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In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) at the Shangdianzi regional background station, China

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Abstract

In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) have been conducted at the Shangdianzi (SDZ) Global Atmosphere Watch (GAW) regional background station, China, from May 2010 to May 2011. The time series for 5 HFCs and 4 PFCs periodically showed high concentration events while background conditions occurred for 36 % (HFC-32) to 83 % (PFC-218) of all measurements. The mean mixing ratios during background conditions for HFC-23, HFC-32, HFC-125, HFC-134a, HFC-152, CF_4, PFC-116, PFC-218 and PFC-318 were 24.5, 5.86, 9.97, 66.0, 9.77, 79.1, 4.22, 0.56, 1.28 ppt (parts per trillion, 10^{-12}, molar), respectively. The background mixing ratios for the compounds at SDZ are consistent with those obtained at mid to high latitude sites in the Northern Hemisphere, except for HFC-32 and PFC-318 for which background mixing ratios were not reported in recent years. All HFCs and PFCs show positive trends at rates of 0.7, 1.4, 1.6, 4.1, 1.1, 0.43, 0.05, 0.01, 0.04 ppt yr^{-1} for HFC-23, HFC-32, HFC-125, HFC-134a, HFC-152, CF_4, PFC-116, PFC-218 and PFC-318, respectively. North-easterly winds were connected with small contributions to atmospheric HFCs and PFCs loadings, whereas south-westerly advection (urban sector) showed increased loadings. Chinese emissions were estimated by a tracer ratio method using CO as tracer with rather well known emissions. The emissions, as derived from our measurement period, were 4.4 ± 0.7, 6.9 ± 0.9, 2.5 ± 0.3, 9.0 ± 1.3, 2.2 ± 0.4, 2.1 ± 0.3, 0.24 ± 0.06, 0.07 ± 0.04, 0.45 ± 0.09 kt yr^{-1} for HFC-23, HFC-32, HFC-125, HFC-134a, HFC-152, CF_4, PFC-116, PFC-218, and PFC-318, respectively. The lower HFC-23 emissions compared to earlier studies may be a result of the HFC-23 abatement measures taken as part of the Clean Development Mechanism (CDM) project that started in 2005.

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1 Introduction

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are greenhouse gases with large global-warming potentials (GWPs) and are included in the Kyoto Protocol. Most HFCs are used in refrigeration, air conditioning, in aerosol spray cans, and as foam blowing compounds (Barletta et al., 2011; McCulloch, 1999) while HFC-23 (CHF_3) is mostly a by-product of the HCFC-22 ($CHClF_2$) production (Montzka et al., 2010; McCulloch and Lindley, 2007; Oram et al., 1998). PFCs are emitted from aluminum smelters (CF_4, PFC-116), and are used and released in the semiconductor industry (Mühle et al., 2010). HFCs and PFCs are replacing chlorinated ozone-depleting gases such as chlorofluorocarbons (CFCs) and hydrofluorochlorocarbons (HCFCs). Emissions of HFCs and PFCs are expected to have increased in China in accordance with the high industrialization and from the substitutions of CFCs and HCFCs. Some emissions were estimated based on measurements at stations downwind of China (Li et al., 2011; Kim et al., 2010; Saito et al., 2010; Stohl et al., 2010; Yokouchi et al., 2006). However, only few atmospheric HFCs and PFCs measurements were made in China, mainly from air collected in canisters during campaigns (Barletta et al., 2006; Chan et al., 2006; Chan and Chu, 2007).

In this study, we report the first in-situ measurement of HFC-23, HFC-32 (CH_2F_2), HFC-134a (CH_2FCF_3), HFC-152a (CH_3CHF_2), HFC-125 (CHF_2CF_3), CF_4, PFC-116 (C_2F_6), PFC-218 (C_3F_8), and PFC-318 (c-C_4F_8) at the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW)'s regional background station Shangdianzi (SDZ) in Northern China from May 2010 to May 2011. Mixing ratios are presented and characterized for both "background" and "polluted" conditions. Additionally, the impact of local surface horizontal advection on the observed compounds has been investigated. Chinese HFCs and PFCs emissions are estimated by a tracer ratio method using a compound with well quantified emission as a reference tracer.

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2 Site description and experimental methods

2.1 Description of the site

The Shangdianzi station (SDZ, 40°39′ N, 117°07′ E, 291.3 m a.s.l.) is located in a mountainous area approximately 100 km northeast of urban Beijing in the North China Plain. Previous studies showed that this site experienced both pollution events influenced by air masses from Beijing and other industrialized areas in the North China Plains and clean air masses from remote areas, such as Siberia, Mongolia, and the Chinese province Inner Mongolia (Lin et al., 2009; Vollmer et al., 2009; Zhang et al., 2010). The wind rose of the observation period is shown in Fig. 1. Influenced by monsoon and local valley topography, the prevailing wind sectors for the whole year are NE/ENE/E (background sectors) and SW/WSW/W (urban sectors) during the observation period, with total frequencies of approximately 40 % and 32 %, respectively.

2.2 Experimental methods

Air samples are analyzed in situ using the "Medusa" automated custom-built gas chromatographic system with mass spectrometric detection (Miller et al., 2008), with relative measurement precisions typically < 2 % for HFCs except for HFC-32 and < 5 % for HFC-32 and PFCs. The system was installed in an air-conditioned container in May 2010. The sample inlet was installed at height of 8 m on a 10 m tall tower located at a distance of 30 m from the container, resulting in a total inlet line < 80 m. The air is continuously drawn through the 10 cm OD Synflex tubing by means of membrane pump resulting in the residence time < 5 min. The Medusa was added to the gaschromatographic measurement system that has been in operation since 2006 (Vollmer et al., 2009; Zhang et al., 2010) to add HFC and PFC measurement to the sampling program. CO was measured in-situ since 2007 by NDIR method (Horiba AMPA-360CE) with resolution of 1 min. Its results are linked to the WMO-2000 calibration scale. All

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the instruments mentioned above share the same inlet. Other greenhouse gases and physical parameters of the atmosphere are also measured at this station.

Each Medusa air sample measurement (every second hour) is bracketed by a reference gas (working standard) measurement to detect and correct for drift in the detector sensitivity. Our measurements are closely tied to the Advanced Global Atmospheric Gases Experiment (AGAGE) (Prinn et al., 2000), and are reported as dry air mole fractions on the calibration scales developed at the Scripps Institution of Oceanography (SIO), and the University of Bristol (UB): SIO-2005 (CF_4, HFC-134a, HFC-152a), SIO-07 (HFC-23, HFC-32, PFC-116, PFC-218), UB-98 (HFC-125), SIO-10-p (PFC-318).

3 Results and discussion

3.1 Time series and background data selection

One-year time series for HFCs and PFCs mixing ratios from May 2010 to May 2011 are shown in Fig. 2 (data gaps were due to instrument malfunction). For most HFCs and CF_4, mixing ratios at SDZ show large episodic events, with elevated concentrations from polluted air masses most likely arriving from urban areas. For the analysis of pollution events, background conditions are distinguished from polluted air by applying a statistical filter of "robust local regression" (Ruckstuhl et al., 2010).

Using the pollution filter approximately 36 % (HFC-32) to 83 % (PFC-218) of all valid measurements have been selected as background data (Table 1). Pollution-classified mixing ratios (grey dots) exhibit large fluctuations compared to the background measurements. The mean mixing ratio difference between pollution and background can be attributed to recent emissions. Of all compounds measured, HFC-134a has the greatest mixing ratio difference between pollution and background. With the exception of CF_4, pollution events for the PFCs are rare and small.

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3.2 Comparison of background mixing ratio and trends

Since the HFCs and PFCs working standards at SDZ are traceable to the standards scale of the AGAGE network, the data are directly comparable to results from the AGAGE stations. Here we compare our results to the four AGAGE stations: Jungfraujoch, Mace Head, Trinidad Head, and Cape Grim. Cape Grim, located in the Southern Hemisphere (SH), is used here as representative for SH air. The other three station, are located at similar latitudes compared to SDZ in the Northern Hemisphere (NH).

The background mixing ratios for HFCs and PFCs at SDZ are consistent with those obtained at other NH stations (Table 2). The differences for the background HFCs mixing ratios between SDZ and Trinidad Head, which are almost located at the same latitude, are within 0.6 ppt (parts per trillion, 10^{-12}, molar) for HFC-23, 0.28 ppt for HFC-125, 1.0 ppt for HFC-134a, 0.21 ppt for HFC-152a, 0.1 ppt for CF_4, 0.03 ppt for PFC-116 and 0.01 ppt for PFC-218.

There are differences for the background mixing ratios of HFCs and PFCs up to several ppts between SDZ and Cape Grim, especially for HFC-134a and HFC-152a due to the difference between NH and SH. Of all the compounds listed in Table 2, HFC-152a shows the biggest relative difference of all stations, due to its shortest lifetime of all measured compound.

The PFC-318 background mixing ratio (1.28 ppt) for the study period is close to the background level (1.2 ppt) of Cape Grim for 2010 as published by Oram et al. (2012) on a different calibration scale (the UEA scale), with currently unknown conversion factor to SIO-10-p scale.

However, there is no recent report about background levels of HFC-32. NH background mixing ratios are estimated from the observation at Mace Head on 2004 and yearly growing rate (Greally et al., 2005), the estimate background mixing ratios from May 2010 to May 2011 are calculated as 3.9 ppt for HFC-32 which are smaller than the background mean mixing ratios by this study. This reveals that this compound has bigger growing rate or regional background of SDZ is higher than Mace Head.

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The annual mean growth rates of HFC-32, HFC-134a, and HFC-125 are achieved by linear curve fitting for the compounds with $R^2 > 0.7$. Figure 3 presents HFC-32 and HFC-125 as example. For other compounds, annual mean growths are obtained from monthly mixing ratio means difference between May 2010 and May 2011.

Both HFCs and PFCs exhibite positive trends. HFCs show higher trends than PFCs. Of all the compounds, HFC-134a shows the biggest yearly grow rate up to 4.1 ppt yr^{-1} while the grow rates of other HFCs are approximately 1 ppt yr^{-1}. Among PFCs, background mixing ratios of CF_4 increased 0.43 ppt yr^{-1}, while other 3 PFCs increased less than 0.1 ppt yr^{-1}.

Table 3 shows the comparison between this study and previous works. There are no big differences for HFC-23, HFC-32, HFC-134a and PFC-218. However, for, CF_4 and PFC-116, the trends are smaller than in other studies. But for HFC-125, HFC-152a and PFC-318, our results show the highest trends for all the site we compare with. However, with just one year of observations, changes in transport patterns could be influencing the trend. Therefore, long-term measurement data are needed to validate a reliable trend of the compounds in this study.

3.3 Impact of local surface horizontal winds on the observed HFCs and PFCs

The combination of in-situ measurements with meteorological data can improve the understanding of the relationship between emissions and transport (Dlugokencky et al., 1993; Zhou et al., 2004). In this study, the impacts of local winds on atmospheric HFCs and PFCs mixing ratios were investigated based on 1-yr of observations. Synchronous hourly surface wind data were calculated based on meteorological measurement from SDZ. The surface wind data was calculated based on the sampling time of the in-situ measurement and was then separated into 16 wind directions.

Anomalies (differences between mixing ratios in each wind sector and their means) and loadings (anomalies multiplied by the wind frequencies) were calculated based on the method described in the previous study (Zhang et al., 2010; Zhou et al., 2003,

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2004). Figure 4 displays statistical anomalies and loadings of the HFCs and PFCs in the 16 wind sectors.

For PFC-218, anomalies for all wind direction are within ±0.01 ppt indicating that there are no distinct emission sources in the region influencing SDZ. For other compounds, mixing ratios are most enhanced in WSW and SW, which are the directions towards downtown Beijing. These two sectors also contribute most to loadings. Winds originating from the northeast sector always exhibited negative mixing ratio anomalies. N/NNE/NNW always show the lowest concentrations. However, the frequencies of these sectors are relatively small so that their loadings do not contribute much. The biggest negative loadings are in sectors NE/ENE which have almost same amount as position contribution of SW/WSW.

Of all HFCs and PFCs, the mixing ratio of HFC-134a is most enhanced (> 5 ppt) in SSW/SW/WSW and loading for SW/WSW is approximately 4000 ppt h. For other HFCs and CF_4, the maximal anomalies and loading are around 0.5 ∼ 2.5 ppt and 700 ∼ 2900 ppt h, while for PFC-116 and PFC-318, the maximal anomalies and loading are less than 0.1 ppt and 120 ppt h.

3.4 Emission estimates by tracer ratio method

The tracer ratio method has been used for the emission estimate of halocarbons in recent studies (Barletta et al., 2011; Kim et al., 2010; Li et al., 2011; Parmer et al., 2003; Saito et al., 2010; Shao et al., 2011; Yokouchi et al., 2006).The method is based on assumption that there is an inherent relationship between the target halocarbons and the tracer. Then the emissions of a halocarbon E_r [kt yr^{-1}] can be calculated from its mixing ratio enhancement over background conditions (ΔC_r in ppt) for the pollution event by:

$$E_r = E_x \times (\Delta C_r / \Delta C_x) \times (M_r / M_x)$$

Here the subscript x is used for the tracer, so E_x is the tracer emissions, ΔC_x is the mixing ratio enhancement, and M_x is its molecular weight. M_r is the molecular weight

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of halocarbon. In this study, we choose CO as the tracer because all HFCs and PFCs measured were statistically very significantly ($p < 0.01$) correlated with in-situ CO measurement. And, CO emissions from China have been studied in several inventories (Zhang et al., 2009; Ohara et al., 2007; Streets et al., 2003). CO emissions during the observation period were estimated to 193.5 $\mathrm{Mt\,yr^{-1}}$ using the estimate by Zhang et al. of 166.9 $\mathrm{Mt\,yr^{-1}}$ for 2006 and a growth rate of 3.4 % $\mathrm{yr^{-1}}$.

The area influencing SDZ covered most of the densely-populated North China Plains, and also extends towards southern parts of China such as Yangtz river region but with much weaker impact on the site (Vollmer et al., 2009).

In the 1-yr dataset from SDZ, the enhanced mixing ratios of 5 HFCs and 4 PFCs were significantly correlated with the enhanced mixing ratios with CO. The emission estimates are list in Table 4. The uncertainty of the emission estimate is given by error propagation:

$$\sigma_{E_r} = E_r \sqrt{\left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_{E_x}}{E_x}\right)^2},$$

where b is given by the slope $\Delta C_r/\Delta C_x$. Here we estimate the uncertainties of CO emission as 10 %. The slope $\Delta C_r/\Delta C_x$ was estimated using weighted least square fits of a straight line with uncertainties in both coordinates (Krystek and Anton, 2007). Prior to the fit enhanced mixing ratios were aggregated to 5-day averages to remove autocorrelation in the time series. The uncertainties of the 5-day aggregates were set to 3 % for CO and 5 % for the HFCs and PFCs with the exception of HFC-23 and PFC-318 were, due to larger noise, the uncertainties were set to 10 %. The correlation of HFC-134a and CO is relatively weak and our uncertainty estimate of HFC-134a emissions seems to be too small in this perspective.

Of all HFCs, HFC-134a has the largest emission, with $9.0 \pm 1.3\,\mathrm{kt\,yr^{-1}}$. Two thirds of the HFC-134a production was used for mobile air condition to replace CFC-12 since 2001 (Wan, 2010). With the rapid increase of Chinese automobile industry and the procedure of phasing out CFC-12, Chinese HFC-134a emission probably will be

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continuously increasing. Bottom-up emission estimate based on difference assumption varies from 13.6 kt to 21.1 kt for 2010 with growing rate of 30 % yr^{-1} (Wan, 2010; Hu et al., 2009). Compared to previous work, our estimate proves the strong growth rate of Chinese HFC-134a emission, but on the other hand, the growth rate might have been overestimated by previous bottom-up projections.

The emission estimate of 4.4 ± 0.7 kt yr^{-1} of HFC-23 is much smaller than 10 ± 4.6 of 2004 by Yokouchi et al. (2006). Considering that HFC-23 is mainly produced as a byproduct of HCFC-22 and some companies have executed the Clean Development Mechanism (CDM) since 2005. Based on the data announced by the United Nations Framework Convention on Climate Change (UNFCCC, http://cdm.unfccc.int), the reduced emission were ∼5.6 kt because of the CDM projects executed by 11 Chinese chemical factories in 2010. That is approximately the difference between the emission estimates by this study and by Yokouchi et al. (2006) for 2004. Investigation of five factories involved in CDM projects found all these factories had more reduced emissions than those they reported to UNFCCC. Though it is quite hard to estimate the over-all reduction, it may partly be compensated by the increase in HCFC-22 production. Top-down estimates by Stohl et al. (2010) for 2008 also found Chinese HFC-23 reduction compared to EDGAR bottom up emissions for 2005. The bottom-up estimate by Wan for 2000 ∼ 2008 also shows that Chinese HFC-23 emissions were decreasing from 9.4 kt (2005) to about 7 kt (2008) (Wan et al., 2010).

HFC-32, HFC-152a and HFC-125 are mainly used as foam blowing agents, aerosol propellants, and in refrigeration mixtures (Velders et al., 2009). The emissions of these three HFCs were 6.9 ± 0.9, 2.2 ± 0.4 and 2.5 ± 0.3 kt yr^{-1}, respectively.

Emission estimates for CF_4, PFC-116, PFC-218 and PFC-318 were 2.1 ± 0.3, 0.24 ± 0.06, 0.07 ± 0.04 and 0.45 ± 0.09 kt yr^{-1}. PFC-116 is only half of the estimate by Saito et al. (2010) and Kim et al. (2010) for 2008 and close to EDGAR report for 2008 (0.263 kt yr^{-1}). Out emission estimate for PFC-318 is between the results by Saito et al. (2010) and EDGAR report. For CF_4 and PFC-218, there are small differences between our estimates and other studies concerning the uncertainties.

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4 Conclusions

Based on the 1-yr measurement at Shangdianzi, we observe the similar baseline levels compared to AGAGE stations at the similar latitude, and positive trends were found of all HFCs and PFCs measured. Compare to the previous study, HFC-134a had replaced HFC-23 to be the dominated HFCs in China. It will strengthen with the execution of CMD project as well as the rapid increase of China's automobile industry. Our estimates by CO ratio method are with large uncertainties with limited spatial and temporal coverage. A network with more stations, especially observations from South China, would improve spatial resolution.

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Table 1. Data analysis of HFCs and PFCs measured at Shangdianzi.

Compounds	NO. of air samples	Percentage of background	background (ppt) Mean	S.D.	Pollution (ppt) Mean	S.D.	10 %	90 %
HFC-23	3438	48.2 %	24.5	0.33	28.8	5.77	25.0	35.3
HFC-32	3444	36.0 %	5.86	0.38	10.7	6.27	6.23	17.8
HFC-125	3414	39.9 %	9.97	0.44	11.4	1.68	9.98	13.8
HFC-134a	3399	36.3 %	66.0	1.20	74.4	8.92	67.0	84.1
HFC-152a	3390	52.9 %	9.77	0.55	13.1	3.37	10.4	17.6
CF_4	3376	48.2 %	79.1	0.23	81.2	2.21	79.5	83.9
PFC-116	3312	59.5 %	4.22	0.04	4.45	0.19	4.30	4.70
PFC-218	2318	83.0 %	0.56	0.02	0.62	0.06	0.59	0.67
PFC-318	3447	59.9 %	1.28	0.02	1.59	0.48	1.31	2.04

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Table 2. Comparison of background mixing ratios at Shangdianzi (SDZ) and 4 other stations during the observation period (mixing ratios are given in ppt).

Compounds	SDZ	Jungfraujoch	Mace Head	Trinidad Head	Cape Grim
Longitude	117.12°	7.99°	−9.90°	−124.15°	144.68°
Latitude	40.65°	46.55°	53.33°	41.05°	−40.68°
Altitude	293 m	3580 m	8 m	120 m	94 m
HFC-23	24.5	24.0	24.0	23.9	22.9
HFC-125	9.97	9.96	9.77	9.69	7.77
HFC-134a	66.0	66.6	65.3	65.0	54.8
HFC-152a	9.77	9.57	9.70	9.56	4.08
CF_4	79.1	79.0	79.0	79.0	78.0
PFC-116	4.22	4.15	4.18	4.19	4.05
PFC-218	0.56	0.55	0.56	0.55	0.53

Data of Mace Head, Thinidad Head and Cape Grim are provided by AGAGE and its members: Scripps Institution of Oceanography (SIO), the University of Bristol and the Commonwealth Scientific and Industrial Research Organisation (CSIRO).

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Table 3. Comparison of annual trends of HFCs and PFCs (ppt yr^{-1}).

Compounds	This study	Mühle et al. (2010)	Greally et al. (2005)	Saito et al. (2010)		Reimann et al. (2008)	Reimann et al. (2004)	Yokouchi et al. (2006)	Oram et al. (2012)
Location	Shangdianzi	NH	Mace Head	Hateruma	Ochiishi	Jungfraujoch		Hateruma	Cape Grim
Period	2010.5–2011.5	1993–2008	2004	2006–2009	2006–2009	2004–2006	2000–2002	2004–2005	2010
HFC-23	0.7		0.7					1.8	
HFC-32	1.4		1.6						
HFC-125	1.6					0.8	0.47		
HFC-134a	4.1					4.7	4.0	4.7	
HFC-152a	1.1					0.7	0.3	0.9	
CF_4	0.43	0.686	0.6						
PFC-116	0.05	0.090 (2004–2008) 0.015 (2007–2008)	0.05	0.10	0.08				
PFC-218	0.01		0.04	0.01	0.01				
PFC-318	0.04			0.02	0.01				0.04

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Table 4. Chinese emission estimates of HFCs and PFCs. Uncertainty estimates for this study represent the 95 % confidence limits.

Compounds	Emission estimate kt yr^{-1}					
	This study	Stohl et al. (2010)	Saito et al. (2010)	Kim et al. (2010)	Yokouchi et al. (2006)	EDGAR V4.2 (2012)
Period	2010.5–2011.5	2008	2006–2009	2008	2004	2008
HFC-23	4.4 ± 0.7	6.2 ± 0.7		12 (8.6–15)	10 ± 4.6	13.0
HFC-32	6.9 ± 0.9			4.3 (3.2–5.9)		0
HFC-125	2.5 ± 0.3			3.2 (2.4–4.4)		0
HFC-134a	9.0 ± 1.3	12.9 ± 1.7		8.7 (6.5–12)	3.9 ± 2.4	1.01
HFC-152a	2.2 ± 0.4	3.4 ± 0.5		5.7 (4.3–7.6)	4.3 ± 2.3	0
CF_4	2.1 ± 0.3			2.3 (1.7–3.1)		1.70
PFC-116	0.24 ± 0.06		0.57 (0.36–0.90)	0.49 (0.37–0.66)		0.263
PFC-218	0.07 ± 0.04		0.08 (0–0.17)	0.09 (0.07–0.12)		0.00073
PFC-318	0.45 ± 0.09		0.73 (0.56–1.26)			0.00036

Emission of China mainland from EDGAR V4.2: http://edgar.jrc.ec.europa.eu/overview.php?v=42.

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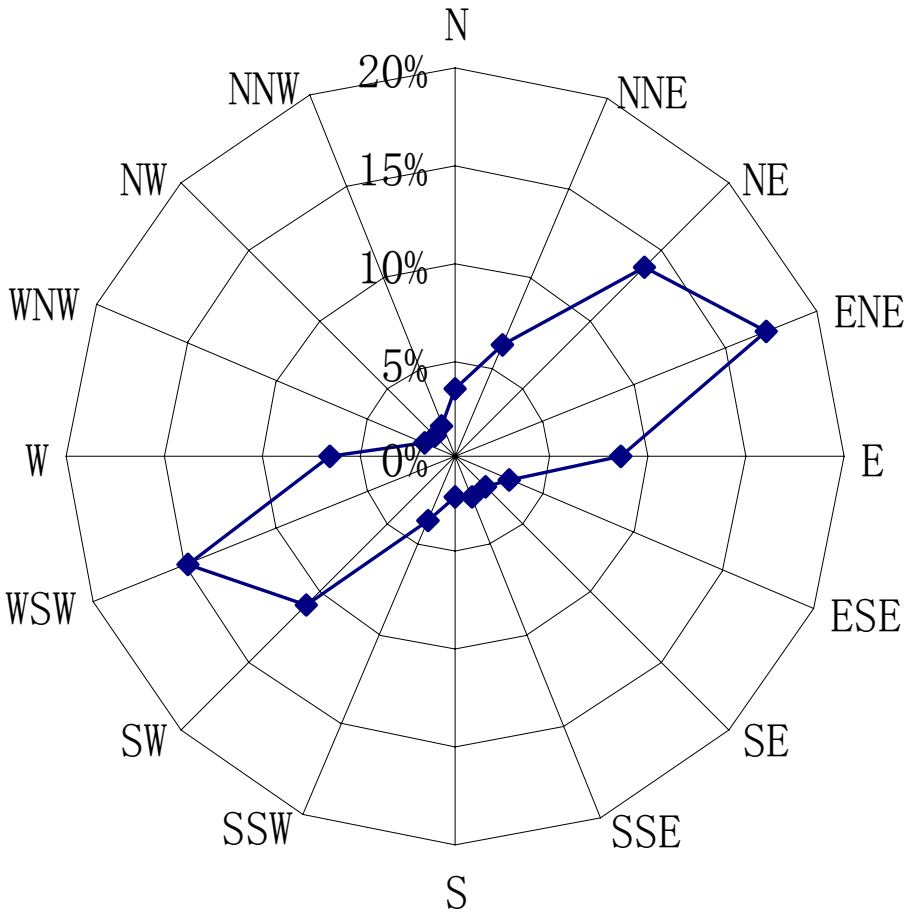

Fig. 1. Probability distribution function of local wind direction (wind rose) at the Shangdianzi station for May 2010 to May 2011 based on hourly data.

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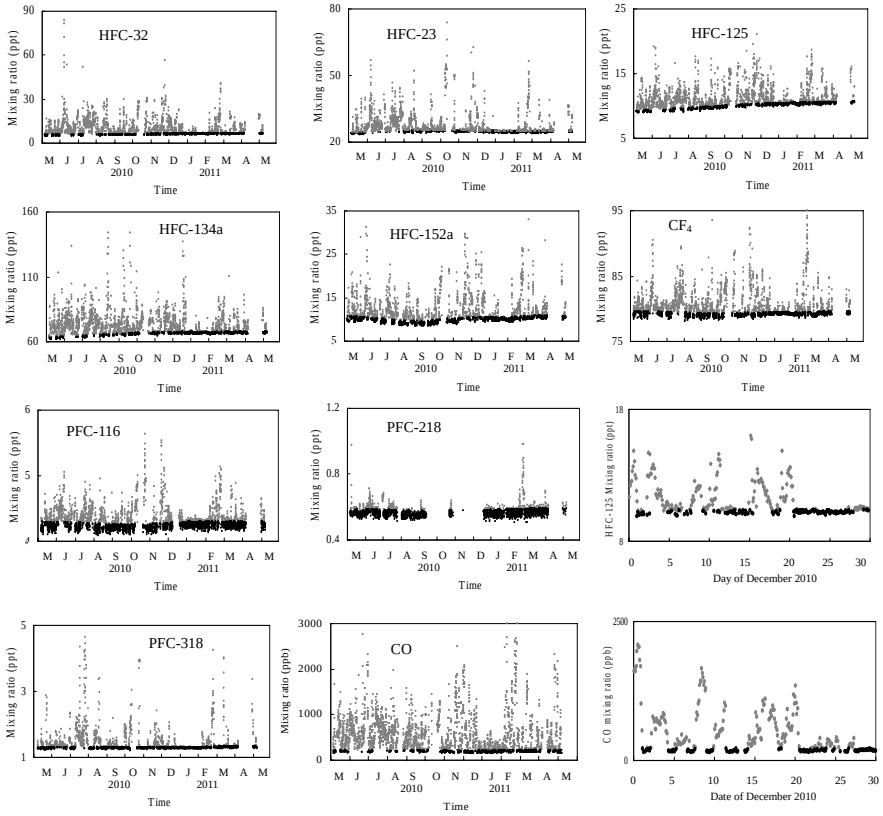

Fig. 2. Time series of HFCs, PFCs and CO at the Shangdianzi station during May 2010 to May 2011 (two panels in the lower right show detailed examples of one month records of CO and HFC-125, grey dots for polluted data and blank dots for background data).

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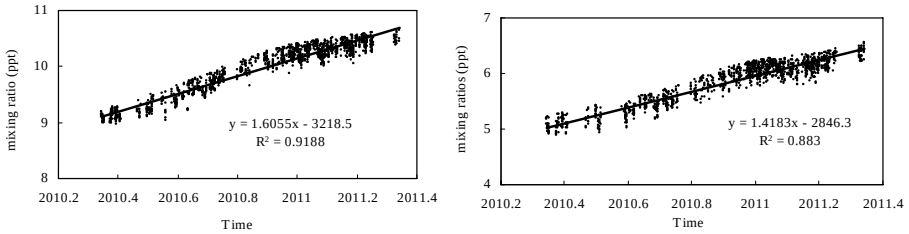

Fig. 3. Annual trends of HFC-125 (left) and HFC-32 (right) at the Shangdianzi station.

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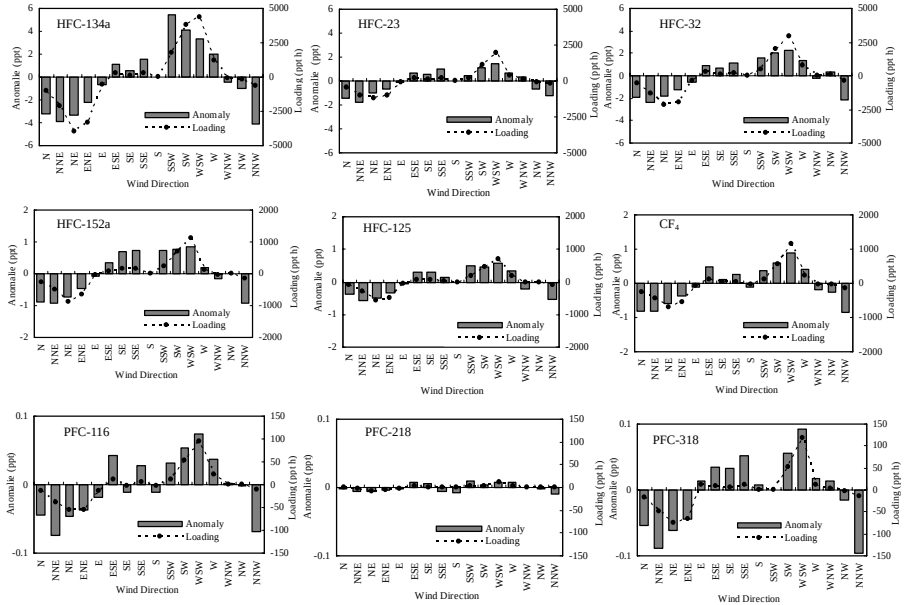

Fig. 4. Statistical anomalies mean mixing ratios for each wind sector and loadings for different wind sectors at the Shangdianzi station from May 2010 to May 2011.

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