Ocean Science
Discussions

Technical Note: A fully automated purge and trap-GC-MS system for quantification of volatile organic compound (VOC) fluxes between the ocean and atmosphere

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Abstract

The oceans are a key source of a number of atmospherically important volatile gases. The accurate and robust determination of trace gases in seawater is a significant analytical challenge, requiring reproducible and ideally automated sample handling, a high

5 efficiency of seawater–air transfer, removal of water vapour from the sample stream, and high sensitivity and selectivity of the analysis. Here we describe a system that was developed for the fully automated analysis of dissolved very short-lived halogenated species (VSLS) sampled from an under-way seawater supply. The system can also be used for semi-automated batch sampling from Niskin bottles filled during CTD (Conduc-

10 tivity, Temperature, Depth) profiles. The essential components comprise of a bespoke, automated purge and trap (AutoP & T) unit coupled to a commercial thermal desorption and gas chromatograph–mass spectrometer (TD-GC-MS). The AutoP & T system has completed five research cruises, from the tropics to the poles, and collected over 2500 oceanic samples to date. It is able to quantify > 25 species over a boiling point range

15 of 34–180 °C with Henry's Law coefficients of 0.018 and greater (CH_2I_2, k_H^{cc} dimensionless gas/aqueous) and has been used to measure organic sulfurs, hydrocarbons, halocarbons and terpenes. In the east tropical Pacific, the high sensitivity and sampling frequency provided new information regarding the distribution of VSLS, including novel measurements of a photolytically driven diurnal cycle of CH_2I_2 within the surface ocean

20 water.

1 Introduction

The ocean covers > 70 % of the Earth's surface and is an important natural source of a wide range of trace gases, notably those containing sulfur, nitrogen and halogens. These play critical roles in global biogeochemical cycling and in a wide range of atmo-

25 spheric processes including marine aerosol formation and modification, tropospheric ozone formation and destruction, and stratospheric ozone loss (Davis et al., 1998;

A number of ocean biological and chemical processes are responsible for the production of marine gases. Very short-lived halogenated species (VSLS), which deliver ozone-depleting reactive halogens to the troposphere and lower stratosphere, can be released from marine macro algae, from phytoplankton, from marine bacteria and detritus and via photochemical breakdown of dissolved organic matter (DOM) in the surface ocean (Sturges et al., 1993; Schall et al., 1994; Tokarczyk and Moore, 1994; Happell and Wallace, 1996; Goodwin et al., 1997; Carpenter et al., 2000; Carpenter and Liss, 2000; Richter and Wallace, 2004; Hughes et al., 2008; Chance et al., 2009; Asare et al., 2012; Ordóñez et al., 2012; Leedham et al., 2013).

Water bodies may also contain anthropogenic components such as trihalomethanes (THMs), aromatic hydrocarbons, pesticides and waste pharmaceuticals which must be closely monitored and have legally enforceable limits (UK, DEFRA, 2000). These contaminants are a direct concern for human health and as such are often targeted by established methods (e.g. U.S.EPA, 2010, WHO – Thompson et al., 2007) and routine measurements of in-land water bodies.

Many marine trace gases exhibit large spatial and temporal variation in their concentrations and emissions, which necessitates the collation of large datasets in order to capture these trends on a global scale and quantify their role in the atmosphere (e.g. https://halocat.geomar.de/). This paper describes an instrument designed to quantify the concentrations of VSLS in the ocean with sufficient temporal resolution to capture diurnal emission profiles and the precision to accurately determine patterns in their spatial distribution.

2 Methods

In-situ VOC seawater measurements are typically made using manual purge and trap-gas chromatography methods (e.g. Ledyard and Dacey, 1994; Quack et al.,

2004; Jones et al., 2009) or via online equilibrator techniques with analysis by pre-concentration GC-MS or chemical ionisation mass spectrometery (Saltzman et al., 2009; Beale et al., 2011; Kameyama et al., 2014). Equilibrator techniques include Weiss-type (Johnson, 1999; Butler et al., 2007; Kameyama et al., 2010), which employ direct contact between the liquid and gas phase, or membrane-type (Groszko and Moore, 1998; Loose et al., 2009; Yang et al., 2014), which physically separates the phases with the analytes able to pass through the gas permeable membrane. The latter offers the advantage of reduced water vapour in the gas phase, especially if a hydrophobic membrane is used.

A disadvantage of the equilibrator technique is that it is limited to analytes with quite high volatilities. Purge and trap samples however can be heated and extensively purged to remove the analytes, such that compounds with boiling points greater than 180 °C can be efficiently sampled. However this often introduces a large amount of water vapour into the instrument, is aggressive toward any biological life in the sample and requires sample preparation and constant operator attention. An automated purge and trap system involves mechanical handling of the sample and requires mechanisms to avoid salt, biological life and debris blocking valves and fouling tubing.

2.1   Instrument design

Manual water sampling is still commonly used for purge and trap systems (Quack et al., 2007; Raimund et al., 2011). Automation of a method removes sources of human error, allows continuous 24 h sampling and can improve reproducibility. Just as important and often overlooked is the reduction of workload automation can bring allowing time for the analyst to concentrate on the upkeep of the instrument and the interpretation of the data.

An automated purge and trap system (AutoP & T) was developed for the analysis of VSLS in seawater. This allows for the measurement of trace gases, not limited to VSLS, in any liquid sample but was designed predominantly for operation on-board research ships sampling seawater from pumped underway supplies and discrete samples taken

directly from the ocean. The AutoP & T was coupled to a commercial thermal desorption unit (TD, Markes Unity2-CIA8), Agilent 6850 gas chromatograph (GC) with 5975C MSD but can be used with any TD-GC instrument.

The system employs the commonly used glass purge tube design with a nitrogen or helium carrier gas for sparging dissolved gases from the liquid sample. The purge tube is thermostatic at 50 °C using PID controlled high temperature heating rope (Omega, FGR). The gas sample is pre-concentrated onto the cooled (-30 °C) absorbent trap (Tenax TA) of the TD unit and desorbed at 250 °C onto the GC column (60 m 320 μm I.D. 1 μm 5 % phenyl film, SGE). The column was held at 40 °C for 2 min, ramped at 20 °C min^{-1} to 207 °C then at 100 °C min^{-1} to 250 °C. The MSD was operated in SIM/SCAN mode with 19 selected ion windows monitoring a total of 46 ions, a qualifier and quantifier per analyte. The MSD source and quadrupole temperatures were increased to 250 and 200 °C, respectively and an enlarged 6 mm draw out plate was fitted to counter MSD sensitivity stability issues associated with water sampling.

2.2 Ship-borne installation and automation

The pumped underway water supply varies with research vessel but usually consists of an inlet positioned at the bow around 6 m below sea level to allow for pitching and rolling of the ship without introduction of air to the inlet. For the RSS *James Clark Ross* (JCR), in which the AutoP & T has been fitted on two occasions, the water is pumped at high flow rate into the laboratories (> 200 L min^{-1}). From this a proportion was diverted to the AutoP & T via a stainless steel mesh filter (400 μm) to remove small particulate matter, drawn by a peristaltic pump (Watson Marlow, 1208/DV). The remaining supply was allowed to flow to waste.

The automated control of the system is achieved using just 3 solenoid valves. A 2-way PEEK diaphragm valve (valve C Fig. 1, BioChem 100T2NC24-62-5P) allows purge gas to flow through the system to waste. Two pinch valves, one dual channel 3-way (BioChem 100PD3MP24-02S) and one single channel 3-way (BioChem 100P3MP24-02S), are used to control the multiple water flow paths through the system and are

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configured to allow a flow at all times to ensure a fresh sample (Fig. 1). The three valves allow the user to filter the sample, fill/empty the glass purge tube, de-gas a liquid to waste, de-gas and trap the analytes for analysis or to flush the purge tube with carrier gas. Pinch valves are used as they have no wetted parts so are robust and the tubing can easily be replaced if contaminated. Early iterations of the instrument used PTFE diaphragm valves (BioChem 150L3MP24-156). However, the soft PTFE diaphragm was easily damaged by flow path debris, causing leaks, and microbial growth could not easily be cleaned from the inside of the valve.

The valves, heated lines and the temperature of the purge tube are controlled by an open-source microprocessor (Arduino Uno) and the programming code is available in the Supplement. A glass water trap is incorporated after the purge tube as an overflow safety and any condensation is emptied by valve C at the end of each run. Water removal is necessary and is incorporated before and after the CIA8 unit of the TD (Fig. 4 and Sect. 2.3).

The system can run in one of two modes, inline or discrete. Inline mode refers to sampling from the underway supply. Discrete samples are introduced manually directly into the purge tube or semi-automated via the offline sample inlet (Fig. 1). In either scenario, sampling is started by a trigger from the TD unit, which in turn waits for the GC system to become ready. The timing of the system is shown in Fig. 3. Purge gas passes through the purge tube, water removal system, TD and out to waste. During this time the water sample is diverted through the filter (0.45 micron PTFE or GF/F application dependent), which has a maximum pore diameter of 0.45 micron, capturing any phytoplankton (larger than 0.45 micron, Bouteiller et al., 1992) and also retaining smaller species such as picoplankton in its smaller pores. Biological matter removal is important as it can produce VOC within the heated purge tube. The carrier gas is then diverted onto the pre-concentration trap and the water sample stream diverted to fill the purge tube. Any VOC de-gassed during the purge tube filling stage are trapped for analysis. During filling the power available for the temperature control of the purge tube is increased to allow rapid equilibration ($\approx 0.5\,^\circ\text{C}$ deviation) of the water sample to

the purge temperature set point. Once the purge tube is filled the sample is purged for the remaining time and the sample flow is diverted to waste. After the sample is completely de-gassed, the flow through the purge tube stops and the pressure increases. This pressure is then used to empty the contents of the purge tube out to waste in preparation for the next sample.

2.3　Water removal

The purging of water at elevated temperatures produces a large amount of water vapour that must be removed before entering the GC-MS. If the absorbent preconcentration trap is cooled to below the dew point of the sample gas, a drying step is required pre-trapping. This was done using two different techniques depending upon which analytes were being monitored. For halocarbons, non-oxygenated saturated hydrocarbons, DMS and isoprene, an ME™-series Nafion® moisture exchanger and a counter-flow MD™-series Nafion® gas drier (Permapure™) were used in series.

For oxygenated, unsaturated hydrocarbons and monoterpenes, in addition to the species mentioned previously, a glass cold trap ("coldfinger") was used to selectively remove the water whilst maintaining sample integrity in comparison with the Nafion, through which these species are lost or transformed. This type of trap has previously been used for hydrocarbon and DMS analyses (Ledyard and Dacey, 1994; Lidster et al., 2014). The analyte recovery using the two sample drying techniques, Nafion and "coldfinger", is listed in Table 1.

The "coldfinger" trap was cooled to $-30\,^{\circ}C$ using either an ethylene glycol chiller (Grant R3) or a free piston Stirling cooler (Twinbird, SC-UD08 FPSC). The latter was implemented for use aboard the research ships, as it does not contain liquid and the power consumption is only around 30 W at $-30\,^{\circ}C$. The glass cold trap system was tested for losses by the analysis of dry standard gas passed through or bypassing the water trap whilst ice from previous samples was present in the trap. No significant losses were observed for any of the analytes of interest. For monoterpene and halo-

carbon integrity it is important that the sample lines are heated as physically close as possible to the cooled water trap and that the transition between hot and cold is very rapid. This minimises the amount of liquid water into which the analytes can partition. It was found that below $-40\,°C$, monoterpenes and xylenes began to be lost in the "coldfinger" trap.

2.4 Reproducibility

In order to reduce the amount of water vapour entering the system, decrease purge time and maximise purge efficiency, the lowest volume of sample should be used that provides a signal above the system's limit of detection (LOD, Table 1). This becomes an important consideration when designing the purge tube as the out-gassing of analytes from the sample is dependent upon partitioning between the liquid and gas phases. Assuming the carrier gas is never saturated, the rate of removal of analyte from the sample is dependent upon four factors: the total surface area of all the bubbles that sparge the sample, its temperature, the time in which the gas contacts the sample and the Henry's law constant of the analyte. Therefore the purge tube was designed long and thin so that the sample filled the tube allowing for a longer gas-liquid contact time. The carrier gas enters the tube through a quartz frit (porosity 3), which produces numerous small bubbles to maximise surface area.

The subtleties of the sparging method can have a significant influence on repro-ducibility. Bubbles reach terminal velocity shortly after formation (Leifer et al., 2000). This terminal velocity is determined by a combination of the bubble's drag and its buoy-ancy. Whereas buoyancy is relative to the gas that forms the bubble, drag is dependent upon bubble size and viscosity of the liquid. Water becomes less viscous at higher tem-peratures, increasing velocity. Increasing temperature also results in oscillation of the bubble, increasing its velocity but reducing its rise time. For bubbles larger than 2 mm, rise time is independent of temperature (Leifer et al., 2000). Bubbles should be small and numerous to ensure maximum surface area. Bubble size generated in this system is dependent upon sparge gas pressure and the porosity of the quartz frit, which are

both kept constant. However, due to its effect upon the analytes Henry's law constant, the bubble's trajectory and the viscosity of the water, it becomes increasingly apparent that accurate temperature control is vital if de-gassing is to be reproducible.

3   Results

3.1   AutoP & T performance

The reproducibility of the system was tested in the laboratory pre- and post-research cruises. Obtaining blank samples for laboratory tests was difficult due to the ubiquitous presence of VOCs, especially halogenated species, in terrestrial water supplies. It was noted during fieldwork that continuous system operation with underway seawater resulted in a "conditioning" of the AutoP & T because deep sea samples from depth profiles contained fewer contaminants than any water available to the laboratory. Replicate analysis of underway samples from unproductive regions also showed very good reproducibility (7 % RSD CCl$_4$, 24 h sampling, 7 Feburary 2012, East Tropical Pacific). For this reason it is likely that reproducibility is actually better during shipboard deployment than during laboratory based trials. For post-cruise performance testing, seawater was collected from the Arctic Ocean at 3000 m depth, filtered and purged to create a blank matrix and spiked with each compound of interest at mid-high ocean representative levels ($\sim$ 0–50 pmol L^{-1}). The reproducibility of the AutoP & T ranged from between 0.1 and 20 % RSD depending on method (see Table 1) but was < 2 % RSD for the majority of compounds in 20 mL sample volumes.

3.2   Purge efficiencies

Purge efficiencies were determined using multiple purges of spiked, blank seawater collected at 3000 m depth (Table 1). Water samples were run as per a usual analysis except not emptied from the purge tube at the end of the sampling time. The degassed

sample was held within the tube and repeatedly analysed until no measurable difference between consecutive samples was observed. The purge efficiency was then calculated using:

$$\% \text{ Purge Eff.} = [\text{analyte}]_{n1} \times 100 \Big/ \sum_{n=1}^{n} [\text{analyte}]_n \qquad (1)$$

Where n is the number of consecutive purges of the same water sample. Two setups were tested for purge efficiency with either 20 or 84 mL sample volumes depending on the target analytes; the results are shown in Fig. 5. The 20 mL volume was optimised for VSLS and used during the Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO) campaign in the East Tropical Pacific. As halocarbons were present in seawater at a high enough concentration to be quantified in 20 mL samples, this smaller volume was used as it could be efficiently degassed in 20 min. Halocarbon purge efficiencies were lower than 100 % in the larger, 84 mL sample volume. Monoterpene concentrations observed in seawater were very low. This, combined with higher limits of detection compared to the halocarbons, prompted the use of an 84 mL sample sparged for 30 min. The relatively high volatility of the monoterpenes resulted in near 100 % purge efficiency even at this large water volume. Where the analytes were not purged completely, their purge efficiencies decreased with decreasing volatility, as expected (Fig. 5).

3.3 Seawater measurements

The AutoP & T was run continuously as an automated on-line instrument sampling under-way surface seawater from NOAA ship Ka'imimoana during the TORERO campaign in January–February 2012. For the first two weeks the ship was in transit between Hawaii and the 110° W TAO (Tropical Atmosphere Ocean) buoy line. Afterward the underway sampling was interspersed with CTD depth profiles. To illustrate the performance of the instrument, Fig. 6 shows chloroiodomethane (CH_2ICl) and diiodomethane

(CH_2I_2) concentrations measured simultaneously in seawater and air. These compounds are important components in global cycling of iodine, with combined emissions comparable to that of methyl iodide (CH_3I) (Jones et al., 2010). Air abundances were measured using the same type of TD-GC-MS as described for the water system. Both water and air phases were calibrated using NOAA standard SX-3570 and inter-calibrated between UK research institutions (Jones et al., 2011). Concentrations of all quantified halocarbons within this cylinder (34 L Essex Cryogenics) were measured as stable for > 4 years from filling. Air concentrations of CH_2ICl and CH_2I_2 were at least partly driven by wind speed and photolysis during the cruise, showing strong diurnal cycles (night-time maxima) and with higher abundances at higher wind speeds (Fig. 6). This is consistent with their short atmospheric lifetimes (Montzka et al., 2011) and the fact that their main source is (largely wind-driven) air-sea exchange. In seawater, CH_2I_2 also showed a clear diurnal cycle in synchrony with the air observations. This is the first time that a VSLS diurnal cycle has been measured in seawater, but is also consistent with expectations since the lifetime of CH_2I_2 in surface seawater is only a few minutes (Jones and Carpenter, 2005). This observation of diurnal cycling was only possible with high temporal resolution, a low background signal and very little sample carry-over of the AutoP & T system.

4 Conclusions

The AutoP & T's low cost and simplicity make it a feasible addition to any TD-GC-MS system and it has been shown to be robust (using pinch valves in later iterations) throughout extended ship-borne sampling campaigns. Filtration of the sample was found to be a large source of potential error. Whereas halocarbons appeared robust toward filtration, DMS was more sensitive (Kiene and Slezak, 2006; Saltzman et al., 2009) and required new filter media per water sample to avoid production occurring on the filter between samples. A further modification to improve the system would be an automated system for filter changing and the addition of an optical sensor for measur-

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ing the purge tube fill volume. Other instrumental issues encountered using this system were largely a result of water vapour ingress beyond the water removal steps. Salt was found to block narrow bore tubing and mass spectrometer sensitivity decreased as water accumulated in the TD-GC system. This highlights that complete water removal is imperative for robust system operation.

The AutoP & T approach of this study is not meant to indicate that this is necessarily the best method for seawater analysis. Equilibrator systems have advantages, such as reduced mechanical and thermal stress on the sample and do not require extensive filtration. However, equilibrators often require more method validation and rely upon the system reaching equilibrium whereas the AutoP & T method can be set up and tested relatively easily, provides an absolute concentration measurement and can be applied to a large range of analytes greater than within the scope of this work.

The AutoP & T system described here has proven capable of determining low levels of atmospherically important trace gases in the ocean. It has been successfully applied to the quantification of ocean–atmosphere fluxes with a 50 min temporal resolution, fast enough to capture gradients in diurnal cycling whilst maintaining a low limit of detection for short-lived gas species. Purge efficiencies were tested at $> 80\%$ for all analytes (within SD) using 20 mL sample volumes at 50 °C and purging with 50 mL min^{-1} N$_2$ for 20 min.

The Supplement related to this article is available online at doi:10.5194/osd-11-2979-2014-supplement.

References

Asare, N. K., Turley, C. M., Nightingale, P. D., and Nimmo, M.: Microbially-mediated methyl iodide production in water samples from an estuarine system, J. Environ., 1, 75–83, 2012. 2981

5 Beale, R., Liss, P. S., Dixon, J. L., and Nightingale, P. D.: Quantification of oxygenated volatile organic compounds in seawater by membrane inlet-proton transfer reaction/mass spectrometry, Anal. Chim. Acta, 706, 128–134, doi:10.1016/j.aca.2011.08.023, 2011. 2982

Bouteiller, A. L., Blanchot, J., and Rodier, M.: Size distribution patterns of phytoplankton in the western Pacific: towards a generalization for the tropical open ocean, Deep-Sea Res. Pt. A,
10 39, 805–823, doi:10.1016/0198-0149(92)90123-B, 1992. 2984

Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J., Mondeel, D. J., Aydin, M., and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons, Global Biogeochem. Cy., 21, GB1023, doi:10.1029/2006GB002732, 2007. 2982

15 Carpenter, L., Malin, G., Liss, P., and Kupper, F.: Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic, Global Biogeochem. Cy., 14, 1191–1204, 2000. 2981

Carpenter, L. J. and Liss, P. S.: On temperate sources of bromoform and other reactive organic bromine gases, J. Geophys. Res.-Atmos., 105, 20539–20547, 2000. 2981

20 Chance, R., Baker, A. R., Küpper, F. C., Hughes, C., Kloareg, B., and Malin, G.: Release and transformations of inorganic iodine by marine macroalgae, Estuar. Coast. Shelf S., 82, 406–414, 2009. 2981

Davis, D., Chen, G., Kasibhatla, P., Jefferson, A., Tanner, D., Eisele, F., Lenschow, D., Neff, W., and Berresheim, H.: DMS oxidation in the Antarctic marine boundary layer: Comparison of
25 model simulations and held observations of DMS, DMSO, $DMSO_2$, $H_2SO_{4(g)}$, $MSA_{(g)}$, and $MSA_{(p)}$, J. Geophys. Res.Atmos., 103, 1657–1678, 1998. 2980

DEFRA: The Water Supply (Water Quality) Regulations 2000, available at: http://dwi.defra.gov.uk/stakeholders/guidance-and-codes-of-practice/WS(WQ)-regs-england2010.pdf (last access: 11 December 2014), 2000. 2981

30 Goodwin, K., North, W., and Lidstrom, M.: Production of bromoform and dibromomethane by giant kelp: factors affecting release and comparison to anthropogenic bromine sources, Limnol. Oceanogr., 42, 1725–1734, 1997. 2981

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Groszko, W. and Moore, R.: A semipermeable membrane equilibrator for halomethanes in sea-water, Chemosphere, 36, 3083–3092, doi:10.1016/S0045-6535(98)00019-8, 1998. 2982

Happell, J. and Wallace, D.: Methyl iodide in the Greenland/Norwegian Seas and the tropical Atlantic Ocean: evidence for photochemical production, Geophys. Res. Lett., 23, 2105–2108, 1996. 2981

Hughes, C., Malin, G., Turley, C., Keely, B., Nightingale, P., and Liss, P.: The production of volatile iodocarbons by biogenic marine aggregates, Limnol. Oceanogr., 53, 867–872, 2008. 2981

Johnson, J. E.: Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases, Anal. Chim. Acta, 395, 119–132, doi:10.1016/S0003-2670(99)00361-X, 1999. 2982

Jones, C. and Carpenter, L.: Solar photolysis of CH_2I_2, CH_2ICl, and CH_2IBr in water, saltwater, and seawater, Environ. Sci. Technol., 39, 6130–6137, 2005. 2989

Jones, C., Hornsby, K., Sommariva, R., Dunk, R., Von Glasow, R., McFiggans, G., and Carpenter, L.: Quantifying the contribution of marine organic gases to atmospheric iodine, Geophys. Res. Lett., 37, L18804, doi:10.1029/2010GL043990, 2010. 2989

Jones, C. E., Hornsby, K. E., Dunk, R. M., Leigh, R. J., and Carpenter, L. J.: Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign, Atmos. Chem. Phys., 9, 8757–8769, doi:10.5194/acp-9-8757-2009, 2009. 2982

Jones, C. E., Andrews, S. J., Carpenter, L. J., Hogan, C., Hopkins, F. E., Laube, J. C., Robinson, A. D., Spain, T. G., Archer, S. D., Harris, N. R. P., Nightingale, P. D., O'Doherty, S. J., Oram, D. E., Pyle, J. A., Butler, J. H., and Hall, B. D.: Results from the first national UK inter-laboratory calibration for very short-lived halocarbons, Atmos. Meas. Tech., 4, 865–874, doi:10.5194/amt-4-865-2011, 2011. 2989

Kameyama, S., Tanimoto, H., Inomata, S., Tsunogai, U., Ooki, A., Takeda, S., Obata, H., Tsuda, A., and Uematsu, M.: High-resolution measurement of multiple volatile organic compounds dissolved in seawater using equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS), Mar. Chem., 122, 59–73, doi:10.1016/j.marchem.2010.08.003, 2010. 2982

Kameyama, S., Yoshida, S., Tanimoto, H., Inomata, S., Suzuki, K., and Yoshikawa-Inoue, H.: High-resolution observations of dissolved isoprene in surface seawater in the Southern Ocean during austral summer 2010–2011, J. Oceanogr., 70, 225–239, 2014. 2982

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Kiene, R. P. and Slezak, D.: Low dissolved DMSP concentrations in seawater revealed by small-volume gravity filtration and dialysis sampling, Limnol. Oceanogr.-Meth., 4, 80–95, 2006. 2989

Ledyard, K. M. and Dacey, J. W.: Dimethylsulfide production from dimethylsulfoniopropionate by a marine bacterium, Mar. Ecol.-Prog. Ser., 110, 95–103, 1994. 2981, 2985

Leedham, E. C., Hughes, C., Keng, F. S. L., Phang, S.-M., Malin, G., and Sturges, W. T.: Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, Biogeosciences, 10, 3615–3633, doi:10.5194/bg-10-3615-2013, 2013. 2981

Leifer, I., Patro, R. K., and Bowyer, P.: A study on the temperature variation of rise velocity for large clean bubbles, J. Atmos. Ocean. Tech., 17, 1392–1402, 2000. 2986

Lidster, R. T., Hamilton, J. F., Lee, J. D., Lewis, A. C., Hopkins, J. R., Punjabi, S., Rickard, A. R., and Young, J. C.: The impact of monoaromatic hydrocarbons on OH reactivity in the coastal UK boundary layer and free troposphere, Atmos. Chem. Phys., 14, 6677–6693, doi:10.5194/acp-14-6677-2014, 2014. 2985

Loose, B., Stute, M., Alexander, P., and Smethie, W. M.: Design and deployment of a portable membrane equilibrator for sampling aqueous dissolved gases, Water Resour. Res., 45, W00D34, doi:10.1029/2008WR006969, 2009. 2982

McFiggans, G., Bale, C. S. E., Ball, S. M., Beames, J. M., Bloss, W. J., Carpenter, L. J., Dorsey, J., Dunk, R., Flynn, M. J., Furneaux, K. L., Gallagher, M. W., Heard, D. E., Hollingsworth, A. M., Hornsby, K., Ingham, T., Jones, C. E., Jones, R. L., Kramer, L. J., Langridge, J. M., Leblanc, C., LeCrane, J.-P., Lee, J. D., Leigh, R. J., Longley, I., Mahajan, A. S., Monks, P. S., Oetjen, H., Orr-Ewing, A. J., Plane, J. M. C., Potin, P., Shillings, A. J. L., Thomas, F., von Glasow, R., Wada, R., Whalley, L. K., and Whitehead, J. D.: Iodine-mediated coastal particle formation: an overview of the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) Roscoff coastal study, Atmos. Chem. Phys., 10, 2975–2999, doi:10.5194/acp-10-2975-2010, 2010. 2981

Montzka, S., Reimann, S., O'Doherty, S., Engel, A., Krüger, K., and Sturges, W.: Ozone-depleting substances (ODSs) and related chemicals, World Meteorological Organization, 2011. 2981, 2989

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G., and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12, 1423–1447, doi:10.5194/acp-12-1423-2012, 2012. 2981

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Quack, B., Atlas, E., Petrick, G., Stroud, V., Schauffler, S., and Wallace, D.: Oceanic bromoform sources for the tropical atmosphere, Geophys. Res. Lett, 31, L23S05, doi:10.1029/2004GL020597, 2004. 2981

Quack, B., Peeken, I., Petrick, G., and Nachtigall, K.: Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling, J. Geophys. Res.-Oceans, 112, C10006, doi:10.1029/2006JC003803, 2007. 2982

Raimund, S., Quack, B., Bozec, Y., Vernet, M., Rossi, V., Garçon, V., Morel, Y., and Morin, P.: Sources of short-lived bromocarbons in the Iberian upwelling system, Biogeosciences, 8, 1551–1564, doi:10.5194/bg-8-1551-2011, 2011. 2982

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature, 453, 1232–1235, 2008. 2981

Richter, U. and Wallace, D.: Production of methyl iodide in the tropical Atlantic Ocean, Geophys. Res. Lett., 31, L23S03, doi:10.1029/2004GL020779, 2004. 2981

Saiz-Lopez, A., Lamarque, J.-F., Kinnison, D. E., Tilmes, S., Ordóñez, C., Orlando, J. J., Conley, A. J., Plane, J. M. C., Mahajan, A. S., Sousa Santos, G., Atlas, E. L., Blake, D. R., Sander, S. P., Schauffler, S., Thompson, A. M., and Brasseur, G.: Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, Atmos. Chem. Phys., 12, 3939–3949, doi:10.5194/acp-12-3939-2012, 2012. 2981

Saltzman, E. S., De Bruyn, W. J., Lawler, M. J., Marandino, C. A., and McCormick, C. A.: A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater, Ocean Sci., 5, 537–546, doi:10.5194/os-5-537-2009, 2009. 2982, 2989

Sander, R.: Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry, Max-Planck Institute of Chemistry, 1999. 2996

Santos, G. S. and Rast, S.: A global model study of natural bromine sources and the effects on tropospheric chemistry using MOZART4, J. Atmos. Chem., 70, 69–89, doi:10.1007/s10874-013-9252-y, 2013. 2981

Schall, C., Laturnus, F., and Heumann, K.: Biogenic volatile organoiodine and organobromine compounds released from polar macroalgae, Chemosphere, 28, 1315–1324, 1994. 2981

Sturges, W., Sullivan, C., Schnell, R., Heidt, L., and Pollock, W.: Bromoalkane production by Antarctic ice algae, Tellus B, 45, 120–126, 1993. 2981

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Thompson, T., Fawell, J., Kunikane, S., Jackson, D., Appleyard, S., Callan, P., Bartram, J., and Kingston, P.: Chemical Safety of Drinking-Water, World Health Organization, 2007. 2981

Tokarczyk, R. and Moore, R.: Production of volatile organohalogens by phytoplankton cultures, Geophys. Res. Lett., 21, 285–288, 1994. 2981

U.S.EPA: Title 40 – Protection of Environment, Code of Federal Regulations (annual edition), 2010. 2981

von Glasow, R., von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J.: Impact of reactive bromine chemistry in the troposphere, Atmos. Chem. Phys., 4, 2481–2497, doi:10.5194/acp-4-2481-2004, 2004. 2981

Yang, M., Beale, R., Liss, P., Johnson, M., Blomquist, B., and Nightingale, P.: Air–sea fluxes of oxygenated volatile organic compounds across the Atlantic Ocean, Atmos. Chem. Phys., 14, 7499–7517, doi:10.5194/acp-14-7499-2014, 2014. 2982

Yang, X., Cox, R., Warwick, N., Pyle, J., Carver, G., O'Connor, F., and Savage, N.: Tropospheric bromine chemistry and its impacts on ozone: a model study, J. Geophys. Res., 110, D23311, doi:10.1029/2005JD006244, 2005. 2981

Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients, Atmos. Chem. Phys., 8, 4559–4593, doi:10.5194/acp-8-4559-2008, 2008. 2996

Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, Atmos. Chem. Phys., 11, 9155–9206, doi:10.5194/acp-11-9155-2011, 2011. 2996

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Table 1. Individual compound purge efficiencies using AutoP&T, associated data, water removal analyte recoveries and limits of detection (LOD).

Label	Compound	Retention time	k_H^{cc}	B. pt. (K) NIST	% purge eff. 84 mL	% RSD 84 mL	% purge eff. 20 mL	% RSD 20 mL	% coldfinger recovery	% Nafion recovery	LOD (pmol L^{-1})
1	Isoprene	219.4	1.461[a]	307	96	1.7	97	0.7	98	99	0.1
2	DMS	229.5	0.085[a]	311	89	2.2	100	0.2	105	92	0.6
3	CH_3I	234.1	0.292[a]	316	92	5.4	83	9.4	100	95	0.05
4	CH_2BrCl	303.5	–	341	85	4.5	100	2.7	104	94	0.05
5	$CHCl_3$	304.9	0.151[a]	334	91	2.9	83	6.9	98	98	0.02
6	CCl_4	335.6	1.076[a]	350	93	4.7	100	0.2	104	98	0.02
7	CH_2Br_2	373.4	0.044[a]	370	68	4.6	98	2.4	102	93	0.06
8	$CHBrCl_2$	378.1	0.102[a]	363	94	2.8	99	3.1	98	99	0.04
9	CH_2ICl	393.3	0.046[a]	381	69	2.8	100	0.7	104	93	0.06
10	$CHBr_2Cl$	449.6	0.056[a]	390	78	2.3	100	1.0	99	92	0.04
11	CH_2IBr	461.2	–	405	53	3.4	98	1.6	100	91	0.06
12	$CHBr_3$	516.8	0.029[a]	422	57	1.8	98	0.4	98	91	0.02
13	α-pinene	531.4	0.835[a]	430	100	1.4	99	1.6	96	1	0.1
14	CH_2I_2	541.9	0.018[a]	279	43	3.1	91	1.5	99	101	0.04
15	Myrcene	554.8	1.290[b]	440	100	9.0	100	20.1	89	0	0.3
16	β-pinene	562.8	0.650[b]	440	100	0.6	96	3.2	90	0	0.2
17	Carene	577.0	0.613[b]	447	100	1.3	94	0.1	93	0	0.2
18	Ocimene	580.6	1.179[b]	448	97	1.8	100	5.2	95	0	0.4
19	Limonene	588.0	0.804[b]	451	100	2.1	98	3.3	89	0	0.3

[a] Where available, Henry's Law constants reproduced from the compiled list by Sander (1999).

[b] Calculated assuming vapour pressure of 0.003 atm and using the AIOMFAC model (http://www.aiomfac.caltech.edu, Zuend et al., 2008, 2011).
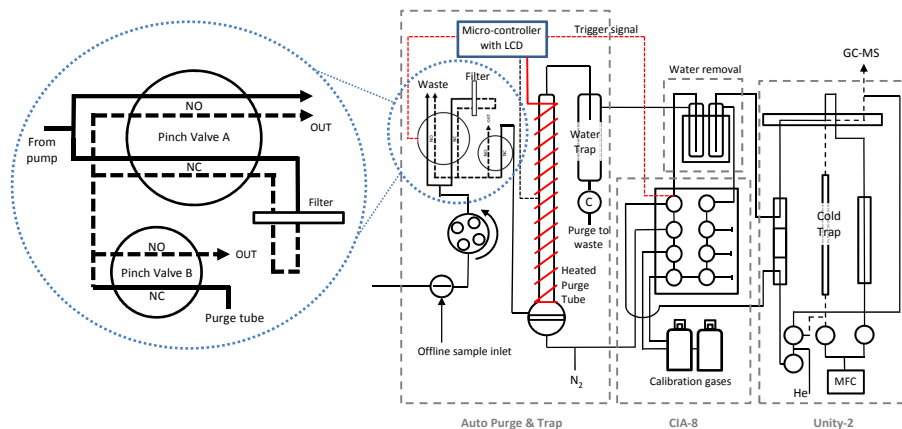
Figure 1. Flow path schematic of the AutoP & T-TD-GC-MS system with "coldfinger" water removal system. Red lines represent electrical connections. Expanded circle: water sample flow paths through the two, 3-way pinch valves used to automate the purge and trap process.
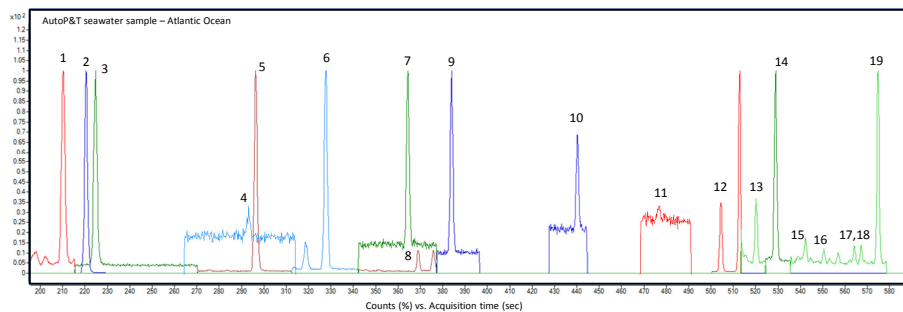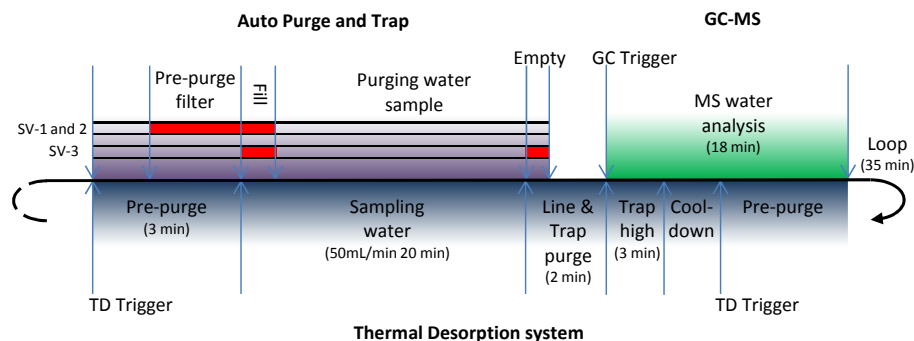
Figure 2. Example Atlantic Ocean seawater chromatogram obtained using the AutoP & T with extracted ions individually scaled. Compound names of peak labels are listed in Table 1.

Figure 3. Graphical representation of the AutoP & T cycle (purple shading) beginning with the trigger from the thermal desorption cycle (blue shading) and its subsequent triggering of the GC-MS run (green shading).
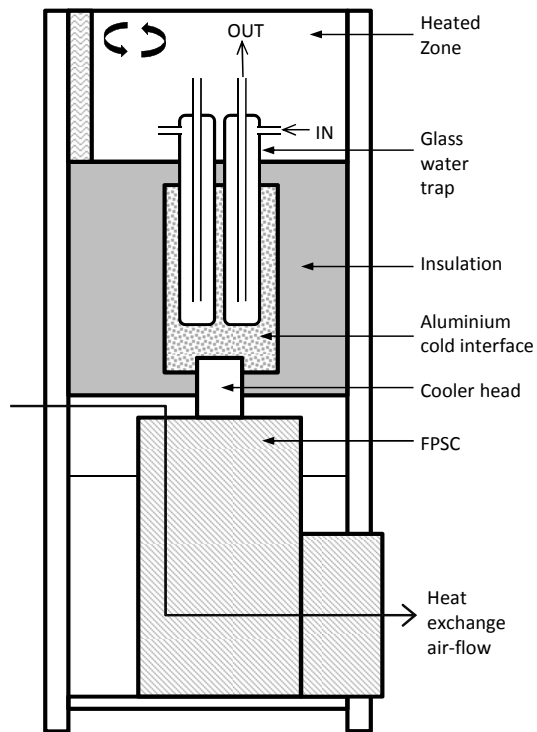
Figure 4. Schematic of the Free Piston Stirling Cooler (FPSC) water trap. Glass water traps cooled to −30 °C via a billet aluminium interface insulated using milled expanded polyurethane foam.
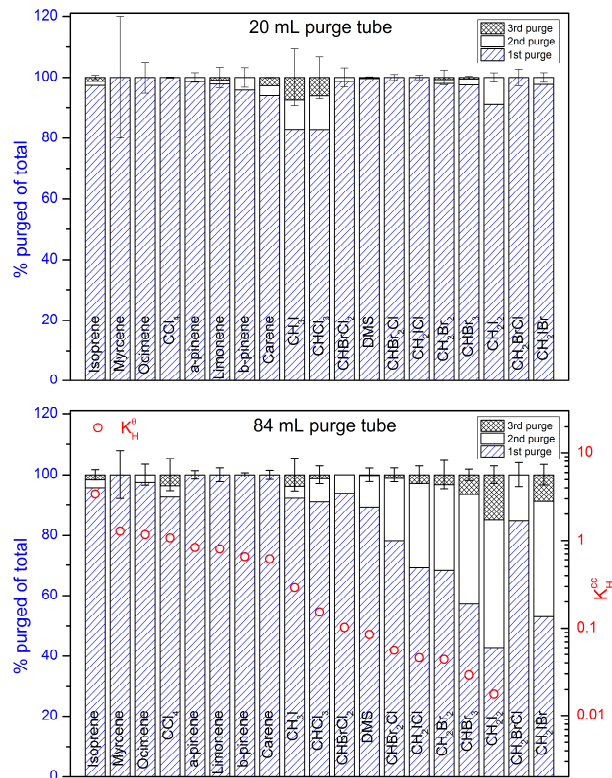
Figure 5. Purge efficiencies for 20 mL (top) and 84 mL (bottom) water samples. Blue bars represent the % purged from the sample in the first purge. Error bars show the run to run reproducibility of the system. For the 84 mL samples K_H^{cc} is plotted as red circles and decreases with purge efficiency.

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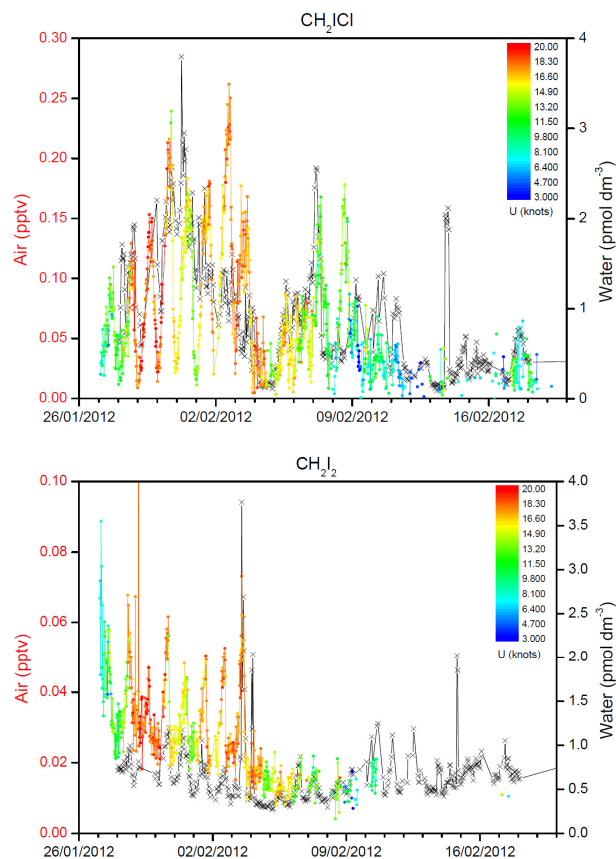Printer-friendly Version

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Figure 6. Example fieldwork data from the East Tropical Pacific using the AutoP & T system. Air concentrations (squares coloured by wind speed) are plotted with water concentrations (black crosses) for CH_2ICl (top) and CH_2I_2 (bottom).

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