

A REVIEW ON THE APPLICATION OF FLUORINATED GREENHOUSE GASES MEASUREMENT TECHNOLOGIES

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Abstract. Fluorinated greenhouse gases (FGHGs) have a high global warming potential, strong greenhouse effect, and long atmospheric lifetime. However, because they are usually < 1 ppb, their measurement is incredibly challenging. This article summarizes international control documents for FGHGs, quantitatively and statistically review the monitoring technologies used in recent FGHG research and summarizes and analyzes the trend in FGHG concentrations. It also reviews the sampling, capture, and detecting instruments used in various stages. In addition, this article introduces some global and regional FGHG research plans and results. Finally, based on the actual monitoring situation of FGHGs in China, we provide targeted suggestions for the subsequent development step.

Keywords: *fluorinated greenhouse gases, observation technology, gas chromatograph/mass spectrometer (GC/MS), spectrum*

Introduction

Fluorinated greenhouse gases (FGHGs) typically include chlorofluorocarbons (CFCs, popularly used refrigerants, foaming agents, and cleaning agents), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF₆), and nitrogen trifluoride (NF₃). In a broader sense, FGHGs also include some ozone-depleting substances (ODSs). Since the earth's outward radiation spectrum is predominantly in the infrared spectrum, S-F and C-F bonds primarily vibrate between 900 and 1300 cm⁻¹, being the most substantial window for earth's outward radiation energy. At the same time, FGHGs have a longer atmospheric lifetime, leading to extremely high global warming potentials (GWPs) and radiative efficiencies. The 100-year GWP of most FGHGs (such as CFC-12, SF₆, and NF₃) is typically more than a thousand (i.e., 11800, 26700, and 18500, respectively) (Hodnebrog et al., 2020).

Most CFCs and HCFCs have relatively long atmospheric lifetimes. Their C-Cl bond can quickly produce Cl free radicals, the leading cause of the ozone hole. Therefore, most countries have banned the emission of these chemicals. As substitutes, HFCs do not directly destroy the ozone layer, although they have a strong greenhouse effect. Thus, they are also being phased out. Similarly, PFCs have a very high GWP. However, they remain indispensable because no feasible substitutes have been found so far for their use as insulating gases in the electrical industry (Sheldon and Crimmin, 2022). Under the current "dual carbon" strategy of achieving a carbon peak before 2030 and carbon neutrality before 2060, the summarization and analysis of past FGHG research results are instructive for studying the development prospects of FGHG monitoring technology and governance measures in China.

This study retrieves Chinese and English literature in the Web of Science database, using search keywords such as HCFCs, HFCs, CFCs, PFCs, and environmental

atmospheric observations. It reviews the literature from three aspects: the species of interest, measurement technology, and changes in different periods. This article organizes and counts the FGHG-related control documents and norms. It clarifies the domestic and foreign FGHG emission control status. The article uses database retrieval to analyze the trend and hotspots of research literature. Additionally, it summarizes the development history of FGHG measurement technology and analyzes the monitoring global networks and the regional distribution characteristics of emissions. Finally, it summarizes and anticipates the development of FGHG monitoring.

Global control measures for fluorinated greenhouse gases

Currently, effective legal regulations for FGHGs are lacking in China. Before 2019, emission restrictions on fluorinated substances as ODSs were already enacted. Yet, there is still a lack of formal technical standards for sampling and detecting related substances. However, with the release of the "IPCC 2006 National Greenhouse Gas Inventory Guidelines 2019 Revised Edition", China has taken control measures for the emission of FGHGs accordingly. In June 2021, the "Kigali Amendment" to the "Montreal Protocol" further enhanced HFC emissions.

Internationally, FGHG emission control mechanisms mainly originate from the "United Nations Framework Convention on Climate Change", the "Paris Agreement", the "Kyoto Protocol", the "Montreal Protocol," and the "Kigali Amendment". These conventions, agreements, and bills gradually include various types of GHGs and stipulate the corresponding emission reduction timetable to control the global temperature rise within 2 °C.

Current status of research on fluorinated greenhouse gases

Trends and hotspots in research literature

Analyzing global literature published since January 2012, monitoring studies (mainly with gas chromatography, mass spectrometry and spectroscopy) on emissions of prohibited CFCs predominated. *Figure 1* illustrates the proportion of research literature that utilizes different methods for measuring FGHGs. The mainstream detection method for CFCs is spectroscopy, with IR being the most common. Among IR methods, FTIR is the majority, with a few instances of GC-IR. Electron capture detector (ECD) is commonly used in the GC/MS system. Similarly, HCFCs are primarily detected via spectroscopy. HFCs are the common substitute for CFCs and HCFCs. Many studies show that HFC-134a, having the highest atmospheric concentration, is currently the focus of HFC monitoring research (Harrison et al., 2021). Meanwhile, SF₆ and NF₃, being FGHGs with no carbons, are widely used for electrical insulation (Harrison, 2020). They are usually examined with GC/MS and IR on formation.

Table 1 shows on one hand that the total number of research publications produced by authors from each country, based on the affiliation of the first author. Secondly, it details the frequency with which each country or region has been monitored and studied within these research articles. In total, 141 papers were reviewed, primarily from the United States, China, and the United Kingdom. Most papers published in the United States focused on the global FGHG issue, while those from China were relatively more inclined toward domestic emissions and background concentration research.

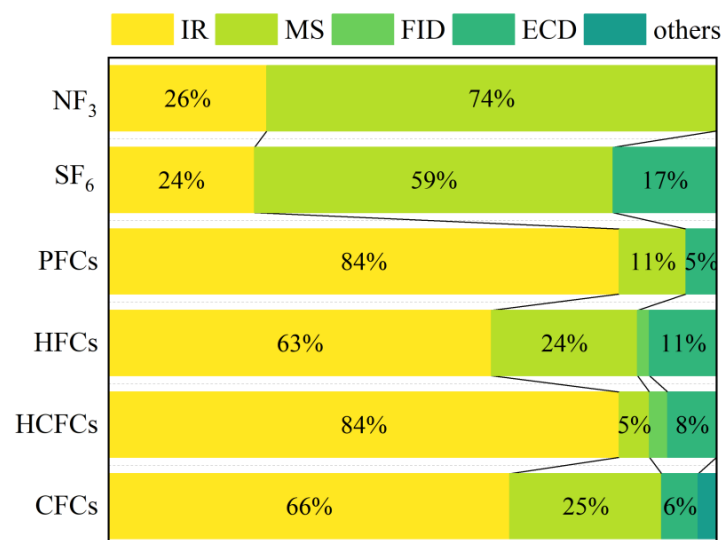


Figure 1. Detectors used for corresponding components in research studies

Table 1. Number of research studies in various international regions or countries over ten years

Author's Country	Number of Articles	Country/Region	Times Studied
United States	45	Global	53
China	29	China	27
United Kingdom	24	United States	9
Switzerland	9	Europe	9
Germany	9	Australia	7
France	7	India	4
Canada	5	East Asia	4
Australia	5	United Kingdom	3
Italy	4	South Korea	3
South Korea	4	France	3

Research on various FGHGs has not shown any significant trend in the past decade. The world and China (specifically) banned CFC emissions in 1995 and 2010, respectively. However, the trend of subsequent changes in atmospheric background concentration is one of the leading research contents. Since the 1990s, HCFCs have been introduced in China as substitutes for CFCs. According to the Montreal Protocol, China will also phase out HCFCs before 2030. Therefore, the emission of these species is a new research hotspot.

Trends in FGHGs concentration

According to the "IPCC 2019", the initial FGHG emissions increased by 0.97 Gt CO₂-equivalent (254%) from 1990 to 2019, when it was 1.4 ± 0.41 Gt CO₂-equivalent. Minx's analysis shows that in the evolution of global FGHG emissions, CFCs were the primary source during the 1980s. However, under the Montreal Protocol, CFC emissions were reduced substantively in 1987, while HCFCs and HFCs began to increase. By 2016, the

CO₂-equivalent emissions of the three species were approximately the same, while other FGHGs contributed relatively small amounts (Minx et al., 2021).

The Advanced Global Atmospheric Gases Experiment (AGAGE) has been monitoring the component concentration changes of various FGHG species for a long time. The output data show a gradual rise in FGHG background atmospheric concentrations (Prinn, 2023).

Figure 2 shows the data of trend of the gas concentration at Gosan Station that the AGAGE public data are used to analyze FGHGs background concentrations in East Asia, and the GWP is ranked, which can represent emissions from eastern China. However, as a potential source of FGHG emissions, the eastern coastal regions of China lack a dedicated monitoring network for specific FGHG emission sources, making it difficult to accurately trace the origin of FGHGs. The HFC-23 concentration is low, but due to its substantially high GWP, it has the highest CO₂-equivalent, followed by HCFC-22. The atmospheric concentrations of HFC-23 and HCFC-22 are related because HFC-23 is a byproduct of HCFC-22 production, meaning their emissions often increase together, the primary emission sources of HCFC-22 are the leakage of refrigerants and the scrapping of refrigeration equipment, while HFC-23 commonly originates from the water washing and maintenance stages of HCFC-22 production (Simmonds et al., 2018; Wu et al., 2022).

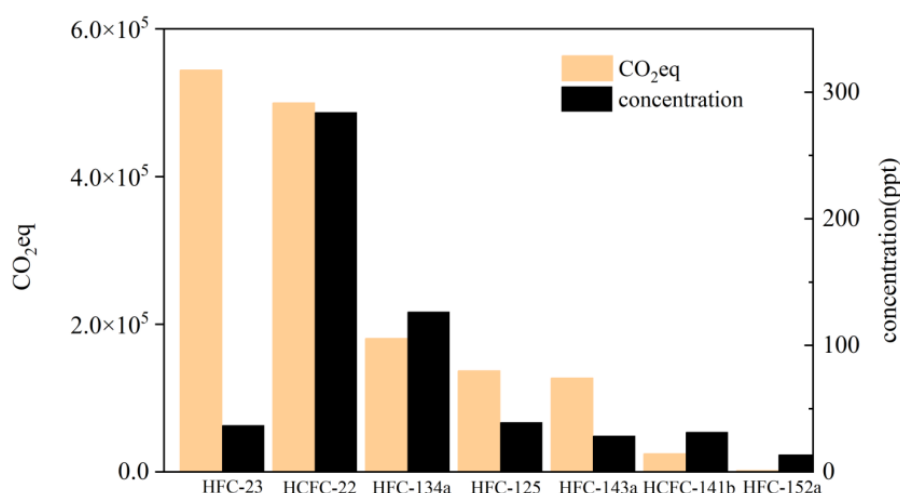


Figure 2. CO₂-equivalent GWP and concentrations of species at Gosan Station in 2020

Figure 3 shows the atmospheric concentration trends of various FGHGs, including HFC-23, HFC-134a, HFC-125, HFC-143a, HCFC-141b, and HFC-152a, at the Gosan station over the years from 2007 to 2020, which can indicate the increasing concentration of FGHGs in east Asia.

The growth rate of FGHG emissions in China from 1990 to 2019 has increased steadily from 5.5 to 200 million tons of CO₂-equivalent emissions (Guo and Fang, 2023). If there are no relevant laws and regulations to restrict FGHG emissions, the total FGHG emissions in China will reach 506–1356 million tons of CO₂-equivalent per year by 2060 (Guo et al., 2023). In recent years, the atmospheric FGHG concentrations have been increasing rapidly. In China, the atmospheric concentration of some species (such as HFC-227a, HFC-236a, and HFC-134a) exceeded 20% during 2018. Compared with 2011, the relative growth rates of HFC-23, HFC-32, HFC-125, HFC-134a, and HFC-152a reached 77%, 295%, 412%, 356%, and 100%, respectively, in 2018 (Xie et al., 2019).

These gases originate primarily from industrial processes and domestic emissions where CFCs are replaced. Among them, HFC-134a is currently the main component of refrigerants and has been the research focus in various regions for decades (Stemmler et al., 2004; Lunt et al., 2015; Yan et al., 2014; Wu et al., 2014; Wu et al., 2013; Li et al., 2011; Stohl et al., 2010; Yokouchi et al., 2006; Yi et al., 2023; Tratt et al., 2021; Harrison et al., 2021). In addition, some studies have found that since 2015, HFC-23 emissions in eastern China have been increasing annually. It could be because the surrounding areas have not successfully reduced the emissions, or there may be unaccounted HCFC-22 productions (Stanley et al., 2020).

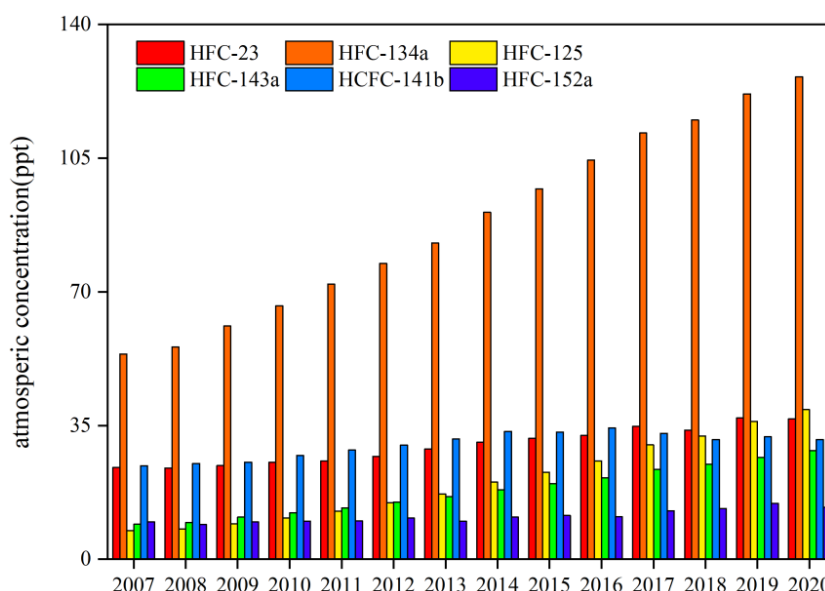


Figure 3. FGHG Concentration Trends at Gosan Station from 2007 to 2020

Further research in China is ongoing on several FGHGs with high GWP, huge emissions, and high background concentrations. According to the China Shangdianzi regional atmospheric background station data, the concentration of HFC-134a and HFC-152a in 2016 was 89.3 and 6.72 ppt; in 2018, the concentrations of HFC-134a and HFC-152a were 110.2 and 10.3 ppt; the concentration of HFC-134a and HFC-152a rises steadily, while HFC-152a exhibits seasonal variations (lows in winter and highs in summer) due to its low atmospheric lifetime of 1.4 years (Xie et al., 2019). According to measurements from the AGAGE Zeppelin station using Medusa GC/MS, the concentrations of HFC-134a and HFC-152a in 2016 were 96.9 ppt and 9.93 ppt, respectively, and in 2018, they were 108.5 ppt and 10.3 ppt. The percentage increase in HFC-134a at the Zeppelin station from 2016 to 2018 is approximately 12%, while for HFC-152a, the increase is around 3.7%. In comparison, the percentage increase at the China Shangdianzi station during the same period was about 23% for HFC-134a and approximately 53% for HFC-152a. These results indicate that the growth rates of both gases were lower at the Zeppelin station, suggesting stronger regulatory measures in the surrounding regions of Zeppelin. In addition, CFCs and other FGHGs that have stopped production have generally shown a steady downward trend over the decades.

From 2005 to 2013, the proportion of HFCs CO₂-equivalent emissions in China's total CO₂ emissions and global HFCs CO₂-equivalent emissions rose rapidly (Zhao et al.,

2022). Details of the HFC emission inventory and the 2050 forecast during this period can be seen in Fang's research (2016). From 2009 to 2019, halocarbons in five Chinese cities (Beijing, Hangzhou, Guangzhou, Lanzhou, and Chengdu) accounted for 75.1% of the ODS-weighted emissions and 58.6% of CO₂-equivalent emissions (Yi et al., 2021). The latest research estimates FGHG emissions in northern China using tracing methods. The results showed that CO₂-equivalent emissions of SF₆ accounted for the highest among all FGHGs (Yi et al., 2023). Elsewhere, Ma's research on FGHG concentrations around typical chemical plants evinced HFC emissions as the largest, followed by PFCs (Ma et al., 2023).

Other countries and regions have also conducted long-term monitoring studies on halocarbons. For example, Rust evaluated halocarbon emissions in Switzerland from 2019 to 2020 based on regional atmospheric observations (Rust et al., 2022). Likewise, Platt detailed the historical measurement results of atmospheric components in the European Arctic at the Zeppelin Observatory over 30 years (Platt et al., 2022).

FGHGs monitoring technology

Monitoring FGHGs is incredibly demanding due to their varieties, low concentrations, and finitely small changes. Any deviation of atmospheric baseline concentration may significantly reduce the emission assessment results (Annadate et al., 2024). For example, the atmospheric baseline concentration of CFC-11 is 230 ppt. Furthermore, its interannual changes and differences between the northern and southern hemispheres are < 10 ppt, requiring an observation accuracy of > 0.5%. Thus, the accuracy requirements for a proper detection technology are incredibly high. According to the conventional instruments used for obtaining steady data and the technical solutions for FGHG monitoring, the reliable technologies that meet the monitoring detection limit, sensitivity requirements, and monitoring frequency include mass spectrometry (Miller et al., 2008), gas chromatography (with specific detectors), gas chromatography-mass spectrometry, and infrared spectroscopy (Hall et al., 2011). These technologies are proven to meet the stringent requirements for monitoring limits, sensitivity, and frequency needed for effective FGHG assessment. *Table 2* summarizes the range of concentrations for various gases, as derived from the literature reviewed in this chapter.

Chromatography mass spectrometry techniques

The electron bombardment ion source (EI) is commonly used in China's ODS-related monitoring standards and applies to FGHGs with similar properties. ECD is a classical technology for detecting CFCs with larger particle cross-sections and does not require any pre-concentration (Prinn et al., 1983; Prinn et al., 1992; Cunnold et al., 1994). Also, ECD is highly sensitive to halocarbons and alkyl nitrates and is widely used to accurately detect related substances, down to ppt level (Ou-Yang et al., 2017; Zheng et al., 2019; Toyoda et al., 1998; Huang et al., 2021).

Moreover, negative ion chemical ionization-mass spectrometry can detect airborne c-PFCs in trace amounts (Begley et al., 1988; Hintsa et al., 2021). By improving the chromatographic column, its detection limit can reach 1.2 fL (Ren et al., 2014), demonstrating the practical application of this technology (Simmonds et al., 2021). Similarly, quadrupole and time-of-flight mass spectrometers have been used to detect CFCs, HFCs, and other FGHGs (Schuck et al., 2018; Sturges et al., 2012).

Table 2. *Species Applicable to Detectors or Detection Limits from the literature*

Column1	Concentration Range in Literature (ppt)				
	CFCs	HCFCs	HFCs	SF ₆	NF ₃
EI		225.49-250.11	1.12-53		1.42-1.88
ECD	7.73-246.47	3-501		6.25-10.46	6.06-6.33
FID				31-231	
FTIR			4.47-25		

Optical and spectral remote sensing techniques

Infrared spectroscopy is a standard spectroscopy monitoring technology. The Interferometric Monitor for Greenhouse Gases remote sensor was used by Coheur et al. (2003) to record the infrared spectrum to evaluate CFCs and their substitutes. Longwave-infrared spectroscopy has been applied to large-scale FGHG measurements to detect high-sensitivity halocarbon emissions (Tratt et al., 2021). This technology was first deployed in 2011 (Hall et al., 2011, 2016). For the first time (in 2019), a concentration measurement system for HFC-236fa using an 8280 nm quantum cascade laser was reported by Yuan et al. (2019) and Wang et al. (2022).

In addition, FTIR is a popular technique for measuring FGHG. More specifically, the atmospheric chemistry experiment-Fourier-transform spectrometer (ACE-FTS), a high-resolution FTIR carried by SCISAT-1 and ACE satellites, is often used for remote sensing monitoring (Coheur et al., 2003; Nassar et al., 2006; Harrison et al., 2021; Dodangodage et al., 2021). As the only current satellite monitoring equipment capable of measuring HFCs, ACE-FTS has continuously provided global HFC-134a monitoring data for over 15 years, complementing the ground-truthing data (Harrison et al., 2021). Further improvements are needed to improve the accuracy of satellite remote sensing FTIR for SF₆ monitoring (Harrison, 2020).

Research methods are available for monitoring atmospheric FGHG concentrations through the tracer ratio method. HFC emission was estimated by monitoring CO concentration using cavity ring-down spectroscopy (Xie et al., 2019).

Monitoring projects of fluorinated greenhouse gases

Research on atmospheric background concentration monitoring

The AGAGE is a multinational cooperative project that has continuously monitored global atmospheric components since 1978. It focuses on essential gases related to the Montreal Protocol (involving ozone layer destruction) and the Paris Agreement (involving climate change) (O'Doherty et al., 2004; Miller et al., 2008). As a pioneer in online FGHG monitoring, the accuracy and precision for various species are > 5% (Cunnold et al., 1994). Currently, AGAGE has 15 sites worldwide that have been monitoring the global FGHG concentrations for a long time, with the trends in FGHG concentrations displayed on the AGAGE website (Simmonds et al., 2017; Prinn et al., 2018). AGAGE network initially measured atmospheric background concentrations of gases using five stations located at Mace Head, Trinidad Head, Ragged Point, Cape Matatula, and Kennaook/Cape Grim. As the project developed, it expanded to include additional stations in Europe—Jungfraujoch, Monte Cimone, Tacolneston, Taunus, and

Zeppelin—and East Asia—Hateruma Island, Cape Ochi-ishi, Gosan, Dongtan, and Xichong. This expansion has resulted in a comprehensive 15-station network that continuously monitors various trace gases crucial for climate change research (Prinn, 2023).

The World Meteorological Organization's Global Atmospheric Watch Program also includes FGHGs. The program publishes bulletins annually that show the trend in GHG levels, intended to address climate change by thoroughly improving the global measurement of heat-trapping atmospheric pollutants (Organization, 2023).

Moreover, the National Oceanic and Atmospheric Administration/Earth System Research Laboratories (NOAA/ESRL) has 58 halocarbon and trace gas monitoring stations in 11 countries, whose primary detection methods are manual analysis and online monitoring. The NOAA publishes the Annual Greenhouse Gas Index (AGGI) annually, intuitively showing the global warming impact of long-lived GHGs (Droste et al., 2020; NOAA, 2023).

Regional emission monitoring research research

Specific regions usually focus on FGHG emission issues. Based on measurement data, the emission volume of the relevant region is inverted. The commonly used inversion models are the Bayesian and FLEXINVERT+ models (Ganesan et al., 2014; Evangeliou et al., 2018).

Yao et al. have been conducting FGHG monitoring at the Shangdianzi monitoring station (Yao et al., 2012a). Their work includes HFC sampling technology, long-term HCFC-22 and HCFC-142b monitoring (Yao et al., 2012b), in-situ PFC monitoring (Yao et al., 2012c), determination of SF₆ atmospheric background concentration (Yao et al., 2014), and inversion of HFC emissions. The results highlight the rapid increase in China's HFC emissions from 2011 to 2017, over this period, HFC-32 emissions increased from 4.4 (3.8–5.0) to 11.3 (10.5–12.0) Gg per year, and HFC-125 emissions increased from 4.7 (3.5–5.9) to 10.8 (9.7–11.9) Gg per year (Yao et al., 2019). Their team also researched other FGHG species (Zhang et al., 2017; Liang et al., 2018; Xie et al., 2019; Fang et al., 2019; Pu et al., 2020; Yi et al., 2021). Some studies in China also focus on various regions or components, such as estimating HFC emissions in the Yangtze River Basin and SF₆ emissions in the electrical industry (Zhou et al., 2018).

East Asia is a hotspot for FGHG research (Stanley et al., 2020). Lunt reported the average CCl₄ emission concentration in East Asia from 2009 to 2016 as 16 ± 7 Gg per year, attributing the primary source to eastern China (Lunt et al., 2018). Similarly, Say's research in India covered top-to-bottom estimates of CFCs, HCFCs, and HFCs, using the same methodologies to reassess HFC-134a emissions in the UK (Say et al., 2016; Say et al., 2019).

In California, a list-based method has been employed to evaluate emissions of CFC-12, HCFC-22, and HFC-134a, revealing that this approach might underestimate CFC-12 emissions and overestimate those of HFC-134a (Gallagher et al., 2014).

In South Africa, Kuyper's research during 2017 focused on the atmospheric concentrations of HCFC-22, HFC-125, and HFC-152a, with emission estimates derived through an inversion model (Kuyper et al., 2019).

Conclusions and prospects

This article reviews the research findings on global FGHGs measurement and monitoring from the literature, including a review of the monitoring equipment used. It also introduces regional monitoring results. We present the following conclusions and recommendations:

- Existing data clearly indicate that the total atmospheric background concentration of FGHGs is continuously rising. The concentrations of CFCs and HCFCs have been decreasing after their emissions were banned, while the concentrations of HFCs, used as substitutes, have significantly increased.
- Some studies point out that East Asia has large FGHG emissions. Researchers have suggested that there may be unreported HFC emissions in China. Therefore, it is necessary to establish a comprehensive monitoring network for FGHGs in the densely populated and industrially developed regions of eastern China and to analyze the collected data.
- For localized FGHGs measurements (e.g., in an industrial park), GC/MS is the optimal choice for monitoring precision, while IR can be a more cost-effective option, allowing for more monitoring points to be set up within limited budgets.
- China currently lacks comprehensive guidelines and technical standards for the accounting and detection of FGHGs. It is urgent to develop technical specifications for the management and disposal of FGHGs.
- For emissions from well-defined sources such as HCFC-22 and its by-product HFC-23, it is crucial to first collaborate with relevant industries to establish monitoring, emission accounting, and reporting systems.

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