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Screening of 1300 organic micro-pollutants in groundwater from Beijing and Tianjin, North China

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HIGHLIGHTS

- First systematic investigation of 1300 chemicals in groundwater in China.
- Seventy eight organic micro-pollutants were detected.
- A range was detected at high concentrations (10^2–10^4 ng L^{-1}).
- Human health impact values were calculated for all detected compounds.
- Seven were found at concentrations with potential adverse effects on human health.

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ABSTRACT

Groundwater contamination in China has become a growing public concern because of the country's rapid economic development and dramatically increasing fresh water demand. However, there is little information available on groundwater quality, particularly with respect to trace organic micro-pollutants contamination. This study was undertaken to investigate the occurrence of 1300 pollutants at 27 groundwater sites in Beijing and Tianjin, North China. Seventy-eight chemicals (6% of the targeted compounds) were detected in at least one sampling point; observed chemicals included polycyclic aromatic hydrocarbons (PAHs), pesticides, plasticizers, antioxidants, pharmaceuticals and other emerging compounds. Chemicals with a frequency of detection over 70% were 2-ethyl-1-hexanol (median concentration 152 ng L^{-1}), benzyl alcohol (582 ng L^{-1}), 2-phenoxy-ethanol (129 ng L^{-1}), acetophenone (74 ng L^{-1}), pentamethylbenzene (51 ng L^{-1}), nitrobenzene (40 ng L^{-1}) and dimethyl phthalate (64 ng L^{-1}). Pesticides with concentrations exceeding the EU maximum residual limits (MRL) of 0.1 μg L^{-1} were 1,4-dichlorobenzene, oxadixyl, diflubenzuron, carbendazim, diuron, and the *E* and *Z* isomers of dimethomorph. Naphthalene and its 7 alkylated derivatives were widely observed at maximum concentration up to 30 μg L^{-1}, which, although high, is still below the Australian drinking water guidelines of 70 μg L^{-1}. The risk assessment indicated there is no human health risk through the oral consumption from most wells, although there were four wells in which total seven compounds were found at the concentrations with a potential adverse health effects. This work provides a wide reconnaissance on broad spectrum of organic micro-contaminants in groundwater in North China.

1. Introduction

Groundwater is the most reliable source of public drinking water supply in many regions of the world because of its good organoleptic properties, microbiological security and resource availability. However, groundwater resources are increasingly threatened by chemical contamination. Tens of thousands of organic chemicals such as pesticides, pharmaceuticals and personal care products (PPCPs), surfactants, flame retardants, plasticizers, steroids and other organics continue to be used in large quantities with a range of purposes by modern society (Lapworth et al., 2012). Although compared to surface water, groundwater often has a high degree of protection from pollution due to physical, chemical and biological attenuation processes (Barnes et al., 2008), there are a

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variety of pathways by which chemicals have the potential to enter the sub-surface aquatic environment, including pesticide and manure application in agriculture, landfills, industry and mining practices (Postigo and Barceló, 2015). Groundwater may become contaminated from various sources on the land surface, such as residential, municipal, commercial, industrial and agricultural activities.

Increasing water demands associated with rapid urban development and expansion in China have led to overexploitation of groundwater resources, and the growing water scarcity has become a big challenge. In north China, groundwater is a critical source, and 400 out of 657 cities use groundwater for drinking water, while 65% of all drinking water originates from groundwater (Ma et al., 2015). Beijing and Tianjin are the most economically important regions in North China, with both highly industrialized areas and intensive agricultural activity. The major water source for Beijing and Tianjin is groundwater, which accounts for 75% and 30% of total water supply, respectively (Ohgaki et al., 2006). Facing increasing pressure on fresh water demands, great efforts have been taken in conserving and augmenting the limited water resources in Beijing and Tianjin, such as waste water irrigation and groundwater recharge using reclaimed water.

The use of recycled wastewater together with soil manure applications and leaching from land fill and contaminated surface water in Beijing and Tianjin could pose a risk to groundwater quality. For instance, Peng et al. (2014) conducted a nation-wide survey on the occurrence of 20 antibiotics across China during groundwater recharge and total concentration in groundwater ranged from 19 to 1270 ng L^{-1}. Chen et al. (2014) reported the levels of antibiotics were significantly greater in wastewater irrigated soils.

Recently, the improvement of chemical analytical detection capabilities has led to the documented occurrence of organic micro-pollutants in water sources (Duong et al., 2014; Pan et al., 2014; Masiá et al., 2013). However, although increased monitoring has shown a large range of organic micro-pollutants in groundwater in Italy (Meffe and de Bustamante, 2014), France (Lopez et al., 2015), UK (Stuart et al., 2011), Spain (Jurado et al., 2012) and USA (Barnes et al., 2008), in China chemical monitoring of groundwater has received little attention and what testing has been undertaken has mainly focused on a limited number of target compounds, including PPCPs and organochlorine pesticides (Li et al., 2015; Peng et al., 2014; Tariq et al., 2004; Wu et al., 2014).

One reason for this lack of data is that there have been few analytical methods capable of screening large number of organic micro-pollutants at low concentrations. When assessing organic substances, many analytical methods may have to be used to cover a large number of known compounds, with the concomitant financial implications associated with operating multiple, definitive chemical analytical screens using gas and/or liquid chromatography-based methods for volatile, semi-volatile, non-polar and polar organic industrial, agricultural and domestic chemicals. 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 (Allinson et al., 2015; Bu et al., 2015; Du et al., 2013; Duong et al., 2014; Pan et al., 2014). 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 949 semi-volatile organic chemicals. More recently an analogous method utilizing liquid chromatography-time of flight mass spectrometry (LC–TOF–MS) in conjunction accurate mass database was developed to allow for screening of a further 303 polar and non-volatile organic chemicals (NVOCs) (Kong et al., 2015). The Automated Identification and Quantification System with Database (AIQS-DB) method (Kadokami et al., 2005) was originally developed for screening unknown pollutants in environmental samples after incidents, e.g. fish kills, food contamination scares, or the unknown number of harmful chemicals discharged into the environment after disasters such as large scale fires and earthquakes, and has since successfully been applied to both water and sediment samples from rivers and estuaries in Japan (Pan et al., 2014), in Vietnam (Duong et al., 2014), Victorian waste water treatment plant effluents in Australia (Allinson et al., 2012), and passive sampler extracts (Allinson et al., 2015). Consequently, when applied to groundwater, as in this study, the GC– and LC–MS database (DB) methods can give a good indication of the presence of many organic micro-pollutants that would not otherwise be identified if samples were to be subjected to only a very limited number of analytical screens for a limited number of target chemicals.

Compared to the numerous efforts undertaken to evaluate trace organic micro-pollutants contamination status of surface waters in North China, the quality of groundwater was relatively poorly understood since it was not considered or known to be significant impacted. As part of continuous effort to collect baseline information, the study was conducted to provide the first detailed survey on 1300 organic micro-pollutants in groundwater from Beijing and Tianjin, North China. The results obtained in this work will help to precede with future development policies of water sources management and regulation.

2. Materials and methods

2.1. Sampling

A total of ten and seventeen domestic wells were sampled during April 2015 throughout Beijing and Tianjin, respectively (Fig. 1). Each well was centrally exploited and distributed to individual households, and the corresponding geological information was unknown. Since little information is available on the suspected contaminated groundwater, there were no strict selection criteria for representative sampling stations. Sites were selected to cover urban, rural and remote areas, and from close to the contaminated surface waters identified by Kong et al. (2015). The results in this study give a preliminary snapshot of groundwater contamination

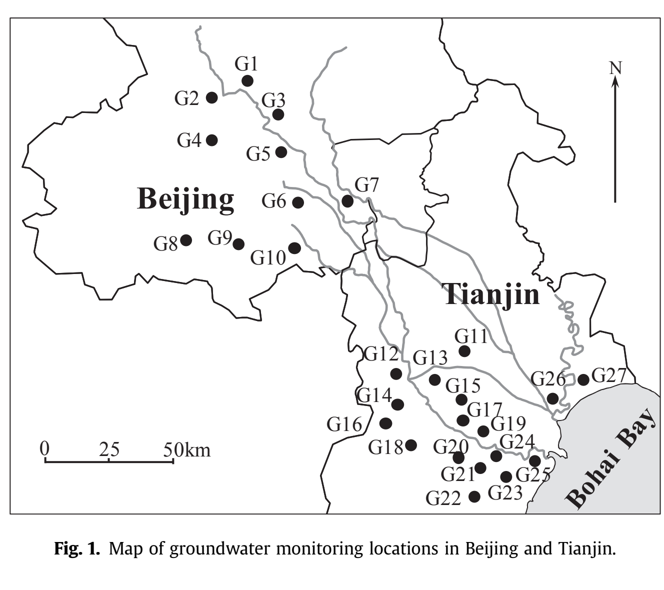

Fig. 1. Map of groundwater monitoring locations in Beijing and Tianjin.