



# A 17-fold increase of trifluoroacetic acid in landscape waters of Beijing, China during the last decade



Zihan Zhai<sup>a</sup>, Jing Wu<sup>a,c</sup>, Xia Hu<sup>a</sup>, Li Li<sup>a</sup>, Junyu Guo<sup>a</sup>, Boya Zhang<sup>b</sup>, Jianxin Hu<sup>a</sup>, Jianbo Zhang<sup>a,\*</sup>

<sup>a</sup> Collaborative Innovation Center for Regional Environmental Quality, State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

<sup>b</sup> School of Public Health, Peking University, Beijing 100191, China

<sup>c</sup> China Waterborne Transport Research Institute, Beijing 100088, China

## HIGHLIGHTS

- Concentrations of TFA in landscape waters after 10 years are reported.
- Atmospheric deposition is the main contribution route for increased TFA in waters.
- Distribution of TFA in waters is simulated by QWASI model.

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## ABSTRACT

The concentrations of trifluoroacetic acid (TFA) were measured in urban landscape waters, tap water and snows in Beijing, China in 2012. Compared with the 2002 measurements, a 17-fold increase from 23–98 ng L<sup>-1</sup> to 345–828 ng L<sup>-1</sup> was observed for TFA concentrations in urban landscape waters, and an obvious increase from not detected (n.d.) to 155 ng L<sup>-1</sup> occurred to TFA in tap water. By flux estimation between air and water interface, the remarkable increase of TFA was attributable to dry and wet deposition. The quantitative water–air–sediment interaction (QWASI) model simulated TFAs in various environmental media and showed that, over 99% of TFA distributed in water bodies. Our results recommend that measures are needed to control the increase of TFA in China.

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## 1. Introduction

As a result of the phase-out of ozone-depleting substances such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) have been substituted as the main class of chemicals with no potential for ozone depletion. Among them, the atmospheric dry mole fractions of 1,1,1,2-tetrafluoroethane (HFC-134a) shows significant growth (NOAA, 2014). The mixing ratio of HFC-134a increased from ~0 parts per trillion (ppt) to ~70 ppt in the past 20 years (NOAA, 2013). HFC-134a is mainly used as a refrigerant for mobile air conditioning systems (McCulloch et al., 2003). In the natural atmosphere, reacting with hydroxyl radical (Vasil'ev et al., 2011) and finally transforming into trifluoroacetic acid (CF<sub>3</sub>COOH, TFA) was revealed as the

major eliminating route of HFC-134a, with the molecular yield of ~7–20% (Wallington et al., 1992, 1996).

As a kind of perfluorinated acid (PFA), TFA has attracted attention in recent years (Kazil et al., 2011; Russell et al., 2012), attributed to both its existence in a wide range of water bodies at concentrations ranging from 0.5 ng L<sup>-1</sup> to 40900 ng L<sup>-1</sup> (Zehavi and Seiber, 1996; Scott et al., 2002), and aquatic toxicity (Davison and Pearson, 1997; Wiegand et al., 2000). Water bodies were regarded as the principal sink of TFA because TFA had low Henry constant [ $1.1 \times 10^{-2} \text{ Pa m}^{-3} \text{ mol}^{-1}$ ] (Bowden et al., 1996), and was miscible in all proportions (Feenstra-Bieders and Olthof, 1992). TFA was resistant to physical and chemical degradation (Visscher et al., 1994; Ellis et al., 2001). Microbial degradation may contributed to TFA removal, but the initial results were proven difficult to repeat by experiments (Visscher et al., 1994; Matheson et al., 1996). TFA tended to accumulate in aquatic ecosystem, especially in some seasonal wetlands (Tromp et al.,

\* Corresponding author. Tel.: +86 10 62753438; fax: +86 10 62760755.

E-mail address: [jbzhang@pku.edu.cn](mailto:jbzhang@pku.edu.cn) (J. Zhang).

1995). The no observed effect concentration (NOEC) of TFA for aquatic ecosystem was  $0.1 \text{ mg L}^{-1}$  (Berends et al., 1999). Although the monitored concentrations of TFA in most water bodies (Zehavi and Seiber, 1996; Berg et al., 2000; Scott et al., 2002, 2006; Zeng et al., 2004; Zhang et al., 2005) were below  $0.1 \text{ mg L}^{-1}$ , some studies suggested that the extensive use of 2,3,3,3-tetrafluoropropene (HFO-1234yf) could dramatically increase the amount of TFA in wetlands (Luecken et al., 2010). There might still be some unknown natural sources in deep waters (Kim and Kannan, 2007; Scott et al., 2010). Simulation studies showed that TFA concentrations would reach  $0.1 \text{ mg L}^{-1}$  in seasonal wetlands in 50 years (Tromp et al., 1995). Accumulation of TFA is potential to occur in unique waters, where there is only inflow, deposition and evaporation but with little outflow or groundwater recharge.

The phase-out of HFC-134a can potentially lead to the increase of TFA concentration if the alternative substances have higher molecular yields. In nowadays, the use of HFC-134a has been rigorously restricted under Kyoto Protocol due to its high global warming potential value as high as 1430 (Metz et al., 2005; Montzka et al., 2011). 2,3,3,3-Tetrafluoropropene (HFO-1234yf) is regarded as the most promising alternatives of HFC-134a (Leck, 2009; Kajihara et al., 2010; Luecken et al., 2010). However, HFO-1234yf degrades to TFA in the atmosphere with a 100% molecular yield (Hurley et al., 2008), much higher than the 7–20% yield of HFC-134a (Wallington et al., 1996). Regional simulations for the degradation of HFO-1234yf were conducted. For instance, there would be 6 to 8-fold increase of TFA concentration in precipitation in Europe by 2020 if HFO-1234yf was substituted for HFC-134a (Henne et al., 2012). Other results also showed that the alternative substances would lead to increased concentrations of TFA in local atmosphere and precipitation (Kajihara et al., 2010; Luecken et al., 2010), and subsequently increase TFA concentrations in surface water (Russell et al., 2012). Therefore, with the increasing consumption of HFO-1234yf, the accumulation of TFA in unique waters will be likely to occur.

According to the “Zhejiang Chemical Engineering Report, 2007”, HFC-134a is mainly used in automotive air conditioning industry, room air conditioner industry (HFC-407A) and the production of medical aerosols in China. Because room air conditioner by HFC-134a is mainly used for export, its emissions occur in the corresponding consumers. Medical aerosols possess a small portion of HFC-134a usage. Therefore, automotive air conditioning industry is the most main emission source of HFC-134a in China. Beijing, the capital of China, is regarded as the HFC-134a emission hotspot because the number of automobiles is up to 5.2 million in 2012 (Beijing Statistical Yearbook, 2013). Based on the monitoring results, the emission and atmospheric concentration of HFC-134a in Beijing is significantly higher than any other cities in China (Fang et al., 2012; Wu et al., 2013). Moreover, evapotranspiration capacity in Beijing is greater than rainfall in most years (Dan et al., 2011). Therefore, the accumulation of TFA is likely to happen in Beijing, especially in urban landscape waters, where there are semi-closed tranquil flow and little evapotranspiration. To carry out continual monitoring of TFA in urban landscape waters is necessary.

As far as we know, Zeng et al. (2004) first determined the concentration of TFA in Chinese waters, and Zhang et al. (2005) reported TFA concentrations in some waters of Beijing in 2002. However, the TFA concentrations in these waters have not been updated in the past decade. Studies about source analysis and environmental distribution of TFA are limited. The concentrations of TFA in current is still unknown.

In this study, the concentrations of TFA in four urban landscape waters in Beijing were reported and compared with results (Zhang et al., 2005) obtained in the same locations in 2002. Furthermore, the increases of TFA concentration in tap water during the past

decade were recorded. Increasing scenario was assumed to explain the increase of TFA concentrations. A water quality model was used to analyze the sources and the contribution proportions of each source. Finally, quantitative water–air–sediment interaction (QWASI) model was used to simulate the transmission rate of TFA in various media, and to determine the distribution characteristics and residence time. To our knowledge, this study is the first time to describe the change of TFA concentrations in the same waters after a decade. Also, by fluxes estimation and model simulation, more information about TFA's behavior in China is given for further studies.

## 2. Materials and methods

### 2.1. Materials and reagents

Standard TFA and perfluoropropionic acid (PFPA) were purchased from Acros Organics Co. (Geel, Belgium). The derivatization agent 2,4-difluoroaniline (2,4-DFAn) was obtained from J&K Chemical Co. (Greensboro, GA, USA). N,N'-dicyclohexylcarbodiimide (DCC) was supplied by the Fluka Chemical Co. (Milwaukee, WI, USA). Organic residue analysis grades of ethyl acetate, hexane, acetone, and methanol were obtained from J.T. Baker Co. (Phillipsburg, NJ, USA). Optima-grade anhydrous sodium sulfate was supplied by Tianjin Jinke Co. (Tianjin, China). Reagent-grade sodium bicarbonate and sodium chloride were obtained from Xilong Chemical Co. (Beijing, China). Silica gel (60 mesh) was purchased from Merck & Co. (Rahway, NJ, USA). The purities of all standards and reagents were >99%.

Anhydrous sodium sulfate was baked overnight at  $600^\circ\text{C}$ . Sodium bicarbonate was immersed in methanol for 10 min, and then in ethyl acetate for 10 min. It was tiled in evaporating dish at room temperature overnight, and then baked at  $80^\circ\text{C}$  for 24 h. The same treating processes applied to sodium chloride except that it was baked at  $450^\circ\text{C}$  for 24 h. Silica gel was immersed in dichloromethane for 1 h, evaporated to dryness at room temperature, and then baked overnight at  $550^\circ\text{C}$ . All glassware was washed with acetone and n-hexane in sequence. All water was deionized and further purified twice by distillation.

### 2.2. Sampling and chemical analysis

Fig. 1 shows the sampling sites. Tap water was collected from the Geological Building at Peking University, Beijing ( $39^\circ59'26''\text{N}$ ,  $116^\circ18'31''\text{E}$ ) on July 8, 2012. The landscape waters were sampled from the same locations (Chaoyang Park, Qingnian Lake, Beihai Park, The Summer Palace) as reported previously by Zeng et al. (2004). The samples of landscape waters were collected between July 8, 2012 and July 10, 2012. For details of the water bodies, please see Table S1 in supporting information.

Samples of landscape waters were collected directly with 1000-mL glass collectors at a depth of 1.0 m below the surface and a distance of 3.0 m off the lakeshore. The water collectors were prewashed by TFA-free water and sonicated for 1 h, then rinsed three times by ultrapure water in the laboratory. At the sampling sites, the collectors were rinsed three times by lake water before collection. After collection, all samples were immediately stored in 1000-mL polyethylene bottles at  $4^\circ\text{C}$  and transported to the laboratory before analysis. Snow and tap water samples from Peking University were collected for comparative purposes. Snow samples were collected on December 14, 2012 and December 21, 2012, respectively. They were taken above ground immediately after the snowfall ended. After removing topsoil and sundries on the surface the snow samples were stored in 1000-mL glass flasks before analysis. Snow samples were melted at room temperature.

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