Atmos. Meas. Tech. Discuss., 4, 2161–2188, 2011
www.atmos-meas-tech-discuss.net/4/2161/2011/
doi:10.5194/amtd-4-2161-2011

Atmospheric Measurement Techniques Discussions

A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons

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Received: 15 March 2011 – Accepted: 17 March 2011 – Published: 8 April 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The isotopic composition of volatile organic compounds (VOCs) can provide valuable information on their sources and fate not deducible from mixing ratios alone. In particular the reported carbon stable isotope ratios of chloromethane and bromomethane from different sources cover a δ^{13}C-range of almost 100‰ making isotope ratios a very promising tool for studying the biogeochemistry of these compounds. So far, the determination of the isotopic composition of C1 and C2 halocarbons others than chloromethane is hampered by their low mixing ratios.

In order to determine the carbon isotopic composition of C1 and C2 halocarbons with mixing ratios as low as 1 pptv (i) a field suitable cryogenic high volume sampling system and (ii) a chromatographic set up for processing these samples have been developed and validated. The sampling system was tested at two different sampling sites, an urban and a coastal location in Northern Germany. The average δ^{13}C-values for bromomethane at the urban site were -42.9 ± 1.1‰ and agreed well with previously published results. But at the coastal site bromomethane was substantially enriched in ^{13}C by almost 10‰. Less pronounced differences were observed for chlorodifluoromethane, 1,1,1-trichloroethane and chloromethane. We suggest that these differences are related to the turnover of these compounds in ocean surface waters. Furthermore we report first carbon isotope ratios for iodomethane (−53.6‰), bromoform (−13.5‰) and other halocarbons.

1 Introduction

Compound specific isotope ratio mass spectrometry (CSIRMS) of non methane volatile organic compounds (NMVOCs) emerged as a powerful tool to distinguish different sources and to provide information on sinks (Rudolph et al., 1997, 2000; Tsunogai, 1998; Thompson, 2002; Goldstein and Shaw, 2003, and references therein; Archbold, 2005; Redeker, 2007; Mead, 2008).

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In particular, stable carbon isotope ratios have been proposed for constraining the origin and fate of atmospheric chloromethane (Harper et al., 2003; Keppler et al., 2005) and bromomethane (Mc Cauly et al., 1999); as the reported carbon isotope ratios of the known sources cover a broad range of $\delta^{13}C$ values from −40‰ for anthropogenic and marine sources to −147‰ for chloromethane synthesized from pectin (cf. Keppler et al., 2005). Tremendous progress has recently been made in the carbon isotopic analysis of dissolved halocarbons (Auer et al., 2006), which now allows to extend this approach to short lived halocarbons such as iodomethane (CH_3I), dibromomethane (CH_2Br_2) and bromoform ($CHBr_3$). Accompanying determination of the carbon isotope ratios of these compounds could provide valuable additional information that can not be derived from the determination of mixing ratios.

For determining carbon isotope ratio of atmospheric VOCs both, air sampling canisters (Rudolph et al., 1997; Tsunogai et al., 1999; Thompson et al., 2002; Archbold et al., 2005; Redeker et al., 2006) and adsorbent tubes (Mead, 2008) have successfully been used. Given a minimum carbon amount between 0.25 ng and 1 ng required for carbon isotope analysis, these sampling methods are sufficient for measurements of chloromethane (Rudolph et al., 1997; Tsunogai et al., 1999; Thompson et al., 2002; Archbold et al., 2005; Redeker et al., 2006; Mead et al., 2008) and several chlorofluorocarbons and hydrofluorocarbons (Thompson et al., 2002; Redeker et al., 2006; Mead et al., 2008) but not for bromomethane and other halocarbons such as bromoform and iodomethane with typical mixing ratios between 0.5 and 10 pptv.

To the best of our knowledge, there is only one study reporting carbon isotope ratios for atmospheric bromomethane (Bill et al., 2004) in which a cryogenic sampling system was used.

The main objective of this study was to develop a simple and robust sampling system appropriate for field work enabling the isotope ratio determination of atmospheric halocarbons in the low pptv range, notably bromomethane, bromoform and iodomethane. Here, we describe the configuration and validation of the developed sampling system and report first results from its application within a survey on air samples from an urban

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(Hamburg, Germany) and a coastal site (Sylt, Germany).

2 Methods

2.1 Overview

Briefly, up to 500 L of air were drawn through a cryo trap. The trap was then heated to 125 °C and the analytes were transferred to an adsorption tube for storage and analysis. A direct analysis of the isotopic composition of the target compounds is not possible due to multiple interferences from other compounds. Therefore, the samples were first pre-separated on a GasPro column and the target compounds were recollected on two cryo traps. For carbon isotope determination each fraction was then separated on a PorabondQ column and analysed on a GC-C-IRMS/MS system.

2.2 Standards and samples

A Scott EPA TO 15/17 standard containing 65 compounds (1 ppm each in nitrogen) was used as a working standard. For further tests single component standards of chloromethane, bromomethane, iodomethane and dichlorodifluoromethane (each 100 ppm in nitrogen) were used.

Three ambient air samples were taken at the institute building in the center of Hamburg, Northern Germany (53.5686° N, 9.9736° W), from 19 to 24 September 2010. The sampling system inlet was placed at 30 m above the ground. Sampling times varied between 10:00 a.m. and 02:00 p.m. local time. Possible local sources include traffic exhaust, emissions from the harbor area and volatiles from laboratory activities in the vicinity.

In addition, three marine influenced air samples were taken at the AWI Wadden Sea Station in List/Sylt, Northern Germany (55.0226° N, 8.4396° W) between 29 August and 5 September. The sampling system was placed directly at the coastline 200 m

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away from the Wadden Sea Station. Sample times varied between 10:00 a.m. and 02:00 p.m. local time. Potential local sources for halocarbons include emissions from salt marshes, tidal flats and, to a minor degree, harbor activities in List.

72 h back trajectories were calculated by Hysplit 4.8 for an arriving height of 30 m (Hamburg samples) and 2 m (Sylt samples) using NCEP's Global Data Assimilation System (GDAS) data (Draxler and Rolph, 2011). The backward trajectories indicate a prevailing marine and coastal influence for the samples taken at Sylt and a prevailing continental influence for the samples taken at Hamburg.

2.3 Sampling system

The sampling system (Fig. 1) was designed with respect to field suitability and integrity of the isotopic composition of the target compounds. To avoid contamination, all system parts were made of stainless steel or silanized glass.

The sampling consists of three consecutive steps: (1) the cryogenic adsorption of the target compounds from ambient air, (2) the transfer of the analytes from the cryo trap to an adsorption tube and (3) the conditioning of the cryo trap.

1. During sampling the valves 1 and 2 were open. 300 to 500 L of ambient air were drawn with a membrane pump (KNF Neuberger N86 KNDC, Freiburg, Germany) through the sampling system with a flowrate between 3 and 5 L min^{-1}. The flowrate and the sampling volume were monitored with a mass flowmeter (Omega FMA-1608A, Deckenpfronn, Germany). The air first passed a particle filter (Sartorius, Teflon membrane filter, diameter: 45 mm, pore size: 0.2 µm) and was then directed through a condenser kept at approximately 5 °C reducing the water vapour of the air. It has previously been shown that a condenser does not affect the recovery of high boiling compounds such as $CHBr_3$ (Christoph et al., 2002). Finally, the target compounds were enriched in the cryotrap at a temperature of ≤ −110 °C provided by a dry shipper.

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2. After sampling, valve 1 and 2 were closed and valve 3 to the adsorption tube was opened. The cryotrap was carefully removed from the dry shipper. Co-trapped argon and traces of O_2 and N_2 were rapidly released into the gas phase. To prevent analyte losses during sample transfer (usually observed at a flowrate >100 mL min^{-1}), a restriction capillary (restriction flow 50 mL min^{-1} at 2 bar) was placed behind valve 2. Without this restriction we observed losses of highly volatile analytes such as chloromethane and dichlorodifluoromethane. After 20 min, valve 4 was opened for 40 min, the cryo trap was heated to 125 °C and flushed with either nitrogen (50 mL min^{-1}) or pre cleaned ambient air. Before entering the adsorption tube, water vapour was removed from the gas stream by a Nafion dryer (Perma Pure Inc.NJ, USA) placed in silica gel. During sample transfer the adsorption tube was cooled to −5 °C using a Peltier cooler to prevent breakthrough of the analytes. Under these conditions non-polar compounds with boiling points as high as 150 °C were completely transferred from the cryo trap to the adsorption tube, while polar water soluble compounds, such as alcohols and aldehydes, were fractionated between the water remaining in the cryo trap and the adsorption tube. After the transfer of samples the adsorption tube was closed and stored at ≤ −80 °C until analysis.

3. After sample transfer, valve 3 was closed and valve 5 was opened for conditioning the cryo trap with a stream of nitrogen (1000 mL min^{-1}) for 30 min at a temperature of 125 °C.

2.3.1 Cryofocussing and design of the cryotrap

Classical cryogenic sampling systems use either liquid nitrogen or liquid argon for the extraction of the target compounds from air (Bill et al., 2004; Pupek et al., 2008; Zuiderweg et al., 2011). More recently, a cryostat has been applied in cryogenic sampling systems (Miller et al., 2008). However, both approaches require a well established technical infrastructure limiting the use of such sampling systems in field campaigns,

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especially for field work in remote areas. In order to overcome the limitations of classical cryogenic sampling systems we employed a dry shipper (Voyageur 12, Air Liquide, Düsseldorf, Germany) as a cooling source. A dry shipper is a dewar that contains an adsorbent taking up liquid nitrogen. The Voyageur 12 can adsorb up to 14 L of liquid nitrogen and provides a temperature of −176 °C for 28 days in the gas phase above the adsorbed liquid nitrogen. It has an approval for air transport allowing cryogenic sampling in remote places where no liquid nitrogen is available. For the sampling system the stopcock of the dry shipper was shortened to 10 cm and a hole of 20 mm diameter was drilled into the stopcock to insert the cryo trap. The effective temperature inside the cryo trap depended on the flushing flow rate and was below −110 °C for flowrates up to 5 L min^{-1}.

The cryo trap consists of an outer stainless steel tube (3/3 inch, 50 cm length) with an air inlet at the side 4 cm below the top and an inner 1/4 inch stainless steel tube that is connected to the sampling pump (Fig. 1).

To achieve complete trapping at −110 °C the space between both tubes is filled with adsorbents separated by plugs of precleaned silanized glass wool. From the top to the bottom the package of the trap was as follows: 0–20 cm: empty; 20–25 cm silanized raschig rings; 25–35 cm silanized glass beads 60–250 µm; 35–41 cm Tenax Ta; 41–47 cm Porapak N; 47–50 cm: empty. The empty space at the top and the silanized glass rings were mainly designated for trapping water vapour and CO_2.

2.3.2 Adsorption tubes

The adsorption tubes were made of stainless steel (1/4 inch outer diameter, 7 inch length) and filled with 77 mg Carboxen 1016®, 215 mg Carbopack X 569®, 80 mg Carboxen® 1003 and 9 mg Tenax® TA in order of the sampling flow direction. The filling was fixed with stainless steel plugs. Silanized glass wool was used for separating the adsorbents. Before use, the packed tubes were conditioned for 24 h in a tube conditioner (TC 1/2, Gerstel, Mühlheim Germany) at 320 °C and a flow of 100 mL min^{-1} of nitrogen.

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2.3.3 Removal of CO_2 and water

Before analysis water and CO_2 must be removed. Chemical traps frequently used in trace gas analysis to remove excessive CO_2, such as Ascarite or Soda lime (Rudolph et al., 1997; Redeker et al., 2007) reduce the recovery of polyhalogenated methyl halides especially of polybrominated compounds and thus have been ruled out. The adsorbents used in the adsorption tubes have a low affinity for CO_2 and most of the CO_2 from the cryo trap passes the adsorbent tubes during sample transfer. Prior to analysis, the adsorbent tubes were flushed with helium at room temperature (2 min, 20 mL min^{-1}) further reducing the CO_2 content of the samples. The remaining CO_2 was removed during the GC pre-separation by an initial flushing step.

Chemical traps such as magnesium perchlorate or phosphorus pentoxide are not suitable for water removal in high-volume sampling systems due to the large amount of water (up to 30 mL m^{-3}) present in ambient air. Water was removed from the sample at three stages during sampling and analysis. First the water vapour pressure in the sampled air was reduced by means of a condenser kept at 5 °C. We found this suitable to prevent clogging of the cryo trap for air samples up to 500 L. The remaining air moisture was frozen out in the cryo trap. During the sample transfer only a small fraction of the water was mobilized from the cryo trap. This water was removed by a Nafion dryer placed in silica gel. Remaining traces of water were finally removed by means of a second Nafion dryer during analysis.

Nafion dryers have the potential for artefact formation. So far, transformation of carbonyl compounds to alcohols and reactions of compounds containing double or triple bonds have been reported (Miller et al., 2008).

During first tests, we attached the Nafion dryer in front of the cryo trap to reduce the water offload to the cryo trap. With this setup we observed elevated levels of bromomethane. Parallel runs with and without the Nafion dryer indicated an artificial formation of bromomethane on the Nafion membrane of up to 10 pptv. Further tests revealed that the sulfonic acid groups of the Nafion membrane can catalyze the

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nucleophilic substitution of methanol to bromomethane in the presence of bromide. Nevertheless, with the Nafion dryer behind the cryo trap we did not observe any artificial formation of bromomethane.

2.4 Carbon isotope ratio determination

A direct analysis of the isotopic composition of the target compounds was not possible due to multiple interferences from other compounds. Therefore, the sample was first pre-separated on a Gas-Pro column and the target compounds were recollected on two cryo traps. For carbon isotope determination each fraction was then separated on a PorabondQ column and analysed on a GC-C-IRMS/MS system. A scheme of the analytical set up is shown in Fig. 2.

2.4.1 Pre-separation

The pre-separation was performed on an 6890N/5975B GC-MS (Agilent, Waldbronn, Germany). The analytes were desorbed from the adsorbent tube into a helium gas carrier at 350 °C (15 min, 25 mL min^{-1}), directed through a Nafion dryer and refocused on a quartz capillary (0.32 i.d, 60 cm length) immersed in liquid nitrogen. Afterwards the analytes were desorbed at 25 °C and separated on a GasPro column (Agilent, 30 m, 0.32 µm i.d.) with helium as a carrier. The flowrate was set to 5 mL for 4 min to remove the CO_2 and then ramped to 2.7 mL min^{-1}. The oven temperature program was as follows: 40 °C, hold for 5 min.; 6 °C min^{-1} to 240 °C, hold for 10 min.

About 20% of the sample were directed into the MS via a split for monitoring the fractionation. The remaining 80% of the sample were directed to a Valco six port valve (Vici, Schenkon, Swiss) and recollected on two cryo traps (Silica steel 1/16#, 0.32 id., 25 cm length), one containing the target compounds and the other containing the remaining components.

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2.4.2 Isotope ratio determination

For the isotope ratio determination each fraction was analysed on a Thermo Finnigan GC-C-IRMS/MS system (Trace GC II; combustion Interface III; DeltaV IRMS and DSQ II) system using a CP-PorabondQ column (Varian, 25 m, 250 µm i.d.) for final separation of the analytes. Again, 20% of the sample were directed to a Quadrupole mass spectrometer (Thermo Finnigan DSQ II) for monitoring the peak purity. The remaining 80% were directed to a commercial combustion interface (GC-combustion interface III; Thermo Finnigan) converting the analytes to CO_2. Water was further removed by a Nafion dryer and about 0.5 mL min^{-1}. of the flow were transferred to an DeltaV isotope ratio mass spectrometer via an open split.

Prior to sample analysis, the performance of the IRMS was evaluated by repeated injections of a certified CO_2 reference gas (Air Liquide, Germany, -26.8 ± 0.2‰) via an open split. The Scott TOC EPA 15/17 standard was used as a daily working standard to monitor the repeatability. Results are only reported for peaks that met the following quality criteria: (i) peak purity better than 90% (ii) peak separation better than 90% valley.

All isotope values are reported relative to the Vienna Pee Dee Belemnite (VPDB) scale and within the lab uncertainties, unless otherwise stated, are reported on the 1σ level.

2.4.3 Identification, quantification and purity control of VOCs

The analytes were identified by comparison of their retention time and mass spectra with known standards. Further compounds were identified by comparison of the obtained mass spectra with the Nist mass spectral database version 2.0. Primary quantification was done on the Agilent system used for pre-separation against the Scotty TOC EPA 15/17 standard. Compounds quantified against a standard were quantified on the IRMS via the CO_2 intensities against chloromethane and bromomethane as internal standards. The overall uncertainty of this procedure is estimated to ±15% on the 1σ level.

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3 Results and discussion

3.1 Trapping and desorption efficiency of the sampling system

The trapping and desorption efficiency was tested for the entire sampling procedure on a 0.2 nmole level by injecting 5 mL of the Scott TOC EPA 15/17 and 50 µL of the iodomethane standard into a stream of nitrogen and pre-concentrating the analytes on the cryo trap at a flow of 5 L min^{-1} for 100 min (total volume 500 L). Extraction was done as described above and the recovery rates were calculated against direct injections of the standard mixture onto the Agilent GC-MS system used for pre-separation and quantification.

The results of these tests are given in Table 1. The recovery rates for the entire sampling procedure averaged 97.8% (range from 87% to 110%) and the reproducibility ranged from 1% to 7%. Our data indicate a slight decrease of the recovery rates with increasing boiling points for compounds with boiling points above 80 °C. However, there are no statistically significant differences between the recovery rates for direct injection on the adsorption tubes and those for the entire sampling process. Therefore, we conclude that no significant losses of the target analytes occur during sampling.

3.2 Reproducibility of the carbon isotope determination

3.2.1 Reproducibility versus concentration

Due to the low mixing ratios of some target compounds such as CH_3Br, CH_3I and $CHBr_3$ (usually <10 pptv), we determined the linearity and reproducibility of the carbon isotope ratios for low levels of carbon in the sub-nmole range. This was performed by injecting chloromethane and bromomethane into the GC-IRMS. The injected carbon amounts ranged from 0.02 to 20 nmol corresponding to mixing ratios between 1 and 1000 pptv for a 500 L sample. The carbon isotope ratio determination was free of a systematic bias for carbon amounts down to 0.02 nmole. Standard deviations ($n = 6$)

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for carbon amounts between 20 and 1 nmole were usually below 0.3‰. However, below 1 nmole the standard deviation increased and was 2.6‰ for chloromethane and 1.8‰ for bromomethane for 0.02 nmole each. This corroborates the study of Rudolph et al. (1997) and Redeker et al. (2007) who observed similar deviations for comparable amounts of carbon.

3.2.2 Reproducibility of the analytical system

Since the sampling procedure showed an excellent recovery of 98 ± 5%, it is expected to be free of analytical artefacts. Thus, the reproducibility of the carbon isotope ratio determination was only tested for the analytical system. The effect of the pre-separation was tested on the 0.2 nmole level with the Scott TOC EPA 15/17 standard. 5 mL of the standard were injected into the GC-MS system, pre-separated and analysed for stable carbon isotope ratios as described in Sects. 3.41 and 3.42. Results were compared to the isotope ratios obtained without pre-separation. Without pre-seperation the isotopic composition could only be determined for 7 compounds because of coelutions and peak overlaps. After pre-separation, isotope ratios for 31 compounds could be determined. The results for these compounds are displayed in Table 1.

Standard deviations ($n = 6$) ranged from 0.5‰ for propene and benzene to 2.8‰ for bromoform and generally decreased with increasing numbers of carbon atoms. The average standard deviation for C_1-compounds, C_2-compounds and C_3-compounds were 1.5‰, 1.1‰ and 0.9‰, respectively. A Mann-Whitney-U-test ($p < 0.05$) revealed usually no significant influence of the pre-separation on the carbon isotope ratios. However, a significant difference between both procedures has been observed for bromoform (direct: -38.6 ± 3.1‰; $n = 6$; pre-separation: -33.8 ± 2.8, $n = 6$; $p = 0.025$) and for 1,1-dichloroethane (direct: -24.0 ± 0‰; pre-separation: -22.3 ± 0.6, $n = 6$; $p = 0.004$).

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3.3 Ambient air samples

The carbon isotope ratios and mixing ratios of the ambient air samples as well as results from previous studies are presented in Table 2. Values are only given for compounds which could be clearly identified either by comparison with standards or by their mass spectra and which met the quality criteria outlined above. In total, we could determine carbon isotope ratios of 37 compounds with mixing ratios between 0.3 pptv for chlorobenzene and up to 1600 pptv for propane. The high amounts of hydrocarbons in urban air samples caused strongly tailing peaks in the IRMS and thus prevented the carbon isotope determination of several organohalogens. This applied for chloroethane, iodomethane, chloroform, and bromoform in all and for carbon tetrachloride and 1,1,2-trichloro-1,2,2-triflouorethane in some of the urban air samples.

3.3.1 Hydrocarbons and oxygenated VOCs

The carbon isotope ratios obtained for the hydrocarbons agree with the results of previous studies (Rudolph et al., 1997; Tsunogai et al., 1999; Redeker et al., 2007). δ^{13}C-values of the alkanes propane, butane, isobutane, pentane and isopentane ranged from −31.8‰ to −25.0‰ with individual standard deviations between 0.8‰ to 2.2‰. Except for butane that co-eluted with 1,2-dichloro-1,1,2,2-tetrafluoroethane, the compounds were well separated. The portion of 1.2-dichloro-1.1.2.2-tetrafluoroethane to the butane carbon was less than 2% in urban samples and therewith negligible. In samples from the coastal site this portion amounted to 5 to 20% and thus may have affected the carbon isotope ratio determination of butane. However, the carbon isotope ratios from both sites showed no significant differences. Even though the average mixing ratios between both sites differed by roughly one order of magnitude (urban site: 304–1620 pptv; coastal site: 11–193 pptv), we observed no significant differences in δ^{13}C-values neither between the alkanes nor between the two sites. This is in line with the small fractionation factors (1.41–3.44‰) reported for the reaction of alkanes with

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OH-radicals (Rudolph et al., 2000). Furthermore, the alkanes most likely stem from local traffic related sources at both sites and therefore obtain similar isotopic signatures.

On average, the alkene, propene and 2-butene were enriched in ^{13}C by 3.0‰ relative to the paraffins, which is conform to previous studies (Redeker et al., 2007). Propadiene and 2-butyne were even more enriched with $\delta^{13}C$-values of -18.1 ± 0.3‰ and -13.6 ± 8.2‰, respectively. Propene, the only unsaturated hydrocarbon that could be determined at both sites, showed no site specific differences in the $\delta^{13}C$ values. As the atmospheric degradation of propene by OH-radicals is assigned with a considerable fractionation factor of 11.7‰ (Rudolph et al., 2000), the lack of a site specific difference in $\delta^{13}C$ thus points towards local sources rather than towards propene transported over a long distance from urban to coastal areas.

We also could determine carbon isotope ratios of several oxygenated compounds including dimethylether (DME), furane, propanal and propenal, which were identified based on their mass-spectra. The carbon isotope ratios of the aldehydes (-25.4 ± 1.6‰) were mainly in the same range as those of the alkenes with the exception of propenal that was strongly enriched in the urban air samples (-17.2 ± 2.3‰). Furane showed $\delta^{13}C$ values of -29.0 ± 1.3‰. DME was depleted relative to the saturated hydrocarbons showing a mean $\delta^{13}C$-value of -34.1 ± 0.8‰ in the urban samples and of -37.2‰ at the coastal site.

3.3.2 Organohalogens

The mixing ratios of the long-lived CFCs and chloromethane generally felt within ±30% of the atmospheric background levels. The average carbon isotope ratios of the organohalogens covered a broad range of $\delta^{13}C$-values. Vinylchloride was strongly enriched in ^{13}C with an average $\delta^{13}C$ value of 0.5‰. In contrast, hexafluoropropene was strongly depleted in ^{13}C with average $\delta^{13}C$ value of -57.1‰.

Dichlorodifluoromethane (CFC-12): The average mixing ratios of dichlorodifluoromethane (614 ± 60 pptv for the urban site and 554 ± 87 pptv for the coastal site) showed no significant difference between the sites. The average $\delta^{13}C$ value was

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−39.6‰ with slightly enriched δ^{13}C values at the urban site (coastal site: −41.2 ± 0.2‰; urban site: −37.9 ± 1.1‰). Our data are in the range reported by Redeker et al. (2007), who gave an average δ^{13}C value of −37.1 ± 3.9‰ from a coastal and an urban area in Ireland, but are depleted in comparison to those reported by Mead et al. (2008) from Bristol, UK (−33.5 ± 0.8‰).

Chloromethane: Chloromethane mixing ratios were 524 ± 36 pptv for the urban and 620 ± 30 pptv for the coastal site. The δ^{13}C value average over both sites was −38.0 ± 4.1‰ ($n = 7$) with a slight difference between the urban (−39.9 ± 1.9‰) and the coastal site (−36.2 ± 0.7‰). The values mirror previously published results. Tsunogai (1999) and co-workers reported an average δ^{13}C of −36‰ for the marine background in the subtropical Pacific. Thompson et al. (2002) determined an average δ^{13}C value of −36.4 ± 1.6‰ from a remote site in the arctic (Alert, Canada). Slightly more depleted values of −39 ± 2.3‰ were reported by Redeker et al. (2007) from Belfast, Ireland.

Bromomethane: The δ^{13}C-values of bromomethane in the urban samples were −41.5 ± 3.3‰ ($n = 4$) being in excellent agreement with the only previous reported values of −43.0 ± 1.7‰ from a suburban site in Berkely, USA (Bill et al., 2004). At the coastal site the δ^{13}C-values averaged −31.0 ± 0.3‰. This isotopic enrichment by 10‰ is accompanied by a decrease of the average mixing ratios from 10 ± 3 pptv at the urban site to 7 ± 1 pptv at the coastal site. However this difference in the mixing ratios is mainly driven by one urban sample showing an elevated mixing ratio and thus we cannot state a systematic relation between the carbon isotope ratios and the mixing ratios.

Iodomethane: Iodomethane coeluted with carbon disulfide, dichloromethane and propenal. Although the mixing ratios in all samples were generally sufficient for the carbon isotope ratio determination we were only able to determine carbon isotope ratios of iodomethane in the coastal samples after a careful adjustment of the time intervals for the fractionation of the samples.

Iodomethane belongs to the few compounds revealing a strong within site variation of the carbon isotope ratios. For the three coastal samples determined, δ^{13}C values

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were −79.8‰, −40.4‰, and −40.8‰. Given the respective mixing ratios of 1.9, 1.0 and 4.9 pptv no clear relation between variations of the δ^{13}C values and of mixing ratios becomes evident. Iodomethane has a relative short atmospheric lifetime of only a few days (Harper and Hamilton, 2003). Therefore both, the mixing ratios and the carbon isotope values, more likely provide a snapshot than an integrated signal, which may explain the lack of any correlation. There are no literature data on carbon isotope ratios of atmospheric iodomethane available to compare with. But own unpublished data from incubation experiments and greenhouse experiments revealed δ^{13}C values of −47 ± 11‰ for iodomethane emitted from different halophytes which correspond with the more enriched atmospheric values in our study. The strongly depleted δ^{13}C value was determined in air masses coming from the open North Sea while the more enriched δ^{13}C values were determined in more coastal influenced air masses. A potential important source in open oceans currently under discussion is the photolytic formation of iodomethane in the sea surface layer (Moore and Zafirou, 1994). Nevertheless, we can currently not substantiate the reasons for the observed large within site variation of the carbon isotope ratios.

Bromoform: A reliable determination of bromoform δ^{13}C values was only possible in the coastal samples. In the urban air samples the determination was hampered by co-eluting C8 hydrocarbons. The average δ^{13}C values of bromoform in the coastal samples was −18.3 ± 4.6‰ (−22.9‰, −13.8‰ and −18.2‰). The isotope ratios reported here were corrected for the isotopic shift observed for the standard (see Sect. 4.2.2). Due to this correction we estimated the overall reproducibility for the δ^{13}C determination of bromoform to ±4.1‰ on the 1σ level. This is close to the natural variability in these samples and it thus remains unresolved weather the variability of the δ^{13}C values for bromoform reflects the natural variability or simply the analytical uncertainty. As for iodomethane, there are no literature data available on the isotopic composition of atmospheric bromoform. However, similar isotope ratios were reported for bromoform produced in incubation experiments by the brown algae *Fucus serratus* (δ^{13}C of −15‰) and the planktonic algae *Dunaliella tertiolecta* (δ^{13}C of −24‰) (Auer et al.,

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2006). In the same study the $\delta^{13}C$ value of dissolved bromoform in a sea water sample from the Baltic Sea was determined to −28‰.

Chloroethane: $\delta^{13}C$ values of chloroethane could only be determined in the samples from the coastal site. In the urban air samples the tailing of the butane peak impeded a reliable carbon isotope ratio determination of this compound. Average mixing ratios were 2.0 ± 0.7 pptv and the $\delta^{13}C$ values (−36.5 ± 1.7‰) were comparable to those of chloromethane.

Vinyl chloride: Vinyl chloride was only detectable in the urban air samples with mixing ratios of 5.3 ± 3.5 pptv. With an average $\delta^{13}C$ value of −0.5 ± 2.1‰ it was strongly enriched in ^{13}C as compared to the other chlorinated compounds. To the best of our knowledge, no isotopic data for atmospheric vinylchloride are so far published. Based on our reference standard one might assume a $\delta^{13}C$ value of −30.1‰ for industrially produced vinyl chloride. In the atmosphere, vinylchloride is rapidly degraded mainly by OH-radicals. The fractionation factor (ε) of this reaction has not been determined yet. As the OH-radical attacks the double bound it may be in the same order as the ε of 11.4‰ reported for the atmospheric degradation of propene by OH-radicals (Rudolph, 2000). In addition, incubation experiments with different soils indicate a large ε of 21.5 to 26.0‰ for the microbial degradation of vinylchloride in soils (Bloom et al., 2000). Thus, this extraordinary high $\delta^{13}C$ value of vinylchloride may result from its rapid atmospheric degradation and/or evasion of isotopically enriched vinylchloride from sources such as landfills.

Chloroform: Chloroform stable isotope ratios could only be determined in the coastal samples due to strong chromatographic interferences from 2-methyl-1-butene in the urban samples. $\delta^{13}C$ values analysed were −33.8‰, −33.1‰ and −44.8‰. The relative enriched isotope ratios were observed in air masses from the North and North East respectively while the depleted ^{13}C value of −44.8‰ was observed in westerly air masses that passed along the Dutch and the German coast. It is noteworthy that this depletion in ^{13}C for chloroform occurred not in the same sample as the depletion in ^{13}C for iodomethane. This depletion in ^{13}C is surprising as it was not accompanied by

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significant differences in the mixing ratios (10.0 ± 2.1 pptv, $n = 3$). Anyhow the mixing ratios found here for chloroform were by almost two orders of magnitude lower than those reported by Redeker et al. (2007) but the carbon isotope ratios found here fell into the range of -37.4 ± 6.4‰ given for chloroform in that study. In contrast, the carbon isotope ratios reported for chloroform by Mead et al. (2008) were on average more than 10‰ enriched in ^{13}C.

Carbontetrachloride: The average found $\delta^{13}C$ value of carbontetrachloride was -28.9 ± 1.9‰ ($n = 3$) and average mixing ratios were 104 ± 8 for the coastal site. This agrees well with the results of Mead et al. (2008) who reported an average $\delta^{13}C$ value of -27.1 ± 1.2‰. The average mixing ratio of carbontetrachloride in the urban samples was 92 ± 25 pptv with a mean $\delta^{13}C$ value of -36.5 ± 5.3‰. The isotopic signal in the urban air samples might be influenced by incomplete recovery of carbontetrachloride in the target fraction (85 and 90%) and thus has to be taken with great care.

Chlorodifluoromethane: In contrast to dichlorodifluoromethane, chlorodifluoromethane was significantly depleted in ^{13}C at the urban site ($\delta^{13}C$ of -53.2 ± 4.6‰) as compared to the coastal site (-44.2 ± 3.3‰). Our values from the coastal site resemble those reported in the study of Redeker et al. (2007) who provided an average $\delta^{13}C$ value of -42.9 ± 5.6‰ for Belfast (Ireland). More enriched $\delta^{13}C$ values of -33.9 ± 1.0‰, have been reported from Bristol, UK. (Mead et al., 2009). Interestingly, Redeker et al. (2007) observed a slight although statistically not significant enrichment of ^{13}C for chlorodifluoromethane in northerly air masses as compared to westerly air masses and air masses from Europe.

Trichlorofluoromethane: The isotope ratios of trichlorodifluoromethane were -29.5 ± 5.3‰ for the urban site and -31.5 ± 2.6‰ for the coastal site. As for dichlorodifluoromethane, no significant differences in $\delta^{13}C$ between the sites were observed. Our values corroborate the results of Redecker et al. (2007) who gave an average $\delta^{13}C$ value of -27.3 ± 4.4‰.

1-Chloro-1,1,difluoroethane (HFC-142b): The average $\delta^{13}C$ value for 1-chloro-1,1,difluoroethane was -24.6 ± 2.8‰ without any significant difference between the

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both sites.

Pentafluoroethane, norflurane and bromotrifluoromethane: Unusually ^{13}C enriched carbon isotope ratios were observed for pentafluoroethane (16.5 ± 5.3‰) and norflurane (4.3 ± 3.3‰). A thorough reanalysis of these data revealed interferences on the *m/z* 45 and *m/z* 46 signal. As both compounds elute shortly after carbonylsulfide in an interval where the *m/z* 46/44 ratio is still affected by sulphur, we presume these interferences to result from the formation of fluoro-sulfur-compounds in the combustion interface or in the ion source. This is further supported by the carbon isotope ratio measurements of bromotrifluoromethane ($CBrF_3$). Interestingly, we observed the opposite effect for bromotrifluoromethane, eluting 15.3 s after carbonylsulfide. In the urban air samples it was recollected in the same fraction as carbonylsulfide and yielded an average $\delta^{13}C$ value of −86.0 ± 0.4‰. Again a reanalysis of our data revealed substantial interferences on the *m/z* 45 and *m/z* 46 signal For the coastal samples, where $CBrF_3$ and carbonylsulfide were recollected in different fractions, we obtained an average $\delta^{13}C$ value of −39.1 ± 10.0‰. and found no indication for interferences. As $CBrF_3$ has an average atmospheric lifetime of 65 years and the mixing ratios for both sites were comparable (3.7 ± 0.2 pptv) this huge discrepancy is rather due to the analytical interferences than to atmospheric degradation or source-related processes.

3.3.3 Variability of the carbon isotope ratios

Our data reveal considerable isotopic differences between the urban and the coastal sampling site for several compounds. A pronounced enrichment in ^{13}C was observed for 1,1-dichloro-1-fluoroethane (10.0‰) and propenal (7.6‰) in urban samples. The mixing ratios of both compounds were significantly elevated at the coastal site as compared to the urban site (22.6 pptv versus 8.0 pptv and 96 pptv versus 6 pptv) pointing towards a strong coastal or marine source. In contrast, a pronounced enrichment in ^{13}C was observed for bromomethane (10.5‰), chlorodifluoromethane (9.0‰), and 1,1,1-triflouroethane (6.7‰) in coastal samples. Concurrently, chloromethane and 1,1,2-trichloro-1,2,2-trifluoroethane were less enriched (3.6‰ and 4.0‰, respectively).

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The 72 h backward trajectories indicate a prevailing marine and coastal influence for the samples taken at Sylt and a prevailing continental influence for the samples taken at Hamburg. The comparison of our data with those reported by Redeker et al. (2007) from Belfast (marine influenced) provide further indication for an isotopic enrichment of these compounds in marine and/or remote air masses. A slight enrichment of chloromethane by 3‰ to 4‰ at urban and rural sites compared to marine and remote sites correspond to previous studies (Goldstein and Shaw, 2003, and references therein; Redeker et al., 2007). Although statistically not significant, the data of Redeker et al. (2007) indicated a small enrichment for chlorodifluoromethane in air masses from the North Atlantic (-39.6 ± 5.6‰) as compared to air masses from western Europe (-42.5 ± 5.2‰). As mentioned before, our data from the coastal station (-44.2 ± 3.3‰) resemble the latter. In contrast, our data from the urban site are enriched by 9.0‰.

These enrichments in ^{13}C at the coastal site were not accompanied by a significant decrease of the mixing ratios which would point towards an enhanced degradation in the marine boundary layer e.g. due to reactions with chlorine radicals. Therefore, we suppose atmospheric degradation processes not to be the decisive factor for these differences. This also holds true for bromomethane, as the elevated average mixing ratio at the urban site is caused by only one single measurement. We assume these isotopic differences are caused by the air sea exchange of these compounds in concert with partial degradation in surface oceans altering the isotopic signatures. Bromomethane from both, intrinsic sources and from the atmosphere, is known to be rapidly degraded in marine surface waters by biotic and abiotic processes with overall degradation rates of up to 20% per day (King and Saltzman, 1997, and references therein). The abiotic degradation due to hydrolysis and transhalogenation is assigned with a large ε of 69 ± 8‰ (King and Saltzman, 1997) and the degradation of bromomethane by methylotrophic bacteria is assigned with an ε of 45 ± 10‰ (Miller et al., 2001). Simultaneously, bromomethane is produced in the surface water. Although the isotopic composition of the intrinsic bromomethane is unknown, it appears reasonable to presume the bromomethane emitted back into the atmosphere to be isotopically enriched

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considering its rapid degradation and the exceptional strong isotopic fractionation of this process.

4 Conclusions

In this study a simple and field suitable cryogenic sampling system for subsequent determination of carbon isotope ratios of a wide range of VOCs was developed. The dry shipper has shown to be a suitable and easy-to-use cooling source that can replace conventional dewars or cryostats in various applications. Up to 30 samples can be taken over a period of two weeks without the need of any technical infrastructure allowing for sampling campaigns in remote areas. Recovery rates for the entire sampling procedure ranged from 92 to 105% with low standard deviations. The overall reproducibility (1σ) for carbon isotope determination on the 0.2 nmole level ranged from 0.5‰ to 2.8‰. With a sampling volume of 500 L, carbon isotope ratios of compounds with typical mixing ratios between 1 and 10 pptv can be determined with a precision better than 2‰. Nevertheless, the determination of these compounds in urban air masses is often hampered by high loads of hydrocarbons.

We reported isotope ratios for a broad range of VOCs in urban and marine air in Northern Germany. Several compounds have not yet been analyzed for their isotopic composition. For the organohalogens having been measured in previous studies the carbon isotope ratios found here are consistent with those previously reported.

The $\delta^{13}C$ values for bromomethane from the urban site of -41.5 ± 3.3‰ are in excellent agreement with those reported by Bill et al. (2004). In contrast, bromomethane $\delta^{13}C$ values were enriched in ^{13}C by about 10‰ in the coastal samples. A similar but less pronounced trend was observed for trichloroethane, chlorodifluoromethane, 1-chloro-1,1difluoroethane and chloromethane. We hypothesize that these differences are related to atmosphere-ocean exchange with fractionating biotic and abiotic degradation processes in the surface ocean and suggest carbon isotope ratio determination as a promising tool for better constraining the role of the ocean in the global cycle of these compounds.

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Acknowledgements. The authors of this article would like to thank the BMBF for funding this work within the framework of Sopran (BMBF grant 03F0611E) We also gratefully acknowledge the support of Justus van Beusekom from the AWI Wadden Sea Station in Sylt during the sampling and the support of our the technical staff members Ralf Lendt, Sabine Beckmann and Peggy Bartsch.

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Table 1. Comparison of the carbon isotope ratios obtained with and without pre-separation for the Scott Speciality Gases TOC 15/17 standard and recovery rates for a sampling volume of 500 L. Results are only given for compounds that were free of interferences from other compounds.

			After pre-seperation							Direct injection			
Compound	CAS =	RT =	Recovery			δ13C				δ13C			
		[s]	mean [%]	±	σ	mean [‰]	±	σ	n	mean [‰]	±	σ	n
Propene	115-07-1	743	93	±	5	−27.9	±	0.5	6				
Chloromethane	74-87-3	744	109	±	3	−61.3	±	1.9	6				
Methanol	67-56-1	790				−39.6	±	1.8	6				
Dichlorodifluoromethane	75-71-8	908	101	±	2	−31.0	±	1.9	6				
Vinylchloride	75-01-04	1026	107	±	2	−30.2	±	1.0	6				
Bromomethane	74-83-9	1096	92	±	7	−61.7	±	1.8	6	−63.6	±	0.8	6
Chloroethane	75-00-3	1196	102	±	3	−30.9	±	0.9	6				
1,2-dichloro-1,1,2,2-tetrafluoroethane	76-14-2	1243				−27.0	±	0.8	6				
Iodomethane	74-88-4	1548	106	±	6	−66.8	±	1.4	6				
Trichlorofluoromethane	75-69-4	1608	98	±	5	−17.0	±	1.4	6				
1,2 Dichloroethene trans	156-60-5	1763	100	±	4	−21.2	±	0.9	6	−21.5	±	1.0	6
1,2 Dichloroethene cis	156-59-2	1884	101	±	4	−20.9	±	1.1	6				
1,1 Dichloroethene	75-35-4	1628	98	±	4	−29.1	±	6.6	6				
1,1 Dichloroethane	75-34-3	1901	99	±	5	−22.3	±	0.6	6	−24.0	±	0.4	6
1,1,2 trichloro- 1,2,2 trifluoroethane	76-13-1	1963	100	±	3	−24.1	±	1.3	6				
Chloroform	67-66-3	1986	100	±	5	−44.3	±	1.6	6	−45.1	±	1.1	6
1,2 Dichloroethane	107-06-2	2094	97	±	4	−26.8	±	0.7	6				
Benzene	71-73-2	2216	97	±	2	−26.8	±	0.5	6				
Carbontetrachloride	56-23-5	2225	96	±	1	−41.1	±	1.1	6				
Hexane	110-54-3	2249				−29.9	±	0.9	6				
Trichloroethene	79-01-06	2252	96	±	2	−39.6	±	0.8	6				
Bromodichloromethane	75-27-4	2295	98	±	2	−50.1	±	0.8	6	−48.6	±	0.5	6
Cyclohexane	110-82-7	2297	93	±	3	−27.3	±	0.6	6				
1,1,2 Trichloroethene	79-00-5	2536	95	±	2	−29.2	±	1.1	6				
Dibromochloromethane	124-48-1	2584	90	±	2	−44.3	±	1.4	6				
1,2 Dibromoethane	106-93-4	2613	92	±	2	−21.2	±	2.5	6				
Heptane	142-82-5	2623	98	±	2	−26.5	±	1.4	6				
Chlorobenzene	108-90-7	2777	93	±	2	−26.4	±	1.1	6				
Bromoform	75-25-2	2856	87	±	4	−33.8	±	2.8	6	−38.6	±	3.1	6
Ethylbenzene	100-41-4	3001	85	±	3	−27.7	±	0.8	6				

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Table 2. Averaged concentrations and isotopic values for all compounds reported in this paper from the coastal and the urban sampling site.

Compound	CAS =	RT = [s]	Coastal site mixing ratio mean ±σ [pptv]	Coastal site $\delta^{13}C$ mean ±σ [‰]	n	Urban site mixing ratio mean ±σ [pptv]	Urban site $\delta^{13}C$ mean ±σ [‰]	n	Other studies mean ±σ
1.1.1 Trifluoroethane*	420-46-2	546	12 ± 0.3	−29.0 ± 1.3	2	13.1 ± 0.4	−35.7 ± 5.3	3	–
Bromotrifluoromethane*	75-63-8	610	3.7 ± 0.2	−39.1 ± 10.3	2				–
Hexafluoropropene*	116-15-4	687	1.2 ± 0.1	−57.1 ± 1.9	2				–
Chlorodifluoromethane	75-45-6	703	231 ± 26	−44.2 ± 3,27	3	222.0 ± 25	−53.2 ± 4.6	3	−42.9 ± 5.6[b]; -33.9 ± 1.0[c]
Propene	115-07-1	743	61 ± 33	−26.3 ± 1.0	3	73 ± 21	−24.3 ± 2.1	3	25.0 ± 2.5[b]; −21.6 ± 4.0[e]
Chloromethane	74-87-3	744	620 ± 30	−36.2 ± 0.7	3	524 ± 36	−39.9 ± 1.9	3	−36.2 ± 0.3[a]; −39.0 ± 2.3[b]; −29 to −45[c]; −37.4[h]
Propane*	74-98-6	819	193 ± 75	−28.1 ± 0.8	3	1615 ± 413	−29.4 ± 1.3	3	−29.8 ± 1.3[b]; −27.1 ± 1.5[e]
Propadiene*	463-49-0	831				10.6 ± 4.1	−18.1 ± 0.3	2	–
Cyclopropane*	75-19-4	834	16 ± 3	−24.9 ± 0.2	2				–
Dimethylether*	115-10-6	893	10.0 ± 8	−36.5 ± 1.9	3	87 ± 36	−34.1 ± 0.8	3	–
Dichlorodifluoromethane	75-78-1	908	554 ± 88	−41.2 ± 0.2	3	614 ± 60	−37.9 ± 1.1	3	−37.2 ± 3.9[b]; −33.5 ± 0.8[c]
Vinylchloride	75-01-4	1026				5.3 ± 3.5	−0.5 ± 2.1	2	–
Bromomethane	74-83-9	1096	7.0 ± 1	−31.0 ± 0.3	3	10.0 ± 3.0	−41.5 ± 3.3	3	−43.0 ± 1.7[f]
1-Chloro-1.1-difluoroethane*	75-68-3	1112	25 ± 2	−24.6 ± 0.1	3	27.3 ± 1.3	−23.5 ± 3.2	3	–
Isobutane*	75-28-5	1171	15 ± 8	−29.4 ± 1.8	3	503 ± 167	−28.2 ± 1.1	3	−29.0 ± 1.2[b]
Chloroethane	75-00-3	1196	2.0 ± 0.7	−36.5 ± 1.7	3				–
Butane*	106-97-8	1243	52 ± 23	−28.3 ± 0.9	3	304 ± 109	−28.0 ± 1.8	3	−28.5 ± 1.1[b]; −28.5 ± 1.7[e]
Propenal*	107-02-8	1319	96 ± 140	−24.6 ± 1.5	3	6.1 ± 2.7	−17.2 ± 2.3	3	–
Propene-methyl*	115-11-7	1336	186 ± 99	−25.5 ± 2.1	3				21.4 ± 3.7[b]
Furane*	110-009	1350	2.1 ± 0.4	−29.3 ± 1.8	3				–
Propanal*	123-38-6	1358	242 ± 86	−24.3 ± 1.8	3				−26.2 ± 2.4[g]
Iodomethane	74-88-4	1377	2.6 ± 2.1	−53.6 ± 22.6	3				–
2-Butene cis	519-18-1	1570	138 ± 31	−25.5 ± 2.1	3				−25.9 ± 4.9[b]; −24.5 ± 6.5[e]
Trichlorfluoromethane	75-69-4	1608	277 ± 14	−31.5 ± 2.6	3	283.0 ± 26	−29.5 ± 5.3	3	−27.3 ± 4.4[b]
1.1-Dichloro-1-flouorethane*	1717-00-6	1646	22 ± 5	−25.7 ± 3.8	3	8.0 ± 0.9	−15.7 ± 2.9	3	–
Isopentane*	78-78-4	1694	32 ± 22	−29.5 ± 1.6		680 ± 210	−31.7 ± 1.2	3	−28.0 ± 1.9[b]
2-Butyne*	503-17-3	1736				0.4 ± 0.2	−13.6 ± 8.2	2	−21.7 ± 4.2[b]
Pentane*	109-66-0	1737	20 ± 10	−31.0 ± 1.2	3	530 ± 100	−28.3 ± 1.4	3	−27.4 ± 2.2[b]; −27.7 ± 1.3[e]
1.1.2-Trichloro-1.2.2-Triflouroethane	76-13-1	1963	69 ± 37	−25.4 ± 1.1	3	72 ± 21	−29.3 ± 4.7	2	−23.3 ± 9.6[a]; −28.1 ± 4.6[b]
Chloroform	67-66-3	1968	10.0 ± 2.1	−37.2 ± 6.5	3				−37.4 ± 6.4[b]; −22.5 ± 1.7[c]
Carbontetrachloride	56-23-5	2225	104 ± 0	−28.9 ± 1.9	3	92 ± 25	−36.5 ± 5.3	2	−27.1 ± 1.2[c]
1.2-Dichloropropane	78-87-5	2396	1.1	−29.5	1				–
Trichloroethene	79-01-06	2536				44	−34.4	1	−18.1 ± 9.1[c]
Toluene	108-88-3	2660	34 ± 16	−26.8 ± 0.6	3				−25.0 ± 1.1
Chlorobenzene	108-90-7	2777	0.3 ± 0.1	−26.9 ± 6.8	2				–
Bromoform	75-25-2	2856	2.4 ± 0.5	−18.3 ± 4.6	3				–

* Mixing ratios have been calculated from the CO_2 intensities on the IRMS against chloromethane and bromomethane as internal standards.
[a] Thompson et al. (2002); [b] Redeker et al. (2007); [c] Mead et al. (2008); [d] Tsunogai et al. (1999); [e] Rudolph et al. (2002); [f] Bill et al. (2004); [g] Giebel et al. (2010); [h] Rudolph et al. (1997)

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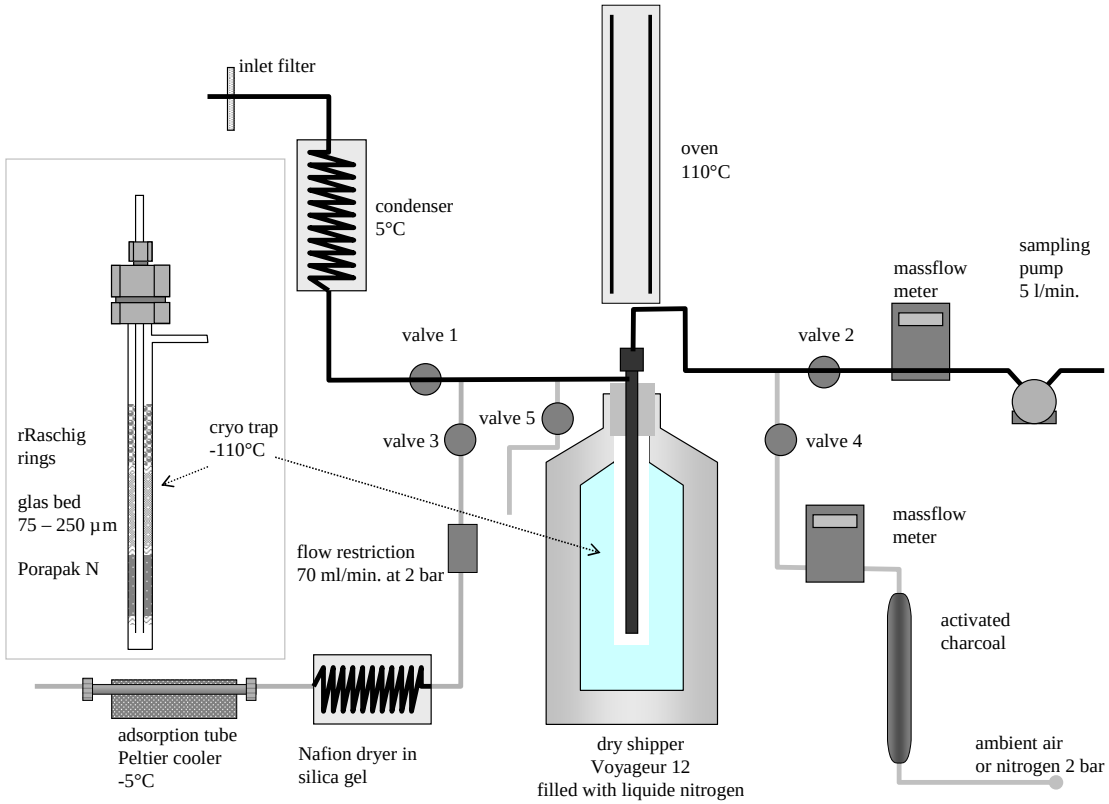

Fig. 1. Scheme of the sampling system.

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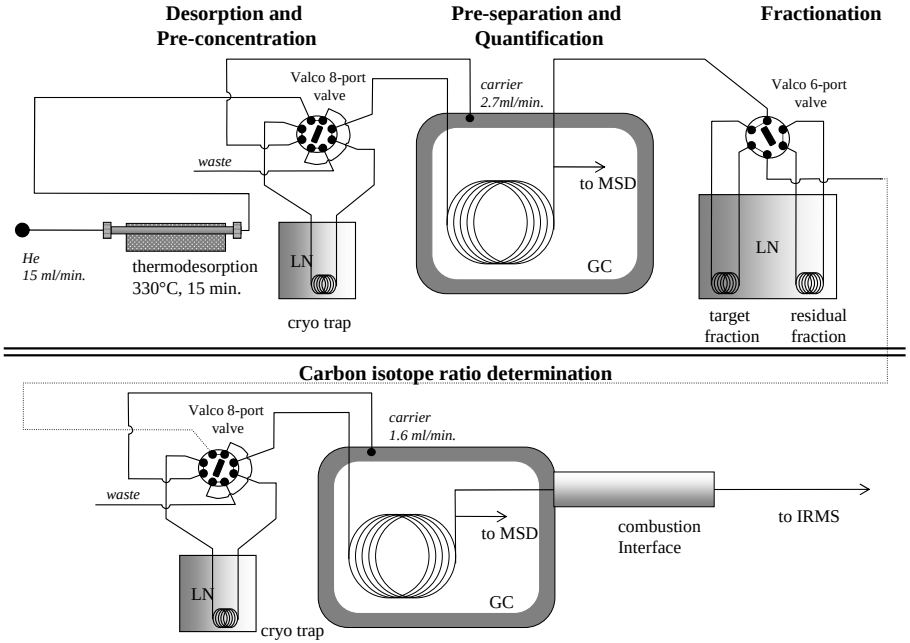

Fig. 2. Scheme of the analytical system.

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