in situ log Koc', the lower equilibrium log Koc' may be due to the laboratory results were obtained under the minimizing other processes such as ...

<table>
<thead>
<tr>
<th>XEDCs</th>
<th>log Kow</th>
<th>log Koc</th>
<th>log Koc'</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
<th>Mean log Koc'</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>4.48*</td>
<td>4.13–4.69</td>
<td>3.88</td>
<td>3.98</td>
<td>3.81</td>
<td>4.36</td>
<td>5.13</td>
<td>4.96</td>
<td>4.35</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>BPA</td>
<td>3.40b</td>
<td>3.02d</td>
<td>4.19</td>
<td>4.14</td>
<td>4.74</td>
<td>4.87</td>
<td>5.00</td>
<td>4.98</td>
<td>4.65</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>

a Data were obtained from literature Ahel and Giger (1993).
b Data were obtained from literature Cousins et al. (2002).
c Data were obtained from literature Navarro et al. (2009). 
d Data were obtained from literature Ying et al. (2003).
volatilization, degradation and chemical bonding etc (Düring et al., 2002). However, considering the Zhengzhou urban zone as the principal discharge source of XEDCs in the study area, the higher log $K_{oc}$ values occurred in the downstream mainly due to the suspended particles with XEDCs deposited to bottom sediment of the downstream and the retransfer of surface sediment from the upstream to the downstream.

Persistence of OP and NP in the anaerobic bed sediment and sewage sludge has been previously reported (Johnson et al., 2000; Ying et al., 2003). Thus, it is reasonable to expect that the long-term accumulation of these chemicals in the downstream also resulted in the high sediment concentrations due to the anoxic conditions in the sediment of the Jialu River.

### 4.3. Estimated mass inventory of XEDCs in sediment along the river

To assess the potential of sediment as a new contaminants source to the downstream and the influences of urban zone on its receiving rivers, the sediment inventory of XEDCs along the Jialu River was estimated. The river was divided into 5 compartments according to the sampling sites. Each of the 5 sampling sites was allocated in the start of one compartment (except S1 and S7) and the average concentration of XEDCs in two adjacent sites was used to represent the entire concentration of the compartment. The inventory ($M_i$, in kg) of XEDCs in sediment along the river was calculated by using the following equation:

$$M_{sediment} = \kappa \rho C_{i0} A_i d$$

where $C_{i0}$ is the average sediment concentration of XEDCs in compartment $i$ ($\mu g \; g^{-1}$); $A_i$ is the area of one compartment $i$ ($m^2$); $\rho$ is the average sediment density of 1.23 g cm$^{-3}$; $\kappa$ is the conversion factor; and $d$ is the thickness of sediment sampled, which was 5 cm in this study. The estimated sediment inventory of XEDCs in the Jialu River was 807 kg with average load of 4.8 kg km$^{-1}$ (Fig. 2). The sediment inventory in the middle and downstream (S4–S7) appeared to be 2.28 times higher than those in the upstream (S2–S4) suggesting that the downstream acts as the net sink of XEDCs to the upper stream.

In order to better understand the accumulation of XEDCs in sediment, we replaced the $C_{i0}$ in eq. (5) with the theoretical $C_{i0}'$, which was deduced from respective XEDCs concentration in surface water at site $i$ under the assumption of sediment—water partition equilibrium, by using the following equation:

$$M_{sediment} = \kappa \rho C_{i0}' A_i d$$

where $C_{i0}'$ is the theoretical sediment concentration of XEDCs in compartment $i$ under partition equilibrium ($\mu g \; g^{-1}$). $K_{oc}$ is the organic carbon-normalized equilibrium partition coefficient. Navarro et al. (2009) showed that the sediment—water log $K_{oc}$ of XEDCs ranged from 4.13 to 4.69 for NP and 3.60–4.19 for OP, which were in good agreement with the ones obtained from both other sorption experiments and empirical correlations. Therefore, in the present study, the log $K_{oc}$ of XEDCs were derived from the experimental results reported by Navarro et al. (2009) and Ying et al. (2003). As shown in Fig. 2, the theoretical mass inventory from S2 to S4 accounted for 72.6% of the total theoretical mass inventory in sediment (S2–S7). Compared with the measured mass inventory, these results provided useful information on the behavior and fate of XEDCs in sediment along the river: (1) since the Zhengzhou urban zone was regarded as the principal source of XEDCs, the higher accumulation of XEDCs in the middle and downstream derived from the retransfer of suspended surface sediment. And the results were in agreement with hydraulic gradient along the river, which was relatively lower in the middle and downstream (mean 0.15‰) than that in upstream of 0.22‰ (Fig. 2); and (2) as for the whole river reach (S2–S7), the measured mass inventory of total XEDCs was about 5.14 times higher than its theoretical values, which can be used as an indicator for reflecting the residual time of XEDCs in the river. That is, the average accumulative time of XEDCs in the river was estimated at about 5 years. In general, a river is a highly complex system and function as a unified whole, the dynamics of which is significantly influenced by several important variables such as discharge, velocity, suspended particles concentrations, and sediment load. Flood disasters frequently occur in the Huaihe River basin and thus, about 5674 reservoirs and 5427 sluices have been constructed in its main stem and tributaries. Heavy rain events in the river catchment basin could cause the floods and change the deposition profile of sediment along the river. Fig. S2 gave the frequency distribution of the rainfall of the Huaihe River basin during the Mei-yu season (mid-Jun to mid-Jul) from 1954 to 2003. The statistic frequency of the rainfall of >300 mm is about 24%, which is in agreement with an average accumulative time of XEDCs in the Jialu River (Fig. S2). Thus, it can be deduced that the big flood, often occurred in the river, would remove the mass loadings of organic contaminants in sediment, which makes the ratio of measured and theoretical mass inventories in sediment was in the one order with the big flood frequency.

On the other hand, the measured sediment concentrations of XEDCs in the middle and downstream were higher than the theoretical mass inventory from S2 to S4 accounted for 72.6% of the total theoretical mass inventory in sediment (S2–S7). Compared with the measured mass inventory, these results provided useful information on the behavior and fate of XEDCs in sediment along the river: (1) since the Zhengzhou urban zone was regarded as the principal source of XEDCs, the higher accumulation of XEDCs in the middle and downstream derived from the retransfer of suspended surface sediment. And the results were in agreement with hydraulic gradient along the river, which was relatively lower in the middle and downstream (mean 0.15‰) than that in upstream of 0.22‰ (Fig. 2); and (2) as for the whole river reach (S2–S7), the measured mass inventory of total XEDCs was about 5.14 times higher than its theoretical values, which can be used as an indicator for reflecting the residual time of XEDCs in the river. That is, the average accumulative time of XEDCs in the river was estimated at about 5 years. In general, a river is a highly complex system and function as a unified whole, the dynamics of which is significantly influenced by several important variables such as discharge, velocity, suspended particles concentrations, and sediment load. Flood disasters frequently occur in the Huaihe River basin and thus, about 5674 reservoirs and 5427 sluices have been constructed in its main stem and tributaries. Heavy rain events in the river catchment basin could cause the floods and change the deposition profile of sediment along the river. Fig. S2 gave the frequency distribution of the rainfall of the Huaihe River basin during the Mei-yu season (mid-Jun to mid-Jul) from 1954 to 2003. The statistic frequency of the rainfall of >300 mm is about 24%, which is in agreement with an average accumulative time of XEDCs in the Jialu River (Fig. S2). Thus, it can be deduced that the big flood, often occurred in the river, would remove the mass loadings of organic contaminants in sediment, which makes the ratio of measured and theoretical mass inventories in sediment was in the one order with the big flood frequency.

On the other hand, the measured sediment concentrations of XEDCs in the middle and downstream were higher than
the respective equilibrium concentrations, which suggested that the non-equilibrium conditions in terms of XEDCs partitioning existed and the sediment may serves as a potential source of XEDCs to river water in the middle and the downstream. Therefore, multimedia mass transfer should be taken into account in predicting the concentration variances of XEDCs and further performing environmental risk assessment in surface water along the river.

4.4. Modeling evaluation of transport of XEDCs in surface water along the river

4.4.1. Model scheme

There are three STPs in urban zone of Zhengzhou and the treated water (about 70 × 10^4 t d⁻¹) was finally discharged into the Jialu River (Table S1). The effluents of the three STPs accounted for 39–71% of the river water discharge at S3 in 2007 and the lowest proportion occurred at September, which was used to represent the high flow season in this study. Under the assumption of discharged XEDCs amount and the river water discharge remaining stable during the sampling period (no rain event happened), the river is treated as a steady state system, that is iC/iOt = 0. Thus, transport of XEDCs in the river can be described by the one-dimension advection–dispersion equation of stable state.

Fugacity models can simplify the analysis of mass fluxes of organic contaminants from one phase to the other such as the air–water and water–sediment exchanges (Kilic and Aral, 2009). The mass transferring processes of different phases mainly include dry/wet deposition, sediment deposition, air–water and water–sediment diffusion and so forth. Because the rain event didn’t happened during the sampling period, the air–water exchange only included the dry deposition and diffusion processes in the present study.

Sampling site S1 was allocated in a spare reservoir of Zhengzhou city, a piedmont upper stream of Zhengzhou urban zone, where the water body is relatively still and immune from human activity. With an assumed air–water exchange equilibrium existing at S1, the calculated atmospheric fugacity (f_a) of OP, NP and BPA were 5.67 × 10⁻⁸, 3.75 × 10⁻⁸ and 1.036 × 10⁻¹¹ Pa and their respective concentrations in atmosphere were 4.83, 338.7 and 0.001 mg m⁻³, respectively. These values were used as the average atmospheric concentrations of XEDCs in the whole Jialu River basin. Therefore, the dry deposition flux (N_ddep) per unit interfacial area can be estimated at 2.52 × 10⁻¹⁰ mol h⁻¹ for OP, 1.66 × 10⁻⁸ mol h⁻¹ for NP and 4.82 × 10⁻¹³ mol h⁻¹ for BPA based on the assumed dry deposition velocity of 10.8 m h⁻¹ (Mackay and Paterson, 1991).

The total mass flux from air and sediment to aqueous phase (N_total, mol h⁻¹ m⁻²) through unit interfacial area can be written as following:

\[
N_{\text{total}} = N_{\text{dif-sw}} + N_{\text{dif-sw}} + N_{\text{dep}}
= (D_{\text{sw}}f_A - D_{\text{sw}}f_A) + (D_{\text{sw}}f_A - D_{\text{sw}}f_A) + N_{\text{dep}}
= D_{\text{sw}}f_A + D_{\text{sw}}f_A - (D_{\text{sw}} + D_{\text{sw}}) f_a + N_{\text{dep}}
\]

(7)

where N_dif-sw and N_dif-sw are air–water and water–sediment diffusive flux (mol h⁻¹) per unit interfacial area (δ, m²), the product of water-surface width (a, m) and unit river length (m, m); D_sw and D_sw are air–water and water–sediment transfer coefficients (mol h⁻¹ Pa⁻¹); f_A, f_w, f_s are the fugacities of air, water and sediment. f_s was calculated from the average concentrations of the XEDCs in all sediment samples and the values were 1.10 × 10⁻⁷ Pa, 1.13 × 10⁻⁵ Pa and 1.11 × 10⁻¹⁰ Pa for OP, NP and BPA, respectively.

Conceptually, the whole river was divided into n sections (the section was defined as a tank with its width and length equal to river width and unit river length) and the completely stirred tank reactors (CSTR) model was applied in each section of the river. For section i, the unit concentration variance (ΔC_i) of XEDCs in aqueous phase, which was caused by the multimedia mass transfer, can be written with the increase of mass flux (Am) per unit water volume:

\[
\Delta C_i = \Delta m/V_i = N_{\text{total,i}}/Q_i = \delta(\alpha - \beta C_i)/Q_i
\]

(8)

Therefore, the final concentration of XEDCs in aqueous phase at each section i can be calculated based on the equation:

\[
C_i = (1 - F) \times (C_i + \Delta C_i)
= \left(1 - \frac{\alpha}{\mu F}\right) \times \left(\frac{\text{max} C_{i-1} \times \left(1 - \frac{\beta}{\mu (Q_i - \text{dep})}\right)}{Q_i} \exp(x - \kappa_{de})\right) \times \left(1 - \frac{\beta}{\mu (Q_i - \text{dep})}\right) + \frac{\delta C_{i-1}}{Q_i} \times \exp(x - \kappa_{de})
\]

(9)

where Q_i is the river water discharge at section i (m³ s⁻¹); C_i is the concentration of XEDCs at section i, which is calculated without consideration of the multimedia mass transfer; C_{i-1} and C_i are the final concentrations of XEDCs in surface water at sections i – 1 and i; V_i is the water column volume in section i, which equal to the product of Q and time (t); x is the simulation distance step (m) and \delta is the interfacial area per unit river length (m²); (1 – F) denotes the partition fraction of XEDCs in aqueous phase within distance step; m and n are the relationship coefficients of river water discharge and water-surface width (Parameterization in supplementary information). α and β denote the formulas (D_sw f_a + D_w a f_s + N_{dep}) and (D_sw f_a + D_w a) respectively. The values of α and β are 3.75 × 10⁻¹⁰ and 0.0012 mol h⁻¹ for OP, 1.68 × 10⁻⁸ and 0.016 mol h⁻¹ for NP, 1.20 × 10⁻⁹ and 5.62 × 10⁻⁵ mol h⁻¹ for BPA.

4.4.2. Sensitivity analysis and model calibration

The sensitivity of important variables in the model were tested by comparing model results without any changed variable with those with only one variable changed by ±10%, which allows us to determine the key parameters and others may remain on default values. Results of sensitivity analysis were shown in Table 3. The results showed that the model was insensitive to the water depth h, water-surface width a, sediment porosity θ and water-side mass transfer coefficient K_{sw} with their changes of <0.1% (except K_{sw} changes of 1.11% and −0.95% for NP). The estimations of XEDCs were moderately sensitive to river water discharge Q and organic carbon-normalized partition coefficients K_{wb} with their changes of <1.0%, whereas the changes of Q were 3.10% and −3.64% for NP. The model was sensitive to other parameters such as river water velocity ν, biodegradation rate constant k_{bio}, dilution factor k_{dil}, and air-side mass transfer coefficient K_{sw}.
And ±10% changes of these parameters can result in >1.0% changes of the model results.

The key model parameters were calibrated using the measured results of BPA in surface water (with 18.6% error). And then, the calibrated parameters were used to run the model for predicting of the concentrations variances of OP and NP in surface water along the river. As shown in Fig. 3, the general trends of the model estimations were in good agreement with the measured results and the relative standard deviation between the simulated and the measured values in all sampling sites were 22.8% for OP and 25.1% for NP. The results indicated that the model fit well with the measured values and can be acceptable.

### 4.4.3. Scenario analysis

In this section, two kinds of different scenarios were simulated: 1) constant discharged amount of XEDCs from urban zone under normal period (average flow of the year 2007), higher water period (the highest water discharge of the year 2007) and lower water period (the lowest water discharge of the year 2007); 2) under the normal period, the amount of discharged XEDCs from urban zone doubles due to the urban development or reduces by half due to improved management of wastewater.

Predicted total concentrations of all the three XEDCs in surface water along the river under different scenarios were plotted in Fig. 4. As for scenario of stable discharge of XEDCs, the concentrations of total XEDCs throughout the river were higher than 1.0 µg L⁻¹ in the year of 2007. Even though under the high water period, the total XEDCs concentrations in almost half of the river reach were more than 2.0 µg L⁻¹ (Fig. 4a). As shown in Fig. 4b, if the discharged XEDCs double, the total XEDCs concentrations in more than 90% river reach would be higher than 3.0 µg L⁻¹ under the normal period. Even though the XEDCs discharged from urban zone could be decreased by half, the total XEDCs concentrations of >1.0 µg L⁻¹ in surface water would persist about 120 km from the discharge source.

Belfroid et al. (2002) reported that the concentrations of BPA in fish were in the range 2–75 µg kg⁻¹ dry weight compared with the corresponding concentrations of <0.01–0.33 µg L⁻¹ in surface water in The Netherlands. Thus, the potential risk of BPA associated with accumulation in the food chain was expected. Zhao et al. (2008) reported that there were some fish such as cyprinoid living in the Zhoukou reach of the Shaying River, where the Jialu River flowed (near S7). Based on the predicted concentrations of BPA at S7 in the year of 2007 and the average annual flow of the Shaying River in Zhoukou reach (125.5 m³ s⁻¹), the estimated concentrations of BPA in surface water of this reach were 0.18–0.28 µg L⁻¹ during 2007. And thus, the bioaccumulation of BPA in fish in the Zhoukou reach of the Shaying River could be expected.

In addition, based on the results of model, the mass loadings of the total XEDCs in surface water along the river can be calculated and the mass loadings (M, in kg yr⁻¹) of XEDCs in surface water vs. distance from discharge source S2 (x, in kilometer) can be described as:

\[
M_{\text{water}} = -7.27x + 2092 (R^2 = 0.98)
\]  

(10)

The result indicated that the amount of the total XEDCs discharged from Zhengzhou urban zone to the river was about

<table>
<thead>
<tr>
<th>Variable</th>
<th>Calibrated values</th>
<th>Variance (%)</th>
<th>OP</th>
<th>NP</th>
<th>BPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ</td>
<td>0.71 m s⁻¹</td>
<td>10</td>
<td>-1.26</td>
<td>-1.90</td>
<td>-3.43</td>
</tr>
<tr>
<td>h</td>
<td>1.56 m</td>
<td>10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Q</td>
<td>20.4 m³ s⁻¹</td>
<td>10</td>
<td>-0.28</td>
<td>-3.64</td>
<td>-0.01</td>
</tr>
<tr>
<td>ω</td>
<td>40.5 m</td>
<td>10</td>
<td>0.23</td>
<td>3.10</td>
<td>0.01</td>
</tr>
<tr>
<td>k_ac</td>
<td>3.16 × 10⁻⁶</td>
<td>10</td>
<td>2.67</td>
<td>2.28</td>
<td>2.52</td>
</tr>
<tr>
<td>K_ac</td>
<td>5 m h⁻¹</td>
<td>10</td>
<td>2.67</td>
<td>2.28</td>
<td>2.52</td>
</tr>
<tr>
<td>K_wu</td>
<td>0.05 m h⁻¹</td>
<td>10</td>
<td>0.01</td>
<td>1.11</td>
<td>0.00</td>
</tr>
<tr>
<td>θ</td>
<td>0.3</td>
<td>10</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>K_ec</td>
<td>-10</td>
<td>0.21</td>
<td>0.14</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>r_bio</td>
<td>-10</td>
<td>-1.26</td>
<td>-1.90</td>
<td>-3.43</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Ratio = 100% × (results with one changed variable – results without any changed variable)/results without any changed variable.

Fig. 3 – Model calibration results for BPA and model validation results for OP and NP in surface water along the Jialu River. Data are simulated (lines) and measured (symbols) concentrations of XEDCs in aqueous phase. BPA (left); OP (middle); NP (right).
2.0 t yr\(^{-1}\) and about 29–65% of the discharged XEDCs were finally dissipated from the aqueous phase in its 170 km downstream. Therefore, the influences of Zhengzhou urban zone on its receiving river were significant and the continuous monitoring and prediction of XEDCs in the Jialu River are necessary.

5. Conclusions

The anthropogenic contaminants XEDCs (OP, NP and BPA) were used as indicators to study the influence of urban zone on its receiving river and thus, the Jialu River seriously polluted by the Zhengzhou urban zone in China was chosen, where the average concentration of NH\(_4^+\) in surface water (near S3) was 63.9 mg L\(^{-1}\) in the year 2007. The concentrations of XEDCs in surface water and sediment were measured and the results suggested that Zhengzhou urban zone can be regarded as the principal discharge source of XEDCs in the catchment. The positive correlation of organic carbon content and XEDCs concentration in sediment were found and the relationship coefficients were 0.77, 0.71 and 0.43 for OP, NP and BPA. The results of in situ sediment–water partition of XEDCs showed that the log \(K_{oc}\) values in the downstream was higher than that in the upstream suggesting that the retransfer of suspended surface sediment was one of reasons why the in situ log \(K_{oc}\) in field was higher than equilibrium value in laboratory.

In order to understand the behavior and fate of XEDCs in sediment, measured and theoretical inventories of XEDCs in sediment were estimated with the thickness of sediment sampled. The results showed that mass inventory of XEDCs in sediment (0–5 cm) was 807 kg, about 70% of which would deposit in the middle and lower reaches. Comparison of measured and theoretical sediment inventories of XEDCs in the whole river suggested that the average residual time of XEDCs was about 5 years. The results were in accord with the big flood frequency of the river indicating that the contaminants in surface sediment would be removed by the big floods in the Jialu River.

To predict the concentration variance of XEDCs in surface water along the river, a fugacity-hydrodynamic model was developed. The hydraulic parameters of the model such as the velocity and depth were calibrated with the data of BPA, and then, predicted results of the calibrated model can agree well with the measured values of OP and NP, within 30% error. Compared with its advantage of numerical simplicity, the main limitation of the model is that the discharge sources of the pollutants are regarded as steady system so that the transport of pollutants can be described by one-dimensional advection–dispersion equation of steady state.

Acknowledgements

This work was supported from the Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science (No. 21300334), the Program of Ministry of Science and Technology, China (2008ZX07010-006-1) and National Key Water Project, China (No.2009ZX07210-006). Authors thank Professor F.D. Li, Dr. S.Q. Wang and Dr. J.R. Liu for their assistance in sample collection.

Appendix. Supplementary information


REFERENCES


