https://doi.org/10.5194/egusphere-2025-3652
Preprint. Discussion started: 19 September 2025

Stable chlorine isotope composition of chlorofluorocarbons and chloromethane in the troposphere

Axel Horst[1*], Steffen Kümmel[2]

[1]Research and Development Centre for Post-Mining Areas, Federal Institute for Geosciences and Natural Resources (BGR), Cottbus, 03048, Germany
[2]Department Technical Biogeochemistry, Helmholtz Centre for Environmental Research−UFZ, 04318 Leipzig, Germany

**Correspondence to*: Axel Horst (axel.horst@bgr.de)

Abstract. Chloromethane (CH_3Cl) and chlorofluorocarbons (CFCs) play an important role in stratospheric ozone loss. Whereas anthropogenic CFC production was banned, CH_3Cl emissions originating primarily from natural sources cannot be regulated. Stable chlorine isotope analysis has the potential to provide valuable insights into the sources and fate of these compounds, but to date only one study has reported atmospheric $\delta(^{37}Cl)$ measurements linked to the isotopic standard of chlorine (SMOC, standard mean ocean chloride). In the current study, we collected tropospheric air samples over the course of one year at an urban site (Leipzig, Germany) and extracted CH_3Cl, CFC-12, CFC-11, CFC-113, and HCFC-22 for stable chlorine isotope analysis. CFCs showed minor $\delta(^{37}Cl)$ variations throughout one year, consistent with long atmospheric lifetimes and ceased production. In contrast, CH_3Cl displayed an annual cycle, with lower $\delta(^{37}Cl)$ in spring and higher $\delta(^{37}Cl)$ in late summer to early fall. This trend likely reflects seasonal variations: increased emission of ^{37}Cl–depleted CH_3Cl by oceans and vegetation in spring and enhanced degradation in summer and fall causing isotope fractionation und thus higher $\delta(^{37}Cl)$. Back trajectory modeling suggested a vertical difference of $\delta(^{37}Cl)$, conceivably due to mixing of freshly emitted and ^{37}Cl–depleted CH_3Cl in the boundary layer. Additionally, stratosphere–troposphere transport of partially degraded and ^{37}Cl–enriched CH_3Cl was hypothesized. While these interpretations remain preliminary until further confirmation, isotopic data reported here represents a crucial step toward establishing $\delta(^{37}Cl)$ fingerprints, which are prerequisites for future source appointment and atmospheric modeling studies.

1 Introduction

Chlorofluorocarbons (CFCs) and chloromethane (CH_3Cl) are responsible for the majority of the chlorine burden in the atmosphere (Seinfeld and Pandis, 2006). Together with other chlorinated and brominated compounds as well as nitrogen species, such as N_2O, they cause the depletion of stratospheric ozone (Carpenter et al., 2014). As a consequence, production of many halogenated substances was banned by the regulations of the Montreal protocol and atmospheric mole fractions have started to decline for a majority of human–made compounds (Prinn et al., 2025). Nevertheless, illegal production and emission of regulated compounds (Rigby et al., 2019) as well as emission of newly detected CFCs and HCFCs (hydrochlorofluorocarbons) was reported (Laube et al., 2014), which may slow down the recovery of the ozone layer.

In contrast, unregulated compounds such as CH_3Cl possess both natural and anthropogenic sources and, despite considerable efforts, it has been very challenging to accurately determine emission and degradation rates for the various sources and sinks. The largest identified natural sources of CH_3Cl are plants (Xiao et al., 2010), oceans (Hu et al., 2013), and biomass burning (Andreae and Merlet, 2001) with minor anthropogenic contributions from coal combustion (McCulloch et al., 1999), industrial emissions (Hu et al., 2022), rice paddies (Lee-Taylor and Redeker, 2005) and even food production (Thornton et al., 2016). When compared to the main sinks, such as reaction with hydroxyl radicals ($OH^·$) in the troposphere (Ko et al., 2013), ocean uptake (Hu et al., 2013), and degradation in soils (Redeker and Kalin, 2012), large gaps in the mass balance persist with sink estimates exceeding those of the sources by about 20 % (Carpenter et al., 2014).

The use of isotopic methods in addition to mole fractions may provide further insights such as process level information or it may help to refine current source and sink estimates for compounds such as CH_3Cl. With the advent of compound–specific stable isotope analysis (CSIA) of carbon three decades ago a variety of studies were carried out to investigate whether this type of additional information might be gained by applying isotopic techniques. For CFCs, for example, these studies reported relatively large ranges of tropospheric $\delta(^{13}C)$ values even though similar values may be expected throughout the troposphere due to ceased production and the long atmospheric lifetimes. Reported atmospheric $\delta(^{13}C)_{VPDB}$ ranged from −27 to −32 ‰ for CFC-11, −34 to −43 ‰ for CFC-12, and −23 to −29 ‰ for CFC-113. (Archbold et al., 2005; Bahlmann et al., 2011; Redeker et al., 2007; Rudolph et al., 1997; Thompson et al., 2002; Zuiderweg et al., 2013). For CH_3Cl, tropospheric $\delta(^{13}C)_{VPDB}$ ranged from −36 to −41 ‰ (Bahlmann et al., 2019; Redeker et al., 2007; Thompson et al., 2002; Tsunogai et al., 1999; Weinberg et al., 2015) despite relatively large variation of potential sources ranging from about -36 ‰ for the emissions by oceans to as low as −83 ‰ for plant emissions (Bahlmann et al., 2019; Saito et al., 2008; Saito and Yokouchi, 2008). This relatively narrow atmospheric $\delta(^{13}C)$ range of CH_3Cl might have been the major hindrance for a more successful application of CSIA of carbon highlighting the need for additional isotopic tools.

Stable chlorine and stable hydrogen isotope analysis in CH_3Cl may provide additional insights especially on the process level. Unlike carbon, chlorine and hydrogen isotope fractionation only occurs if a reaction cleaves the corresponding C–Cl or C–H bond, respectively, causing a primary isotope effect (Melander and Saunders, 1980). Adjacent bonds are subject to secondary isotope effects, which are usually negligible. It was shown in two former studies that microbial degradation occurring in oceans, soils, and on leaf surfaces of plants are associated with considerable chlorine but negligible hydrogen isotope fractionation (Hartmann et al., 2023; Keppler et al., 2020). In contrast, reaction of CH_3Cl with hydroxyl radicals in the troposphere showed large hydrogen but negligible chlorine isotope fractionation (Keppler et al., 2018, 2020). Stable carbon isotope measurements alone did not reveal such differences because carbon is involved in both, the cleavage of the C–Cl bond and the C–H bond resulting in isotopic fractionation in both cases. Hence, progress in measuring Cl and H isotopes in atmospheric CH_3Cl is essential to gain new insights.

Stable chlorine isotope values of atmospheric organic compounds have only been reported in a few studies due to the difficulties associated with collecting the large volumes of air that are required to perform such measurements. Volpe (1998) determined a $\delta(^{37}Cl)$ of −6.2 ‰ relative to SMOC for tropospheric CH_3Cl sampled at a coastal site in La Jolla (California, USA). This value likely reflects a strong influence of marine CH_3Cl emissions from algae in the Pacific Ocean. There are also records of stable chlorine isotope measurements of CFC-11, CFC-12, and CFC-113 in stratosphere, troposphere, and in firn air (Allin et al., 2015; Laube et al., 2010). However, these values were not linked to the SMOC scale due to unavailability of appropriate reference materials. Apart from atmospheric measurements, $\delta(^{37}Cl)$ values have also been determined for several CH_3Cl sources. Emissions from royal fern (*Osmunda regalis*) showed a $\delta(^{37}Cl)_{SMOC}$ of −0.9±0.9 ‰ (Hartmann et al., 2023), while two individual samples of industrially manufactured CH_3Cl exhibited a $\delta(^{37}Cl)_{SMOC}$ of +6.0±0.1 ‰ (Keppler et al., 2020). Stable chlorine isotope signatures of other potential sources of CH_3Cl, CFCs, and HCFCs have not yet been reported, underscoring the need for further isotopic characterization of both natural and anthropogenic sources.

In this study, we collected and analyzed air samples to get a first glance of the stable chlorine isotope composition of tropospheric CH_3Cl as well as the most abundant CFCs and HCFC-22. In particular, we intended to investigate whether chlorine isotopes in tropospheric CH_3Cl show sufficient variability to be of potential use for identification and quantification of sources and fractionation processes in the atmosphere.

2 Materials and methods

2.1 Chemicals and isotopic reference materials

A set of halogenated chemicals was purchased in order to test the sampling and extraction methods for potentially occurring isotope fractionation effects and for determining the $\delta(^{37}Cl)$ values of these industrially manufactured compounds. HCFC-22 (chlorodifluoromethane, $CHClF_2$), CFC-12 (dichlorodifluoromethane, CCl_2F_2), HCFC-21 (dichlorofluoromethane, $CHCl_2F$), CFC-114 (1,2-dichlorotetrafluoroethane, $C_2Cl_2F_4$), CFC-11 (trichlorofluoromethane, CCl_3F), combined in a Supelco freon mix (10000 µg/mL in ethyl acetate), were purchased from Sigma Aldrich (Germany). A second batch of undiluted CFC-11 as well as tetrachloromethane (CCl_4) were purchased from Sigma Aldrich (Germany). Chloromethane (CH_3Cl) was purchased from Linde AG (Germany). A gaseous sample of HCFC-22 originated from SynQuest Laboratories (USA).

We used in-house reference materials to link $\delta(^{37}Cl)$ values to the SMOC scale and to correct for potential scale compression caused by the method. In-house reference materials chloromethane (CM: +5.53 ‰), trichloroethene (TCE2: −1.03 ‰; TCE6: +2.17 ‰), and trichloromethane (TCM: −5.48 ‰) were isotopically characterized against the USGS perchlorate ($KClO_4$) reference materials USGS37 and USGS38 (Böhlke et al., 2017). Both perchlorates and organic chemicals were first converted to silver chloride (AgCl), followed by reaction with iodomethane (CH_3I) to chloromethane (CH_3Cl) using classic offline conversion methods described in detail elsewhere (Eggenkamp, 2025; Gilevska et al., 2015). Produced chloromethane gases were finally analyzed by gas chromatography multi–collector inductively coupled plasma mass spectrometry (GC–MC–ICPMS) to determine their $\delta(^{37}Cl)$.

2.2 Air sampling and extraction of halogenated organic compounds

Air sampling for collection of CFCs and CH_3Cl was accomplished by combining two previously published methods (Bill et al., 2004; Davidson et al., 2021). In a first step, target compounds were trapped cryogenically in a coiled PFA tube (length 900 cm, outer diameter 0.635 cm, inner volume 90 mL) immersed in liquid nitrogen. A diaphragm pump (KNF, Freiburg, Germany) was used to pull up to 1800 L of air through the cryotrap applying a pumping rate of 7 L min^{-1}. A mass flow controller was used to record the amount of air flowing through the trap (Omega, Deckenpfronn, Germany). Air was sampled through an air inlet of the LSI (Laboratory for Stable Isotopes) at the campus of the UFZ in Leipzig, Germany (51.35231 °N, 12.43155 °E). Sampled air first passed a glass wool filter and then entered a water trap held at −35 to −40 °C using cooled methanol. Subsequently, the air passed the PFA coil cooled to −196 °C with liquid nitrogen. The pressure in the trap was adjusted to 600 mbar with a needle valve installed at the trap inlet to prevent nitrogen, oxygen, and argon from condensing in the trap, thus enabling the removal of 99.9 % of these unwanted gases at this stage. After cryosampling was complete, all collected compounds were transferred into a pre-evacuated 250 mL septum bottle crimp sealed with a blue butyl rubber stopper. A disposable luer lock needle was used to perforate the stopper, connecting the PFA-coil via a custom-made adapter to the sample bottle. Once connected, the bottom of the septum bottle was cooled with liquid nitrogen and the PFA-coil was immersed in warm water (60 °C). The transfer of the target compounds was facilitated by the relatively large amounts of CO_2 freezing out in the septum bottle together with the target compounds. Transfer was considered complete when the pressure in the PFA-trap had dropped below 100 mbar. Septum bottles with samples were stored at +5 °C until further extraction.

In a second step, separation of target compounds from more abundant co-trapped gases such as CO_2 was achieved by adapting a method reported by Davidson et al (2021). A cooled stainless steel adsorbent trap (250 mm x 6.35 mm OD; −75 °C) filled with Tenax TA (Sigma Aldrich, Germany) was used to trap halogenated organics and thus to separate CO_2. To achieve this separation, samples were transferred from the septum bottles to 0.5 L Tedlar bags (Restek, Germany). After transfer, Tedlar bags were connected to the adsorbent trap. A KNF diaphragm pump was used to pull the sample gas through the cooled Tenax trap (−75 °C) using a flow rate of 50 mL/min. The sample was then transferred to a liquid nitrogen-cooled cryotrap (3.2 mm OD x 200 mm length) by pulling helium through the Tenax trap, which was heated to 200°C. After cryotrapping, target compounds were transferred via a custom-made luer adapter and luer lock needle to a pre-evacuated 10 mL septum vial crimp sealed with a blue butyl rubber stopper.

2.3 Creation of synthetic air samples for evaluation of isotopic fractionation

Synthetic air was generated by filling a 100 L Tedlar bag (Restek, Germany) with 80 L of nitrogen, 20 L of oxygen, 1 L of argon, 400 mL of CO_2, and 2 mL of water. The excess CO_2 was used to simulate cryotrapping conditions for about 1000 L of air, which was the usual target volume within this study. This synthetic air was then spiked with CH_3Cl, CFC-11, and CCl_4 to characterize isotopic fractionation of compounds with boiling points ranging from −24 °C to +77 °C, thus representing most of the measured compounds. Synthetic air samples were cycled through the sampling system and extracted compounds were treated in the same way as described in section 2.2 to evaluate isotopic fractionation due to sampling and separation of target compounds. Recovery rates and isotopic fractionation were evaluated by measuring standards against samples in a standard–sample bracketing approach. Standards were prepared by spiking 10 mL septum vials with the same amount of compound as added to the synthetic air samples. Areas of the transient signals and isotopic ratios of standards were compared with those measured for synthetic samples cycled through the sampling system.

2.4 Identification of target compounds

Identification of target compounds and optimization of chromatographic separation parameters was carried out using gas chromatography (HP6890, Agilent Technologies, Germany) coupled to ion trap mass spectrometry (PolarisQ, Thermo Finigan, Germany). Baseline separation of chlorinated compounds was achieved by using a PoraBOND Q column (50 m x 0.32 mm x 5 µm, Agilent J&W, Germany) applying the following temperature program: hold for 10 minutes at 40°C, ramp to 120°C with 5°C/min, hold for 10 minutes, ramp to 250 °C with 10 °C/min, hold 15 minutes. A constant carrier gas flow of 1.5 mL He per minute was applied. A chromatogram of an atmospheric sample is shown in Fig. 1(b) representing all compounds that produce ions with a mass-to-charge ratio of 35 to 200. This test was necessary to make sure that target compounds did not co-elute with other chlorine-free gases, which would not be detectable with MC-ICPMS. Chlorine-free gases might cause isobaric interferences if they contained large amounts of hydrogen thus producing $^{36}Ar^{1}H^{+}$ dimers that would be recorded by the same Faraday cup as $^{37}Cl^{+}$ ions. The chromatograms in Fig. 1 indicate an overall good separation for the most abundant CFCs (HCFC-22, CFC-12, CFC-11, CFC-113) and chloromethane (CH_3Cl). Hence, it was assumed that target compounds may be measured accurately without disturbance by isobaric interferences.

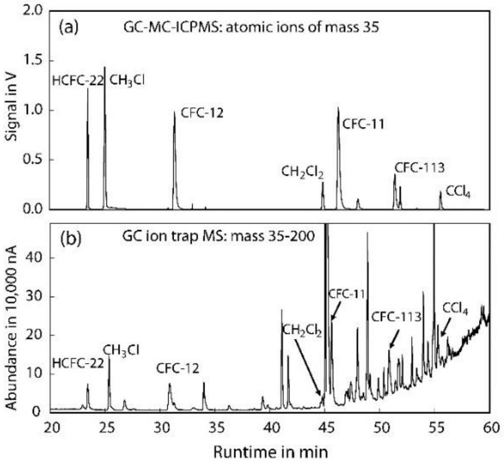

Figure 1. Mass traces recorded during analysis of atmospheric samples using GC-MC-ICPMS (a) and GC ion trap MS (b). Ion trap analysis (b) was carried out to verify baseline separation and retention times of target compounds not containing Cl but potentially causing interferences. Panel (a) shows the mass trace recorded by the software of the MC-ICPMS only showing Cl containing compounds as recorded by the Faraday cups.

https://doi.org/10.5194/egusphere-2025-3652
Preprint. Discussion started: 19 September 2025

2.4 Stable chlorine isotope analysis

Stable chlorine isotope analysis was accomplished by GC-MC-ICPMS according to Horst et al. (2017) and Renpenning et al. (2018) applying modifications of this method as described in Keppler et al. (2020) and Hartmann et al. (2023). Briefly, up to 7.5 mL of sample gas were extracted with a gastight 10 mL syringe from the sample vial (Vici Precision Sampling, Baton Rouge, USA) and injected into the injector of the GC in splitless mode (Thermo Fisher Scientific, Germany). Compounds were then trapped on the column to remove excess–He and to refocus the sample for optimized peakshape. Trapping was accomplished by immersing 20 cm of the column into methanol cooled to −70 °C. The column was sheathed by a 1.59 mm (OD) stainless steel tube for protection. Two minutes after injection, the column trap was immersed in 60 °C warm water. Released compounds were then separated on the GC-column and ionized in the plasma. The resulting signals of ^{35}Cl and ^{37}Cl collected by the two corresponding Faraday cups were recorded by the Multicollector Software 3.2 as ASCII files. Isotopic ratios were calculated via regression analysis; that is, the intensity recorded for ^{37}Cl was plotted versus ^{35}Cl with the resulting slope indicating the ^{37}Cl/^{35}Cl isotopic ratio (Horst et al., 2017; Renpenning et al., 2018). To be comparable with other measurements, ^{37}Cl/^{35}Cl isotopic ratios are commonly expressed as $\delta(^{37}\mathrm{Cl})$ relative to standard mean ocean chloride (SMOC):

$$\delta(^{37}\mathrm{Cl}) = \frac{\mathrm{R_{sample}}}{\mathrm{R_{reference}}} - 1 \qquad (1)$$

where $\mathrm{R_{sample}}$ indicates the isotopic ratio of a sample and $\mathrm{R_{reference}}$ the isotopic ratio of a reference compound linked to the SMOC scale (Coplen, 2011). Delta values may be expressed in Ur (urey), ‰ (permil), or parts per thousand. In this study, the permil nomenclature was used. Delta values were linked to the SMOC scale by, in a first step, referencing sample isotope ratios against isotope ratios of the in-house reference compound chloromethane (CM), which was injected in triplicates between two consecutive sample analyses. In a second step, a linear two-point normalization approach was applied to raw-$\delta(^{37}\mathrm{Cl})$ to correct for potential scale compression effects. In-house reference materials chloromethane (CM), trichloroethene (TCE2, TCE6), and trichloromethane (TCM) were analyzed daily to determine the scale.

2.6 Back trajectories

Back trajectories were calculated using the HYSPLIT model (version 5.3.0 with GUI) (Draxler and Hess, 1997; Stein et al., 2015) to reconstruct travel paths of the air parcels 96 hours prior to arrival at the sampling location and to identify correlations between these travel paths and stable chlorine isotopic data of CH_3Cl. We used GDAS1 meteorological input data, which offers a one-degree longitude–latitude resolution. The starting point (sampling point) of the simulation was set to 500 meters above ground level (m.a.g.l.) being located well within the boundary layer. It was demonstrated before that a relatively high starting point for the simulation is better suited to model bulk air movement as it may be less influenced by local topography (Gebhart et al., 2005). Graphical output files are provided in (Supplement S1)

3 Results and discussion

3.2 Evaluation of isotopic fractionation caused by the sampling method

Sampling and extraction of organic compounds from large volumes of air might cause changes of the isotopic composition affecting the accuracy of such data. Fractionation caused by the sampling process was evaluated by creating synthetic air samples (control samples) with known isotopic compositions of CH_3Cl, CFC-11, and CCl_4. Measured isotopic signatures of these compounds cycled through the sampling and extraction system were compared with the isotopic signatures of the pure phase chemicals used to create the synthetic mixtures (standards). Results indicated that sampling by this method was often not quantitative with recovery rates of control samples ranging from 11 % to 90 % for CH_3Cl and CFC-11 and 6 to 20 % for CCl_4 (Table 1). These losses may be due to incomplete cryotrapping and/ or incomplete adsorption in the Tenax trap. Despite these losses, only small effects on the isotopic composition of these three compounds were observed. CH_3Cl and CFC-11, respectively, showed an average isotopic difference of ±0.4 ‰ and ±0.2 ‰ from directly measured stock gas mixtures (standards). For CCl_4 the $\delta(^{37}Cl)$ varied within ±1 ‰ from directly measured stock gas mixtures.

Table 1: Recovery rates and isotopic difference between control samples and standards ($\Delta(^{37}Cl)_{control/standard}$) obtained for isotope fractionation control experiments.

	CH3Cl		CFC-11		CCl_4	
	$\Delta(^{37}Cl)_{control/standard}$ ‰	recovery rate %	$\Delta(^{37}Cl)_{control/standard}$ ‰	recovery rate %	$\Delta(^{37}Cl)_{control/standard}$ ‰	recovery rate %
control 1	+0.51	13.0	+0.27	11.0	+1.17	6.3
control 2	+0.27	73.5	+0.18	73.2	+0.42	20.4
control 3	+0.38	90.8	+0.19	61.0	+1.09	11.1

The absence of significant isotopic fractionation for cryotrapping methods was previously documented in the literature for CFCs (Horst et al., 2015; Laube et al., 2010) and other volatile organic compounds (Thornton et al., 2013; Zwank et al., 2003). Similarly, incomplete sorption is unlikely to significantly change the isotopic composition as reported in several studies (Schüth et al., 2003; Slater et al., 2000; Wanner et al., 2017; Zwank et al., 2003). Both sorption and freezing belong to the non-degradative physical processes usually not causing large fractionation due to the relatively small mass differences of the different isotopologues. Larger isotopic fractionation is characteristic for bond-breaking chemical or biochemical reactions such as hydroxyl radical reactions or nucleophilic substitution in CH_3Cl, which produced significant chlorine isotope fractionation (Horst et al., 2019; Keppler et al., 2020). Overall, our tests indicated some isotopic variability due to the entire sampling and measurement procedure. To account for such variation, we assume an overall uncertainty of ±1 ‰ for $\delta(^{37}Cl)$ determination of an individual atmospheric sample, which is a conservative estimate combining the uncertainties caused by sampling, extraction, and isotopic analysis including linkage of raw-$\delta(^{37}Cl)$ values to the SMOC scale.

3.2 Stable chlorine isotope composition of pure-phase CFCs, HCFCs, and CH_3Cl

Before analyzing atmospheric samples, we measured pure-phase compounds in order to get an impression of expectable $\delta(^{37}Cl)$ of these compounds and to obtain a probable source signature. Especially CFCs and HCFCs are human-made compounds without any significant natural sources. Hence, industrially produced compounds are considered the sole source of atmospheric CFCs and HCFCs (Carpenter et al., 2014). Atmospheric CH_3Cl, in contrast, has mainly natural sources. Contributions of industrially produced CH_3Cl to the atmospheric budget are considered small but isotopic techniques might be applied to identify unaccounted anthropogenic emissions, which were reported in the past (Hu et al., 2022; Li et al., 2017).

In the current study, we purchased CFCs, HCFCs, and CH_3Cl and measured their $\delta(^{37}Cl)$. There are no comparable values for CFCs and HCFCs in the literature because previous studies focused on reporting isotopic fractionation due to atmospheric processes without linking delta values to the SMOC scale (Allin et al., 2015; Laube et al., 2010). In the current study, $\delta(^{37}Cl)$ values of commercially available CFCs and HCFCs, ranged from −2.08 ‰ for HCFC-21 up to +3.28 ‰ relative to SMOC for CFC-12 (Table 2). CH_3Cl showed a value of +5.53 ‰, which is similar to a published value of about +6 ‰ reported in a previous study (Keppler et al., 2020). At this point, these values may only serve as a first reference point for the stable chlorine isotope composition of CFCs, HCFCs, and CH_3Cl because only 1–2 different samples were available for measurement. Further measurements of pure phase compounds are required to obtain a more representative $\delta(^{37}Cl)$ source signature.

Table 2: Source $\delta(^{37}Cl)$ relative to SMOC of pure-phase CFCs, HCFCs, and CH_3Cl compared to tropospheric measurements

compound	origin	$\delta(^{37}Cl)_{SMOC}$	σ	n	origin	$\delta(^{37}Cl)_{SMOC}$	σ	n
HCFC-22	Freon mix Supelco	+1.44	0.10	5	tropospheric	+0.24	0.33	30
HCFC-22	SynQuest Laboratories	+0.87	0.05	3				
CFC-12	Freon mix Supelco	+3.28	0.16	5	tropospheric	+2.83	0.20	30
HCFC-21	Freon mix Supelco	−2.08	0.09	5				
CFC114	Freon mix Supelco	+0.18	0.07	5				
CFC-11	Freon mix Supelco	+2.50	0.14	5	tropospheric	+1.86	0.26	22
CFC11	Sigma Aldrich	+2.21	0.05	4				
CFC-113					tropospheric	+1.57	0.28	8
CH_3Cl	Linde AG	+5.53	0.10	11	tropospheric	+3.24	0.61	30

3.3 Stable chlorine isotope composition of tropospheric CFCs and HCFCs

In air samples, stable chlorine isotope compositions were determined for HCFC-22, CFC-12, CFC-11, and CFC-113. Other compounds such as CH_2Cl_2 and CCl_4 were also detected but signals were too low for reliable determination of $\delta(^{37}Cl)$. Overall, CFCs and HCFCs showed relatively little variability throughout the measurement period of one year (Fig. 2). Average $\delta(^{37}Cl)_{SMOC}$ ranged between +0.24 ‰ for HCFC-22 and +2.83 ‰ for CFC-12 (Table 2). The standard deviation of the measurements of HCFCs and CFCs ranged between 0.20 ‰ for CFC-12 and 0.33 ‰ for HCFC-22. Such small variation was expectable for CFC-11, CFC-12, and CFC-113 because these compounds are officially not produced anymore and emissions from legacy sources should be small. The small variation of $\delta(^{37}\mathrm{Cl})$ also is an indication for the negligible influence of isotopic fractionation throughout the campaign. Fractionation in CFCs is mainly caused by destruction of these compounds in the stratosphere but reaction rates are slow and resulting changes of mole fractions (< 3 pmol mol^{-1}) are, according to our results, not reflected in $\delta(^{37}\mathrm{Cl})$ over the course of one year.

HCFC-22 has a shorter lifetime of about 11 years but continued emissions occur from legacy sources (Carpenter et al., 2014). Hence, tropospheric $\delta(^{37}\mathrm{Cl})$ values of HCFC-22 are influenced by both, isotopic fractionation due to degradation and mixing of freshly emitted compound. Despite these processes, constant monthly mole fractions of 257 pmol mol^{-}1 were reported for 2022 for HCFC-22 measured at Jungfraujoch (Prinn et al., 2025)). Continued emission and degradation of HCFC-22 caused slightly larger variability of $\delta(^{37}\mathrm{Cl})$ of HCFC-22 compared with CFCs, which is reflected in a standard deviation of 0.33 ‰ throughout the measurement campaign (Table 2).

Over longer timescales, variations in $\delta(^{37}\mathrm{Cl})$ of CFCs are likely to emerge due to mixing of stratospheric and tropospheric air (e.g.(Boothe and Homeyer, 2017; Stohl et al., 2003). Whereas CFCs are nearly stable in the troposphere, photodegradation occurs in the stratosphere for which Laube and coworkers (2010) reported a considerable shift of $\delta(^{37}\mathrm{Cl})$ of CFC-12 ($\varepsilon_{\mathrm{Cl}} = -12.1$ ‰) toward more ^{37}Cl–enriched values in stratospheric samples taken at higher altitudes. Mixing of tropospheric with stratospheric CFCs would hence cause a gradual shift of $\delta(^{37}\mathrm{Cl})$ of CFCs over time, which may eventually be measurable in tropospheric air. Hence, application of stable chlorine isotope analysis of CFCs and more short-lived compounds might be a method providing additional insights in troposphere–stratosphere dynamics if data are collected regularly on larger temporal and spatial scales.

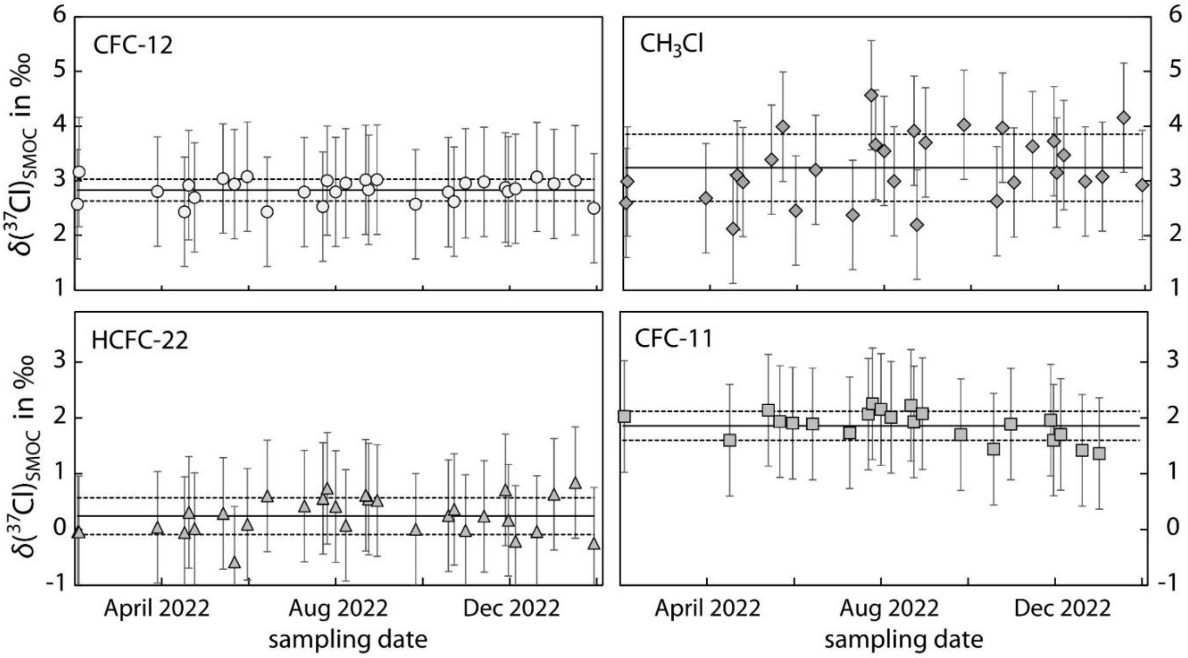

Figure 2: Measured $\delta(^{37}Cl)$ of CH_3Cl, CFC-12, CFC-11 and HCFC-22 relative to SMOC throughout the period of one year. Solid lines indicate the mean $\delta(^{37}Cl)$ of all samples and dashed lines indicate the standard deviation. CFC-113 is not shown because only eight samples could be determined due to lower contents in the samples. Error bars represent the uncertainty for an individual measurement (1 ‰).

3.4 Stable chlorine isotope composition of tropospheric CH_3Cl

3.4.1 Annual cycle of $\delta(^{37}Cl)$ of tropospheric CH_3Cl

CH_3Cl measurements revealed an average $\delta(^{37}Cl)_{SMOC}$ of +3.24 ‰ and a standard deviation of 0.61 ‰ thus indicating a larger variability of isotopic values compared to CFCs and HCFC-22 (Fig. 2). This larger isotopic range is likely related to the changing strengths of individual sources and degradation processes over the course of the year. In the Northern Hemisphere, oceans and plants are strong emitters in spring (March–May). This fact is also reflected in the annual cycle of tropospheric mole fractions (Fig. 3(b)) as measured by the AGAGE network (Advanced Global Atmospheric Gases Experiment) at Jungfraujoch, Switzerland (Prinn et al., 2025). In September, mole fractions reach their minimum due to higher activity of degradation processes such as reaction with hydroxyl radicals and uptake by soils and oceans and decreasing source emissions. Monthly means of $\delta(^{37}Cl)$ values of CH_3Cl indicate an opposite trend with lowest $\delta(^{37}Cl)$ values in spring and maximum $\delta(^{37}Cl)$ values in fall (Fig. 3). For simultaneously measured CFC-12 no such trend is discernable, verifying that this trend is not an analytical artefact.

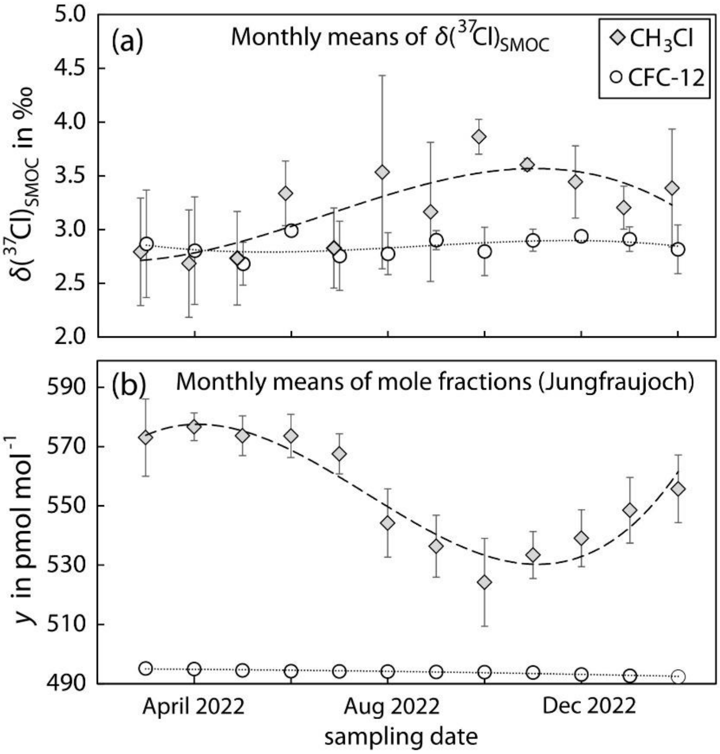

Figure 3: Monthly means of measured $\delta(^{37}Cl)_{SMOC}$ compared to monthly means of CH_3Cl mole fractions measured at Jungfraujoch, Switzerland (Prinn 2025). The dashed and the dotted trendlines indicate the polynomial fit (3rd degree) of mean CH_3Cl and CFC-12 values, respectively. Error bars represent the standard deviation of individual measurements carried out in the corresponding month.

This isotopic annual cycle of CH_3Cl may be explained with known isotopic signatures of the largest sources and sinks of CH_3Cl. First isotopic measurements of CH_3Cl produced in oceans and by plants hinted toward ^{37}Cl–depleted $\delta(^{37}Cl)_{SMOC}$ values of −6.2 ‰ (Volpe, 1998) and −0.9 ‰ (Hartmann et al., 2023), respectively. Mixing of freshly emitted but ^{37}Cl–depleted CH_3Cl could explain the minimum of monthly averages of $\delta(^{37}Cl)$ in spring. In late summer/early fall, decreasing emission and increasing degradation by plants, oceans, and soils might cause the maximum $\delta(^{37}Cl)$ when reaction rates rise due to higher temperatures. Previous studies showed that degradation by microorganisms populating plant surfaces as well as by aerobic microbial communities in fresh and marine water causes a shift toward more positive (higher) $\delta(^{37}Cl)$ values due to fractionation between heavy and light isotopes (Hartmann et al., 2023; Keppler et al., 2020). Isotopic fractionation expressed as ε_{Cl} reached −5.7 ‰ for degradation by plants and between −9.4 and −10.9 ‰ for two bacterial strains. Hence, it is conceivable that the maximum of $\delta(^{37}Cl)$ values in late summer is caused by microbial degradation and concomitantly decreasing production by plants and oceans towards fall. It should be noted at this point that reaction with hydroxyl radicals, the most important abiotic degradation process in the troposphere, does not cause measurable chlorine isotope fractionation (Keppler et al., 2020) because this reaction splits the C–H bond and not the C–Cl bond. Hence, hydroxyl radical reaction is unlikely to have contributed to this $\delta(^{37}\mathrm{Cl})$ maximum in summer. Also, abiotic degradation in oceans was found to be too slow to be a relevant process even though isotopic fractionation ($\varepsilon_{\mathrm{Cl}}$) was as large as −5.3 ‰ (Horst et al., 2019).

Whereas these stable chlorine isotope measurements represent a significant scientific achievement, it is worth noting that the correlation in Fig. 3 only reveals a first glimpse on the relation between atmospheric mole fractions and $\delta(^{37}\mathrm{Cl})$. Unfortunately, precise mole fractions could not be determined within this study. Determination of CH_3Cl mole fractions in conjunction with stable chlorine isotope ratios will be imperative in future studies to reveal a more nuanced picture of the $\delta(^{37}\mathrm{Cl})$ annual cycle in CH_3Cl.

3.4.2 Origin of air masses and potential correlations with $\delta(^{37}\mathrm{Cl})$

Back trajectories calculated by the HYSPLIT model were used to identify any correlations between the origin of the air masses contributing to the samples and their isotopic composition. CH_3Cl is primarily emitted by natural sources such as plants, biomass burning, and oceans, which are either ubiquitously present in the sampling region (e.g. plants) or located further away (e.g. marine sources). Hence, contributions from these sources may be considered rather well-mixed with background air. Anthropogenic point sources such as emissions due to manufacturing of this chemical are likely too small to be detectable in the source regions. Consequently, it was assumed that variations of $\delta(^{37}\mathrm{Cl})$ in CH_3Cl were caused by mixing of larger air masses and sink processes instead of local injection of CH_3Cl by point sources.

When considering horizontal travel paths, isotopic values seem to show a relationship to back trajectories in some instances. Air masses travelled to the sampling location primarily from western and northern directions as well as eastern direction in some instances (Fig. 4(a)) with the majority of trajectories representing the prevailing western wind directions. Most of the samples (27 out of 30) span an isotopic range of +2.12 to +3.99 ‰ relative to SMOC with corresponding trajectory plots not indicating an isotopic preference for a certain direction. The three samples exhibiting the highest $\delta(^{37}\mathrm{Cl})_{\mathrm{SMOC}}$ values of +4.03 to+ 4.57 ‰ were exclusively associated to western travel paths, which cannot be linked to any particular source or process at this point.

Some more differences seem to emerge when samples are grouped according to meteorological seasons (Fig. 4(b)). Spring samples (4 out of 6) traveled to the sampling location primarily from Scandinavia and eastern Europe, with $\delta(^{37}\mathrm{Cl})_{\mathrm{SMOC}}$ values ranging between +2.12 and +3.10 ‰ thus always showing lower than average values. Samples travelling via southwestern Europe were dominated by fall samples with $\delta(^{37}\mathrm{Cl})_{\mathrm{SMOC}}$ values ranging between +2.63 and +3.97 ‰, which tended to be above the average of +3.24 ‰. Hence, results seem to indicate preferential travel paths with associated isotopic tendencies depending on the season. However, samples taken in summer and winter showed very similar travel paths, mostly originating in the West and North-West without a recognizable pattern for higher or lower isotopic values. This might indicate that the preferential travel paths in spring and fall are rather attributable to the relatively low number of samples and coincidental collection of air masses originating in similar regions. In order to derive more information from horizontal back trajectories it will be crucial to collect more samples to gain a statistically more relevant number of observations.

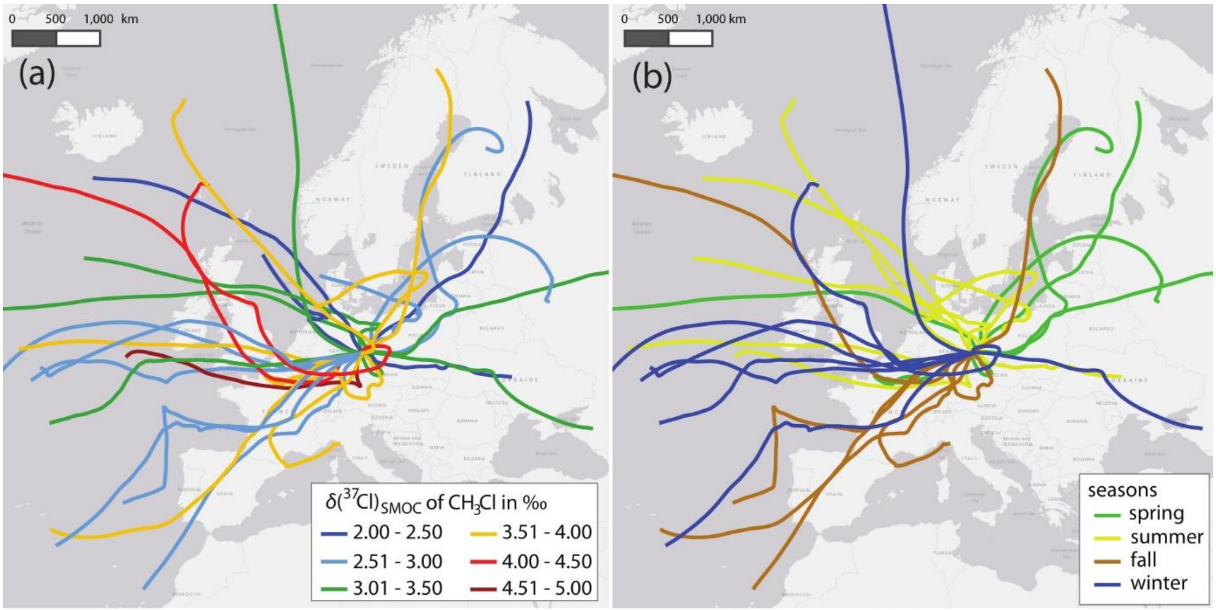

Figure 4: Back trajectories calculated for each sample. In (a) colors represent different isotopic values. In (b) colors represent the meteorological seasons spring (March–May), summer (June–August), fall (September–November), and winter (December–February).

In contrast to horizontal patterns, a more distinct relation between $\delta(^{37}Cl)$ and travel height of the air parcels became apparent on a vertical scale. Sampled air that resided exclusively in the boundary layer ($h_{max} \leq 1000$ m) during the 96 hours before arrival showed, on average, lower $\delta(^{37}Cl)$ values compared to air masses that had also travelled in the free troposphere above 1000 m (Fig. 5). Even though such a differentiation is based on rather simple and coarse assumptions (e.g. fixed boundary layer thickness), the fact that isotopic differences between these groups became apparent deserved a closer examination. Lower $\delta(^{37}Cl)$ of air travelling exclusively below 1000 m can be rationalized with larger contributions of freshly emitted CH_3Cl. CH_3Cl is solely produced and emitted within the boundary layer with the largest known sources producing $\delta(^{37}Cl)_{SMOC}$ values of about −6 and −1 ‰ SMOC for oceans and plants, respectively (Hartmann et al., 2023; Volpe, 1998). These emissions are lighter (more negative $\delta(^{37}Cl)$) than any measured atmospheric value found in the current study. Hence, a mixture containing larger amounts of freshly emitted CH_3Cl would potentially result in more depleted, that is, lower $\delta(^{37}Cl)$ values in the boundary layer. Heavier, more positive $\delta(^{37}Cl)$ values for samples with travel paths reaching above 1000 m can be explained with larger contributions of aged background CH_3Cl as it might be present in the free troposphere. Such aged CH_3Cl may have been subject to partial degradation by the various sinks (oceans, plants, soils) before rising to higher tropospheric levels where no further degradation affects chlorine isotopes and where no additional CH_3Cl is emitted.

An additional conceivable process influencing stable chlorine isotopes in CH_3Cl could also be stratosphere–troposphere transport (STT) carrying partially degraded CH_3Cl back into the troposphere. Our isotopic data might deliver evidence of this well-known phenomenon often studied in the context of stratosphere–troposphere ozone fluxes, for example (Boothe and Homeyer, 2017; Holton et al., 1995; Li et al., 2024; Ruiz and Prather, 2022; Stohl et al., 2003). Chemical reactions affecting the δ(^{37}Cl) of CH_3Cl occur in the boundary layer only due to degradation by plants, oceans and soils. Once CH_3Cl reaches the free troposphere, hydroxyl radical reaction is the sole degradation process, which does not change the δ(^{37}Cl). Hydroxyl radicals cleave the C–H bond in CH_3Cl and thus leave the chlorine isotope composition virtually unchanged because only secondary isotope effects are involved (Keppler et al., 2020). In contrast, photolytic degradation in the stratosphere splits the C–Cl bond in CH_3Cl, which directly affects the chlorine isotope composition due to a primary isotope effect (Melander and Saunders, 1980). Hence, STT might shift stable chlorine isotope values of CH_3Cl in the upper troposphere toward more positive δ(^{37}Cl) values by mixing partially degraded stratospheric CH_3Cl with tropospheric CH_3Cl. Even though the net transport of CH_3Cl to the stratosphere is relatively small (146 Gg yr^{-1}) compared with loss by hydroxyl radical reactions (2830 Gg yr^{-1}) (Carpenter et al., 2014), more substantial amounts of CH_3Cl might be transported to the stratosphere in tropical regions and, after partial degradation, mix back into the troposphere in temperate regions (Holton et al., 1995). The relatively long stratospheric lifetime of CH_3Cl of about 35 years (Umezawa et al., 2015) and the associated low degradation rates would require a large isotope effect in order to be detectable in CH_3Cl in mixed tropospheric air. Laube et al. (2010) measured an apparent isotopic fractionation (ε_{Cl}) of −12.1 ‰ for degradation of CFC-12 in the stratosphere. If CH_3Cl showed similar chlorine isotope fractionation due to photolysis, transport and mixing of even small amounts of stratospheric CH_3Cl could measurably change the chlorine isotopic composition of tropospheric CH_3Cl.

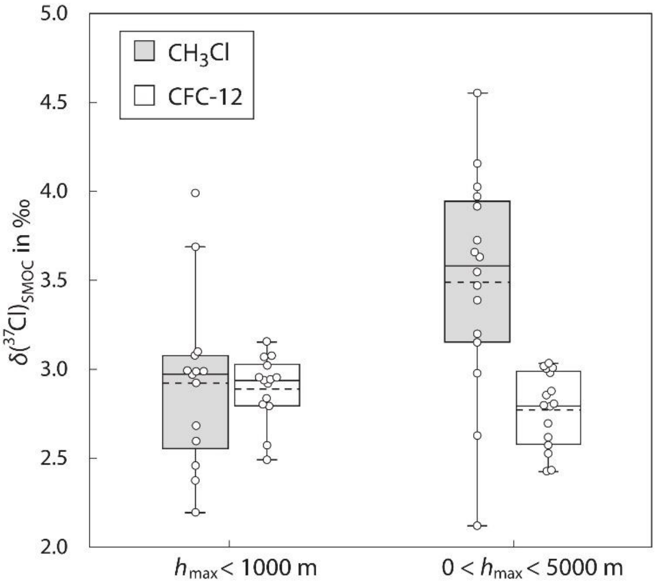

Figure 5: δ(^{37}Cl) values of CH_3Cl and CFC-12 grouped according to their travel path. White circles indicate individual measurements, the dashed lines in boxplots indicate the mean and solid lines the median of δ(^{37}Cl) values. For air parcels that traveled at heights of less than 1000 m (above ground), a larger influence of boundary layer air is assumed. Travel paths that include heights of more than 1000 m, a larger influence of free tropospheric air may be present causing the measured isotopic offset in CH_3Cl. CFC-12 does not exhibit such an offset.

In Fig. 6 samples were grouped according to meteorological seasons and travel heights to further explore potential influences of STT on isotopic values. Figure 6 indicates that in spring and fall no apparent difference between samples with low ($h_{\mathrm{max}} <$ 1000 m) and mixed ($0 < h_{\mathrm{max}} < 5000$ m) travel paths is visible. If at all, there is even a tendency toward lighter isotopic values for samples with higher travel paths. It should be noted, however, that the variance in each of these groups is rather large with only a small number of observations in each group (3–6). Despite these limitations, summer and winter samples indicate a quite clear isotopic difference between low and mixed samples. Studies investigating exchange of air between stratosphere and troposphere generally found an overall seasonal maximum of exchange (upward and downward) in late spring/early summer and a minimum in early fall (Holton et al., 1995; Ruiz and Prather, 2022; Stohl et al., 2003). Boothe and Homeyer (2017) compared four reanalysis models of climatological data and their results indicated a maximum downward stratosphere–troposphere transport (STT) generally occurring in late winter in mid-latitudes of the northern hemisphere. These findings would agree with the isotopic offset observed between low ($h_{\mathrm{max}} <$ 1000 m) and mixed ($0 < h_{\mathrm{max}} < 5000$ m) winter samples assuming an influx of partially degraded CH_3Cl into the troposphere causing more positive $\delta(^{37}Cl)$ values for samples with larger proportions of CH_3Cl from higher traveling paths. However, minimum STT was described for summer suggesting a minimum influx of stratospheric air and thus of ^{37}Cl–enriched CH_3Cl. Yet, the isotopic offset between samples with low and mixed traveling paths is similar to that observed for winter samples. This discrepancy does not necessarily exclude STT as a cause for ^{37}Cl–enriched isotopic values in samples with mixed traveling paths. Presented data in this study might rather be the result of an interplay of several processes: production of CH_3Cl by the various sources and destruction by degradation reactions, each governed by individual annual cycles. The simplified approach of separating rather few samples into two groups might not be accurate enough to gain further information at this point. Still, STT might be an additional process changing the $\delta(^{37}Cl)$ of CH_3Cl, which, if significant, would have to be considered in budget estimates based on isotopic methods.

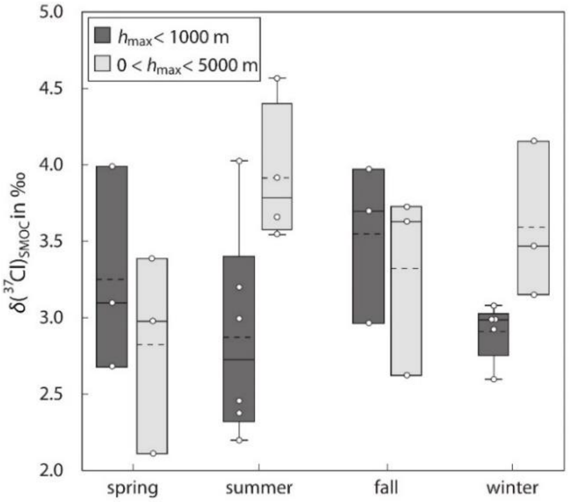

Figure 6: $\delta(^{37}Cl)$ values of CH_3Cl grouped according to meteorological seasons. White circles indicate individual measurements, the dashed lines indicate the mean. Samples taken in summer and winter exhibit a clear difference between the two groups (travel height < 1000 m and travel height 0 to 5000 m) whereas spring and fall samples are not distinguishable based on travel heights

https://doi.org/10.5194/egusphere-2025-3652
Preprint. Discussion started: 19 September 2025

4 Conclusions

In this study, we presented stable chlorine isotope data of CFCs, HCFC-22, and CH_3Cl collected during an annual campaign in 2022 and 2023. Even though we were not able to measure mole fractions of these compounds in air, the isotopic data alone provides a first view on the stable chlorine isotope composition and, especially for CFCs, a first isotopic fingerprint in air. Such records are essential prerequisites for future studies aimed at assessing long-term changes of $\delta(^{37}Cl)$ in these slowly degrading compounds in the atmosphere.

Whereas CFCs showed little variability within one year, consistent with long atmospheric lifetimes, CH_3Cl exhibited more pronounced seasonal variations in $\delta(^{37}Cl)$. On average, data showed an annual cycle with lower, more negative $\delta(^{37}Cl)$ in spring and higher, more positive $\delta(^{37}Cl)$ in late summer and early fall. Considering mole fractions of analyzed compounds, this cycle might be interpreted with increased emissions of sources such as oceans and plants in spring and enhanced degradation, most likely by hydroxyl radicals, during summer and fall. Further identification of emissions and robust source apportionment were not possible because $\delta(^{37}Cl)$ characterization has currently only been carried out for few sources. Despite these limitations, we were able to differentiate air masses on a horizontal but especially on a vertical scale using back trajectories analysis by HYSPLIT. However, using the available data and methods it remains unclear if vertical isotopic differences resulted from ^{37}Cl–depleted CH_3Cl emissions in the boundary layer, mixing with ^{37}Cl–enriched stratospheric CH_3Cl, or if a combination of both processes was responsible for the observed differences. Yet, the mere existence of the described isotopic offset provides sufficient reason to investigate this phenomenon further in future studies. It should be noted that the influence of stratosphere–troposphere transport on measured $\delta(^{37}Cl)$ in CH_3Cl, as hypothesized in this study, would add an additional layer of complexity when using chlorine isotopes to refine atmospheric budget estimates of CH_3Cl. On the other hand, chlorine isotopes in CH_3Cl and related halogenated compounds such as $CHCl_3$ and CH_2Cl_2 might provide an additional technique to study stratosphere–troposphere interactions.

A more refined understanding of $\delta(^{37}Cl)$ variability in CH_3Cl in the atmosphere could be achieved through more frequent sampling over longer time periods. Coordinated efforts by established monitoring networks, such as AGAGE, would be most beneficial. Participating stations routinely perform high-precision analysis of atmospheric mole fractions of CFCs, CH_3Cl, and other compounds in diverse settings, such as at high altitude sites (Jungfraujoch, Switzerland, 3500 m), marine environments (Mace Head, Ireland), and remote regions (Ny Ålesund, Svalbard). While the current sampling method is not appropriate for high-frequency analysis of $\delta(^{37}Cl)$ in CH_3Cl, the advent of laser absorption spectrometry, as routinely applied in CH_4 and N_2O studies (Ibraim et al., 2018; Rennick et al., 2021), may facilitate routine in situ isotope measurements in the near future. Hence, isotopic analysis on gases collected at such stations would substantially improve our understanding of CH_3Cl sources, sinks, and atmospheric transport processes. Particularly useful, in this respect, would be the simultaneous measurement of hydrogen isotopes in CH_3Cl, which are indicative for hydroxyl radical reactions without being affected by photolysis or microbial degradation thus helping to identify and quantify individual processes. Such integrated approaches will be critical to advance the application of stable isotopes in atmospheric trace gas research and to constrain global halocarbon budgets more robustly.

Appendix A: Meteorological data and isotopic values collected in Leipzig, Germany (WGS84: 51.35231 °N, 12.43155 °E), during the sampling campaign. Meteorological data represents values recorded at noon of the corresponding sampling day. Height represents the maximum traveling heights of sampled air 96 hours prior to arrival at the sampling site as calculated by the HYSPLIT model.

date	air sampled	T	p	relative humidity	height	$\delta(^{37}\text{Cl})$ vs. SMOC				
						HCFC-22	CH_3Cl	CFC-12	CFC-11	CFC-113
	L	°C	hPa	%	m	‰	‰	‰	‰	‰
03 Feb 2022	300	6	1011	69	$h_{\max} \leq 1000$	-0.05	2.60	2.57		
04 Feb 2022	354	7	1018	93	$h_{\max} \leq 1000$	-0.05	2.99	3.16	2.02	
31 March 2022	970	4	1002	80	$h_{\max} \leq 1000$	0.04	2.68	2.80		
19 April 2022	1040	10	1014	53	$0 \leq h_{\max} \leq 5000$	-0.06	2.12	2.43	1.60	
22 April 2022	1000	11	1008	82	$h_{\max} \leq 1000$	0.31	3.10	2.92		
26 April 2022	1000	15	1016	48	$0 \leq h_{\max} \leq 5000$	0.01	2.98	2.69		
16 May 2022	1295	25	1017	42	$0 \leq h_{\max} \leq 5000$	0.29	3.39	3.04	2.14	
24 May 2022	1505	21	1005	60	$h_{\max} \leq 1000$	-0.58	3.99	2.94	1.93	1.20
02 June 2022	1100	19	1021	49	$h_{\max} \leq 1000$	0.09	2.46	3.08	1.90	
16 June 2022	1512	25	1019	41	$0 \leq h_{\max} \leq 5000$	0.60	3.20	2.43	1.89	1.68
12 July 2022	1890	23	1024	47	$h_{\max} \leq 1000$	0.42	2.38	2.79	1.73	1.40
25 July 2022	1770	34	1010	30	$0 \leq h_{\max} \leq 5000$	0.56	4.57	2.53	2.07	1.89
28 July 2022	1631	23	1019	41	$0 \leq h_{\max} \leq 5000$	0.74	3.66	3.00	2.25	
03 Aug 2022	1840	32	1016	34	$0 \leq h_{\max} \leq 5000$	0.41	3.55	2.80	2.15	
10 Aug 2022	1800	26	1027	39	$h_{\max} \leq 1000$	0.07	2.99	2.95	2.01	
24 Aug 2022	1700	27	1020	64	$0 \leq h_{\max} \leq 5000$	0.61	3.92	3.02	2.22	1.12
26 Aug 2022	900	27	1013	66	$h_{\max} \leq 1000$	0.54	2.20	2.84	1.93	1.86
01 Sept 2022	1866	20	1022	49	$h_{\max} \leq 1000$	0.52	3.70	3.02	2.08	1.59
28 Sept 2022	1700	10	996	76	$0 \leq h_{\max} \leq 5000$	0.00	4.03	2.57	1.70	
21 Oct 2022	1215	15	1010	100	$0 \leq h_{\max} \leq 5000$	0.25	2.63	2.79	1.44	
25 Oct 2022	1200	16	1017	72	$0 \leq h_{\max} \leq 5000$	0.36	3.97	2.62		
02 Nov 2022	960	14	1021	55	$h_{\max} \leq 1000$	-0.02	2.97	2.95	1.89	1.82
15 Nov 2022	1050	15	1006	55	$0 \leq h_{\max} \leq 5000$	0.24	3.63	2.98		
30 Nov 2022	1400	3	1023	90	$0 \leq h_{\max} \leq 5000$	0.71	3.73	2.88	1.96	
02 Dec 2022	1370	0	1023	93	$0 \leq h_{\max} \leq 5000$	0.16	3.15	2.81	1.60	
07 Dec 2022	1200	4	1011	81	$0 \leq h_{\max} \leq 5000$	-0.21	3.47	2.85	1.70	
22 Dec 2022	1470	11	1002	100	$h_{\max} \leq 1000$	-0.04	2.99	3.07	1.42	
03 Jan 2022	1200	8	1028	76	$h_{\max} \leq 1000$	0.63	3.08	2.94	1.36	
18 Jan 2022	1700	0	993	86	$0 \leq h_{\max} \leq 5000$	0.84	4.16	3.01		
31 Jan 2022	1630	5	1015	75	$h_{\max} \leq 1000$	-0.25	2.92	2.50		

Data Availability

All relevant data is included in the article and the supplement.

Author Contribution

AH conceptualized the research idea and designed the air sampling method based on existing methods. AH and SK collected the samples and performed the isotopic measurements. AH executed HYSPLIT model calculations. AH took the lead in writing the manuscript supported by SK.

Competing Interest

The authors declare that they have no conflict of interest

Acknowledgments

We thank ProVIS (Centre for Chemical Microscopy) at the UFZ for using the MC-ICPMS. ProVIS was funded by European Regional Development Funds (EFRE-Europe funds Saxony) and the Helmholtz Association. The authors are grateful for the use of the analytical facilities of the Laboratories for Stable Isotopes (LSI) of the Helmholtz Centre for Environmental Research. Measurements of CH_3Cl and CFC-12 at Jungfraujoch were provided by M. Vollmer and S. Reimann (Empa) as part of the Swiss National Program CLIMGAS-CH (Swiss Federal Office for the Environment, FOEN) with additional support by the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG).

Financial Support

A. Horst received funding through an HGF recognition award (ERC-RA-0039), which was financed by the Initiative and Network Fund (IVF) of the Helmholtz Association, Germany

References

Allin, S. J., Laube, J. C., Witrant, E., Kaiser, J., McKenna, E., Dennis, P., Mulvaney, R., Capron, E., Martinerie, P., Röckmann, T., Blunier, T., Schwander, J., Fraser, P. J., Langenfelds, R. L., and Sturges, W. T.: Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air, Atmospheric Chemistry and Physics, 15, 6867–6877, https://doi.org/10.5194/acp-15-6867-2015, 2015.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochemical Cycles, 15, 955–966, https://doi.org/10.1029/2000GB001382, 2001.

Archbold, M. E., Redeker, K. R., Davis, S., Elliot, T., and Kalin, R. M.: A method for carbon stable isotope analysis of methyl halides and chlorofluorocarbons at pptv concentrations, Rapid Communications in Mass Spectrometry, 19, 337–342, https://doi.org/10.1002/rcm.1791, 2005.

Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis, W.: A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons, Atmospheric Measurement Techniques, 4, 2073–2086, https://doi.org/10.5194/amt-4-2073-2011, 2011.

Bahlmann, E., Keppler, F., Wittmer, J., Greule, M., Schöler, H. F., Seifert, R., and Zetzsch, C.: Evidence for a major missing source in the global chloromethane budget from stable carbon isotopes, Atmospheric Chemistry and Physics, 19, 1703–1719, https://doi.org/10.5194/acp-19-1703-2019, 2019.

Bill, M., Conrad, M. E., and Goldstein, A. H.: Stable carbon isotope composition of atmospheric methyl bromide, Geophysical Research Letters, 31, https://doi.org/10.1029/2003GL018639, 2004.

Böhlke, J. K., Mroczkowski, S. J., Sturchio, N. C., Heraty, L. J., Richman, K. W., Sullivan, D. B., Griffith, K. N., Gu, B., and Hatzinger, P. B.: Stable isotope analyses of oxygen (18O:17O:16O) and chlorine (37Cl:35Cl) in perchlorate: reference materials, calibrations, methods, and interferences, Rapid Communications in Mass Spectrometry, 31, 85–110, https://doi.org/10.1002/rcm.7751, 2017.

Boothe, A. C. and Homeyer, C. R.: Global large-scale stratosphere–troposphere exchange in modern reanalyses, Atmospheric Chemistry and Physics, 17, 5537–5559, https://doi.org/10.5194/acp-17-5537-2017, 2017.

Carpenter, L. J., Reimann, S., Engel, A., Montzka, S., Burkholder, J. B., Clerbaux, C., Hall, B., Yvon-Lewis, S. A., Blake, D. R., Dorf, M., Dutton, G. S., Fraser, P. J., Froidevaux, L., Hendrick, F., Hu, J., Jones, A., Krummel, P. B., Kuijpers, L. J., Kurylo, M. J., Liang, Q., Mahieu, E., M?hle, J., O?Doherty, S., Ohnishi, K., Orkin, V. L., Pfeilsticker, K., Rigby, M., Simpson, I. J., and Yokouchi, Y.: Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project-Report No.55, 416 pp., World Meteorological Organiz, NIST, 2014.

Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, Rapid Communications in Mass Spectrometry, 25, 2538–2560, https://doi.org/10.1002/rcm.5129, 2011.

Davidson, C., Amrani, A., and Angert, A.: Tropospheric carbonyl sulfide mass balance based on direct measurements of sulfur isotopes, Proceedings of the National Academy of Sciences, 118, e2020060118, https://doi.org/10.1073/pnas.2020060118, 2021.

Draxler, R. R. and Hess, G. D.: Description of the HYSPLIT_4 modeling system. NOAA Tech. Memo. ERL ARL-224, NOAA Air Resources Laboratory, Silver Spring, MD, 24 pp., 1997.

Eggenkamp, H.: The Geochemistry of Stable Chlorine and Bromine Isotopes, Springer Nature Switzerland, Cham, https://doi.org/10.1007/978-3-031-75633-7, 2025.

Gebhart, K. A., Schichtel ,Bret A., and and Barna, M. G.: Directional Biases in Back Trajectories Caused by Model and Input Data, Journal of the Air & Waste Management Association, 55, 1649–1662, https://doi.org/10.1080/10473289.2005.10464758, 2005.

Gilevska, T., Ivdra, N., Bonifacie, M., and Richnow, H.-H.: Improvement of analytical method for chlorine dual-inlet isotope ratio mass spectrometry of organochlorines, Rapid Communications in Mass Spectrometry, 29, 1343–1350, https://doi.org/10.1002/rcm.7220, 2015.

Hartmann, S. C., Keppler, F., Greule, M., Lauer, R., and Horst, A.: Triple-Element Stable Isotope Analysis of Chloromethane Emitted by Royal Fern and Degraded by Club Moss, Journal of Geophysical Research: Biogeosciences, 128, e2022JG007256, https://doi.org/10.1029/2022JG007256, 2023.

Holton, J. R., Haynes, P. H., McIntyre, M. E., Douglass, A. R., Rood, R. B., and Pfister, L.: Stratosphere-troposphere exchange, Reviews of Geophysics, 33, 403–439, https://doi.org/10.1029/95RG02097, 1995.

Horst, A., Lacrampe-Couloume, G., and Sherwood Lollar, B.: Compound-Specific Stable Carbon Isotope Analysis of Chlorofluorocarbons in Groundwater, Anal. Chem., 87, 10498–10504, https://doi.org/10.1021/acs.analchem.5b02701, 2015.

Horst, A., Renpenning, J., Richnow, H.-H., and Gehre, M.: Compound Specific Stable Chlorine Isotopic Analysis of Volatile Aliphatic Compounds Using Gas Chromatography Hyphenated with Multiple Collector Inductively Coupled Plasma Mass Spectrometry, Anal. Chem., 89, 9131–9138, 2017.

Horst, A., Bonifacie, M., Bardoux, G., and Richnow, H. H.: Isotopic Characterization (2H, 13C, 37Cl, 81Br) of Abiotic Degradation of Methyl Bromide and Methyl Chloride in Water and Implications for Future Studies, Environ. Sci. Technol., 53, 8813–8822, https://doi.org/10.1021/acs.est.9b02165, 2019.

Hu, L., Yvon-Lewis, S. A., Butler, J. H., Lobert, J. M., and King, D. B.: An improved oceanic budget for methyl chloride, Journal of Geophysical Research: Oceans, 118, 715–725, https://doi.org/10.1029/2012JC008196, 2013.

Hu, X., Yao, B., and Fang, X.: Anthropogenic emissions of ozone-depleting substance CH3Cl during 2000–2020 in China, Environmental Pollution, 310, 119903, https://doi.org/10.1016/j.envpol.2022.119903, 2022.

Ibraim, E., Harris ,Eliza, Eyer ,Simon, Tuzson ,Béla, Emmenegger ,Lukas, Six ,Johan, and and Mohn, J.: Development of a field-deployable method for simultaneous, real-time measurements of the four most abundant N2O isotopocules*, Isotopes in Environmental and Health Studies, 54, 1–15, https://doi.org/10.1080/10256016.2017.1345902, 2018.

Keppler, F., Bahlmann, E., Greule, M., Schöler, H. F., Wittmer, J., and Zetzsch, C.: Mass spectrometric measurement of hydrogen isotope fractionation for the reactions of chloromethane with OH and Cl, Atmospheric Chemistry and Physics, 18, 6625–6635, https://doi.org/10.5194/acp-18-6625-2018, 2018.

Keppler, F., Barnes, J. D., Horst, A., Bahlmann, E., Luo, J., Nadalig, T., Greule, M., Hartmann, S. C., and Vuilleumier, S.: Chlorine Isotope Fractionation of the Major Chloromethane Degradation Processes in the Environment, Environ. Sci. Technol., 54, 1634–1645, https://doi.org/10.1021/acs.est.9b06139, 2020.

Ko, M., Newman, P., Reimann, S., and Strahan, S.: SPARC (Stratosphere-troposphere Processes And their Role in Climate), SPARC Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, 2013.

Laube, J. C., Kaiser, J., Sturges, W. T., Bönisch, H., and Engel, A.: Chlorine Isotope Fractionation in the Stratosphere, Science, 329, 1167–1167, https://doi.org/10.1126/science.1191809, 2010.

Laube, J. C., Newland, M. J., Hogan, C., Brenninkmeijer, C. A. M., Fraser, P. J., Martinerie, P., Oram, D. E., Reeves, C. E., Röckmann, T., Schwander, J., Witrant, E., and Sturges, W. T.: Newly detected ozone-depleting substances in the atmosphere, Nature Geosci, 7, 266–269, https://doi.org/10.1038/ngeo2109, 2014.

Lee-Taylor, J. and Redeker, K. R.: Reevaluation of global emissions from rice paddies of methyl iodide and other species, Geophysical Research Letters, 32, https://doi.org/10.1029/2005GL022918, 2005.

Li, S., Park, M.-K., Jo, C. O., and Park, S.: Emission estimates of methyl chloride from industrial sources in China based on high frequency atmospheric observations, J Atmos Chem, 74, 227–243, https://doi.org/10.1007/s10874-016-9354-4, 2017.

Li, Y., Xia, Y., Xie, F., and Yan, Y.: Influence of stratosphere-troposphere exchange on long-term trends of surface ozone in CMIP6, Atmospheric Research, 297, 107086, https://doi.org/10.1016/j.atmosres.2023.107086, 2024.

McCulloch, A., Aucott, M. L., Benkovitz, C. M., Graedel, T. E., Kleiman, G., Midgley, P. M., and Li, Y.-F.: Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory, Journal of Geophysical Research: Atmospheres, 104, 8391–8403, https://doi.org/10.1029/1999JD900025, 1999.

Melander, L. and Saunders, W. H.: Reaction Rates of Isotopic Molecules. John Wiley and Sons, New York, 391 + xiv pp., 1980.

Prinn, R., Weiss, R., Arduini, J., Choi, H., Engel, A., Fraser, P., Ganesan, A., Harth, C., Hermansen, O., Kim, J., Krummel, P., Lo, Z., Lunder, C., Maione, M., Manning, A., Mitrevski, B., Mühle, J., O'Doherty, S., Park, S., Pitt, J., Reimann, S., Rigby, M., Saito, T., Salameh, P., Schmidt, R., Simmonds, P., Stanley, K., Stavert, A., Steel, P., Vollmer, M., Wagenhäuser, T., Wang, H., Wenger, A., Western, L., Yao, B., Young, D., Zhou, L., and Zhu, L.: The dataset of in-situ measurements of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gas Experiment (AGAGE) and affiliated stations (20250123), https://doi.org/10.60718/0FXA-QF43, 2025.

Redeker, K. R. and Kalin, R. M.: Methyl chloride isotopic signatures from Irish forest soils and a comparison between abiotic and biogenic methyl halide soil fluxes, Global Change Biology, 18, 1453–1467, https://doi.org/10.1111/j.1365-2486.2011.02600.x, 2012.

Redeker, K. R., Davis, S., and Kalin, R. M.: Isotope values of atmospheric halocarbons and hydrocarbons from Irish urban, rural, and marine locations, Journal of Geophysical Research: Atmospheres, 112, https://doi.org/10.1029/2006JD007784, 2007.

Rennick, C., Arnold, T., Safi, E., Drinkwater, A., Dylag, C., Webber, E. M., Hill-Pearce, R., Worton, D. R., Bausi, F., and Lowry, D.: Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision In Situ Analysis of δ13C and δ2H from Ambient Air Methane, Anal. Chem., 93, 10141–10151, https://doi.org/10.1021/acs.analchem.1c01103, 2021.

Renpenning, J., Horst, A., Schmidt, M., and Gehre, M.: Online isotope analysis of 37Cl/35Cl universally applied for semi-volatile organic compounds using GC-MC-ICPMS, J. Anal. At. Spectrom., 33, 314–321, https://doi.org/10.1039/C7JA00404D, 2018.

Rigby, M., Park, S., Saito, T., Western, L. M., Redington, A. L., Fang, X., Henne, S., Manning, A. J., Prinn, R. G., Dutton, G. S., Fraser, P. J., Ganesan, A. L., Hall, B. D., Harth, C. M., Kim, J., Kim, K.-R., Krummel, P. B., Lee, T., Li, S., Liang, Q., Lunt, M. F., Montzka, S. A., Mühle, J., O'Doherty, S., Park, M.-K., Reimann, S., Salameh, P. K., Simmonds, P., Tunnicliffe, R. L., Weiss, R. F., Yokouchi, Y., and Young, D.: Increase in CFC-11 emissions from eastern China based on atmospheric observations, Nature, 569, 546–550, https://doi.org/10.1038/s41586-019-1193-4, 2019.

Rudolph, J., Lowe, D. C., Martin, R. J., and Clarkson, T. S.: A novel method for compound specific determination of δ13C in volatile organic compounds at ppt levels in ambient air, Geophysical Research Letters, 24, 659–662, https://doi.org/10.1029/97GL00537, 1997.

Ruiz, D. J. and Prather, M. J.: From the middle stratosphere to the surface, using nitrous oxide to constrain the stratosphere–troposphere exchange of ozone, Atmospheric Chemistry and Physics, 22, 2079–2093, https://doi.org/10.5194/acp-22-2079-2022, 2022.

Saito, T. and Yokouchi, Y.: Stable carbon isotope ratio of methyl chloride emitted from glasshouse-grown tropical plants and its implication for the global methyl chloride budget, Geophysical Research Letters, 35, https://doi.org/10.1029/2007GL032736, 2008.

Saito, T., Yokouchi, Y., Kosugi, Y., Tani, M., Philip, E., and Okuda, T.: Methyl chloride and isoprene emissions from tropical rain forest in Southeast Asia, Geophysical Research Letters, 35, https://doi.org/10.1029/2008GL035241, 2008.

Schüth, C., Taubald, H., Bolaño, N., and Maciejczyk, K.: Carbon and hydrogen isotope effects during sorption of organic contaminants on carbonaceous materials, Journal of Contaminant Hydrology, 64, 269–281, https://doi.org/10.1016/S0169-7722(02)00216-4, 2003.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change., 2nd Edition., Wiley, Hoboken, N.J, 2006.

Slater, G. F., Ahad, J. M. E., Sherwood Lollar, B., Allen-King, R., and Sleep, B.: Carbon Isotope Effects Resulting from Equilibrium Sorption of Dissolved VOCs, Anal. Chem., 72, 5669–5672, https://doi.org/10.1021/ac000691h, 2000.

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System, Bulletin of the American Meteorological Society, 96, 2059–2077, https://doi.org/10.1175/BAMS-D-14-00110.1, 2015.

Stohl, A., Bonasoni, P., Cristofanelli, P., Collins, W., Feichter, J., Frank, A., Forster, C., Gerasopoulos, E., Gäggeler, H., James, P., Kentarchos, T., Kromp-Kolb, H., Krüger, B., Land, C., Meloen, J., Papayannis, A., Priller, A., Seibert, P., Sprenger, M., Roelofs, G. J., Scheel, H. E., Schnabel, C., Siegmund, P., Tobler, L., Trickl, T., Wernli, H., Wirth, V., Zanis, P., and Zerefos, C.: Stratosphere-troposphere exchange: A review, and what we have learned from STACCATO, Journal of Geophysical Research: Atmospheres, 108, https://doi.org/10.1029/2002JD002490, 2003.

Thompson, A. E., Anderson, R. S., Rudolph, J., and Huang, L.: Stable carbon isotope signatures of background tropospheric chloromethane and CFC113, Biogeochemistry, 60, 191–211, https://doi.org/10.1023/A:1019820208377, 2002.

Thornton, B. F., Horst, A., Carrizo, D., Holmstrand, H., Andersson, P., Crill, P. M., and Gustafsson, Ö.: A High-Volume Cryosampler and Sample Purification System for Bromine Isotope Studies of Methyl Bromide, Journal of Atmospheric and Oceanic Technology, 30, 2095–2107, https://doi.org/10.1175/JTECH-D-12-00228.1, 2013.

Thornton, B. F., Horst, A., Carrizo, D., and Holmstrand, H.: Methyl chloride and methyl bromide emissions from baking: an unrecognized anthropogenic source, Science of The Total Environment, 551–552, 327–333, https://doi.org/10.1016/j.scitotenv.2016.01.213, 2016.

Tsunogai, U., Yoshida, N., and Gamo, T.: Carbon isotopic compositions of C2-C5 hydrocarbons and methyl chloride in urban, coastal, and maritime atmospheres over the western North Pacific, Journal of Geophysical Research: Atmospheres, 104, 16033–16039, https://doi.org/10.1029/1999JD900217, 1999.

Umezawa, T., Baker, A. K., Brenninkmeijer, C. a. M., Zahn, A., Oram, D. E., and van Velthoven, P. F. J.: Methyl chloride as a tracer of tropical tropospheric air in the lowermost stratosphere inferred from IAGOS-CARIBIC passenger aircraft measurements, Journal of Geophysical Research: Atmospheres, 120, 12,313-12,326, https://doi.org/10.1002/2015JD023729, 2015.

Volpe, C. M.: Stable chlorine isotope variations in the atmosphere, Dissertation, University of San Diego, 1998.

Wanner, P., Parker, B. L., Chapman, S. W., Aravena, R., and Hunkeler, D.: Does sorption influence isotope ratios of chlorinated hydrocarbons under field conditions?, Applied Geochemistry, 84, 348–359, https://doi.org/10.1016/j.apgeochem.2017.07.016, 2017.

Weinberg, I., Bahlmann, E., Eckhardt, T., Michaelis, W., and Seifert, R.: A halocarbon survey from a seagrass dominated subtropical lagoon, Ria Formosa (Portugal): flux pattern and isotopic composition, Biogeosciences, 12, 1697–1711, https://doi.org/10.5194/bg-12-1697-2015, 2015.

Xiao, X., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Weiss, R. F., O'Doherty, S., Miller, B. R., Salameh, P. K., Harth, C. M., Krummel, P. B., Porter, L. W., Mühle, J., Greally, B. R., Cunnold, D., Wang, R., Montzka, S. A., Elkins, J. W., Dutton, G. S., Thompson, T. M., Butler, J. H., Hall, B. D., Reimann, S., Vollmer, M. K., Stordal, F., Lunder, C., Maione, M., Arduini, J., and Yokouchi, Y.: Optimal estimation of the surface fluxes of methyl chloride using a 3-D global chemical transport model, Atmospheric Chemistry and Physics, 10, 5515–5533, https://doi.org/10.5194/acp-10-5515-2010, 2010.

Zuiderweg, A., Holzinger, R., Martinerie, P., Schneider, R., Kaiser, J., Witrant, E., Etheridge, D., Petrenko, V., Blunier, T., and Röckmann, T.: Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland, Atmospheric Chemistry and Physics, 13, 599–609, https://doi.org/10.5194/acp-13-599-2013, 2013.

Zwank, L., Berg, M., Schmidt, T. C., and Haderlein, S. B.: Compound-Specific Carbon Isotope Analysis of Volatile Organic Compounds in the Low-Microgram per Liter Range, Anal. Chem., 75, 5575–5583, https://doi.org/10.1021/ac034230i, 2003.