Environmental Pollution xxx (2016) 1–10

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Screening and health risk of organic micropollutants in rural groundwater of Liaodong Peninsula, China☆

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A R T I C L E I N F O

Article history:
Received 2 February 2016
Received in revised form
21 July 2016
Accepted 30 July 2016
Available online xxx

Keywords:
Organic micropollutants
Groundwater
Health risk assessment
Carcinogenic risk
Noncarcinogenic risk

A B S T R A C T

Groundwater serves as a main drinking water source for rural residents in China. However, little is known regarding the pollution of organic micropollutants in groundwater that may pose health risks. In this study, more than 1300 organic micropollutants were screened in the groundwater samples collected from 13 drinking water wells distributed across five rural regions of Liaodong Peninsula in China. A total of 80 organic micropollutants including 12 polycyclic aromatic hydrocarbons, 11 alkanes, 9 pesticides, 7 substituted phenols, 7 perfluoroalkyl acids, 6 heterocyclic compounds, 5 alcohols, 5 phthalic acid esters, 5 pharmaceutical and personal care products, 3 ketones, 2 polychlorinated biphenyls (PCBs), 2 alkylbenzenes and 2 chlorinated benzenes were detected, with their total concentration of 32–1.5 $\times$ 10^4 ng/L. Noncarcinogenic and carcinogenic risks of a part of pollutants were assessed. Exposure through skin absorption and oral ingestion was considered in the assessment. Generally the risks are within the acceptable limits, except for that the carcinogenic risk at two sites in Jinzhou is higher than 10^{-6}. To the best of our knowledge, this is the first report on health risks of groundwater micropollutants in China.

1. Introduction

Groundwater is one of the most important drinking water sources in the world (Kolpin et al., 1998; US Census Bureau, 2011; USEPA, 2009a). In China, groundwater was used by about 70% of the population, 95% of which are rural residents (http://www.mlr.gov.cn/xwdt/jrxw/201012/t20101206_799699.htm). Direct use of raw groundwater is a general practice because drinking water treatment plants are not fully popularized in the rural areas in some developing countries. Hence, it is of importance to know whether groundwater has been polluted so as to protect human health.

In recent years, the pollution of groundwater by organic micropollutants has become a growing concern (Lapworth et al., 2012; Stuart et al., 2012; EU Water Framework Directive, 2008; Desimone, 2009), and some reviews have summarized the sources, occurrence and potential risks of organic micropollutants in groundwater (Lapworth et al., 2012; Postigo and Barceló, 2015; Meffe and Bustamante, 2014; Jurado et al., 2012; Stuart et al., 2012). The occurrence of a variety of organic micropollutants in groundwater has been reported, including polar organic persistent pollutants (Loos et al., 2010), perfluoroalkyl acids (PFAAs) (Post et al., 2013; Schaider et al., 2014), pharmaceuticals and organophosphate flame retardants (Schaider et al., 2014), and organochlorine pesticides (Wu et al., 2014). Although these pollutants occur in low to very low concentrations in groundwater, they pose nonnegligible risks to human and ecosystem health (Schwarzenbach et al., 2006; Ondarza et al., 2014; Meng et al., 2014). Nevertheless, the information about organic micropollutants in groundwater is still insufficient compared with those in surface waters.

To fully understand the occurrence of organic micropollutants, high throughput screening of organic micropollutants in groundwater samples becomes necessary. The Automated Identification and Quantification Database System (AIQS), in which retention time, calibration curves and mass spectra of more than 1000 compounds were registered (Kadokami et al., 2004, 2005, 2012,

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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http://dx.doi.org/10.1016/j.envpol.2016.07.070
0269-7491/

2013), is one of the high throughput screening systems that has been widely and successfully employed to screen organic micropollutants in surface water and sediment samples (Kadokami et al., 2012; Kong et al., 2015; Duong et al., 2015). Using the screening analysis with AIQS, more than 1000 organic compounds can be identified and quantified simultaneously, and its reproducibility and accuracy have been verified (Miyazaki et al., 2011).

To ensure safety of drinking water from groundwater, it is important to assess the risks of organic micropollutants to human health (USEPA, 1989; Weinstein et al., 2010). The method of health risk assessment recommended by the US EPA has been widely adopted in assessing carcinogenic and noncarcinogenic risks caused by an individual pollutants (Leung et al., 2013; Viana et al., 2009; Lee et al., 2004; Liu et al., 2014; Etchepare and van der Hoek, 2015; Gaffney et al., 2015). However, the hazard posed by chemical mixtures is difficult to quantify because the toxicity pathways (TP) or adverse outcome pathways (AOP) of many chemicals are not known (Williams et al., 2012). Considering the worst scenario, some studies calculated the sum of risk quotient of each pollutant to characterize the health risk of mixtures (Shi et al., 2011; Zhang et al., 2011).

This study aimed to identify the occurrence of organic micropollutants in groundwater from rural areas of Liaodong Peninsula in China and to assess their health risks. We collected groundwater samples in 13 drinking water wells, and screened more than 1300 organic chemicals, including 949 semi-volatile organic compounds (SVOCs) detected by GC-MS combined with AIQS, 20 organochlorine pesticides (OCPs) and 59 polychlorinated biphenyls (PCBs) detected with GC-MS-MS, 265 polar organic compounds [79 pharmaceutical and personal care products (PPCPs), 180 pesticides and 6 industrial compounds] with LC-TOF-MS and 16 perfluoroalkyl acids (PFAAs) with LC-MS-MS.

2. Materials and methods

2.1. Sampling sites

Liaodong Peninsula is the second largest peninsula in China located in the south of Liaoning province. The area of Dalian accounts for more than 60% of the whole peninsula. As shown in Fig. 1, the sampling sites were set in Dalian rural areas, including three county-level cities (Wafangdian, Pulandian and Zhuanghe) and two districts (Lvshun and Jinzhou). In these regions, the groundwater mainly derives from bedrock fissures, including both unconfined and confined aquifers.

According to the National Geological Archives of China (http://www.ngac.org.cn/Document/Map.aspx?MapId=EC7E1A7A75291954E0430100007F182E), most groundwater in Dalian rural regions is potable except for that in Jinzhou (J1, J2, J3, X1 and X2) and a part of Pulandian (P1) and Zhuanghe (Z1), where the groundwater is undrinkable but can be used for industry and agriculture. Agriculture is a main non-point polluter of the groundwater in rural areas, while factories and industry zones can be significant point sources. Herein, site J3 is 4.2 km away from Wolong industry zone, which can be a main pollution source of organic micropollutants. To assess human health risks of organic micropollutants in groundwater, the samples were collected from the wells used as drinking water sources of local residents.

2.2. Sample collection

Thirteen wells at 11 villages (Yinggeshi, Qijiatun, Xialianjia, Nanwangtun, Xietun, Zuotun, Liutun, Zhongjia, Dongbeishan, Nanlingzi and Dadi village) distributed in Dalian rural areas of the Liaodong Peninsula were selected as the sampling sites (Fig. 1). Detailed information on the sampling sites and water quality (water temperature, pH and electrical conductivity) are listed in Tables S1 and S2. Shallow groundwater samples were collected from the wells in March 2013, and conserved in 4 L ultra-clean brown glass sampling bottles; while for PFAAs analysis, the samples were stored in 1 L polypropylene bottles. All the sampling vessels were pre-cleaned with ultrapure water and acetone. Before sampling, the vessels were rinsed with the well waters from the point of collection. The samples were kept in dark during transport, stored at 4 °C, and treated within 48 h.

2.3. Sample pretreatment

Disk solid phase extraction (SPE) equipment (Glassware and Manifolds, 47 mm, GL Science) and column SPE equipment (Aqua Loader Twin SPL 698, GL Science) were employed for water sample treatment. More than 1300 target organic compounds were classified into three categories for the pretreatment and analysis. For 949 SVOCs (Table S3), 20 OCPs and 59 PCBs (Table S4) (Kadokami

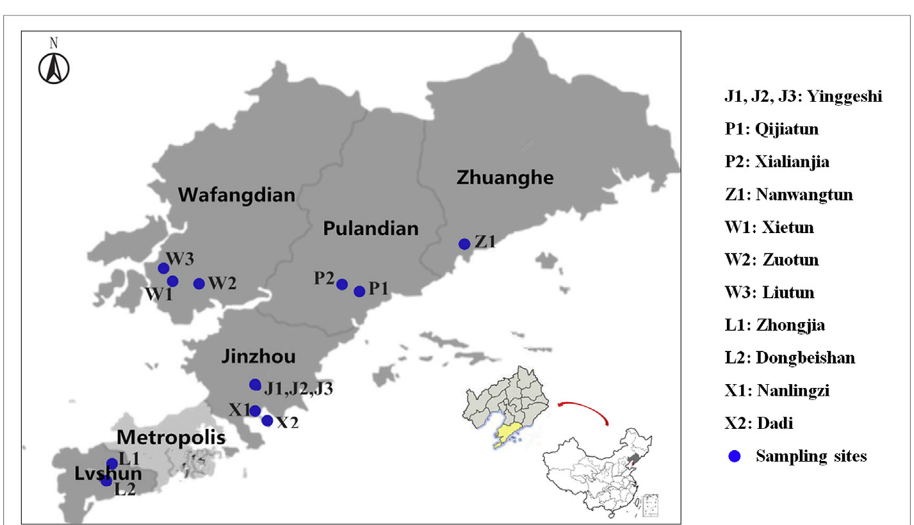

Fig. 1. Sampling sites in Dalian rural areas of Liaodong Peninsula.

Please cite this article in press as: Li, X., et al., Screening and health risk of organic micropollutants in rural groundwater of Liaodong Peninsula, China, Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.07.070