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Risk assessment and source identification of perfluoroalkyl acids in surface and ground water: Spatial distribution around a mega-fluorochemical industrial park, China

Zhaoyang Liu [a,b], Yonglong Lu [a,*], Tieyu Wang [a], Pei Wang [a], Qifeng Li [a,b], Andrew C. Johnson [c], Suriyanarayanan Sarvajayakesavalu [d], Andrew J. Sweetman [c,e]

[a] State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Centre for Ecology & Hydrology, Maclean Building, Crowmarsh Gifford Wallingford, Oxon, OX 10 8BB, UK
[d] SCOPE (Scientific Committee on Problems of the Environment) Beijing Office, P.O. Box 2871,18 Shuangqing Road, Haidian District, Beijing 100085, China
[e] Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

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ABSTRACT

Perfluoroalkyl acids (PFAAs) can be released to water bodies during manufacturing and application of PFAA-containing products. In this study, the contamination pattern, attenuation dynamics, sources, pathways, and risk zoning of PFAAs in surface and ground water was examined within a 10 km radius from a mega-fluorochemical industrial park (FIP). Among 12 detected PFAAs, perfluorooctanoic acid (PFOA) dominated, followed by shorter-chained perfluoroalkyl carboxylic acids (PFCAs). PFAA-containing waste was discharged from the FIP, with levels reaching 1.86 mg/L in the nearby rivers flowing to the Bohai sea together with up to 273 μg/L in the local groundwater in the catchment. These levels constitute a human health risks for PFOA and other shorter-chained PFCAs within this location. The concentrations of ∑PFAAs in surface water strongly correlated with the local groundwater. The dominant pollution pathways of PFAAs included (i) discharge into surface water then to groundwater through seepage, and (ii) atmospheric deposition from the FIP, followed by infiltration to groundwater. As the distance increased from the source, PFAAs levels in groundwater showed a sharp initial decrease followed by a gentle decline. The contamination signal from the FIP site on PFAAs in groundwater existed within a radius of 4 km, and at least 3 km from the polluted Dongzhulong River. The major controlling factor in PFAA attenuation processes was likely to be dilution together with dispersion and adsorption to aquifer solids. The relative abundance of PFOA (C8) declined while those of shorter-chained PFCAs (C4–C6) increased during surface water seepage and further dispersion in groundwater.

1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in manufacturing processes and products, such as surfactants and surface protectors, performance chemicals, lubricants and pesticides, due to their unique properties, including surface activity, heat and acid resistance, and water and oil repellency (Giesy and Kannan, 2001, 2002). However, concerns have been raised due to the environmental persistence, toxicity, long-range transport and bioaccumulation properties of PFAAs (Lescord et al., 2015; Liu et al., 2015; Wang et al., 2015). Continuous release of these substances from various products and applications has made them ubiquitous in environments, such as air (Taniyasu et al., 2013a), water (Wang et al., 2012), sediment (Yeung et al., 2013), wildlife (Persson et al., 2013) and even the human body (Kannan et al., 2004). In addition, water has become the primary reservoir of PFAAs and the major medium for their transportation due to the relatively high polarity and solubility of ionic PFAAs (Prevedouros et al., 2006; Sharma et al., 2015). Because of these physicochemical properties, PFAAs can even be used as useful chemical tracers of global circulation of ocean waters (Yamashita et al., 2008).

PFAAs can be released to the surrounding environment during manufacturing and the application of PFAA-containing products (Wang et al., 2014b). The presence of perfluorooctane sulfonate (PFOS) in the environment is usually associated with discharge from industries such as metal plating, textile treatment and PFOS manufacture, while most perfluorooctanoic acid (PFOA) is derived from PFOA production and fluoropolymer manufacturing and processing (Xie et al., 2013b; Li et al., 2015). Manufacturing facilities are major sources for PFAAs in surface and ground water, the contamination can continue even if the facilities have terminated the production of PFAA-related products (Xiao et al., 2012a). PFAA levels in groundwater affected by a former manufacturing facility from the 1940s to 2002 are still as high as 24 μg/L for PFOA and 1.6 μg/L for PFOS (Xiao et al., 2015). Moreover, PFAAs are also discharged from domestic sewage (Xie et al., 2013a). The

* Corresponding author.
E-mail address: yllu@rcees.ac.cn (Y. Lu).

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mobility of long-chained PFAAs is reduced by their sorption to soil and sediment, while the less hydrophobic, short-chained, PFAAs are more likely to undergo long-distance transport in surface water or penetrate to groundwater (Ahrens et al., 2009). The generally slow movement of groundwater makes this environment more of a sink, while contamination of surface water can lead to widespread dissemination (Lin et al., 2015). High concentrations of PFAAs in surface and ground water could pose not only a potential health risk via consumption of drinking water but also a risk to wildlife in aquatic ecosystems (Mak et al., 2009; Giesy et al., 2010). PFAAs are not readily removed by conventional drinking-water treatment processes (Eschauzier et al., 2012; Xiao et al., 2013). Hence, it is very important to identify and control PFAA contamination and prevent it entering drinking water sources.

Although the production of PFAA-related chemicals has been discontinued in Europe and America (UNEP, 2009; USEPA, 2013), it continues to increase in China due to the domestic and international demands. A previous study has shown that the main sources of PFAAs in the South Bohai coastal region were located in the Xiaoqing River basin (Wang et al., 2014a). The major source is a mega-fluorochemical industrial park (FIP), a fluoropolymer production centre with an annual capacity of 50,000 tons of tetrafluoroethylene (TFE), 37,000 tons of polytetrafluoroethylene (PTFE), 10,000 tons of hexafluoropropylene (HFP) and more than 200,000 tons of different types of fluorinated refrigerants (Dongyue Group Limited, 2012). Previous studies demonstrated that fluoropolymer manufacturers can seriously contaminate surface water with PFAAs (Heydebreck et al., 2015; Shi et al., 2015), but less is known about local groundwater contamination by such industrial sites and the relationship with polluted surface water.

The purpose of this paper was to study the environment around the fluoropolymer production facility (FIP) with particular emphasis on (i) groundwater monitoring of PFAAs pollution, (ii) PFAA contamination pattern and attenuation dynamics, (iii) analyzing PFAA sources and pathways, (iv) determining extent of local pollution from the FIP, and (v) conducting a risk analysis for the local surface and ground water with regard to human drinking water safety and ecology.

2. Materials and methods

2.1. Sampling design and collection

Beneath the FIP in Huantai County, Shandong Province, China, groundwater can be found at an average depth of 12.5 m from the surface. This is an alluvial sandy aquifer which is unconfined or micro-confined with a depth of less than 90 m. The groundwater samples were collected from a series of boreholes which had been installed two years previously. Sampling was done using a submersible pump, with over 100 L being pumped and discarded before taking the actual sample in 1-L polypropylene bottles. Surface water samples were collected from the Dongzhulong River and Xiaoqing River together with groundwater samples from the Dongzhulong River catchment (Fig. 1). The study area is a major grain-producing zone with large tracts of farmland and scattered villages, while surface and ground water played an important role for human consumption and irrigation. In October 2014, 10 samples of surface water and 37 samples of groundwater were collected. Collected samples were stored in an icebox during transport, all samples were extracted within 1 week after arrival in the lab, and the remainder stored at −20 °C for long-term reference. Parameters, including pH, dissolved oxygen, conductance, water temperature and salinity, were determined in situ using a HQd Portable and Benchtop Meter Configurator (HACH Company, USA) (Table S1). Before analysis, all the samples were allowed to stand for 24 h to settle any sediment and then 400 mL of supernatant was taken from each

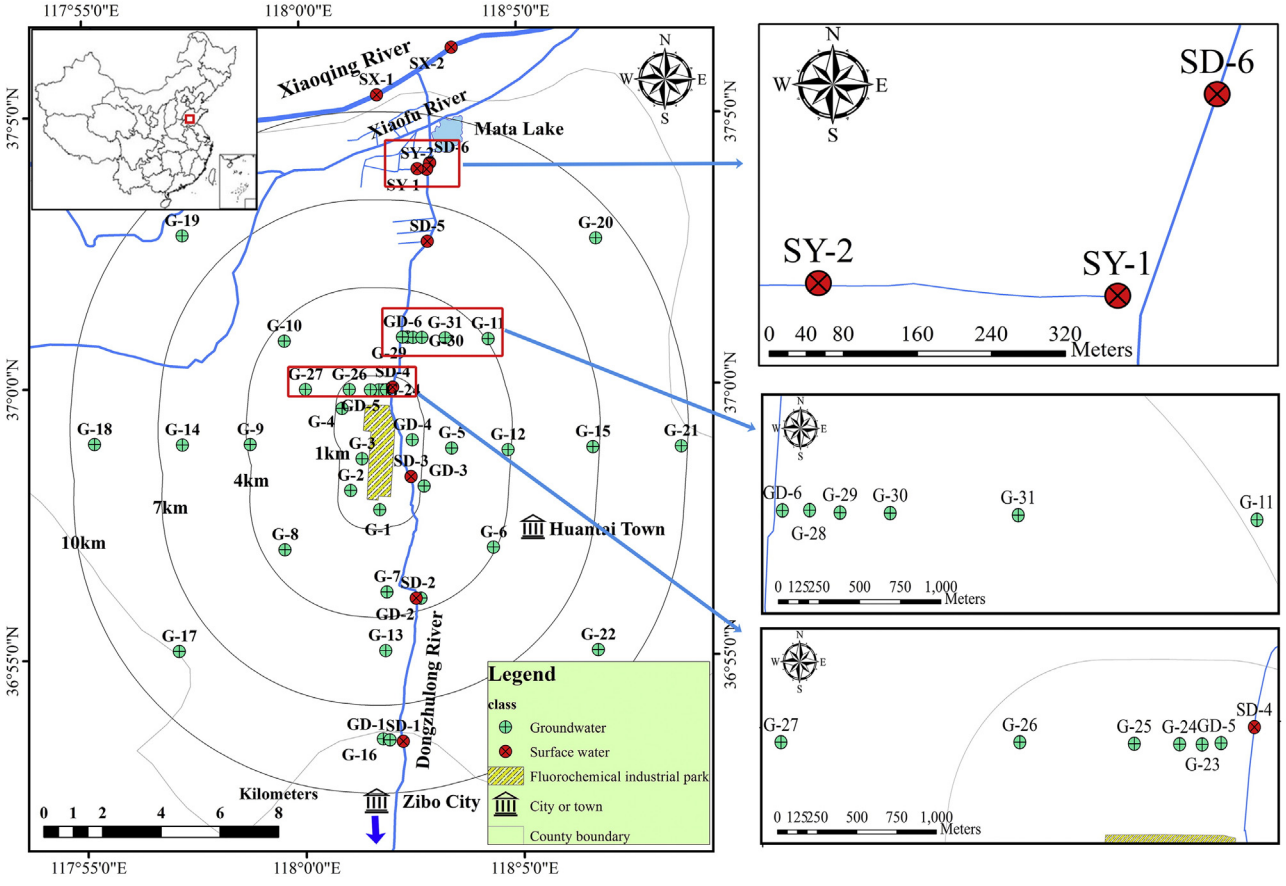

Fig. 1. Map of the sampling locations for surface water and groundwater in Huantai County.