

Stable carbon isotope analysis of selected halocarbons at parts per trillion concentration in an urban location

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Environmental context. Halocarbons can have significant effects on the atmosphere and the environment, particularly with regard to ozone depletion and climate change impacts. The determination of isotopic concentrations for selected halocarbon species should provide useful information to identify and constrain halocarbon sources and sinks within the urban environment. In the present study, a new instrumental method is described to determine these isotope ratios for selected halocarbons and the resultant data are interpreted in terms of local sources and sinks.

Abstract. $\delta^{13}\text{C}$ values of a suite of halocarbons have been determined in an urban background site in Bristol, UK. A novel mobile preconcentration system, based on the use of multi-adsorbent sample tubes, has been developed for trapping relatively large-volume air samples in potentially remote areas. An Adsorption Desorption System–Gas Chromatography–Electron Capture Detector was used to measure the mixing ratios of the selected halocarbon species, while a Gas Chromatography–Combustion–Isotope Ratio Mass Spectrometer was used to determine $\delta^{13}\text{C}$ values. For the species with strong local sources, the variation of isotope ratios has been observed over the experimental period. Some of the results reported in the present study differ from previously reported values and reasons for this are discussed. The reporting of different $\delta^{13}\text{C}$ values for selected halocarbons from different areas in the present study suggests that $\delta^{13}\text{C}$ values may be used to determine the relative magnitudes of anthropogenic and biogenic sources.

Additional keywords: Adsorption Desorption System (ADS), Automated Thermal Desorber (ATD), Electron Capture Detector (ECD), Gas Chromatography (GC), Isotope Ratio Mass Spectrometry (IRMS).

Introduction

Atmospheric halocarbons including chlorofluorocarbons (CFCs), hydrochlorofluorocarbon (HCFCs), methyl halides (CH_3X ; X = Cl, Br or I), dichloromethane (CH_2Cl_2), chloroform (CHCl_3), perchloroethylene (PCE, C_2Cl_4) and trichloroethylene (TCE, C_2HCl_3) show a significant effect on the atmosphere and the environment by depleting the stratospheric ozone layer^[1,2] and by changing the climate in the troposphere.^[3] Despite research into the sources, sinks and distributions of halogenated species (both anthropogenic and biogenic), many uncertainties still persist. Recently, several studies have been undertaken to investigate various aspects of the carbon isotope composition of several halocarbons and hydrocarbons in the environment.^[4–9] Variations in the carbon isotope composition of certain compounds have been used to investigate biogeochemical cycles and global source–sink relationships and their underlying mechanisms.^[10–13] Carbon isotope ratio mass spectrometry has also been used to define relative levels of contribution from specific reservoirs to the atmospheric budget for CO_2 ,^[14] CH_4 ,^[15] CO ^[16] and N_2O .^[17] The use of $\delta^{13}\text{C}$ values has also been suggested as one further possible tool for the constraint of budgets for species such as CH_3Cl ,^[5,18] CH_3Br .^[5] Any patterns in variation, such as diurnal shifts, may also help to broadly differentiate between anthropogenic and biogenic

or abiotic sources. Although there is major uncertainty in the budget of many halocarbons, little work to date has been undertaken into the determination of $\delta^{13}\text{C}$ values of these compounds. Atmospheric trace halocarbons typically reside at concentrations between 1 and 600 parts per trillion (ppt). However, for measurements at such low concentrations, it is necessary to use sample preconcentration techniques. In the present study, a preconcentration system suitable for large-volume sample collection was deployed in the Bristol urban area.^[19] A new instrumental method is described that enables the application of Automated Thermal Desorber–Gas Chromatography–Combustion–Isotope Ratio Mass Spectrometry (ATD-GC-C-IRMS) to the isotope ratio measurement of selected halocarbons at ppt concentrations. Here we present $\delta^{13}\text{C}$ values and mixing ratios of selected halocarbons from an urban background site in the city of Bristol, UK, generated using ATD-GC-C-IRMS and Adsorption Desorption System–Gas Chromatography–Electron Capture Detector (ADS-GC-ECD) systems in tandem.

Experimental

Sampling methodology

The mixing ratios and carbon isotope values of a suite of halocarbons were measured at an urban background site in the

Bristol area during March 2005. The sampling site was ~3–5 km (~2–3 miles) from the nearest known natural and anthropogenic sources (e.g. Severn Estuary and Avonmouth docks to the west and various small industrial sources around the city and its environs). For measuring the carbon isotope ratios of halocarbons, samples were collected using a preconcentration unit primarily composed of a 16-port valve (Valco Instruments Inc., Houston, TX, USA), pump (KNF Neuberger, Germany, P_{\max} 150 kPa (1.5 bar)), mass flow controller (Unit 7000 Industrial MFC, Unit Instruments Ltd, Dublin, Ireland), in-line filter (7 μm), temperature sensor (0–50°C), Nafion dryer system (with a 5-Å molecular sieve as a ‘counter-purge’ drying agent rather than a dry nitrogen gas flow) and a computer with microprocessor based electronics (Arcom, Cambridge, UK; software: Reef Technology Ltd., Hampshire, UK); Swagelok fittings were used throughout (Swagelok Co., Cleveland, OH, USA). The preconcentration unit was designed to be run from a suite of electronics that can be preprogrammed before sampling. Each program was made up of a series of events (a valve position change or a flow-rate change) and a start time and date. The program was started automatically when the system had been set to run.

By using the preconcentration unit, the air samples were collected in each of the 16 multi-bed adsorbent tubes (Carbograph 1TD-Carboxen 1000-Carbosieve SIII, Markes International Ltd., Pontyclun, UK) at a flow rate of 100 mL min⁻¹ for 30 min. The preconcentration unit also took four samples from a standard canister. Two were taken before air sampling and two were taken directly after. The methodology was adapted so that trends in urban background concentrations for key species could have $\delta^{13}\text{C}$ values assigned to them over a 1-day period. This period was chosen to satisfy the limited time available for use of the GC-C-IRMS apparatus while still being of suitable length for possible variations in the urban background to be recorded and analysed.

As tube samples were being taken in the preconcentration unit, the ADS-GC-ECD system was operated concurrently for measuring the mixing ratios of selected halocarbons using a modified sequence program. The ADS, which is interfaced with the GC-ECD system through a transfer line, incorporates all of the electrically actuated valves, mass flow controllers, air sampling pump, microtrap, Peltier unit and ancillary electronics and software to enable analysis of standard and air samples. The ADS system was set up to run a standard and then an air sample in a cycle of 20 repetitions. A modified time-scale was used so that air samples were acquired simultaneously on the ADS and preconcentration unit. Air samples for both the ADS and the preconcentration unit were taken from the same sample line.

Halocarbon standard

The use of standards to bracket air runs allowed quantitative analysis of the air samples and the monitoring of any drift in sensitivity to be made. The standard used contained selected halocarbons in nitrous oxide (N₂O) (Linde Gas, Stoke-on-Trent, UK), diluted to near-ambient atmospheric concentrations and calibrated using a SOGE (System for Observation of Greenhouse Gases in Europe) primary standard, which is a pressurised Mace Head, Ireland, air sample, assigned trace gas concentrations in the SIO-98 scale (Scripps Institution for Oceanography-1998) for CFC-11 (CFCl₃), CFC-12 (CF₂Cl₂), CFC-113 (C₂F₃Cl₃), CHCl₃, CCl₄ and CH₃CCl₃, and the UB-98 scale (University of Bristol-1998) for all other species.^[20]

Mixing ratio measurement

A Hewlett Packard 6890 gas chromatography (Agilent Technologies UK Ltd., Cheshire, UK) equipped with an ECD was used to determine the mixing ratios of the targeted halocarbons present in the ambient background atmosphere. The sample was injected onto the GC column (CPSil-5CB, Varian-Chrompack, Palo Alto, CA, USA, 110 m × 0.32 mm internal diameter (i.d.), 5 μm dimethylpolysiloxane film thickness) after passing through an ADS, based on the design described in the previous study.^[21] The adsorbents used in the microtrap of the ADS system were 4 mg of Carboxen 1000 and 6 mg of Carboxen 1003 (Supelco Ltd., Bellefonte, CA, USA), separated by silanised glass beads (60–80 mesh, BDH chemicals, Poole, UK).

Determination of $\delta^{13}\text{C}$ values

Preconcentrated samples in sample tubes were analysed by using a Turbomatrix (Turbomatrix HS, PerkinElmer Inc. Analytical Instruments, Wellesley, MA, USA) automated thermal desorber (ATD) attached to a Varian 3400 gas chromatograph (Varian-Chrompack) coupled to a Finnigan MAT Delta S (Bremen, Germany) isotope ratio MS (IRMS; electron ionisation, 100 eV electron voltage, 1 mA electron energy, three Faraday cup collectors m/z 44, 45 and 46) via a modified Finnigan MAT Mark I combustion interface. A length of column (CPSil-5CB, Varian-Chrompack, 0.32 mm i.d., 5 μm film thickness) was used in the heated transfer line (Turbomatrix HS). One end of this column length was directly attached to the heated valve assembly in the ATD system and the other was connected to the GC column using a Supelco butt connector (Supelco-Sigma-Aldrich, St. Louis, MO, USA). The helium carrier gas used in this system was first passed through a gas-cleaning filter jacket to remove organics and water, and was then passed through a molecular sieve filter to remove any residual hydrocarbons, moisture and oxygen. The Delta S helium flow was teed to feed the Turbomatrix ATD system.

The essential parameters for the analysis method in the ATD system were selected as: tube desorption temperature of 380°C for 5 min, tube oven temperature of 150°C, transfer line temperature of 200°C, flow rate of carrier gas of 5 mL min⁻¹, cold trap desorption temperature of 300°C for 5 min. The column used was a gas-liquid WCOT (wall-coated open tubular) CPSil5-CB non-polar capillary column (Varian-Chrompack) (120 m × 0.32 mm i.d. with 5 μm film of dimethylpolysiloxane). The GC oven temperature program was set at 33°C held for 12 min followed by an increase to 160°C at a rate of 10°C min⁻¹ and held there for 30 min.

The trap on the ATD system was checked by running trap heat cycles, thereby establishing that the sample chromatograms were not affected by artefacts in the system. The multi-bed tubes exhibited no residual traces of any components at the analysis desorption temperature of 380°C^[19] precluding any sample carry-over between the consecutive runs. Previous studies have shown that traps containing Ascarite II do not alter the $\delta^{13}\text{C}$ values obtained for CH₃Cl.^[22] It has also been shown that Carbosorb traps do not significantly affect the stable carbon isotope signatures of methyl halides and CFCs.^[23] It is assumed that the isotopic signatures of the targeted halocarbons are not affected by these traps based on the prior work on different species.

Carbon isotope ratios of the analytes were internally calibrated against a reference gas containing CO₂ (chemically pure grade CO₂, BOC, Linde Gas) of known isotopic composition ($\delta^{13}\text{C} = -34.58\%$) with an instrumental precision of 0.3%.

CO₂ standards were infused directly into the ion source four times during each analysis, two times before and two times after the analytes had eluted from the GC. The high precision associated with the standard CO₂ measurement reveals that the GC-C-IRMS system itself was working correctly and that results were reproducible. This ensured that recorded isotope ratio values were not related to internal production of artefacts but were determined by the introduced sample.

The Finnigan MAT Delta S system is dedicated to stable carbon isotope ($\delta^{13}\text{C}$) analysis and features a customised combustion interface. The GC-C-IRMS separates different components in the sample according to retention time, followed by in-line combustion to form CO₂, which is then passed to an IRMS via a He stream. This allows for the determination of discrete $\delta^{13}\text{C}$ values for the target compounds. $\delta^{13}\text{C}$ values were reported relative to the Vienna Pee Dee Belemnite limestone standard (PDB). Data was acquired and processed using ThermoFinnigan *Isodat NT* software.

Table 1. Precision of the standard halocarbons by using the Adsorption Desorption System–Gas Chromatography–Electron Capture Detector (ADS-GC-ECD) and Automated Thermal Desorber–Gas Chromatography–Combustion–Isotope Ratio Mass Spectrometer (ATD-GC-C-IRMS) system

RSD, relative standard deviation. See text for compound details

	RSD (%) for mixing ratios ($n = 15$)	RSD (%) for $\delta^{13}\text{C}$ values ($n = 4$)
CFC-12	1.9	1.2
H-1211	4.4	2.1
CH ₂ Cl ₂	2.4	2.5
CHCl ₃	5.1	0.3
CCl ₄	5.0	2.7
TCE	5.4	0.4
PCE	5.5	1.6
HCFC-22	3.1	0.7

Table 2. Summary of statistics for the target halocarbons mixing ratios in ppt recorded between 1200 hours 15 March 2005 and 1500 hours 16 March 2005

For all halocarbons, $n = 14$. See text for compound details. NH, Northern Hemisphere

	CFC-12	H-1211	CH ₂ Cl ₂	CHCl ₃	CCl ₄	TCE	PCE	HCFC-22
Average	580.2	2.8	136.6	19.8	83.0	32.8	15.6	133.2
Maximum	655.5	4.6	247.0	39.2	118.3	74.0	34.5	245.4
Minimum	548.3	1.3	79.6	7.2	46.0	8.2	7.2	44.5
Standard deviation	34.8	0.7	33.2	7.0	17.6	11.2	6.7	38.8
NH background ^[24]	545.0	4.5	33.5	10.8	91.9	5.2	1.1	177.1

Table 3. Summary of statistics for the target halocarbons $\delta^{13}\text{C}$ values determined between 1200 hours 15 March 2005 and 1500 hours 16 March 2005

All values are in mL. For CH₂Cl₂, $n = 11$; for CHCl₃, $n = 13$; for other halocarbons, $n = 14$. See text for compound details

	HCFC-22	CFC-12	H-1211	CH ₂ Cl ₂	CHCl ₃	CCl ₄	TCE	PCE
Average (air)	−33.9	−33.5	−31.7	−49.7	−22.5	−27.1	−18.1	−27.4
Average (standard)	−32.2	−31.8	−34.9	−39.9	−22.7	−17.0	−9.3	−28.7
Maximum (air)	−32.8	−32.5	−28.9	−14.3	−17.6	−25.6	−7.2	−21.4
Minimum (air)	−36.3	−35.0	−35.0	−122.2	−24.4	−28.7	−35.6	−32.2
Median (air)	−33.7	−33.4	−30.9	−39.9	−22.9	−27.7	−16.1	−27.7
Standard deviation (air)	1.0	0.8	3.8	30.7	1.7	1.2	9.1	3.8
90% confidence	0.4	0.3	1.7	13.5	0.8	0.5	4.0	1.7

Results and discussion

Accuracy and precision of the analytical system

The precision of the mixing ratios and $\delta^{13}\text{C}$ determination for selected halocarbons is shown in Table 1. The reproducibilities are expressed as the relative standard deviations (RSD) and were derived from repeat analysis of the standard halocarbon samples, which were all within 5% and 3‰ for the concentrations and $\delta^{13}\text{C}$ values for the selected halocarbons, respectively. The standard halocarbon samples show that the concentrations and isotope ratio values assigned to the species in the current study had reproducible baseline values.

Concentration data

Table 2 shows the average, minimum, and maximum mixing ratios of the target halocarbons recorded from the ADS-GC-ECD system over a 26-h period (from 1200 hours 15 March 2005 to 1500 hours 16 March 2005). The average atmospheric mixing ratios of some halocarbons are higher than background values from the northern hemisphere site at Mace Head in Ireland.^[24] These elevated concentrations are most likely due to local sources. Previous study^[25] suggested that there were a large variety of potential sources and sinks in the Bristol area. Previous study (M. A. H. Khan et al., unpubl. data)^[25] also reported that CHCl₃, CH₂Cl₂, PCE and TCE concentrations in the Bristol area are elevated during low wind speed, suggesting very close local sources. The recorded average concentration of H-1211 (CF₂BrCl), HCFC-22 (CHF₂Cl) and CCl₄ values in the Bristol urban background area are lower than the Northern Hemisphere (NH) background values. The baseline data for Mace Head are derived from clean Atlantic air that has not experienced interactions with a terrestrial surface for many days at least but has been exposed to ocean surfaces. Therefore, it may be that there are losses for these compounds associated with terrestrial biomes reflected in the Bristol data. The mixing ratios for CFC-12, CHCl₃, CH₂Cl₂, PCE and TCE are relatively

Carbon isotope ratios of halocarbons

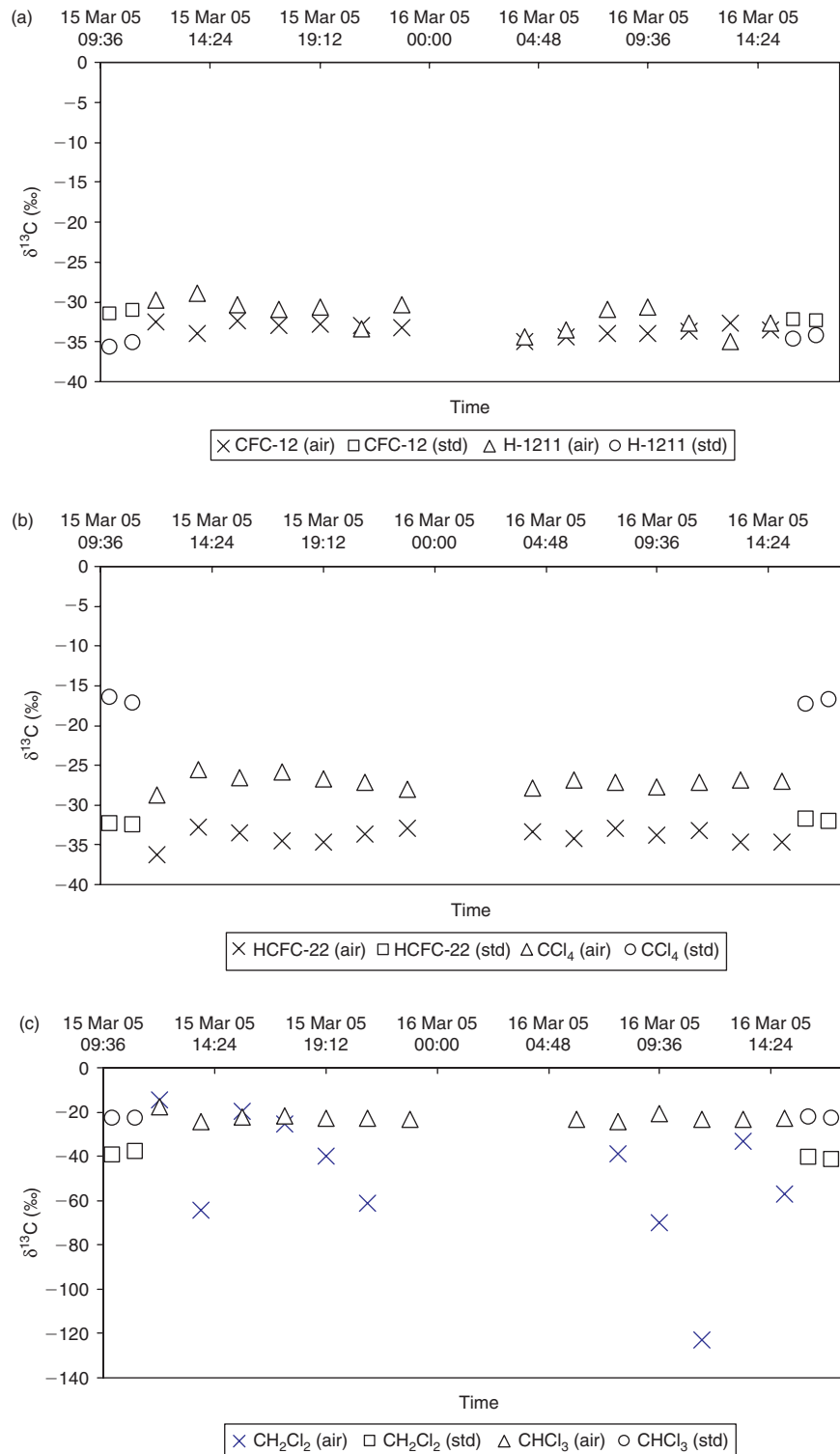


Fig. 1. Comparison of the halocarbon's $\delta^{13}\text{C}$ values between standard (std) and air sample over the time period of 1200 hours 15 March 2005 to 1500 hours 16 March 2005, (a) CFC-12 and H-1211, (b) HCFC-22 and CCl₄, (c) CH₂Cl₂ and CHCl₃, (d) TCE and PCE. (Note: Three missing data points from CH₂Cl₂ and one missing data point from CHCl₃ are the result of a calibration problem.)

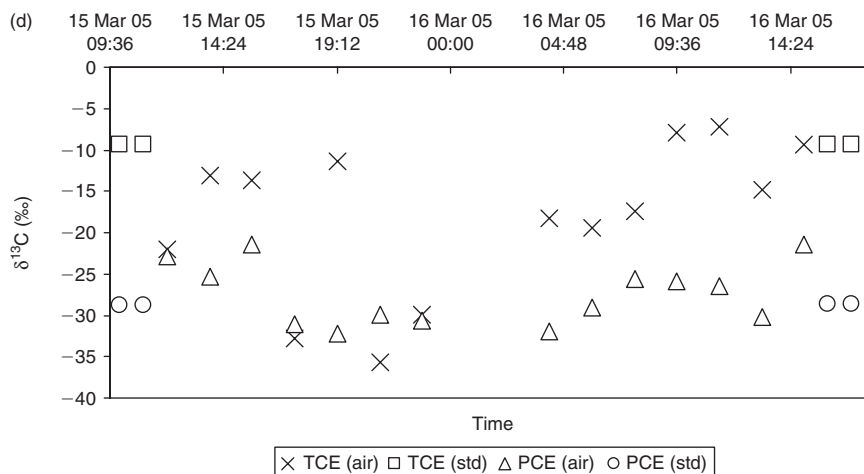


Fig. 1. (Continued)

higher in the Bristol urban site compared with the NH background site, indicating the existence of local anthropogenic and biogenic sources in the Bristol area. The elevated concentrations of biogenic halocarbons are associated with the nearby estuary and the anthropogenic halocarbons from industrial activity at Avonmouth (M. A. H. Khan et al., unpubl. data).

Carbon isotope ratio data

Table 3 shows the average, maximum and minimum $\delta^{13}\text{C}_{\text{PDB}}$ values of the target halocarbons taken using the ATD-GC-C-IRMS system from tube samples taken between 1200 hours 15 March 2005 and 1500 hours 16 March 2005. The $\delta^{13}\text{C}$ values for some of the halocarbons in the present study are less depleted than in previous studies^[22,25] owing to the different source strengths and sinks of these compounds in the Bristol area or in differences in the analytical systems used in previous studies, including the pre-concentration system. We have ruled out signal influence from the pre-concentration system because standard sample analysis gave similar peaks whether samples were injected directly into the IRMS or went through the pre-concentration system. Fig. 1 shows a comparison between the $\delta^{13}\text{C}$ values of selected halocarbons from air and standard samples *v.* time. It should be noted that the $\delta^{13}\text{C}$ values of the target halocarbons for the standard sample are less depleted than the urban background sample.

The trends of the $\delta^{13}\text{C}_{\text{PDB}}$ values for anthropogenic compounds CFC-12, HCFC-22, H-1211 and CCl_4 showed virtually no variation over the whole experiment; some of the compounds, CHCl_3 and PCE, showed some variation over the period. Notably, CH_2Cl_2 and TCE showed large variability as both have a common, local source in an industrial area where they are used as solvents. Previous study (M. A. H. Khan et al., unpubl. data) also observed a correlation between CHCl_3 and CH_2Cl_2 and suggested that they could be emitted from a nearby estuarine oceanic source. The isotopic composition of halocarbons in the atmosphere is dependent on the isotopic signature of the sources, the mixing of air from different sources and the isotopic fractionation processes during atmospheric degradation by OH or possibly degradation in soils. Comparatively, in the present study, the long-lived and entirely anthropogenic compounds CFC-12, HCFC-22, H-1211 and CCl_4 show no variability in isotopic fractionation. The other compounds, CHCl_3 , CH_2Cl_2 , PCE and

TCE, have lifetimes of less than a year and are emitted from biogenic and anthropogenic sources; they exhibit variability in their isotope fractionation indicating the involvement of a range of sources (solvents, soils, oceanic algae, landfill sites, biomass burning, etc.) and sinks (oceanic, soil) in the Bristol region.

The maximum value (-32.8‰) for HCFC-22 from the current study is within the range of values as given by the study of Redeker et al.^[26] (-30.6‰), but the average value (-33.9‰) for the present work is less depleted compared with the value of the study of Redeker et al.^[26] (-43.2‰). The maximum value (-32.4‰) for CFC-12 falls within the range recorded by the study of Redeker et al.^[26] (-29.1‰) and the average value (-33.5‰) is very similar to the value of the study of Redeker et al.^[26] (-37.2‰) and from the study of Archbold et al.^[23] (-37.0‰). The less depleted value (-22.5‰) for CHCl_3 in the present study, compared with the study of Redeker et al.^[26] (-37.4‰), could be due to the different sources (solvents, oceanic algae) and possibly sinks (estuarine) in Bristol urban area. The average $^{13}\text{C}/^{12}\text{C}$ value (-49.7‰) for CH_2Cl_2 has been recorded that is more depleted when compared with the value of the study of Redeker et al.^[26] (-35.6‰), implying that CH_2Cl_2 in the Bristol area is significantly more depleted than in the Belfast area. Currently there are no published data for comparison with our values for H-1211. Our recorded CCl_4 and TCE carbon isotope ratios are less depleted than the values recorded for those collected from different manufacturers by the study of Auer and Schulz-Bull.^[27] Previous studies suggest that TCE could be emitted from coating and respraying processes in the Bristol area (M. A. H. Khan et al., unpubl. data)^[25] and the estuary could be a potential sink for CCl_4 (M. A. H. Khan et al., unpubl. data). For PCE, the values are quite similar to the study of Auer and Schulz-Bull,^[27] indicating industrial sources of the compound in the Bristol area.

The degree of linear relationship between mixing ratios and carbon isotope ratios of the halocarbons is reflected by the value of the Pearson product momentum correlation, *R*. The Pearson correlation has a value of between +1 and -1, where +1 is a perfect positive linear relationship and -1 is a perfect negative linear relationship (an anticorrelation). Any value of -0.5 (or less) or +0.5 (or more) is classed as significant. Fig. 2 shows the correlation between the halocarbon mixing ratios and their carbon isotope ratios. A good correlation was observed for CH_2Cl_2

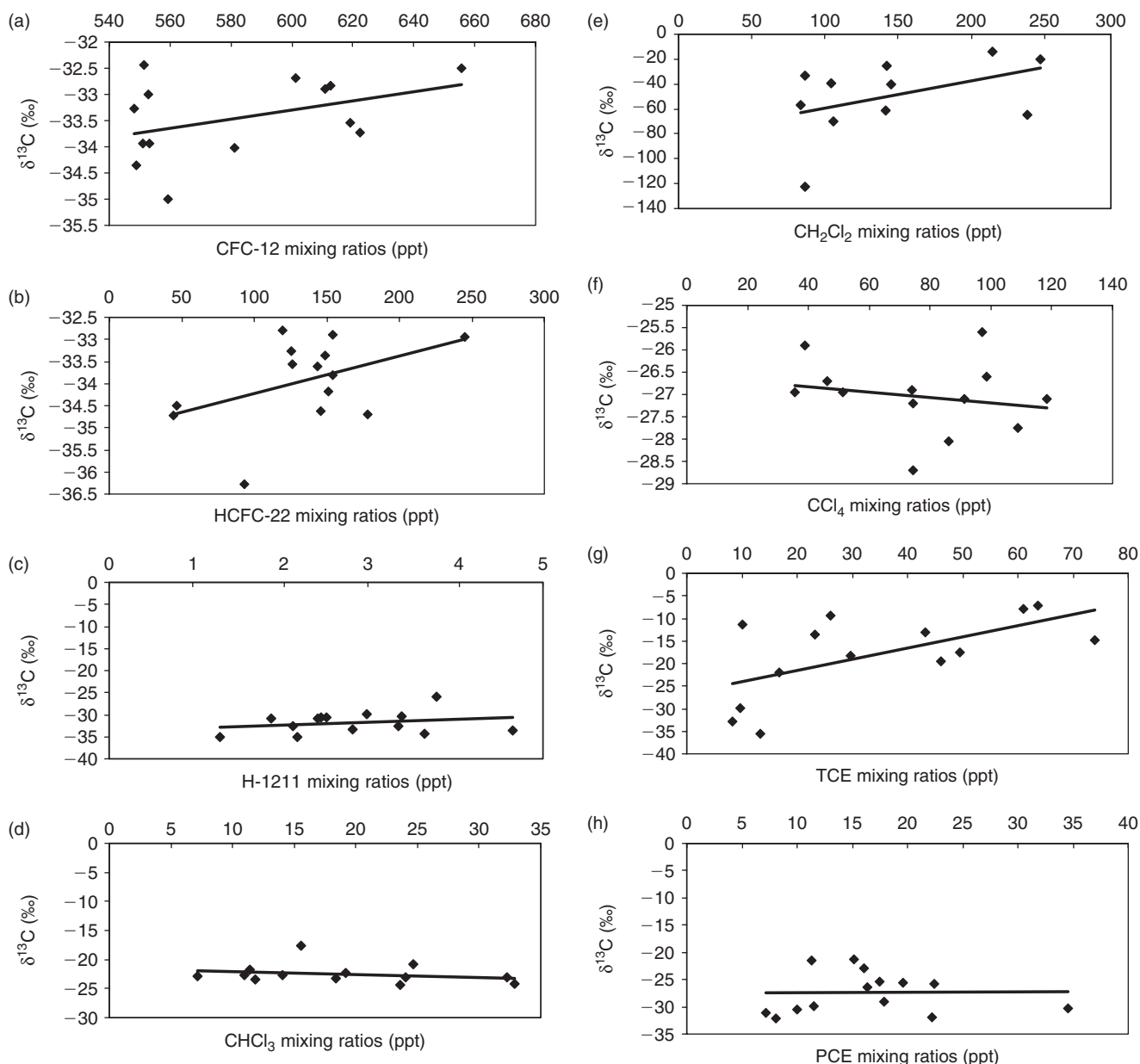


Fig. 2. The correlation between selected halocarbon mixing ratios and their carbon isotope ratios: (a) CFC-12, (b) HCFC-22, (c) H-1211, (d) CHCl_3 , (e) CH_2Cl_2 , (f) CCl_4 , (g) TCE, (h) PCE. See text for compound details.

($r = 0.5$), TCE ($r = 0.6$) and HCFC-22 ($r = 0.5$), whereas no correlation was observed for PCE ($r = 0.1$), CHCl_3 ($r = -0.2$) and CCl_4 ($r = -0.2$). For PCE, CHCl_3 and CCl_4 , the estuary could be a possible sink (M. A. H. Khan et al., unpubl. data), which can degrade the compounds with the preferential fractionation of the lighter isotopes. The emission sources predominate over the sinks in the Bristol area for CH_2Cl_2 , TCE and HCFC-22, giving an enriched isotope ratio in ^{13}C with the higher mixing ratios. At lower concentrations, the isotope ratio becomes enriched in ^{13}C that could be due to the degradation of the compounds as preferential fractionation of the lighter isotopes will take place^[5,28] resulting in the remaining compounds being enriched in ^{13}C .

Conclusion

An ATD-GC-IRMS system was used to analyse carbon isotope ratios of a suite of halogenated compounds in an urban

background area and allowed the measurement of carbon isotope composition for some of the halocarbons at the ppt level. Also in the current study, we report the first carbon isotope ratio measurements of H-1211, PCE, TCE, CCl_4 and CH_2Cl_2 from the urban background area. This method could potentially provide a useful tool in determining carbon isotope ratios of some other biogenic halocarbons and also hydrocarbons in the urban background area. For several species such as CFC-12, H-1211 and CCl_4 that are known to be long-lived in the atmosphere, the isotope ratio varies very little, which is reassuring, and for species with strong local sources, there is indeed a variation of isotope ratio. The reasons for these variations may be in the sources and sinks of these compounds or in differences in their method of manufacture. Further work is required to utilise these values to allow interpretation of sinks and sources in general.

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