



## Screening for over 1000 organic micropollutants in surface water and sediments in the Liaohe River watershed



Qingwei Bu <sup>a,c,d</sup>, Qian Luo <sup>b</sup>, Donghong Wang <sup>b,\*</sup>, Kaifeng Rao <sup>c</sup>, Zijian Wang <sup>c</sup>, Gang Yu <sup>d</sup>

<sup>a</sup> School of Chemical & Environmental Engineering, China University of Mining & Technology-Beijing, Beijing 100083, China

<sup>b</sup> Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

<sup>c</sup> State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

<sup>d</sup> School of Environment, POPs Research Center, State Key Joint Laboratory of Environment Simulation and Pollution Control, Tsinghua University, Beijing 100084, China

### HIGHLIGHTS

- The reliability and usefulness of high throughput screening method was evaluated.
- The massive qualitative data help unveil pollution profiles among different sites.
- The semi-quantification results agree well with those from target analysis.
- The high throughput method is proven to be a valuable tool in watershed management.

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### ABSTRACT

High throughput screening method has gained attractive prospects because it offers a fast and effective approach to obtain a holistic picture of organic micropollutant (OM) pollution in a site specific environment. However, reliability and usefulness of the generated data sets for OM pollution profiles and occurrence levels have not been fully evaluated. In this paper, we screened 1030 OMs in surface water and sediments from the selected rivers of the Liaohe River watershed to (1) examine the usefulness of using qualitative data to gain insights into source identification and (2) further evaluate the reliability of the semi-quantification results in a field study. The results showed that 81 and 89 OMs at concentrations up to 5670 ng/L and 6714 ng/g were identified in surface water and sediments, respectively. Qualitative data could be used to identify the similarity (or dissimilarity) of pollution sources at different locations for surface water, which could provide insights for source back tracking of water contamination. Accuracy tests showed that our semi-quantification results agree well with those from previously reported values and our target analysis. Though our results for the majority of newly quantified OMs need to be further confirmed, we have demonstrated that this method is suitable for understanding the pollution characteristics and occurrence levels of OMs in the environment for environmental scientists and managers.

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### 1. Introduction

Thousands of organic chemicals have been produced and released into the aquatic environment, and new chemicals are being continuously introduced (Bu et al., 2013a). Some of these contaminants pose risks to human health and/or the environment even at extremely low concentrations [known as organic micropollutants (OMs)] (Feron et al., 2002; Long et al., 1995; Sharpe, 2001; Sharpe and Irvine, 2004). Due to the increasing sensitivity of

analytical methods, the number of OMs detected in the aquatic environment is on the rise over the past decade (Schwarzenbach et al., 2010). However, our knowledge of OM contamination levels in the aquatic environment is still limited because only a small fraction of OMs can be probed by the vast majority of traditional target analysis. The target analysis used to assess OM contamination levels usually covers few compounds and is time-consuming and costly. Alternatively, methods that fulfill the goal of high throughput screening of OMs in environmental samples are gaining attractive prospects for environmental scientists and managers, because the screening method could analyze several hundreds or even more OMs simultaneously.

\* Corresponding author.

E-mail address: [dhwang@rcees.ac.cn](mailto:dhwang@rcees.ac.cn) (D. Wang).

Several methods for screening organic micropollutants in the aquatic environment have been reported (Gómez et al., 2009; Kadokami et al., 2012, 2005) and are proven to be useful for screening environmental samples (Duong et al., 2014; Kadokami et al., 2013; Pan et al., 2014). In our previous study, a method for screening 50 phenols in water was established and applied in the case of Taihu Lake (Zhong et al., 2010). Further, this method was modified for qualitative screening of 1093 OM<sub>s</sub> in water of the Danjiangkou reservoir (Bu et al., 2014a). More recently, we introduced a set of quantification internal standards (QIS<sub>s</sub>) to improve the quantification ability of the method, and results showed that the high throughput semi-quantification method was feasible for comprehensive analysis of OM<sub>s</sub> in sediments quantitatively (Bu et al., 2014b). The high throughput screening analysis could produce a database comprising of a large pool of both qualitative and quantitative data of contaminants, which can help understand the pollution characteristic and occurrence level of OM<sub>s</sub> in the investigated sites. However, usefulness and reliability of the data sets generated from the high throughput method have not been fully demonstrated.

One of our goals is to examine the usefulness of using qualitative data to gain insights into source identification. Generally, pollution characteristics of sampling sites are related to the source types, especially the point source types at a local scale. The hypothesis is that the acquired qualitative data could be used to differentiate pollution characteristics of different sites, and further to offer a basis for source identification. Here we did not aim to identify emission sources for individual OM<sub>s</sub> and their contribution to each sampling site, because our straight goal is focused on how to get the maximum use of qualitative data to identify similarity (or dissimilarity) of pollution sources for different locations. Another goal of this work is to further evaluate the reliability of the semi-quantification results in a field study. To this end, quantitative data generated from this semi-quantification method was compared to those obtained by target analysis. To accomplish these goals, we reported an application of our previously proposed high throughput semi-quantification method (Bu et al., 2014b) for screening OM<sub>s</sub> in surface water and sediments from selected rivers of the Liaohe River watershed.

## 2. Materials & methods

### 2.1. Chemicals and materials

All solvents (including methanol, acetone, dichloromethane, *n*-hexane) were HPLC grade (J.T Baker, Phillipsburg, NJ, USA). All standards were purchased from AccuStandard Inc. (New Haven, Connecticut, USA). All glassware was washed with acetone and water, soaked overnight in concentrated sulfuric acid containing 5% K<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub> solution, and baked at 550–600 °C for five hours after washing with ultra-pure water.

### 2.2. Study sites and sampling

Liaohe River watershed is located in the Northeastern China and originates from the Qilaotu Mountain, runs about 1345 km into Liaodong Bay, covering an area of 191,900 km<sup>2</sup>. A large number of municipal and industrial facilities are located in the catchment, especially in the lower reaches in Liaoning Province, which is one of the most heavily polluted regions in China. Therefore, four main streams in Liaoning Province including Liaohe River, Hunhe River, Taizihe River, and Daliaohe River provide an ideal setting to explore the goals of this work (Fig. S1). Based on the goal of evaluating the usefulness of qualitative data in source identification, twelve national monitoring cross-sections which accept various

types of sewages, were selected (Table 1). At each section, surface water and respective sediment samples were collected in April 2011 along the riverside. At each sampling site, surface water (0–20 cm depth, >2 L) was collected by a stainless sampler (5 L) and filtered using Millipore glass microfiber filters (0.7 μm, Millipore, USA) immediately. After that, they were preserved in amber glass bottles at 4 °C until analysis. Surficial river sediment samples (0–10 cm depth) were collected using a grab sampler (15 × 15 cm) and immediately transported to the laboratory and stored at –20 °C.

### 2.3. Sample pretreatment

The analytical procedures for surface water samples were performed according to Bu et al. (2014a) and Zhong et al. (2010). Briefly, two liter of water was extracted by solid phase extraction with C18 (500 mg, 6 ml; Supelco, Bellefonte, PA, USA) coupled with Oasis<sup>®</sup> hydrophilic-lipophilic balance (HLB, 500 mg, 6 ml; Waters, Milford, MA, USA) cartridges. The cartridges were eluted by 10 ml of dichloromethane. The extract was concentrated under a gentle stream of nitrogen and thereafter, the solvent was changed from dichloromethane to hexane (0.5 ml) for instrumental analysis.

OM<sub>s</sub> in the sediment were analyzed using the method of Bu et al. (2014b). In short, the freeze-dried sediment (5 g) was extracted with dichloromethane/acetone (1:1, v/v) using an accelerated solvent extraction system (Dionex ASE350, Dionex, Sunnyvale, California, SA). The extract was cleaned-up by the gel permeation chromatography (GPC) equipped with a Bio-Beads SX3 column (Bio-Rad Laboratories, Hercules, California, USA) using cyclohexane/ethyl acetate (1:1, v/v) as mobile phase. Thereafter, the solvent as changed to hexane in approximately 1 ml under a gentle stream of highly pure nitrogen. The hexane concentrate was applied to a Florisil (500 mg, 6 ml; Supelco, Bellefonte, PA, USA) cartridge for further cleanup process. The cartridge was eluted by 5 ml of mixture of dichloromethane/acetone (1:1, v/v). The solution of the cleaned extract was changed to hexane (0.2 ml) before instrumental analysis.

### 2.4. Instrumental analysis and semi-quantification

The sample analysis was carried out using an Agilent 6890N-5975D gas chromatography–mass selective detector (GC–MSD; Agilent Technologies, Santa Clara, California, USA) equipped with a DB-5 ms capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific, USA). High purity helium (99.9999%) was used as the carrier gas. Data acquisition and processing were based on retention time locking and deconvolution technologies, which was accessed in ChemStation Software (version E.0200.493; Agilent Technologies, USA). One complete run lasted 48 min, details of the GC–MSD method was described in previous studies (Bu et al., 2014b; Bu et al., 2014a).

The database used for screening analysis included 1030 OM<sub>s</sub> as that in Wylie (2006) and Quimby and Szelewski (2006), which are also listed in detail in Table S1. Deconvolution was run to identify OM<sub>s</sub> according to the following two criteria: the automated mass spectral deconvolution and identification system match values were higher than 60%; the expected retention time value differed from the observed one in less than 10 s. The extracted spectrum was also reverse-matched with the National Institute of Standards and Technology library to further confirm the positive identification. For semi-quantification, the 1030 OM<sub>s</sub> were categorized into 15 groups according to their chemical classes, and for each class a QIS was assigned (Table S1). Then quantification was conducted by comparing the peak area of identified OM to the respective QIS assigned by its chemical classes. The method

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