



Monitoring of 1300 organic micro-pollutants in surface waters from Tianjin, North China



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HIGHLIGHTS

- First systematic investigation of 1300 chemicals in surface waters, China.
- 227 Organic micro-pollutants were found.
- Benzothiazoles, 2-naphthol and metformin were detected with high concentrations.
- Principal components analysis identified 4 factors for contamination origin.
- This comprehensive analytical method is a useful tool for environmental survey.

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ABSTRACT

In spite of the quantities and species of chemicals dramatically increased with rapid economic growth in China in the last decade, the focus of environmental research was mainly on limited number of priority pollutants. Therefore, to elucidate environmental pollution by organic micro-pollutants, this work was conducted as the first systematic survey on the occurrence of 1300 substances in 20 surface water samples of Tianjin, North China, selected as a representative area of China. The results showed the presence of 227 chemicals. The most relevant compounds in terms of frequency of detection and median concentration were bis(2-ethylhexyl) phthalate (100%; 0.26 $\mu\text{g L}^{-1}$), siduron (100%; 0.20 $\mu\text{g L}^{-1}$), lidocaine (100%; 96 ng L^{-1}), antipyrine (100%; 76 ng L^{-1}), caffeine (95%; 0.28 $\mu\text{g L}^{-1}$), cotinine (95%; 0.20 $\mu\text{g L}^{-1}$), phenanthrene (95%; 0.17 $\mu\text{g L}^{-1}$), metformin (90%; 0.61 $\mu\text{g L}^{-1}$), diethyl phthalate (90%; 0.19 $\mu\text{g L}^{-1}$), quinoxaline-2-carboxylic acid (90%; 0.14 $\mu\text{g L}^{-1}$), 2-(methylthio)-benzothiazole (85%; 0.11 $\mu\text{g L}^{-1}$) and anthraquinone (85%; 54 ng L^{-1}). Cluster analysis discriminated three highly polluted sites from others based on data similarity. Principle component analysis identified four factors, corresponding to industrial wastewater, domestic discharge, tire production and atmospheric deposition, accounting for 78% of the total variance in the water monitoring data set. This work provides a wide reconnaissance on broad spectrum of organic micro-contaminants in surface waters in China, which indicates that the aquatic environment in China has been polluted by a large number of chemicals.

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1. Introduction

Water quality in China has deteriorated in the last decade as a result of the rapid expansion of industrialization and urbanization. For example, 100 tons of benzene, aniline, nitrobenzene and other toxicants were spilled into the Songhua River following a plant explosion in 2005 (He et al., 2013). In January 2013, more than 39 tons of aniline leaked into rivers in Shanxi province, posing a

great threat to the safety of drinking water for downstream provinces (Aredy, 2013). Tianjin is the fourth largest city in China, with a population of over 10 million. The city is located on the north west coast of Bohai Bay, and covers about 11 200 km^2 of land. As a coastal city, Tianjin suffers from a lack of water resources, and the wastewater that is discharged into surface waters from major industries without effective treatment has caused serious pollution to the aquatic environment. Surface waters passing through Tianjin also provide important drainage and wastewater discharge functions for Beijing City and Hebei Province, ultimately entering into Bohai Bay and pose a significant threat to local ecosystems.

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The presence of xenobiotic compounds especially organic micro-pollutants, such as pesticides, pharmaceuticals, phthalate esters and polycyclic aromatic hydrocarbons (PAHs) in aquatic ecosystems is a major concern worldwide, especially where drinking water supplies and amenity waters are contaminated by multiple chemicals for which human health based guideline values are not available (Kolpin et al., 2002; Zhang et al., 2007). Although most trace organic micro-pollutants are reported at low concentrations in the aquatic environment, the components of complex mixtures raise considerable toxicological concern since they have largely unknown combinative long-term effects on aquatic life and human health (Kümmerer, 2009). Also unknown is how many organic chemicals are used, although in the European Union, there are more than 100000 registered chemicals, of which 30000–70000 are in daily use (EINECS, European Inventory of Existing Chemical Substances) (Loos et al., 2009). To date, most studies of trace organic chemicals in the aquatic environment have focused on a limited number of priority pollutants, because widespread screening for hundreds of organic chemicals in surface water is technically and financially challenging. Such screening, however, is urgently needed to better understand water quality and pollution sources in water resource limited areas, and to allow for the implementation of sustainable water use management strategies.

Recent progress in technology has improved the ability to detect and quantify a large variety of chemicals in environmental samples, although there are as yet few papers reported (Du et al., 2013; Hanh et al., 2013; Kadokami et al., 2009; Loos et al., 2009; Vryzas et al., 2009). In that context, Kadokami et al. (2005) developed a novel, automated screening gas chromatographic–mass spectrometric (GC–MS) method capable of operating in both selected ion monitoring (SIM) and total ion monitoring (TIM) in conjunction with a mass spectral database for simultaneous identification and quantification of nearly 1000 semi-volatile organic compounds (SVOCs). This GC–MS method was employed in this study, along with an analogous method utilizing liquid chromatography–time of flight mass spectrometry (LC–TOF–MS) in conjunction accurate mass database to allow for screening of around 300 compounds.

Targeted 1300 compounds are chemicals regulated by environmental protection laws and foods protection laws, and compounds that have been reported to be frequently detected in the aquatic environment and marker substances of pollution sources. Since we used the AIQS-DB (Kadokami et al., 2005), which can determine targets without the use of standard substances, we measured nearly 1000 substances by GC–MS. On the other hand, the number of substances measured by LC–TOF–MS is 300 because there is no AIQS-DB for LC–TOF–MS, we should use conventional measurement method for determination of the targets: preparing calibration curves before sample analysis, which restricts the number of substances measured simultaneously.

Monitoring programs for thousands of organic micro-pollutants inevitably generate complicated data matrix associated with a large number of parameters. Multivariate statistical techniques such as cluster analysis (CA) and principal component analysis (PCA) offer an attractive approach to interpret the datasets and refine the inventory information.

The aims of this study were to use the GC–MS and LC–TOF–MS methods to provide a more extensive picture of trace organic chemical contamination than might otherwise be obtainable using more conventional analytical chemistry, and in doing so to confirm the usefulness and effectiveness of the newly developed comprehensive analytical methods. The results obtained in this study provide valuable information to refine pollutants inventories and develop appropriate strategies for water sources management.

2. Materials and methods

2.1. Sample collection

A total of 20 sampling sites were selected, including locations in three watersheds (Jiyun River, Hai River and Dulu River) and two sewage canals (Fig. 1); these sites were chosen to represent the dominant surface water quality in Tianjin. Sites J1–J6 were located in the Jiyun River watershed; site J6 (Luann River) is the primary drinking water supply for Tianjin inhabitants. Eleven sites (H1–H11) were along Hai River watershed, the largest catchment in the northern China. Site D1 was in the Dulu River. Stations S1 and S2 were on the north and south sewage canals, respectively. Samples were taken from surface waters no deeper than 1.0 m depth using amber glass bottles in December 2013. All sampling vessels were pre-cleaned with acetone, purified water, and water from the point of collection. After collection, samples were kept in the dark and cooled with icepacks during transport to a laboratory where the water samples were stored at 4 °C for a maximum of 48 h until treatment.

2.2. Solid-phase extraction

Samples were prepared for measurement of both 949 SVOCs (Table S1) by GC–MS and 81 persistent organic pollutants (POPs, Table S2) by GC–MS/MS following the same method from Jinya et al. (2013). In short, surface water samples (1 L), spiked with surrogate standards (Table S3) were passed through a stack of multiple SPE disks (in ascending order, a glass membrane fiber disk (GMF 150, 47 mm, Whatman, Maidstone, UK), a styrene-divinylbenzene disk (Empore™ SDB-XD, 47 mm, 3 M Co., St. Paul, MN, USA), and an activated carbon disk (Empore™ AC, 47 mm, 3 M Co., St. Paul, MN, USA), after which the disks were subjected to vacuum for 30 min to remove water. The GMF and XD disks were eluted sequentially with acetone and dichloromethane, whereas the AC disk was eluted with only acetone. Both eluates were mixed and concentrated to 1 mL, then reconstituted to 5 mL with hexane. The final volume was reduced to 0.4 mL under a gentle stream of nitrogen, and mixed internal standards (Table S1) were added prior to instrumental analysis.

Samples were prepared for measurement of 303 polar and/or non-volatile organic chemicals (NVOCs, Table S4) by filtration of surface water (1 L) through a 47 mm glass microfiber filter GF/C (Whatman, Maidstone, UK) after adding surrogate standards (Table S3). The suspended solid (SS) was subjected to sonication extraction with methanol twice. The filtrate was passed through a PS 2 Sep-Pak cartridge and an AC 2 Sep-Pak cartridge (Waters Associates, Milford, MA, USA) at a flow rate of 10 mL min⁻¹. The cartridges were eluted with methanol and dichloromethane. After combining the eluates and the extract from SS extraction, the mixture was concentrated to 50 µL under a gentle stream of nitrogen. Mixed internal standards (Table S4) were added and reconstituted to 1 mL with purified water prior to LC–TOF–MS analysis.

2.3. Chemical analysis

Monitoring of 949 SVOCs (Table S1) was performed with a GC–MS (Shimadzu, QP-2100 Plus, Kyoto, Japan) in both selected ion monitoring (SIM) and total ion monitoring (TIM). Target SVOCs information and GC–MS conditions were described in Tables S1 and S5, respectively. Total ion current chromatograms obtained by a GC–MS were treated with a novel Automated Identification and Quantification System with a GC–MS database (AIQS-DB) in order to identify and quantify of 949 SVOCs (Kadokami et al., 2005). GC retention times, calibration curves and standard mass

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