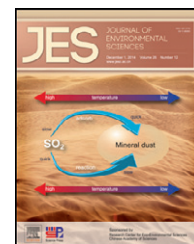


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Atmospheric sulfur hexafluoride *in-situ* measurements at the Shangdianzi regional background station in China

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ABSTRACT

We present *in-situ* measurements of atmospheric sulfur hexafluoride (SF₆) conducted by an automated gas chromatograph–electron capture detector system and a gas chromatography/mass spectrometry system at a regional background site, Shangdianzi, in China, from June 2009 to May 2011, using the System for Observation of Greenhouse gases in Europe and Asia and Advanced Global Atmospheric Gases Experiment (AGAGE) techniques. The mean background and polluted mixing ratios for SF₆ during the study period were 7.22×10^{-12} (mol/mol, hereinafter) and 8.66×10^{-12} , respectively. The averaged SF₆ background mixing ratios at Shangdianzi were consistent with those obtained at other AGAGE stations located at similar latitudes (Trinidad Head and Mace Head), but larger than AGAGE stations in the Southern Hemisphere (Cape Grim and Cape Matatula). SF₆ background mixing ratios increased rapidly during our study period, with a positive growth rate at $0.30 \times 10^{-12} \text{ year}^{-1}$. The peak to peak amplitude of the seasonal cycle for SF₆ background conditions was 0.07×10^{-12} , while the seasonal fluctuation of polluted conditions was 2.16×10^{-12} . During the study period, peak values of SF₆ mixing ratios occurred in autumn when local surface horizontal winds originated from W/WSW/SW/SWS/S sectors, while lower levels of SF₆ mixing ratios appeared as winds originated from N/NNE/NE/ENE/E sectors.

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Introduction

Sulfur hexafluoride (SF₆) is an inert halogenated greenhouse gas that is used as a dielectric and insulator in high voltage electrical equipment, and also released from the magnesium and aluminum industries and semiconductor manufacturing (Ko et al., 1993; Maiss and Brenninkmeijer, 1998; Niemeyer and Chu, 1992). SF₆ is the most potent of the greenhouse gases, with a global

warming potential of 23,900 (Forster et al., 2007) over a 100-year time horizon, and thus its emissions were regulated under the Kyoto Protocol.

SF₆ increased slowly from a very low estimated pre-industrial concentration of ca. 6×10^{15} to 0.03×10^{-12} in 1970 (Vollmer and Weiss, 2002). Then, the global mean SF₆ concentration increased with a growth rate of 8.3% per year to 2.8×10^{-12} in 1992 (Maiss and Levin, 1994). The SF₆ growth rate was relatively stable from the late 1990s to 2004, with $(0.24 \pm$

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0.01×10^{-12} per year for early 1996 (Geller et al., 1997) and 0.25×10^{-12} per year for 2004 (Greally et al., 2005). The concentration of atmospheric SF₆ reached a global background mixing ratio of around 7.26×10^{-12} (mol/mol, hereinafter) in 2011, with a high growth rate of up to 0.28×10^{-12} per year from 2005 to 2011 based on Advanced Global Atmospheric Gases Experiment (AGAGE) measurements (Forster et al., 2007). Considering its long atmospheric lifetime of 3200 years (Stocker et al., 2013), the SF₆ concentration will not decrease over human timescales (Ravishankara et al., 1993). Thus, it is important to conduct long-term atmospheric SF₆ measurements for further emission estimation and to study its climate effect. The National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) and AGAGE established their global SF₆ observation networks in the 1990s and early this century, respectively, by means of gas chromatograph–electron capture detector (GC–ECD) and gas chromatography/mass spectrometry (GC/MS) systems (Rigby et al., 2010; NOAA/ESRL/HATS, 2014; AGAGE, 2014).

As the largest developing country in the world with rapid industrialization, China contributed 22.8% to global SF₆ emission in 2008, with accelerated emission growth rates from 1990 to 2010 (Fang et al., 2013). However, only limited atmospheric SF₆ measurements in China have been presented previously, and all were short-term case studies (Fang et al., 2010; Wang and Wang, 2010).

In this study, we made two continuous years of *in-situ* measurements of SF₆ at the Shangdianzi (SDZ) station in Northern China from June 2009 to May 2011. We compare the performance of GC–ECD and GC/MS systems, and report mixing ratios for both “background” and “polluted” conditions. Background levels and trends are compared with other stations. Additionally, seasonal variations and the impacts of local surface horizontal winds on the observed SF₆ mixing ratios are discussed.

1. Site and measurement

1.1. Site description

Shangdianzi (SDZ, 40°39'N, 117°07'E, 291.3 m asl (above sea level)) is one of the regional background stations of the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW) run by the China Meteorological Administration, and also an affiliated station of AGAGE and the System for Observation of Greenhouse gases in Europe and Asia (SOGE–A) network. It is approximately 100 km northeast of urban Beijing in Northern China, and its topography and climate have the typical characteristics of the North China region (An et al., 2012a). There are no densely populated or industrial areas within a distance of 30 km around the station. The detailed topography and emission source regions influencing the station were described by Lin et al. (2008), Zhang et al. (2010) and An et al. (2012b). During the study period (June 2009 to May 2011, hereinafter), the dominating wind directions of the station (Fig. 1) were NE/ENE/E (background sectors) and W/WSW/SW (urban sectors), which were consistent with previous studies.

1.2. Instruments and methods

Air samples were analyzed *in-situ* using an automated system consisting of a gas chromatograph (6890N, Agilent Technologies Inc., USA) equipped with two electron capture

detectors (ECDs) and a custom-built sample preparation system (SPS) operating since 2006 as part of the SOGE–A program (Vollmer et al., 2009; Yao et al., 2012a). SF₆ was trapped at room temperature in a 2 mL sample loop and then separated on a molecular sieve (MS) 5A column (4 m, 1/8 in. OD, custom-made) located in an auxiliary oven at 90°C, and detected by ECD. The system also measures chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), Halons and chlorinated solvents. The CFC and HCFC measurements made by this system were reported by Zhang et al. (2010) and Yao et al. (2012a).

An air inlet was installed at 8 m height on a 10-m tower that was 30 m distant from the air conditioned container where the system was installed. Ambient air was drawn through a continuously flushed sampling tube (10 mm OD, Synflex-1300, Eaton, Switzerland) by means of a membrane pump (N86, KNF Inc., USA) with response time <5 min.

An automated custom-built “Medusa” gas chromatographic system with mass spectrometric detection (5975C, Agilent Technologies Inc., USA) (Medusa-GC/MS) (Miller et al., 2008) installed in May 2010 has been measuring SF₆ and a suite of more than 50 trace gases as part of the AGAGE network. The Medusa-GC/MS system used a similar sampling mechanism, sharing the same inlet and sampling tubing with GC–ECD system. The HFC and PFC measurements made by this system were reported by Yao et al. (2012b).

1.3. Data process and quality control

Techniques transferred from AGAGE were used for the data processing and quality control in our study. Each air sample measurement (every 80 min for GC–ECDs and every other hour for Medusa-GC/MS) was bracketed by a reference gas (working standard) measurement to detect and correct for drift in the detector sensitivity. Our measurements were linked to AGAGE and reported as dry air mole fraction on the

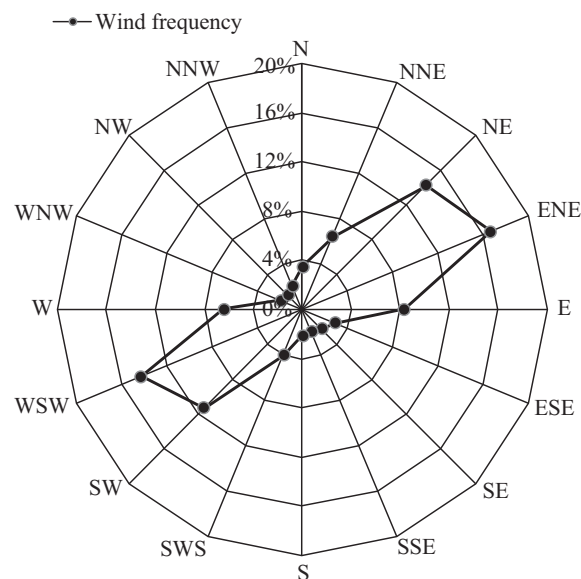


Fig. 1 – Wind rose at Shangdianzi station.

Table 1 – Results of tank calibration by gas chromatograph–electron capture detector (GC–ECD) and gas chromatography/mass spectrometry (GC/MS).

Method	C-133			C-135		
	N total	Mean ($\times 10^{-12}$)	S.D. ($\times 10^{-12}$)	N total	Mean ($\times 10^{-12}$)	S.D. ($\times 10^{-12}$)
GC–ECD	16	7.14	0.04	19	7.11	0.04
GC/MS	11	7.15	0.05	9	7.13	0.05

N: number of valid data; S.D.: standard deviation (one sigma).

Scripps Institution of Oceanography (SIO)-2005 calibration scale (Miller et al., 2008; Prinn et al., 2000).

Additionally, weekly measurements of two system blanks were conducted on each instrument to check for potential instrument-internal contamination. Nonlinear detector response was characterized using a dynamic dilution system and data were corrected with calculated nonlinearities. Both systems were fully automated and controlled by commercially available chromatography software developed by AGAGE (GCWerks, GC Soft Inc., La Jolla, USA).

2. Results and discussion

2.1. Comparison between performance of GC–ECD and GC/MS systems

Both GC–ECD and GC/MS systems were used to calibrate two tanks (C-135 and C-133, filled at SDZ with ambient air) using the same analytical technique as for ambient air samples. As shown in Table 1, the precisions of the two systems were both within 0.05×10^{-12} . The differences between the two tanks calibrated by the two systems were 0.01×10^{-12} (C-133) and 0.02×10^{-12} (C-135), respectively, both within the precisions of the systems.

The results of co-located *in-situ* measurements at SDZ for a whole year from May 2010 to April 2011 were compared. The differences between 10th, 25th, and 75th percentiles of the two time series of SF₆ were all within 0.04×10^{-12} , while the difference between 90th percentiles was relatively greater, at 0.09×10^{-12} .

Considering the different time resolutions of the two systems, a time window of 4 hr was chosen. In each time window, 3 and 2 air samples were measured by the GC–ECD and GC/MS systems, respectively. In total, 1083 time windows were chosen with valid data for comparison. As shown in Fig. 2, the time series of SF₆ obtained by the two systems at the same time window show similar patterns. The differences between averaged mixing ratios of the two methods in the same time windows were statistically analyzed. The results demonstrated no significant differences ($p > 0.05$) between the two systems by the Welch Two Sample t-test. For 36.92% of the time windows, the differences between the two methods were within $\pm 0.04 \times 10^{-12}$, however, for 4.89% of the time windows, the differences between the two methods were larger than 0.5×10^{-12} .

SF₆ concentrations could increase rapidly due to its pulsed emissions pattern. Taking the pollution event from

December 3 2010 to December 5 2010 as an example, the SF₆ concentrations increased from ca. 7×10^{-12} to ca. 25×10^{-12} in 6 hr, with growth rate reaching $3 \times 10^{-12} \text{ hr}^{-1}$ (Fig. 2). Considering the difference of sampling time between the two systems (possibly as long as 1 hr), the rapidly changing rate might account for some individual examples with relatively large differences between the two methods.

Generally, GC/MS and GC–ECD show similar and acceptable precision for measuring atmospheric SF₆. No significant differences were found between average mixing ratios for the two methods in the same time window. Moreover, it might be helpful to capture the detailed features of SF₆ pollution events by improving the time resolution of the measurement.

2.2. SF₆ mixing ratios over two years

Fig. 3 exhibits the dataset compiled by using the results from the GC/MS system in September 2010 and data from the GC–ECD system from the rest of the study period because the GC–ECD system was malfunctioning in September 2010. The discussion below is all based on the combined SF₆ time series.

Background conditions were distinguished from polluted values using a “robust local regression” mathematic procedure (Ruckstuhl et al., 2012). The details of the procedure were described by Yao et al. (2012b). Approximately 63% of the valid results had been selected as non-background data. Large episode events with elevated SF₆ mixing ratios at SDZ were mainly ascribed to polluted air masses transported from urban or industrialized areas. As shown in Fig. 3, background data displayed low mixing ratios and smooth changes, but polluted data showed high values and large variations. Table 2 lists SF₆ mean mixing ratios of both background and polluted data together with the standard deviations, and also median values, 10% and 90% percentiles.

2.3. Mean SF₆ background mixing ratios at SDZ compared with AGAGE sites

SF₆ mean background mixing ratios were derived from monthly data during the study periods at Mace Head (MHD), Trinidad Head (THD), Cape Matatula (SMO) and Cape Grim (CGO) as listed in Table 3. The measurements at all these AGAGE stations were traceable to the SIO-2005 calibration scale, hence data could be compared directly.

At SDZ, the averaged SF₆ background mixing ratio was 7.22×10^{-12} from June 2009 to May 2011, consistent with THD

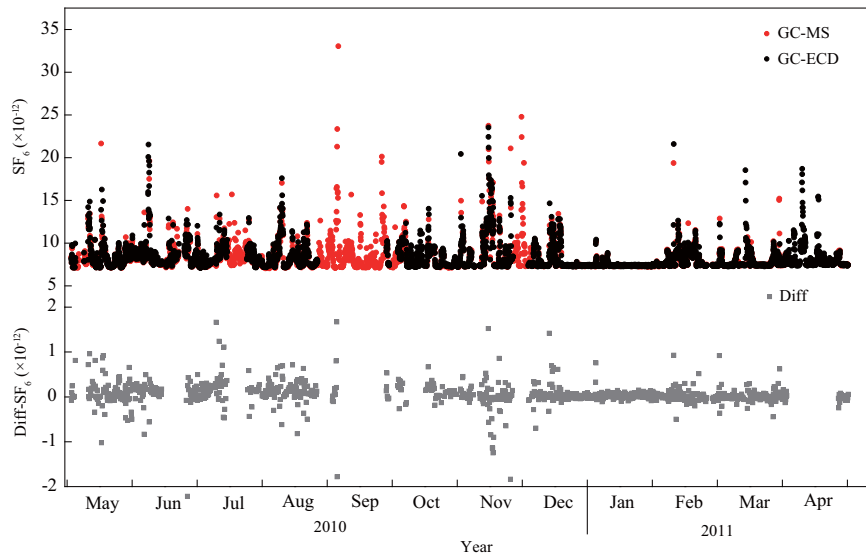


Fig. 2 – Time series for the average mixing ratios by gas chromatography/mass spectrometry (GC/MS) and gas chromatograph-electron capture detector (GC-ECD) at the time window of 4 hr (top panel) and the difference between the two methods (mixing ratios by GC/MS minus mixing ratios by GC-ECD) at the same time windows (bottom panel) at SDZ for a whole year from May 2010 to April 2011.

(7.18×10^{-12}) and MHD (7.17×10^{-12}) during the same observational period. All these three sites were located at middle or high northern latitude. The differences between SDZ and the two stations in the southern hemisphere were 0.36×10^{-12} (SMO) and 0.44×10^{-12} (CGO), respectively (Table 3), reflecting the hemispheric gradient of SF_6 , mainly owing to ~90% anthropogenic and industrial sources being contributed from the northern hemisphere (Maiss et al., 1996; Olivier et al., 2005).

2.4. Trends

As shown in Fig. 4, the long-term trends were estimated based on linear curve fitting of the daily average of SF_6 background mixing ratios (open circles). In our study, the average growth rate of SF_6 at SDZ was 0.30×10^{-12} per year, which was in excellent agreement with THD (0.30×10^{-12} per year) and MHD (0.29×10^{-12} per year) from June 2009 to May 2011, and also in good agreement with the growth rate (0.29×10^{-12}

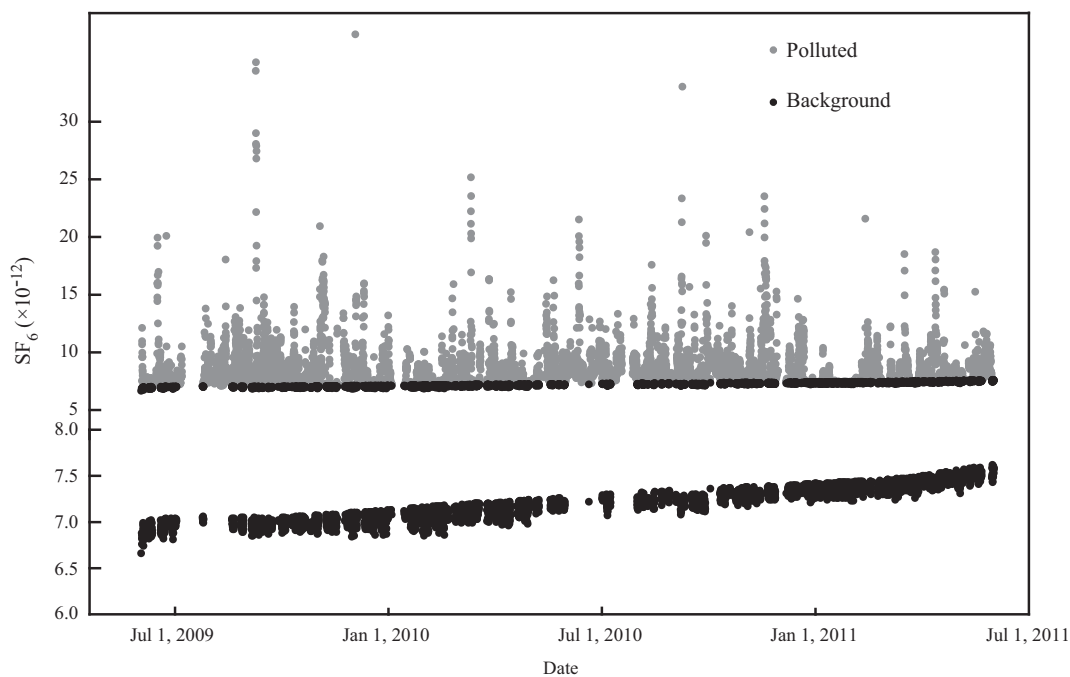


Fig. 3 – Time series for background and polluted SF_6 mixing ratios at Shangdianzi. The top panel presents the combined time series from June 2009 to May 2011. Data for September 2010 is measured by gas chromatography/mass spectrometry, and the rest by gas chromatograph-electron capture detector. The bottom panel presents the background mixing ratios in larger axis.

Table 2 – Statistics of SF₆ mixing ratios at the Shangdianzi from June 2009 to May 2011.

Data	N total	Mean ($\times 10^{-12}$)	S.D. ($\times 10^{-12}$)	10% ($\times 10^{-12}$)	90% ($\times 10^{-12}$)	Median ($\times 10^{-12}$)
Background	3759	7.22	0.18	6.88	7.43	7.24
Polluted	6468	8.66	1.97	7.28	10.49	8.09

N: number of valid data; S.D.: standard deviation (one sigma); 10%: 10th-percentile; 90%: 90th-percentile.

Table 3 – Mean SF₆ background mixing ratios at Shangdianzi and four AGAGE stations from June 2009 to May 2011.

Station	Mace Head	Trinidad Head	Shangdianzi	Cape Matatula	Cape Grim
Station ID	MHD	THD	SDZ	SMO	CGO
Latitude	53.3°N	41.1°N	40.6°N	14.2°S	40.7°S
Longitude	9.9°W	124.2°W	117.1°E	170.6°W	144.7°E
Mean mixing ratio ($\times 10^{-12}$)	7.17	7.18	7.22	6.86	6.78

Mean mixing ratio: Mean background mixing ratios of SF₆ were based on monthly data from June 2009 to May 2011 at 4 AGAGE sites which was available on http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current_archives/.

per year) at AGAGE northern hemisphere monitoring sites for 2008 (Rigby et al., 2010). Therefore, it was inferred that the increasing SF₆ concentration might have been accelerated recently, which may be due to the increasing global SF₆ emission from 6.3 ± 0.6 Gg/year in 1995 to 7.4 ± 0.6 Gg/year in 2008 (Rigby et al., 2010).

2.5. Mean annual cycle of SF₆

Fig. 5 shows the average seasonal cycle of SF₆ background mixing ratios during the study period at SDZ and THD. We first presented the time series of “detrended” monthly data sets by subtracting a linear secular trend, then averaged these available monthly values throughout the study period to obtain a mean value for each month. As shown in Fig. 5, maximum and minimum values of the mean seasonal SF₆ cycle at SDZ appeared in July and September, respectively. The peak to peak amplitude was 0.07×10^{-12} . The seasonal amplitude at SDZ was very similar to that at THD (ca. 0.07×10^{-12}), yet the phases of the SF₆ seasonal cycle were slightly different from THD. At THD, maximum and minimum values occurred in May and September, respectively.

Fig. 6 shows the seasonal variations of polluted conditions based on the average monthly data at SDZ during the study period. The seasonal fluctuation (difference between maximum and minimum values) for polluted SF₆ mixing ratios was 2.16×10^{-12} , which was much stronger than the background conditions, even in relative terms. SF₆ polluted mixing ratios displayed a peak value in November. In China, SF₆ emission was from the electrical equipment sector (70%), the magnesium production sector (10%), the semi-conductor manufacturing sector (10%) and the SF₆ production sector (10%) (Fang et al., 2013). Unlike other greenhouse gases such as CH₄, CO₂ and N₂O, SF₆ is generally thought to be a predominantly anthropogenic component with negligible natural sources (Harnisch and Eisenhauer, 1998). Therefore, we deduced that more anthropogenic emissions of SF₆ probably occurred in November during our study periods around SDZ.

2.6. Impact of local surface horizontal winds on SF₆

This section elucidates the seasonal variation of surface horizontal wind and its impact on SF₆ mixing ratios at SDZ, which could improve understanding of the air-mass transport

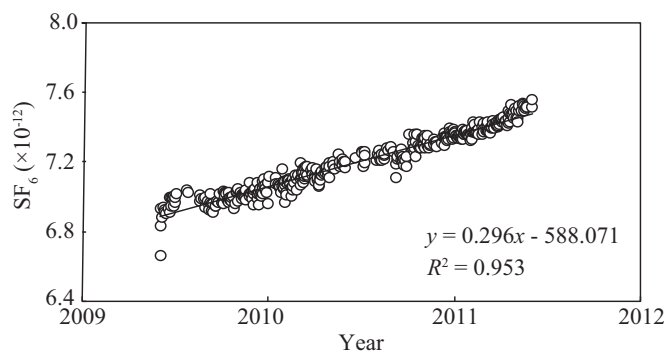


Fig. 4 – Estimated trends for SF₆ at Shangdianzi from June 2009 to May 2011. Open circles represent daily average values of SF₆, solid line represents the long-term estimated trends.

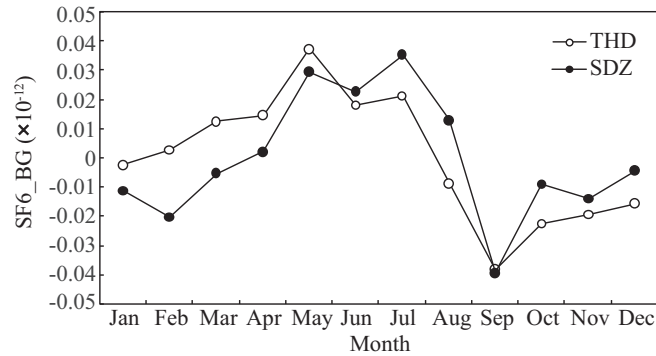


Fig. 5 – Average seasonal cycles of SF₆ background mixing ratios at Shangdianzi and Trinidad Head during the study period.

paths and help deduce the SF₆ emission source regions. The seasonal wind frequency of 16 wind directions at SDZ over the study period is shown in Fig. 7a. The prevailing surface horizontal wind directions in autumn and winter were NE/ENE/E, with about 42% and ~54% of the total wind frequency respectively; whereas in spring and summer, SW/WSW/W were the dominating wind directions, with ~38% and ~44% of the total frequency, respectively.

Fig. 7b exhibits the distribution of SF₆ mixing ratios over 16 wind directions in different seasons. Pollution events often occurred in W/WSW/SW/SWS/S sectors, while lower levels of SF₆ mixing ratios appeared in N/NNE/NE/ENE/E sectors. It could be concluded that polluted air masses were transported to SDZ from W/WSW/SW/SWS/S wind directions, where densely populated urban areas such as Beijing were located. Airflow that originated from N/NNE/NE/ENE/E sectors was thought to be clean and inferred to represent SF₆ background conditions. As seen in Fig. 7b, SF₆ mixing ratios were obviously higher in autumn than in other seasons, probably owing to more SF₆ emissions in November, when the maximum value of the seasonal cycle was observed, as shown in Fig. 6.

3. Conclusions

In-situ measurement of SF₆ mixing ratios was made by GC-ECD and GC/MS at SDZ from June 2009 to May 2011. GC/MS and GC-ECD showed a similar precision for measuring

atmospheric SF₆. Time series of SF₆ mixing ratios based on the combined data from the two instruments are presented in this study, showing numbers of pollution events with higher concentrations and larger fluctuations than background conditions, as this station was influenced by polluted air flows from urban and industrial-related areas in northern China. SF₆ background mixing ratios increased throughout the study period. The averaged SF₆ background mixing ratios were in good agreement with other AGAGE sites located at middle or high northern latitude such as MHD and THD, but higher than SMO and CGO located in the southern hemisphere, because of inter-hemispheric differences caused by predominant NH emissions. The seasonality of SF₆ pollution exhibited a maximum value in November. It was also observed at SDZ that airflow from W/WSW/SW/SWS/S sectors exhibited positive contribution to SF₆ levels, with peak values in autumn. Lower SF₆ concentrations appeared especially when local surface horizontal winds were from N/NNE/NE/ENE/E sectors.

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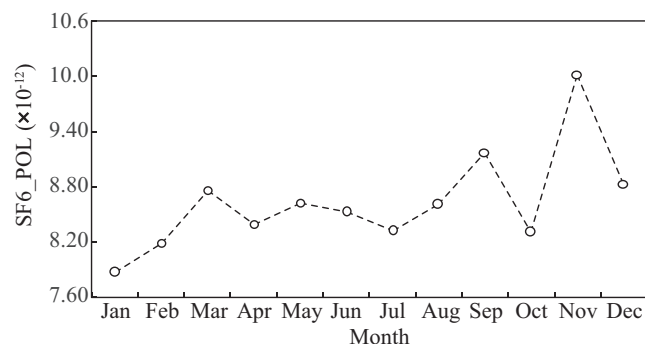


Fig. 6 – Seasonal variations of polluted conditions for SF₆ at Shangdianzi during the study period.

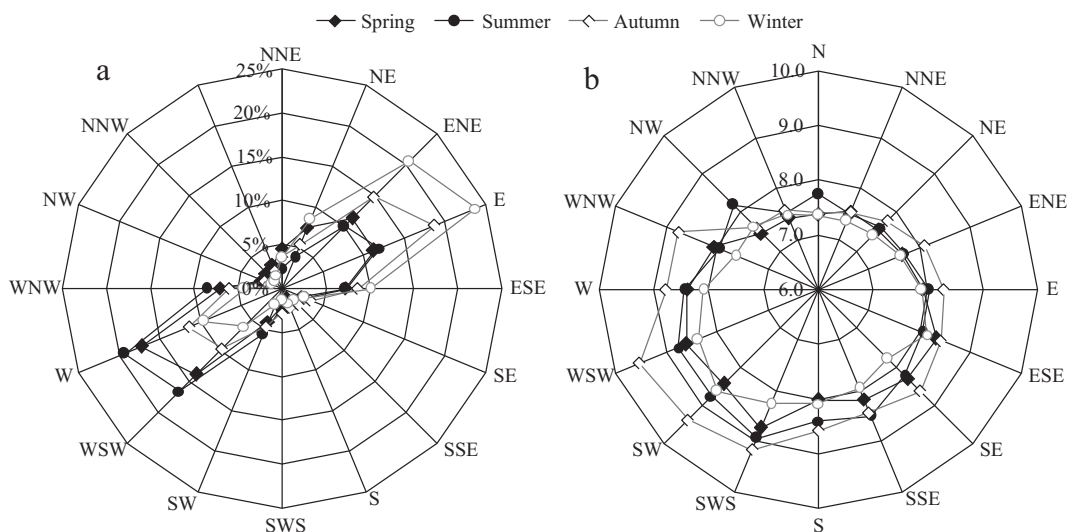


Fig. 7 – Seasonal wind frequency (a) and SF₆ mixing ratio (unit: 10⁻¹²) distribution over 16 wind directions (b) at Shangdianzi during the study period.

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