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Rainwater trifluoroacetic acid (TFA) in Guangzhou, South China: Levels, wet deposition fluxes and source implication

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HIGHLIGHTS

- Rainwater TFA was monitored in Guangzhou during 2007–2008.
- Rainwater TFA predominantly originated from HCFCs/HFCs and fluoropolymers.
- HFC-134a alone contributed 55.9–90.0% of the observed rainwater TFA.

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ABSTRACT

The origin of trifluoroacetic acid (TFA) occurring in hydrosphere has long been a controversial issue. Hydrochlorofluorocarbons and hydrofluorocarbons (HCFCs/HFCs) as replacements of chlorofluorocarbons (CFCs) are precursors of TFA in the atmosphere, their contribution to rainwater TFA is a concern as their ambient mixing ratios are continually growing. Here we present rainwater TFA monitored from April 2007 to March 2008 in urban Guangzhou, a central city in south China's highly industrialized and densely populated Pearl River Delta region. Rainwater TFA levels ranged 45.8–974 ng L⁻¹ with a median of 166 ng L⁻¹. TFA levels negatively correlated with rainfall amount, the yearly rainfall-weighted average for TFA was 152 ng L⁻¹. The annual TFA wet deposition flux was estimated to be 229 g km⁻² yr⁻¹, and the total wet deposition of TFA reached ~1.7 t yr⁻¹ in Guangzhou. The Two-Box model was applied to estimate attributions of HCFCs/HFCs and fluoropolymers to rainwater TFA assuming TFA generated was proportional to gross domestic product (GDP), gross industrial product (GIP) or number of private cars. The results revealed that the degradation of HCFCs/HFCs and fluoropolymers could explain 131.5–152.4 ng L⁻¹ rainwater TFA, quite near the observed rainfall-weighted annual mean of 152 ng L⁻¹, suggesting rainwater TFA in Guangzhou was predominantly originated from these anthropogenic precursors. HCFCs/HFCs accounted for 83.3–96.5% of rainwater TFA observed, while fluoropolymers' contributions were minor (~5%). HFC-134a alone could explain 55.9–90.0% of rainwater TFA, and its contribution would be greatly enhanced with its wide use in mobile air conditioning systems and rapid increase in ambient mixing ratios.

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1. Introduction

As replacement products for the ozone depleting CFCs, HCFCs/HFCs exhibit growing mixing ratios in the atmosphere (WMO, 2011). Some HCFCs/HFCs, such as HCFC-123 (CF₃CHCl₂), HCFC-124 (CF₃CHClF) and HFC-134a (CF₃CH₂F), can react with hydroxyl (OH) radical to yield CF₃COX (X = F or Cl), which will result in the formation of trifluoroacetic acid (TFA) through in-cloud hydrolysis (Wallington et al., 1992, 1994; Franklin, 1993; Tuazon and Atkinson, 1993; Kanakidou et al., 1995; Boutonnet et al., 1999). Due to its low Henry's Law constant (Bowden

et al., 1996) and high solubility (Boutonnet et al., 1999), TFA is expected to be removed from the atmosphere primarily by washout. Wet deposition via rain, snow and fog is thus the most important pathway of TFA's transfer from atmosphere into hydrosphere.

TFA has become a ubiquitous contaminant and has been detected in a variety of environmental media, such as air (Frank et al., 1996), precipitation (Jordan and Frank, 1999; Scott et al., 2006; Zehavi and Seiber, 1996), fog (Römpp et al., 2001), surface waters (Cahill and Seiber, 2000; Scott et al., 2000, 2002; Zhang et al., 2005), soils and pine needles (Cahill et al., 1999; Scott et al., 2005b), oceans (Frank et al., 2002; Scott et al., 2005a) and even in the snow of the Arctic and Antarctica (Von Sydow et al., 2000). TFA is extremely stable in the ambient and highly resistant to chemical and biological degradation under normal environmental condition (Emptage et al., 1997; Boutonnet et al., 1999). The persistence and water solubility of TFA make it potentially accumulate

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in some aquatic ecosystems where TFA may concentrate through water evaporation, especially in landlocked lakes (Tromp et al., 1995; Cahill et al., 2001; Wu and Chau, 2006), or in some hydrometeors, particularly in fog (Römpp et al., 2001). Previous results displayed that TFA was of mildly phytotoxic (Berends et al., 1999; Boutonnet et al., 1999). Although the observed TFA levels in aqueous environment were all below the safety level of 0.10 mg L^{-1} (Berends et al., 1999), high levels have been reported as early as in 1990s. For instance, TFA concentrations were reported as high as $40,900 \text{ ng L}^{-1}$ in Pyramid Lake of the United States (Zehavi and Seiber, 1996); and the levels beyond 1000 ng L^{-1} were also recorded in rainwater around the world (Frank et al., 1995; Wujcik et al., 1998; Von Sydow et al., 2000; Berg et al., 2000; Scott et al., 2006). Due to the continual input to the environment and the accumulation in terminal water bodies, TFA levels in aqueous environment would keep increasing in the coming decades and more attention should be paid on its potential adverse effects (Berends et al., 1999; Boutonnet et al., 1999; Wiegand et al., 2000). Thus, it is important to acquire information about the fate and sources of TFA in the environment.

Atmospheric degradation from HCFCs/HFCs has been regarded as an important source of environmental TFA due to globally large use and emission of these CFC-replacements (Wallington et al., 1994, 1996). HFC-134a, for example, as the most widely used HFCs in the world and also an important TFA precursor, was a cooling agent for mobile air conditioning systems (MACs) used in more than 80% of passenger cars and commercial vehicles worldwide (Velders et al., 2009). HFC-134a would release from seals and pipelines during the whole life cycle of a car, including production, normal operation, repair and maintenance, and end-of-life disposal (Siegl et al., 2002; Stemmler et al., 2004). The global production and sales of HFC-134a grew from $<0.2 \text{ Gg yr}^{-1}$ in 1990 up to 158.2 Gg yr^{-1} in 2007, with faster increase after the year of 2000 (AFEAS, 2007). The total production of HFC-134a had reached 1831.5 kt during 1990–2007 (AFEAS, 2007), with an emission rate of more than 100 kt yr^{-1} (Ashford et al., 2004; Stohl et al., 2010). The accumulation of HFC-134a in the atmosphere would certainly result in more TFA generated and eventually accumulating in the hydrosphere. However, previous studies showed that the degradation of these halocarbons cannot explain well the observed TFA in precipitation (Boutonnet et al., 1999; Jordan and Frank, 1999). As model predicted, in the year of 2010 the global average of HCFC-123, HCFC-124 and HFC-134a would reach 1.1 pptv, 9.8 pptv and 80 pptv, respectively, resulting in a global average of 120 ng L^{-1} TFA in rainwater (Kotamarthi et al., 1998). However, many studies around 1995 (e.g. Frank et al., 1995, 1996; Wujcik et al., 1998; Jordan and Frank, 1999; Berg et al., 2000) revealed rainwater TFA levels close to or even higher than 120 ng L^{-1} while atmospheric concentrations of these halocarbons at that time were much lower than the predicted levels. HCFC-123 and HCFC-124 concentrations around 1995 were both at sub-pptv level globally (Ashford et al., 2004), and HFC-134a just started its use as a CFC-replacement especially in MACs, with a background concentration of less than 3 pptv on a global scale (Montzka et al., 1996; Oram et al., 1996; <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>). Thus, CFC-alternatives could be not regarded as the sole source of TFA, and there should have sources other than HCFCs/HFCs.

Ellis et al. (2001) found that the thermolysis of fluoropolymers in industrial processes and other high-temperature applications was another important pathway to bring TFA into the environment. As their model estimated, fluoropolymers thermolysis alone explained over 80% of TFA observed in the rainwater of Toronto (Ellis et al., 2001). Other fluorochemicals, such as fluorinated inhalation anesthetics (halothane, desflurane, and isoflurane) and pesticides with trifluoromethyl-substituted aromatic ring, were also considered as the potential precursors of TFA (Jordan and Frank, 1999). Moreover, some chemical industries using TFA as a reagent could also directly or indirectly give off TFA to the ambient (Jordan and Frank, 1999; Boutonnet et al., 1999). Even so, all these sources mentioned above

still could not explain huge reserve of TFA in oceans. During 1998–1999 when HCFCs/HFCs and fluoropolymers were comparatively less used, TFA levels of about 200 ng L^{-1} were homogeneously distributed in ocean waters of the Mid-Atlantic Ocean and the Southern Ocean, even in the depth of below 4,000 m (Frank et al., 2002). Harnisch et al. (2000) pointed out that TFA was a naturally occurring chemical with unknown natural sources. Based on the observed TFA profiles in the Arctic, Atlantic, and Pacific oceans, Scott et al. (2005a) proposed that deep-sea vents might be a possible natural source of TFA. Until now the global mass balance of TFA is still a problem. Therefore, surveys on present situation of TFA in the environment are essential to trace its sources and further evaluate its impacts on ecosystems.

The Pearl River Delta (PRD) region in south China is a densely populated and highly industrialized region with $\sim 1/200$ of China's land area but $\sim 1/10$ of China's GDP. Higher consumption, storage and emissions of HCFCs/HFCs, as well as larger fluoropolymers usage in industrial processes and domestic applications, are thus supposed to occur in this region. Meanwhile, in this tropical/subtropical region, high air temperature ($\sim 23 \text{ }^\circ\text{C}$, annual mean), high relative humidity ($\sim 70\%$, annual mean) and more sunshine ($\sim 1600 \text{ h}$, annual) are all favorable meteorological characteristics for the formation of TFA from HCFCs/HFCs in atmosphere. Higher concentrations of oxidants like OH radical in this subtropical/tropical region (Prinn et al., 1995) should also promote the degradation of precursors to produce TFA. The abundance of rainfall in PRD ($\sim 1900 \text{ mm}$, annual) would facilitate TFA removal from the atmosphere through wet precipitation as the major pathway for final removal of TFA in the atmosphere (Kotamarthi et al., 1998). China government implemented one compulsory policy since 2002 to convert previously CFC-12 based MACs to HFC-134a based MACs. This would consequentially result in much more release of HFC-134a and its degradation product TFA, particularly in the megacities like the PRD region.

Till present, although the levels, spatial distribution and flux estimation of TFA in rainwater have been studied in many regions all over the world, a large reservoir of TFA in the hydrosphere is not well explained by known industry sources. In China, the production and consumption of TFA precursors, like HFC-134a, are increasing rapidly in recent years, but there are only a few studies about TFA in the surface or sea waters (Zhang et al., 2005; Wang et al., 2010; Wang and Wang, 2011), and no results are available about TFA in rainwater as well as its contribution from HCFCs/HFCs. In this present study, rainwater TFA was monitored in urban Guangzhou, the capital city of Guangdong province and the central city of PRD. The aim of this work was (a) to obtain rainwater TFA data from extensive field monitoring and hence to estimate its wet deposition in this region and (b) to assess source contributions to rainwater TFA, particularly the role played by CFC-replacement HCFCs/HFCs.

2. Experimental section

2.1. Chemicals and reagents

Trifluoroacetic acid (TFA, $>99.5\%$) and perfluoropropionic acid (PFPA, $>99\%$) were purchased from Lancaster Chemical Company (the United Kingdom). The derivatization agent 2,4-difluoroaniline (DFA, 99%) was obtained from Acros Chemical Company (Belgium). *N,N'*-dicyclohexylcarbodiimide (DCCI, $>99.0\%$) used as catalyst was from Fluka Chemical Company (Switzerland). All other chemicals and solvents were supplied by Guangzhou Chemical Company (China) in analytical reagent (AR) grade, except concentrated (37%) hydrochloric acid (HCl) and toluene in guaranteed reagent (GR) grade.

All the solvents (n-hexane, methanol and ethyl acetate) were redistilled before use. Sodium bicarbonate (NaHCO_3) and sodium chloride (NaCl) were soaked and rinsed by re-distilled methanol and ethyl acetate subsequently, and then baked for 10 h at $80 \text{ }^\circ\text{C}$ (NaHCO_3) and $450 \text{ }^\circ\text{C}$ (NaCl), respectively. Sodium sulfate (Na_2SO_4) was baked at $450 \text{ }^\circ\text{C}$ for

12 h. All glassware and rainwater collection containers were solvent rinsed before use. Reagent water was double distilled purified water, and excluded for possible TFA contamination that might occur in laboratory environment.

2.2. Rainwater sampling

The rain sampling location is shown in Fig. 1. Rainwater samples were simultaneously collected by two glass containers on the rooftop of a 4-story building in the campus of Guangzhou Institute of Geochemistry (23° 08' 40" N, 113° 21' 53" E) with an elevation of 37.5 m above sea level. The glass containers (50 cm cube) were opened once a rain event started and closed when the rain stopped for avoiding dry deposition. Except for keeping separately as parallel samples, two rainwater samples for each rain event were combined and transferred to a 1-L polypropylene bottle immediately as one sample and stored at 4 °C in dark until analysis. After sampling, the glass containers were carefully cleaned by methanol and then by ethyl acetate to avoid cross contamination in next collection. If rainwater samples collected were less than 100 mL during small rains, they were combined to the nearest rainwater samples. A total of 40 rainwater samples were collected from April 2007 to March 2008. The data of rainfall amount, air temperature and relative humidity (RH) for each rainy day were obtained from the Guangzhou Meteorological Satellite Ground Station (GMSS), which is less than 2 km away from our sampling site.

2.3. Laboratory analysis

Before analysis, rainwater samples were warmed to room temperature. Since the pH values of rainwater samples were less than 7, NaHCO₃ was added into samples to adjust pH values to 9 for ensuring that all TFA molecules were ionized and avoiding the loss of TFA. After addition of 8 µL of the internal standard (PPFA, 156.1 µg mL⁻¹), each sample was reduced from ~500 mL to about 50 mL in volume using a rotary evaporator (IKA RV05, Germany) at 50 °C water bath.

Similar to the analytical method previously described (Scott and Alae, 1998; Scott et al., 2002), TFA was derivatized using DFA. In brief, there were three steps: i) *Adjusting pH*. Concentrated HCl was added drop by drop to each concentrated sample until its pH value was slowly adjusted to 1. ii) *Derivatization*. 1 g of NaCl was dissolved in sample to enhance the ion strength. 35 mL of ethyl acetate was added to sample as solvent followed by adding 43 µL of pure DFA and 400 µL of 0.23 g mL⁻¹ DCCI solution into ethyl acetate phase. The mixed solution was vigorously stirred for 1 h. Then another 5 g of NaCl was added, shaking until it was completely dissolved. iii) *Purification*. After the aqueous and the organic phases in the mixture came to

equilibrium, they were separated. The former was stirred a further 10 min with an additional 15 mL of ethyl acetate, and the two parts of organic phases (ethyl acetate phase) were combined and washed first with 10 mL of 20% HCl solution, then with 10 mL of saturated NaHCO₃ and 10 mL of saturated NaCl solution subsequently. After filtering through a funnel with Na₂SO₄, the ethyl acetate solution was gently reduced to dryness with a rotary evaporator. 10 mL of toluene was added to extract the precipitate absorbed in glass wall. After filtration, sample was finally reduced to 1 mL in volume and kept at -20 °C until analysis.

Derivatized samples were analyzed by a Hewlett-Packard 5972 gas chromatograph (GC)/mass selective detector (MSD) equipped with a 50 m FFAP capillary column (0.32 mm i.d., 0.5 µm film thickness) in the electron impacting (EI) ionization and selected ion monitoring (SIM) mode. Helium was used as carrier gas with a flow rate of 1.5 mL min⁻¹. 2 µL of each sample was injected in the splitless mode. The oven temperature was initially maintained at 100 °C for 2 min, then raised at a rate of 7 °C min⁻¹ to 215 °C, and kept isothermally for 10 min. The target ion selected for the 2,4-difluoroanilide derivatives of TFA was m/z 225. The calibration curve obtained from seven standard samples (different levels of TFA along with a fixed amount of PPFA was spiked in 50 mL reagent water and treated the same as rainwater) showed very good linear correlation ($R^2 = 0.997$). During the instrumental analysis, a calibration run was performed each day to determine the response factor (RF). Re-calibration was required if the relative deviation of the RF was beyond 10%. The method detection limit (MDL) of TFA in the current study was calculated to be 1.7 ng L⁻¹ based on 500 ml sample, which was similar to 1 ng L⁻¹ based on 1 L sample reported in literature (Scott et al., 2002).

Three laboratory blank samples (reagent water) were treated in the same way as rainwater samples. TFA were less than MDL in these blank samples, indicating that no TFA was introduced by either inevitable exposure to laboratory air or the multi-step sample treatment processes. Recoveries of spiked blank samples (TFA spiked in reagent water, $n = 7$) and spiked rainwater samples (TFA spiked in rainwater, $n = 4$) were $87 \pm 6\%$ and $83 \pm 6\%$, respectively. Duplicate samples (rainwater in glass containers was not combined but analyzed separately, $n = 4$) showed relative standard deviation less than 10%.

3. Results and discussion

3.1. Rainwater TFA levels

TFA levels in collected rainwater samples ranged from 45.8 to 974 ng L⁻¹ with a median concentration of 166 ng L⁻¹ and an average of 225 ng L⁻¹ (Fig. 2), exceeding annual average levels of about 120 ng L⁻¹ as predicted for the year 2010 (Kotamarthi et al., 1998). As shown in Table 1, quite a lot studies about rainwater TFA were conducted around 1997 with few reports available after 2000. TFA levels in rainwater from Guangzhou were about one order of magnitude higher than those in Mace Head, Ireland in 1996 (Von Sydow et al., 2000), and were much higher than those reported in Baikal, Siberia (30–215 ng L⁻¹) and Hanoi, Vietnam (4–150 ng L⁻¹) in 1996 (Berg et al., 2000), but in similar range with those reported in Tübingen (Frank et al., 1995), Beijing (Zhang et al., 2005), California and Nevada (Wujcik et al., 1998). The average level in this study was even lower than that in Central Valley, California in 1996 (Wujcik et al., 1998).

Higher TFA concentrations were related to lower rainfalls, as can be obviously seen from the samples on April 9, 2007, February 4, 2008, and March 28, 2008. TFA level exhibited a significant negative correlation with rainfall ($p < 0.01$) during our sampling period. Larger rainfall will probably dilute TFA in rainwater and result in relatively lower concentrations observed. This relationship between TFA levels and rain amount also indicated that an arithmetic mean of rainwater concentration is not proper for comparison of TFA levels in different locations, or for the calculation of TFA wet precipitation flux. Instead, especially for

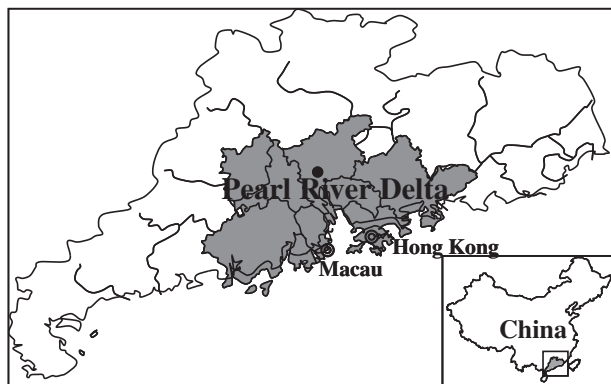


Fig. 1. Location of the Pearl River Delta region (grey) and the sampling site (solid circle). The bottom right corner is the location of Guangdong province in south China.

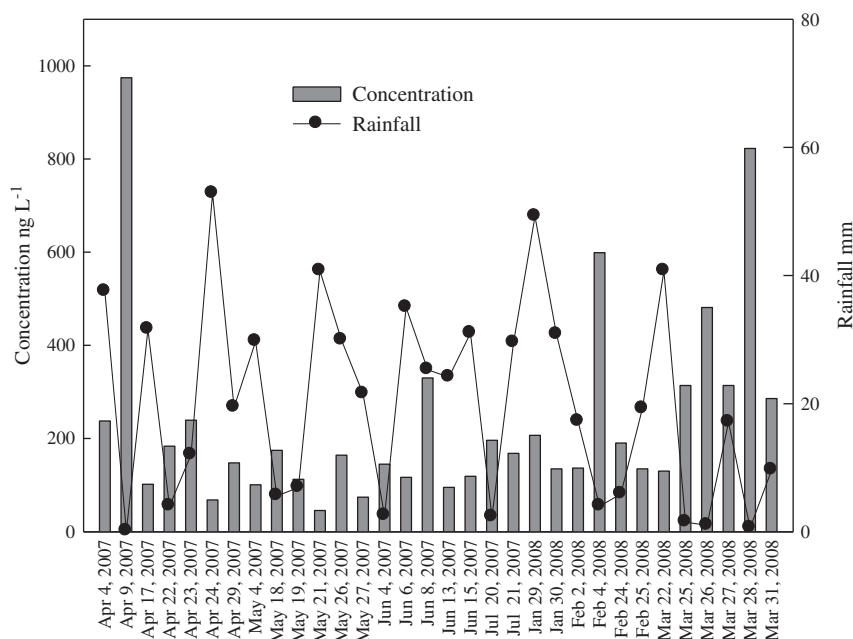


Fig. 2. Observed rainwater TFA levels and rainfall from April 2007 to March 2008.

flux estimation, rainfall-weighted average concentration at a site should be used and calculated as:

$$C_{\text{rainfall-weighted}} = \frac{\sum C_i P_i}{\sum P_i} \quad (1)$$

where C_i and P_i are the rainwater TFA level and rain amount, respectively, in rain event i . An accurate TFA wet deposition during a time interval should be the sum of fluxes that pertain to each rain event; therefore a better estimation of annual TFA wet deposition should be annual rainfall amount multiplying the annual rainfall-weighted average concentration, instead of the simple arithmetic average of collected samples. Also, rainfall-weighted average concentration instead should be used for comparing levels from different sites, especially for long-term monitoring results. In the present study, while the arithmetic average of TFA levels reached 225 ng L^{-1} , the rain-fall weighted average concentration was only 152 ng L^{-1} . Similarly, a study in Switzerland reported an average TFA level of 151 ng L^{-1} in rainwater, but calculated rainfall-weighted average was 116 ng L^{-1} using their rainfall and TFA data (Berg et al., 2000). It should be noted that Kotamarthi et al. (1998) predicted global annual average rainwater TFA of 120 ng L^{-1} for the year 2010, and higher rainwater TFA levels with a range from 150 to 200 ng L^{-1} occurred in the northern middle latitudes due to CF_3COF converting to TFA with so short lifetime that production of TFA maximizes in these areas. In this study, the annual rainfall-weighted average TFA level of 152 ng L^{-1} in Guangzhou fell within the range predicted by Kotamarthi et al. (1998) for the year 2010 in the northern middle latitudes.

Due to the accumulation of CF_3COX or TFA in non-raining days, TFA levels should be the highest at the beginning of a rain event and then decrease with time. To check the washout effect for TFA, continuous sampling during one rain event was also conducted. Two continuous samples (sampling in the morning and in the afternoon, separately) during one event were collected in each of two rainy days. A sharp decrease (42.9% on March 22, 2008 and 41.7% on March 31, 2008) of TFA levels were clearly observed from morning to afternoon. The gradual decrease of TFA levels was observed during a thunder storm (29.9 mm rainfall within only 20 min) on May 26, 2007. TFA concentrations in the three continuous samples collected during 0–2 min, 2–10 min and 10–20 min were 176, 164 and 154 ng L^{-1} , respectively. Washout effect was also found in samples

collected in continuous rainy days, e.g. May 18–19, 2007 and January 29–30, 2008. Such a washout effect was also reported in California and Nevada (Wujcik et al., 1998) and Beijing (Zhang et al., 2005).

Due to the influence of monsoons, the PRD has a clear division between the arid and rainy seasons. The rainy season, accounting for about 80% of annual total rainfall, is typically from April to September, while other months, from October to next March, belong to the arid season. Rainfall-weighted rainwater TFA level in arid seasons (191.3 ng L^{-1}) was higher than that in rainy seasons (135.1 ng L^{-1}). In rainy seasons including summer, higher temperature, elevated RH and more intensive solar radiation would result in relatively higher photochemical oxidants (Prinn, et al., 1995; Cai et al., 2008), and therefore promote the formation of TFA from precursors. However, more rainfall amount in the rainy season would lead to comparatively lower rainwater TFA levels due to frequent washout and more dilution. On the contrary, with lower rainfall washout in arid seasons, TFA in the atmosphere could accumulate in non-rainy days and lower rainfalls will further lead to elevated rainwater TFA levels during arid season.

3.2. Annual TFA wet deposition estimation in the region

In the PRD region, since there is no snow and fog rarely occur all the year, wet deposition is predominantly through rainfall. The TFA deposition for each rain event, calculated by TFA level multiplying rainfall amount, ranged from 97 to $10,177 \text{ ng m}^{-2}$ in this study. When the number of days without rain before each rain event is figured out, significant positive correlation can be observed between TFA deposition and non-rainy days before rainfall ($r = 0.54$, $p < 0.05$). The extreme high deposition, $10,177 \text{ ng m}^{-2}$, occurred on January 29, 2008, largely due to a long time (23 days) accumulation of CF_3COX or TFA in non-rainy days.

Taking the calculated rainfall-weighted average level (152 ng L^{-1}) as the annual rainfall-weighted average concentration of TFA in Guangzhou, with the total rainfall of 1500 mm during April 2007 to March 2008, the annual wet deposition flux of TFA in Guangzhou was estimated to be $229 \text{ g km}^{-2} \text{ yr}^{-1}$, which was almost the same as $230 \text{ g km}^{-2} \text{ yr}^{-1}$ reported for Switzerland (Berg et al., 2000). According to this annual wet deposition flux, there would be 1.7 t yr^{-1} of TFA deposited through rainfall in Guangzhou within an area of $7,434 \text{ km}^2$. The PRD has an area

Table 1
Comparison of the observed rainwater TFA concentrations with those reported in other studies.

Sampling location	Duration	TFA (ng L ⁻¹)	Average (ng L ⁻¹)
Tübingen, Germany ^a	Jan–June, 1994	<3–1400	
Reno, Nv and Santa Rosa CA ^b	Sep 28 and Dec 28, 1994; Jul 17, 1995	31–90	
Sonoma County, California ^c	Dec 28–29, 1994	48 and 55	
Bayreuth, Germany ^d	Mar–Dec, 1995	25–280	100
Selma, CA ^e	Jan–Feb 1996		215.3
Central Valley, California ^c	Jan 30, 1996–Mar 28, 1996	40–1160	253
Mace Head, Ireland ^f	Feb–Mar 1996	2–92	
Gdansk, Poland ^f	May 1996	26–1100	
Washoe County, Nevada ^c	Sep 1994–May 1996	31–796	
Hanoi, Vietnam ^g	Aug 1996	4–150	
Baikal, Siberia ^g	Jun 1996, Dec 1996	30–215	
Switzerland ^g	May 1996–Jul 1997	<3–1550	151
Reno, NV ^f	Jun 13, 1997	196	
Rohnert Park, Sonoma county, CA ^b	Dec 1996–Sep 1997	25.1–158	46.6 ^k
Selma, Fresno County, CA ^g	Dec 1996–Sep 1997	20.7–463	63.9 ^k
Reno, Washoe County, NV ^h	Dec 1996–Sep 1997	108–763	136 ^k
Smith Island Maryland, USA (near urban) ⁱ	1998	23–620	
	1999	21–200	
Lewes, Delaware, USA (near urban) ⁱ	1998	10–170	
	1999	17–2400	
Ithaca, New York (rural U.S.) ⁱ	1998	3–110	
	1999	9–360	
Underhill, Vermont (rural U.S.) ⁱ	1999	8–250	
Beijing, China ^j	May 2000–July 2001	25–235	
Kejimkujik, Nova Scotia, Canada (remote) ⁱ	2002	4–100	
Algoma, Ontario, Canada (remote) ⁱ	2002	8–220	
Saturna Island, British Columbia (rural Canada) ⁱ	2002	5–140	
Egbert, Ontario, Canada (near urban) ⁱ	Oct–Dec 2003; Sep–Dec 2004	43–170	
North Toronto, Ontario, Canada (urban) ⁱ	May 2003–Aug 2004	87–270	
Guangzhou, China (Urban, this study)	Apr 2007–March 2008	45.8–974	225

^a (Frank et al., 1995).

^b (Zehavi and Seiber, 1996).

^c (Wujcik et al., 1998).

^d (Frank et al., 1996).

^e (Wujcik et al., 1999).

^f (Von Sydow et al., 2000).

^g (Berg et al., 2000).

^h (Wujcik et al., 1999).

ⁱ (Scott et al., 2006).

^j (Zhang et al., 2005).

^k Median TFA concentration.

of 42,898 km² with the annual average rainfall of about 1900 mm (Guangdong Provincial Bureau of Statistics, 2009). When extrapolated to PRD using the annual wet deposition flux observed, annual wet deposition of TFA in PRD reached 12.1 t yr⁻¹.

3.3. Source implication

The “Two-Box model” by Ellis et al. (2001) was also adopted here to evaluate the contributions of precursors, such as HCFCs/HFCs and fluoropolymers, to rainwater TFA in Guangzhou. The two boxes were set in the model with the smaller box representing Guangzhou city within the larger one representing China (Fig. 3). The fluxes of TFA into and out of the smaller box (Guangzhou) and the larger box (China) were all considered to establish steady-state equations. The details of the model and the calculation were described in Supplementary Material (Appendix A). In this model calculation, a key parameter is the proportion of TFA generated in the small box to that in the large box. As presented in Table 2, here we allocate generated TFA assuming that it was proportional to 1) gross domestic production (GDP), 2) gross industrial production (GIP), and 3) number of private vehicles possessed.

The model results revealed rainwater TFA of 131.5–152.4 ng L⁻¹ (Table 2) in Guangzhou altogether from three halocarbons (HFC-134a, HCFC-123, HCFC-124) and fluoropolymers, assuming the mass of TFA generated was proportional to the GDP, GIP or number of private cars. These levels were quite near the observed annual rainfall-weighted mean TFA of 152 ng L⁻¹ in Guangzhou. This suggests

that the degradation of HCFCs/HFCs and fluoropolymers could explain well TFA in rainwater, and rainwater TFA in Guangzhou was therefore predominantly anthropogenic in its origin.

The three HCFCs/HFCs altogether accounted for 83.3–96.5% of the rainfall TFA in Guangzhou. Among them HFC-134a alone contributed 84.9–98.3 ng L⁻¹ or 55.9–64.7% of rainwater TFA (Table 2) observed in Guangzhou, suggesting that it was already the dominant halocarbon precursor of TFA in this region. If the mixing ratio of atmospheric HFC-134a in China was higher than the average background level in the northern hemisphere as expected, its contribution to rainwater TFA would reach up to 90% (in Supporting Information). With the regulation of ozone-depleting substances (ODS) under Montreal Protocol and its Amendments, CFCs in the region are declining while HCFCs/HFCs as replacement-products are increasing rapidly (Zhang et al., 2010). Since Jan 1st, 2002, all automobiles manufactured in China are required to assemble with HFC-134a based MACs instead of CFC-12 based ones. According to the 2008–2010 Analysis Report on Development of China's Fluorine Chemical Industry, the national consumption of HFC-134a increased from 4,000 t in 2001 to 15,000 t in 2008, with an annual growth rate of 30%. Hu et al. (2009) also estimated that the consumption would reach to 20,000 t in 2010 and 35,000 t in 2015. Such a huge consumption of HFC-134a would inevitably result in a large amount of emission and therefore a dramatic increase of its mixing ratio in the atmosphere. A snapshot of ambient halocarbons in 45 Chinese cities in 2001 revealed an average HFC-134a concentration of 23 pptv, 50% higher than the global mean surface mixing ratio level by

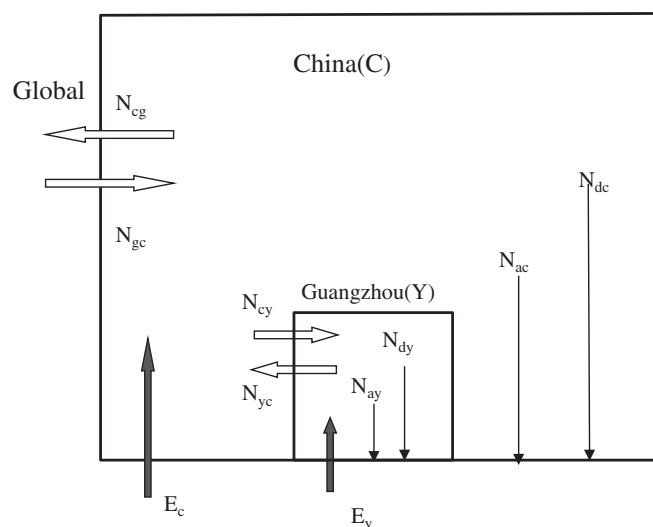


Fig. 3. The Two-Box model employed: E_c and E_y are emission/generation of TFA in the gas phase to the atmosphere through the atmospheric degradation of halocarbons and the thermal degradation of fluorinated polymers in China and in Guangzhou, respectively; N_{cg} and N_{gc} are the amount of material moving between the continent of China and the globe and vice versa; N_{cy} and N_{yc} are the amount of material moving between the continent of China and the Guangzhou area and vice versa; N_{dy} and N_{dc} are rain deposition of TFA to Guangzhou and to the continent of China, respectively; N_{ay} and N_{ac} are dry deposition of TFA on to water bodies within Guangzhou and the continent of China, respectively.

mid-2000 (Barletta et al., 2006; WMO, 2006). In the PRD region, a median of 19 pptv for HFC-134a in autumn 2000 was reported in urban area (Chan and Chu, 2007), and the level reached 49 pptv by 2004 in suburban Guangzhou (Chan et al., 2006). During 2008–2009, air samples were collected concurrently at 84 sites over the whole PRD region

Table 2
Contribution of precursors to TFA as estimated by the Two-Box Model.

Compound	Atmospheric mixing ratio (pptv)	Yearly molar yield for TFA	Generated TFA in rainwater (ng L ⁻¹)	Contribution to rainwater TFA
<i>Scheme 1: TFA generated is proportional to GDP (Guangzhou/China = 2.85%)</i>				
HCFC-123	0.3 ^a	100% ^c	31.8	20.9%
HCFC-124	0.7 ^a	100% ^c	16.6	10.9%
HFC-134a	50.0 ^b	20% ^d	98.3	64.7%
Fluoropolymers ^e	–	0.1% ^f	5.7	3.7%
Total			152.4	100%
<i>Scheme 2: TFA generated is proportional to GIP (Guangzhou/China = 2.44%)</i>				
HCFC-123	0.3 ^a	100% ^c	27.4	18.0%
HCFC-124	0.7 ^a	100% ^c	14.3	9.4%
HFC-134a	50.0 ^b	20% ^d	84.9	55.9%
Fluoropolymers ^e	–	0.1% ^f	4.9	3.2%
Total			131.5	86.5%
<i>Scheme 3: TFA generated is proportional to numbers of private vehicles (Guangzhou/China = 2.63%)</i>				
HCFC-123	0.3 ^a	100% ^c	29.5	19.4%
HCFC-124	0.7 ^a	100% ^c	15.4	10.1%
HFC-134a	50.0 ^b	20% ^d	91.2	60.0%
Fluoropolymers ^e	–	0.1% ^f	5.3	3.5%
Total			141.4	93.0%

^a (Ashford et al., 2004).

^b The average mixing ratio of HFC-134a in the north hemisphere (<http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>).

^c (Boutonnet et al., 1999; Kotamarthi et al., 1998).

^d (Wallington et al., 1996).

^e The reserve of fluoropolymers in China in the last 5 years was estimated to be 181,000 t (see Supporting Information).

^f Per year the percentage of fluoropolymers that ultimately undergo thermal degradation (Ellis et al., 2001).

(Zhang et al., n.d.), and the results revealed an average HFC-134a mixing ratio of 81.6 pptv (Wang and Wang, 2013), significantly (51%) higher than the global background level of 54 pptv in the Northern Hemisphere and 48 pptv in the Southern Hemisphere during the similar period (<http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>). With the rapid growth of automobile produced and possessed in the PRD region, HFC-134a release would certainly be enhanced, leading to higher HFC-134a mixing ratios in the atmosphere and subsequently higher TFA in rainwater.

Based on fluoropolymers data available around 2008, the thermolysis of fluoropolymers contributed 1.7–5.7 ng L⁻¹ of TFA (Table 2), less than 5% in the observed rainwater TFA. This percentage from fluoropolymer thermolysis in Guangzhou was much lower compared to that of over 80% in Toronto (Ellis et al., 2001). Fluoropolymers are primarily used for thermal application, especially in areas of high thermal stress, like ovens, cookware, industrial and car engines, heat exchanges, and high-temperatures circuits (Johns and Stead, 2000). According to the 2008–2010 Analysis Report on Development of China's Fluorine Chemical Industry, the total production of fluoropolymers in China was ~36,000 t in 2006, lower than the total amount (40,000 t) in North America around 2000 (Ellis et al., 2001). Moreover, organic fluorine manufacturers in China were centered in eastern China. A survey for TFA in surface water over China showed that eastern China had much higher levels of TFA, e.g. up to 7,850 ng L⁻¹ in river water in Shanghai, probably due to the influence of fluoropolymers manufacturing there (Wang and Wang, 2011). Since there were few organic fluorine manufacturers in the PRD region, the contribution of fluoropolymers thermolysis to rainwater TFA was minor.

Besides three HCFCs/HFCs compounds and fluoropolymers, other organo-fluorinated chemicals like HFC-227ea (CF₃CHFCF₃), halothane and isoflurane anesthetics were also reported to produce TFA (Boutonnet et al., 1999). But halothane and isoflurane anesthetics formed TFA mainly through metabolism other than oxidative degradation in the atmosphere. Mixing ratios of HFC-227ea reported in the northern mid-latitude upper troposphere were lower than 1.0 pptv (Laube et al., 2010; Vollmer et al., 2011). Besides, HFC-227ea has a lifetime of 34 years (<http://www.epa.gov/ozone/science/ods/index.html>) and TFA molar yield of 50% (Boutonnet et al., 1999). Therefore, its potential contribution to TFA was also negligible. The PRD region is adjacent to the South China Sea, which is a large reservoir of TFA (Wang et al., 2010). However, owing to its strong solubility, TFA in seawater is difficult to re-evaporate to atmosphere and transfer to coast area (Römpp et al., 2001). The re-evaporation from the South China Sea could not contribute to rainwater TFA in Guangzhou.

4. Conclusion

A year-round monitoring of rainwater TFA from April 2007 to March 2008 in urban Guangzhou revealed that rainwater TFA levels ranged 45.8–974 ng L⁻¹ with a median concentration of 166 ng L⁻¹ and a rainfall-weighted annual average of 152 ng L⁻¹. The annual TFA wet deposition flux was estimated to be 229 g km⁻² yr⁻¹, and the total wet deposition of TFA reached ~1.7 t yr⁻¹ in Guangzhou.

By applying the Two-Box model with the assumption that TFA generated was proportional to GDP, GIP or number of private cars, we found that the degradation of HCFCs/HFCs and fluoropolymers could explain 131.5–152.4 ng L⁻¹ rainwater TFA, quite near the observed rainfall-weighted annual average of 152 ng L⁻¹, suggesting rainwater TFA in Guangzhou was predominantly anthropogenic. HCFCs/HFCs were precursors that could explain 83.3–96.5% of observed rainwater TFA, while fluoropolymers' contributions were minor. HFC-134a alone could explain 55.9–64.7% of rainwater TFA, even up to 90.0%, and a larger contribution would be expected with rapid growth of its ambient mixing ratios over China for its prevalent use as cooling agent in MACs. As a strongly persistent and hydrophilic compound, TFA would eventually accumulate in the hydrosphere. Although observed TFA levels in aqueous environment are so far well below the safety level of 0.10 mg L⁻¹, great concern

should be paid on its increasing in water bodies due to multi-year accumulation. It is worth noting that if the mixing ratios of precursor halocarbons were determined when collecting rainwater samples, and if we have more understanding about regional emission of HCFCs/HFCs and release of TFA from fluoropolymers, we should have source attribution of improved accuracy and better time-resolution for TFA in rainwater. These aspects should therefore be incorporated into future field campaigns.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.08.055>.

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