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Sorbent Tube Sampling and an Automated Thermal Desorption System for Halocarbon Analysis

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ABSTRACT

Development and deployment of the analytical system, ATD-GC-ECD has been established to monitor a suite of halogenated compounds found in the atmosphere at trace concentrations. The instrument has been used to monitor urban background emission flux levels in Bristol, UK as well as Yellowstone National Park, USA and an indoor rainforest (Wild Walk@Bristol, UK). The newly established sorbent tube sampling system is small and easily portable and has been used for large volume sample collection from remote areas. Automated Thermal Desorption (ATD) provides routine atmospheric measurements without cryogenic pre-concentration. The instrument provides good precision where the detection limit was 3 pptv for the species of interest and the reproducibility was within 4% for all of the selected halocarbons. The results from two field experiments have also provided insight about natural missing sources of some ozone depleting halocarbons.

Key words: Automated Thermal Desorption (ATD), Pre-sampling unit, Sorbent tube, Gas Chromatography (GC), Electron Capture Detector (ECD)

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1. INTRODUCTION

Air sampling using adsorbents followed by thermal desorption and Gas chromatographic analysis with either ECD (Electron Capture Detection) or Mass Spectrometric (MS) detection has been established as a common method for detecting many volatile organic compounds (VOCs) in ambient outdoor and indoor environments (Tang et al. 1995; Ma et al. 1997; Pankow et al. 1998; Peng and Batterman 2000). An ECD offers good sensitivity for halogenated compounds while a MS enables the positive identification of peaks in the chromatogram and takes advantage of the characteristic nature of bromine and chlorine containing ion fragments (Wevill and Carpenter 2004). Trace atmospheric halocarbon levels were usually determined by the cryogenic pre-concentration of large volumes of air before analysis. The use of liquid cryogen was limited by their cost, availability and problems with automation of such systems. The air sampling, using sorbent tubes precludes the necessity for liquid cryogens allowing for the development of a more robust 'stand alone' system. Sorbent tube sampling can achieve high recovery of polar and reactive compounds, which can pose problems for whole air samples collected in canisters (Batterman et al. 1998). Sorbent tubes are small in size, facilitating collection, transport and storage. They can be conditioned easily and conveniently reused. The associated pre-sampling systems are also small, easily portable and can be used in remote areas and are relatively inexpensive.

Automated Thermal Desorption (ATD) is an automated and unattended analysis system for up to 50 samples. Thermal desorption of sorbents offers cost savings and high sensitivity. The system provides cryogen-free operation down to -30 C, reducing operating costs. The tube and the sample flow path can be purged with helium gas at ambient temperature to remove oxygen and moisture, which prevents analyte and sorbent oxidation thus minimising artefact formation, ensuring data quality and extending tube lifetimes. The system also helps to minimize sample losses by checking the system flow path for leaks so they can be corrected prior to initiating a run. The instrument also preserves

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sample integrity by sealing sample tubes before and after desorption. Risk of ice blockage is minimal in the cold trap and the moderate cooling temperatures required may be obtained using Peltier coolers rather than liquid cryogen. Break through in sampling and artefact formation during analysis can be minimized by using the appropriate sorbent tubes (Peng and Batterman 2000).

This study provides a selection of appropriate sorbents and cold traps for halocarbon trapping and analysis methods using an automated thermal desorption system followed by GC-ECD with the aim of demonstrating the applicability of the analytical system. The study also includes the analysis of eleven C_1-C_3 ozone depleting and long lived halocarbons in areas including Yellowstone National Park, USA. The major aim of this study is to derive the unknown natural sources of halocarbons, which will reduce discrepancy in the global budget of halocarbons.

2. METHODS AND MATERIALS

2.1 Sorbent Tube Selection

Three-bed sorbent tube (Markes Int. Ltd., UK) (Approximately 500 mg) containing a series of sorbents, Carbograph 1TD, Carboxene 1000 and Carbosieve SIII separated by quartz wool was selected. This combination of sorbent quantitatively retains the target compounds from a volume of air sampled and releases the compounds back quantitatively when heat is applied and flow of carrier gas reversed. Sampling flow and desorption flow are in opposite directions to prevent the contamination of the strongest absorbent with analytes from the weakest adsorbent during heating. Analytical sensitivity and precision were largely determined by sample trapping efficiency, desorption efficiency and the level of interferences. A selection of the sorbents in this study and their associated characteristics are presented in Table 1.

2.2 Tube Conditioning

The freshly packed 3-bed tubes were carefully conditioned using a carrier gas such as He at a flow rate of 10 ml min^{-1}. 3-bed tubes were conditioned starting at a fairly low temperature and increasing this step by step in order to remove oxygen and water completely without damaging the sorbent. By using the conditioning methods adopted in the ATD, the tubes were initially conditioned by holding at 200 C for 30 minutes, 300 C for 30 minutes and then finally 380 C for 15 minutes.

2.3 Capping and Tube Handling

After air sampling, the tubes were capped using standard PTFE storage end caps (PerkinElmer Inc Analytical Instruments Wellesley, MA, USA). The tubes must have these caps fitted before being loaded onto the ATD sample carousel prior to analysis. In the case of remote sampling, 1/4 inch brass Swagelok end fittings were used. These caps were tightened finger tight and a quarter turn. These type of seals ensured minimum ingress of external artefacts and minimal loss of sampled components over long term storage.

2.4 Pre-Sampling System

The automated sampling apparatus for the URGENT Tracer campaign developed by Cooke et al. (2000) has been modified and then used for pre-sampling in this study. The pre-sampling system, itself, consists of a 16-position multiport valve (Valco Instruments Co. Inc., Houston), a 24V DC pump (KNF Neuberger. Type N86. Pmax 1.5 bar), mass flow controller (Unit 7000, Unit Instruments Ltd., Ireland), a 7 micron in-line filter, a temperature sensor (0 - 50 C), a Nafion dryer system (with 5A molecular sieve as 'counter-purge' drying agent rather than a dry nitrogen gas flow), an electronic control system (CGL Technology Ltd., UK) (See Fig. 1).

16 valve positions are available in the pre-sampling system, 15 tubes can be loaded for sampling. Tubes were fitted with the port through stainless steel swage locks which were tightened finger tight. Sample volumes were measured during the program run by integrating the flow rate. The flow rate sample time is measured to the nearest ms and is nomi-

Table 1. Different sorbents with characteristic features.

Sorbent	Strength	Max. Tem. (°C)	Cond. Tem. (°C)	Specific Surface area (m^2 g^{-1})	Features
3-Bed: Carbograph 1TD	Medium/Weak	400	350	100	Not inert, hydrophobic, Low artefacts (< 0.1 ng)
Carboxen 1000	Very strong	400	350	> 1200	Inert, hydro-philic, high artefacts (> 10 ng)
Carbosieve SIII	Very strong	400	350	> 800	Some hydrophilicity, low artefacts (< 0.1 ng)

nally 1 sec. Temperature was monitored by using the temperature sensor which was displayed on the program run menu.

2.5 Automated Thermal Desorption (ATD)

The thermal desorption system used in this study was the Turbomatrix ATD produced by PerkinElmer (PerkinElmer Inc Analytical Instruments Wellesley, MA, USA). The system has programmable pneumatic control which allows for inlet and outlet flow split flow rates, desorb flow rates and carrier pressure to be pre programmed and controlled accurately. The system basically incorporates a desorption oven, quartz cold trap, heated valve assembly, pneumatics assembly, sample carousel and a heated transfer line for the transfer of analytes to the GC oven for separation. The transfer line used was the Turbomatrix HS long heated transfer line (PerkinElmer Inc Analytical Instruments Wellesley, MA, USA), which has a maximum operation temp of 50 - 300 C and for this study a length of Zebron CPSil5 column (0.32 mm internal diameter, 5 m film thickness) was inserted. The transfer line tubing is coated with Sulfinert™ as standard (Restec Bellefonte, PA, USA). The length of the column was connected at either end with a Supelco (Supelco® Sigma-Aldrich, St. Louis, MO USA) butt connector. This allowed for the transfer of analytes from the cold refocusing trap via the transfer line to the column in the GC oven with minimal or no losses. The Sample tubes were ballistically heated to desorb analytes from the sample tube with an operational temperature range of between 50 and 400 C for time periods of 1 - 999 minutes. After desorption from the sample tube, analytes pass onto the quartz cold trap. The cold trap is adsorbent-based in order to ensure compatibility with samples containing significant amounts of water. This process enhanced resolution, providing sharper peaks that are easier to integrate. Figure 2 shows the schematic diagram of the automated thermal desorption system.

The central heated valve body in the ATD is constructed of stainless steel and an inert Valcon™ T-type rotor. There is a minimal sample flow path where connections for the cold trap and the transfer line pass directly through the heated block of the valve and into the valve itself. The pneumatic function was driven by compressed air (at 90 psi from zero air generator; Parker Balston) which was consumed at a rate of between 0.5 - 0.7 ml min^{-1}. The carrier gas used was He and the desorption flow rate was varied depending on the sample under analysis. The carrier gas was also used as a purge at ambient temperature, the effluent from the purge is passed over the cold trap to remove air and minimise loss of volatile analytes.

2.6 Cold Trap Selection

A temperature of -30 C is sufficient for quantitative retention of the components of interest, provided a suitable trap packing is selected. Tenax TA 60/80 cold trap filled by Tenax TA sorbent with mesh size 60/80 and Turbomatrix 40/110 air toxic tube filled by graphitized carbon black (carbopack X/carbograph 5-TD) and carbon molecular sieves (Carboxen 1003/Carboxen 569/Carbosieve SIII) were used as cold traps in this study. The cold trap is cooled with a Peltier cooler to temperatures between -30 and +150 C. Before starting sample analysis, the cold trap was conditioned by heating to 300°C for 30 minutes at a He flow rate of 50 ml min^{-1}.

Figure 3 shows the comparative standard sample's chromatogram for different cold traps with the solid line

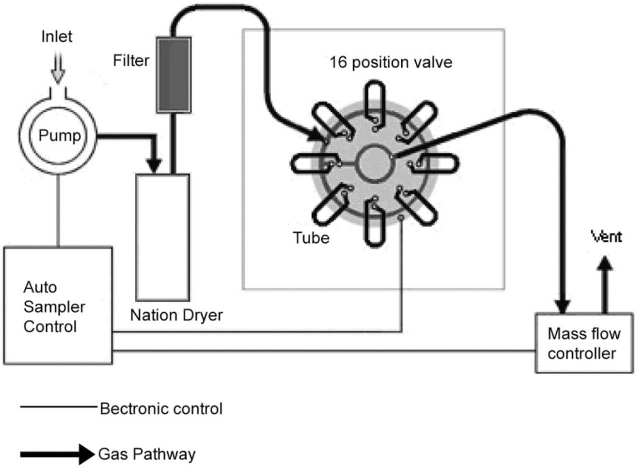

Fig. 1. Schematic of the pre-sampling apparatus.

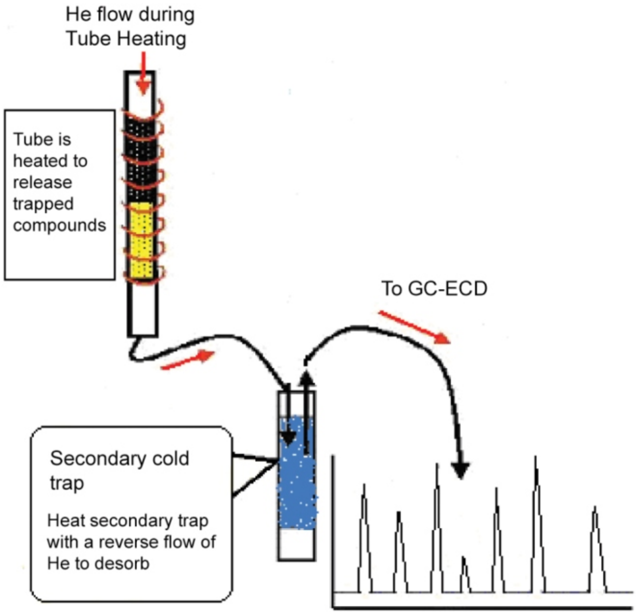

Fig. 2. Outline schematic of the turbomatrix automated thermal desorption system.

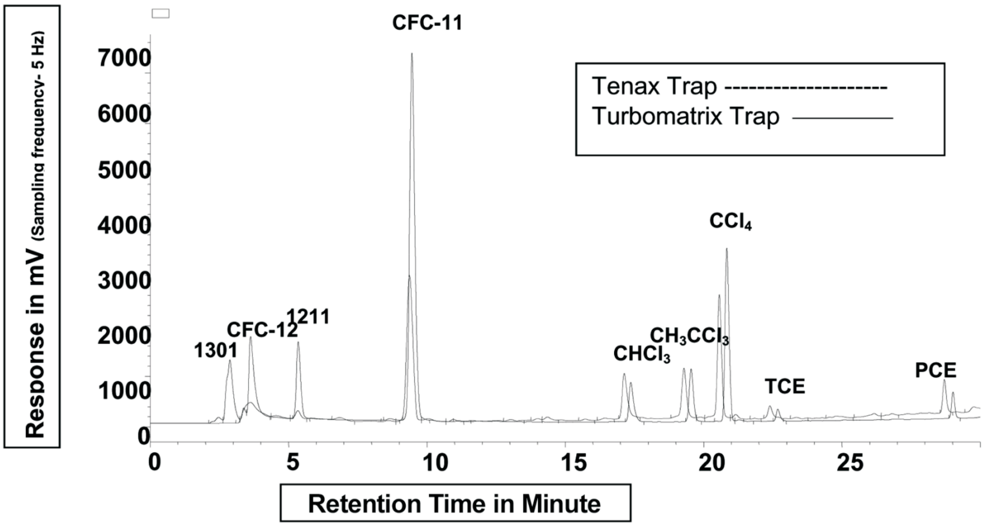

Fig. 3. A comparison of the standard sample chromatograms for different cold traps.

corresponding to the Turbomatrix trap and the broken line to the Tenax TA trap. The Turbomatrix 40/110 (Air Toxic Tube) trap gave better results over the TenaxTA trap as it increased the trapping efficiency over of the less volatile components, recovery of target compounds and also improved the baseline of the chromatogram. There is a quick desorption of the heavier compounds (CH_3CCl_3, CCl_4, TCE, PCE) from the Tenax trap resulting in comparatively less retention time than the Turbomatrix trap (See Fig. 3). The chlorinated compounds have a relatively high affinity with the Tenax cold trap, due to hydrogen-bond interactions making desorption less efficient (Stanetzek et al. 1996).

2.7 GC-ECD

Gas chromatography with Electron Capture Detection (ECD) was used for detecting $C_1 \rightarrow C_3$ halogenated organic compounds present in the ambient background atmosphere. In this work, a gas chromatograph (HP6890) is equipped with twin linked ECDs, one of which is oxygen doped (Bassford 1998). The eluent then passes through the non doped ECD before passing through the second, oxygen doped ECD. An integrator measures the signal from the detectors; the areas from which are then converted to concentrations. Figure 4 shows a typical chromatogram for a 3-litre standard sample measured by ATD-GC-ECD system.

2.8 Halocarbon Standards

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 14 halocarbons in N_2O (Linde gases, UK) diluted to near ambient concentration and was calibrated in an Agilent 6890/5973 GC-MS with ADS by using standard H-074 (SOGE Gold standard) which is a fully calibrated Mace Head air sample (filled December 2003) assigned on calibration scales SIO-98 for AGAGE-MD species (CFC-11, CFC-12, CFC-113, $CHCl_3$, CCl_4, and CH_3CCl_3) or UB-98 for most other species (Prinn et al. 2000).

2.9 Air Sampling

2.9.1 @Bristol Wild Walk Campaign

Thirteen 3-bed tubes were used for taking sample from an ant colony in the @Bristol Wild Walk Science Centre, using the pre-sampling system on 27 June 2005. Before sampling, the tubes were conditioned. A 24V battery (Two 12V lead-acid type rechargeable batteries, Yuasa Battery Ltd, UK parallel connected to make 24V) was used for running the pump. The first five of the tubes sampled were from the greenhouse in the late morning (9:45 to 10:39) and the second five were from the greenhouse in the early afternoon (13:00 to 15:20) and another three were from inside the ant colony. 3-litre samples were taken in each tube by using the mobile pre-sampling system. Two tubes were used for standard sampling; one was taken before the air sampling and another after finishing the air sampling.

2.9.2 Yellowstone Campaign

Thirty 3-bed tubes were used for the Yellowstone 'volcano' site sampling. Samples were taken at different locations of the site at the end of July, 2005. Five sites were chosen for sampling. One of these sites was on the eastern side of the Yellowstone Plateau in the vicinity of the mud volcano feature, three were on the western side in the Gibbon meadows area and the last one was the campsite based in the Canyon Village area. 10 tubes were used for sampling taken from a background site based in the Canyon Village area

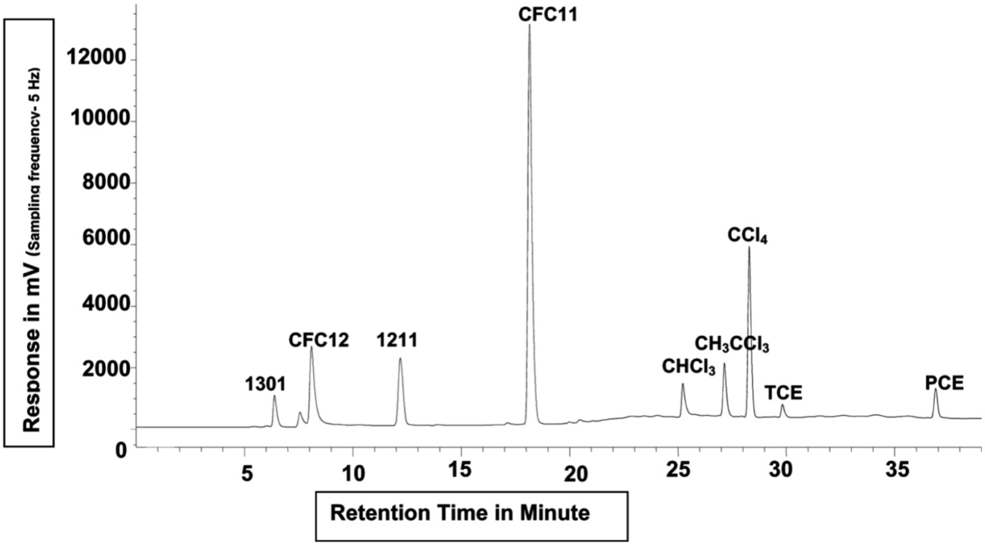

Fig. 4. A standard sample chromatogram analyzed by ATD-GC-ECD system.

(forested, mainly lodgepole pine), 7 from the Hot Hill site based in the vicinity of the Mud Volcano feature, 4 from the Washer site, 4 from the Little Hottie site and the remaining 5 from Gibbon Meadow traverse site. The last three sites were located in the Sylvan Springs area about 2 - 3 hr hike from the head of the Gibbon Valley. The sample sites chosen were just behind (North of) the Washer feature, at the Little Hottie feature and a traverse of the Gibbon Meadows (a large boggy area between the Sylvan Springs and the head of the Gibbon Valley). 5 tubes were used for standard sampling.

3. RESULTS AND DISCUSSION

3.1 Analytical Performance Evaluation

Analyte 'break through' tests were performed to optimize the sample volume, tube temperature, desorption time, trap hold time and desorption flow rate. After sampling via the pre-sampling system, the analysis of each tube was carried out straight after a conditioning run and chromatograms analyzed to see whether any sample remained. The 3-bed tubes exhibited no residual traces of any components at the analysis desorption temperature. Some empty tubes (without sample) have also been analysed. Blank emission during thermal desorption of tubes has been detected possibly due to sorbent degradation, incomplete conditioning of the sorbent tubes, contamination from the carrier gas, and/or contamination of the upstream flow path of the cryotraps. When compared with the analysis of standard halocarbons, the blank traces did not interfere with the peak of the standard halocarbons. A desorption flow rate of 10 ml min^{-1} allowed good analyte recovery and proper desorption. If the flow rate increases from 10 ml min^{-1}, analyte peak responses decreases indicating that the analyte was desorbing from the other end of the cold trap and no longer being quantitatively trapped. Break-through volume tests have also been performed to select the amount of sample taken in the sorbent tubes. Table 2 shows the final analytical conditions that were set for air sample analysis.

3.2 Method, Detection Limit, Reproducibility and Desorption Efficiency

The detection limit for the analytical systems was calculated for a signal to noise ratio of 3 and is shown in Table 3. The reproducibility's expressed as the relative standard deviation (RSD) were all within 4% for each component. Successive desorptions confirmed that there were no residual traces of any components following two desorptions, demonstrating that one thermal preconditioning cycle was sufficient to prevent sample carryover occurring between consecutive runs.

3.3 Air Sample Analysis

@Bristol Wild Walk and Yellowstone volcano samples were analysed using the ATD-GC-ECD system. Table 4 shows the average, maximum and minimum halocarbon concentration values of the ant colony, background of the colony and also the ratio of the average colony and background from the measurements at @Bristol Wild Walk. The concentrations of anthropogenic halocarbons e.g., Halons, CFCs, CCl_4, CH_3CCl_3 in @Bristol Wild Walk are very much closer to the Global Average value and indeed ambient levels in Bristol. CH_3Br levels are significantly higher in the ant colony compared with the background of the colony (see Table 4). CH_2Cl_2 and $CHCl_3$ are also elevated in the colony whereas for other species, the ratios of colony and

Table 2. The analytical conditions for the air sample analysis by ATD-GC-ECD system.

Sampling system	3-bed tube	3 L at a flow rate of 300 ml min^{-1}
ATD	Tube Desorption Temperature	380°C
	Tube Conditioning Method	380°C for 15 minutes at a He flow rate of 7.5 ml min^{-1}
	Tube Oven Temperature	150°C
	Transfer Line Temperature	200°C
	Cold Trap (low)	-30°C
	Trap Heating Rate	5°C s^{-1} (low) or at up to 40°C s^{-1} (fast)
	Trap Desorption Temperature	300°C
	Trap Desorption Time	5 minutes
	Purging Time	1 minute
	Helium Carrier Gas Pressure	24.3 psi
	Column (He) Flow	1.9 ml min^{-1}
	Desorption Flow	5 ml min^{-1}
GC	Column	CPSil5 (110 m × 0.32 mm i.d. with 5 μm film of dimethylpolysiloxane)
	Oven Initial Temperature	30°C for 12 minutes
	Ramp rate	10°C min^{-1}
	Oven End Temperature	150°C for 15 minutes
ECD	Detector Temperature	300°C
	Make-up (N_2) Gas Flow	25.1 ml min^{-1}

Table 3. Precision of halocarbon standard by using ATD-GC-ECD system.

Compound	%RSDs (n = 20)	Limit of Detection (pptv)
Halon 1301	1.2	0.20
CFC-12	2.4	0.60
H-1211	1.1	0.08
CH_3Br	4.2	3.12
CFC-11	3.2	0.05
CH_2Cl_2	4.4	1.27
$CHCl_3$	3.0	0.12
CH_3CCl_3	1.9	0.18
CCl_4	1.4	0.06
TCE	2.3	0.19
PCE	1.6	0.09

background are very close to unity. The fungi from the leaf cutter ant colony in @Bristol Wild Walk was identified as the most likely source of these elevated levels (Mead 2006; Mead et al. 2008). The measurements made by Mead et al. (2008) at various stages of the ant colony life-cycle suggest that the levels of these halocarbons are elevated during the active phases of the ant colony life cycle.

Table 5 shows the average, maximum and minimum concentrations of the selected halocarbons from all sites, background, Hot Hill and Gibbon meadows of Yellowstone volcano site. In the Yellowstone campaign, the recorded concentrations of the CFC-11 and CFC-12 for Hot Hill and Gibbon Meadow were much higher than the urban background values and also background values from the AGAGE network suggesting that volcanic emissions could be a source of these CFCs. Previous studies (Isidorov et al. 1990; Jordan et al. 2000; Schwandner et al. 2004) reported the emission of CFCs from volcanoes. Isidorov et al. (1990) reported 0.4 - 1.5 ppbv of CFCs in solfataric air and Jordan et al. (2000) detected CFC-11 in gas samples of volcanoes at concentrations of up to 1 ppbv. Schwandner et al. (2004)

Table 4. Mean, maximum and minimum halocarbon mixing ratios (in pptv) of the ant colony and the background of the colony and their ratio from the measurements at @Bristol Wild Walk.

	1301	**CFC12**	**1211**	**CH_3Br**	**CFC11**	**CH_2Cl_2**	**$CHCl_3$**	**CH_3CCl_3**	**CCl_4**	**TCE**	**PCE**
Ant Colony (n = 3)											
Mean	5.0	533.3	2.5	760.1	255.1	63.9	79.0	17.1	74.3	21.5	13.4
Maximum	5.1	543.8	2.7	791.8	260.8	67.0	81.7	18.9	78.5	23.9	15.4
Minimum	4.9	522.9	2.4	728.4	246.3	60.8	76.4	16.4	70.3	19.1	7.9
Background (n = 10)											
Mean	5.1	572.8	2.6	152.5	283.2	36.4	51.5	21.0	87.1	112.0	18.5
Maximum	6.1	596.7	3.9	325.2	291.1	49.1	68.8	22.1	92.0	126.9	31.0
Minimum	4.8	536.3	2.2	24.4	272.5	31.8	46.7	20.5	83.1	39.4	11.5
Colony:Background	1.0	0.9	1.0	5.0	0.9	1.8	1.5	0.8	0.9	0.2	0.7

Table 5. Average, maximum and minimum halocarbon levels at various sampling sites in Yellowstone National Park. All values are in pptv.

Site	**1301**	**CFC12**	**1211**	**CH_3Br**	**CFC11**	**CH_2Cl_2**	**$CHCl_3$**	**CH_3CCl_3**	**CCl_4**	**TCE**	**PCE**
Background (n = 10)											
Average	3.2	553.1	2.7	72.7	258.9	117.9	99.2	32.4	88.0	5.8	17.1
Maximum	3.4	558.5	3.1	108.4	280.4	124.5	111.4	33.8	106.6	6.2	23.9
Minimum	2.9	542.3	2.2	44.7	223.9	108.8	84.6	30.4	79.8	5.3	10.1
Hot Hill (n = 7)											
Average	3.0	681.3	2.5	543.3	316.3	105.5	86.3	23.4	78.1	13.1	3.7
Maximum	3.1	708.5	2.8	832.6	400.7	112.9	94.5	28.1	98.9	15.8	8.7
Minimum	2.9	629.2	2.2	48.2	258.9	96.6	79.8	20.9	70.2	11.4	2.0
Gibbon Meadows (n = 13)											
Average	4.4	618.0	4.7	394.7	373.0	105.8	92.1	22.6	89.7	13.2	1.2
Maximum	4.8	634.5	5.8	543.2	417.4	110.2	100.1	26.9	99.8	14.7	2.3
Minimum	3.4	564.3	3.1	43.8	301.2	99.9	87.4	18.0	72.5	11.9	0.9
All sites (Average)	3.5	617.5	3.3	336.9	316.1	109.7	92.5	27.0	85.3	10.7	7.3

also observed 1200 and 3700 pptv of CFC-11 in diffuse emissions from the active volcano and dry fumarolic gas, respectively. The current study suggests that the maximum concentrations of CFC-12 and CFC-11 in the Yellowstone volcano sample are 1.3 and 1.7 times higher than background values. Extremely high concentrations were also recorded for CH_3Br at Hot Hill and the Washer site compared with background levels indicating the volcano site may be one of the missing sources of CH_3Br. There may have been an additional input of CH_3Br from large amounts of buffalo dung that could increase the concentration of CH_3Br at the Hot Hill site. The recorded CH_3CCl_3 concentrations in the background area are very similar to remote background concentrations and slightly higher than the volcano sites, which suggest that CH_3CCl_3 is not being emitted by the volcano. The concentrations of CH_2Cl_2 and $CHCl_3$ recorded were highly elevated at all sites especially the background area, which is forested (mainly lodgepole pine trees) indicating that the volcano could be a potential source of them. Previous studies (Isidorov et al. 1990; Schwandner et al. 2004) detected higher CH_2Cl_2 and $CHCl_3$ concentrations in the volcanic gas samples. Schwandner et al. (2004) suggested that the increased CH_2Cl_2 concentrations in the volcanic gas were associated with elevated ground resistivities indicating a subsurface origin. These compounds are also known to have terrestrial sources and these observations are consistent with this. Previous studies (Mead 2006; Khan et al. 2009) suggest that there is a common biogenic source of CH_2Cl_2 and $CHCl_3$ in the Bristol urban background area. Khan et al. (2009) proposed the biogenic emission of these compounds in the Bristol area from the sea water of the nearby estuary.

4. CONCLUSION

A laboratory and two field campaign tests have been used to evaluate the performance of an air sampling system using 3-bed sorbent tubes, and an automated thermal desorption system for identification and quantification of target halocarbons by using a GC-ECD system. The air sampling system has been demonstrated to be an effective method for remote sample collection, particularly in corrosive environments such as that at Yellowstone and also for large volume sample collection. The system is small, easily portable and relatively inexpensive. ATD has also been proved to be an important device for the measurement of halogenated compounds with a very wide range of boiling points. No carry-over problems were identified in the analytical system. The method was highly automated and the precision of the system was better than 4% for all of the selected halocarbons. The system has been applied to two sample campaigns (@Bristol Wild Walk and Yellowstone) and the results from the two campaigns also give information regarding natural missing sources of halocarbons. Both CFC-11 and CFC-12 and CH_3Br are elevated in the vicinity of volcanic out-gassing and may well be a significant source of these compounds.

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