

Interactive comment on “Technical Note: A fully automated purge and trap-GC-MS system for quantification of volatile organic compound (VOC) fluxes between the ocean and atmosphere” by S. J. Andrews et al.

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We thank you for your in-depth and constructive comments.

The responses are listed below in the format: Referee comment, Author response, Changes to text in response to Referee comment.

Comment 1 from referee: The manuscript describes an automated purge and trap inlet system to a GC-MS for measuring dissolved very short-lived halogenated species from seawater in discrete or continuous mode. The description of the analytical system

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and its performance characteristics are well documented and it appears that this is a system that, despite its size and complexity, (large GC-MS and inlet system) is readily able to go to sea, as the authors report that it has collected good quality data on 6 cruises. I think it is a nice contribution to the body of literature on sea-going purge and trap systems and the total number of analytes captured is also impressive. It would be valuable to build large data sets of these VOC fluxes over the ocean. I have only one major concern that I would like the authors to clarify, and a few minor comments about the text. The paper concerns itself primarily with describing the PT system and extraction of gases from seawater. However, the title refers to VOC fluxes, and in the last figure (Figure 6) indeed we see air-side concentrations of two VOCs. What is not clear, is whether these air-side measurements were made with the same system or whether they require a different system altogether. I see no part of the diagram in Figure 1 where air is inlet to the system for GC-MS analysis and no discussion of air sampling to avoid VOC contamination from shipboard activities. Do you have to trap and preconcentrate air samples for GC-MS analysis of these VOCs? If the air-side samples were collected with the same system, this should be indicated in Figure 1 and in the text with adequate description of how that was done. If those measurements require a separate method/apparatus that is not part of this system, then the authors should make that clear in the text, in Figure 6.

Response 1 from authors: We agree that this was an oversight. We have modified Fig. 1 (below) to show how air samples were processed. We have also added text to the end of section 2.2 to describe how air samples were collected by the instrument between each water sample

Authors changes to manuscript in response to referee: "In order to calculate ocean-atmospheric fluxes, air samples were acquired between each water sample. Air was drawn from a bow inlet through 1/2" PFA tubing at approx. 35 L min⁻¹ using a diaphragm pump (KNF, N035.1.2AN.18). Before the air reached this pump it was drawn through a clean stainless steel bellows pump (Senior Aerospace, MB-158) and pres-

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surised into the thermal desorption unit at 10 psi with the majority of flow vented via a proportional relief valve." In section 2.1 we will add "As for direct air analysis, the gas sample is pre-concentrated..." to confirm that the same instrumental method was used for both air and water samples.

Comment 2 from referee: Further, the authors should change the title of the manuscript to more accurately reflect what their system can do, something like "A fully automated purge and trap-GC-MS system for quantification of volatile organic compound (VOC) compounds in water and seawater".

Response 2 from authors: The change of title to omit the word "fluxes" is not required due to the addition of a description of air sampling to the text.

Authors changes to manuscript in response to referee: None

Comment 3 from referee: 3.1 Line 8: Is it not possible to obtain VOC-free water from a MilliQ system? I would expect careful distillation would have a similar effect.

Response 3 from authors: Due to the addition of halogens to domestic water supplies we have found that they contain a large quantity of all the halocarbon analytes we measure. MilliQ machines do not remove this and produce water with concentrations much higher than open ocean levels. We have purchased ultrapure water for LC-MS systems and this too is unsatisfactory. The best results we have had are from 3000 m deep seawater (described in the text) or mineral water purged with VOC free- pure air generated using a heated platinum catalyst.

Authors changes to manuscript in response to referee: None, although additions to manuscript following author comment number 4 are applicable.

Comment 4 from referee: 3.1 Line 10: What is meant by "conditioning" of the P&T system. If this is some kind of system memory effect, a much more detailed description is required.

Response 4 from authors: The conditioning relates to the previous point about obtain-
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ing halocarbon-free water. Generally the first few samples at the beginning of a cruise are high compared to subsequent samples. This is likely due to a combination of the purge tube "conditioning" or adapting to the low concentrations in open ocean water after being ran in the lab with water containing much higher concentrations and the conditioning of the ships seawater supply which sits idle in dock and is only turned on once sailing in unpolluted waters. These first few data points are flagged as erroneous.

We feel that this is a very fair comment and the text would benefit from clarification. The text has been changed to the following:

Authors changes to manuscript in response to referee: Section 3.1 line 6 "The reproducibility of the system was tested in the laboratory pre-, during and post-research cruises. Obtaining blank samples for laboratory tests was difficult due to the ubiquitously high concentrations of VOCs, especially halogenated species, in domestic and laboratory water supplies (Milli-Q, Fisher Scientific Optima LC-MS, etc.). It was noted during fieldwork that the first few seawater samples collected from the ship's continuous supply were usually higher than average – these data points were discarded. Continual system operation with underway seawater resulted in a 'conditioning' of either the AutoP&T and/or the ship's underway water supply, as suggested by stabilization of concentrations after 2-3 hours. Duplicate analysis of underway samples from unproductive oceanic regions showed very good reproducibility (7 % RSD for CCl₄, 24 hrs sampling, 07/02/2012, East Tropical Pacific). This is due to the system being optimised to trace levels far below those present in commercially available water and for this reason it is likely that reproducibility is actually better during shipboard deployment than during laboratory based trials and system performance testing should be carried out in the field. For post cruise performance testing, seawater was collected from 3000 m depth in the Arctic Ocean, filtered, sparged with N₂ and used as a blank matrix, spiked with each compound of interest at mid-high ocean representative levels (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.

Comment 5 from referee: Figure 4 – Figure 4, sentence starting with “Glass water traps..” seems to be missing an adverb or something. Response 5 from authors: inserted “Glass water traps are”

Authors changes to manuscript in response to referee: inserted “Glass water traps are”

Comment 6 from referee: Page 5, lines 5-15. References indicating that the VOCs of interest are quantitatively trapped at -30°C should be included here. Response 6 from authors: Sorbent breakthrough tests on Tenax TA at -30°C were carried out as standard with thermal desorption for all analytes of interest. Although references do exist for these compounds and sorbents, in reality this is system dependent and as such we will add the following text to confirm that we carried out these tests on our system.

Authors changes to manuscript in response to referee: Page 5 line 7 “The gas sample is preconcentrated onto the cooled (-30°C) adsorbent trap (Tenax TA) of the TD unit. All analytes were quantitatively trapped in breakthrough tests up to 3 L sample volume at these conditions. The sample was desorbed at 250°C onto the GC column (60 m $320\ \mu\text{m}$ I.D. $1\ \mu\text{m}$ 5% phenyl film, SGE) which was held at ...”

Comment 7 from referee: Page 6, Line 5-10. You indicated PTFE valves are easily damaged. Please include the make/model of the valves that you found to work well. Response 7 from authors: In the previous paragraph, Page 5 line 26 it is stated that we used pinch valves and model numbers are listed

Authors changes to manuscript in response to referee: None

Interactive comment on Ocean Sci. Discuss., 11, 2979, 2014.

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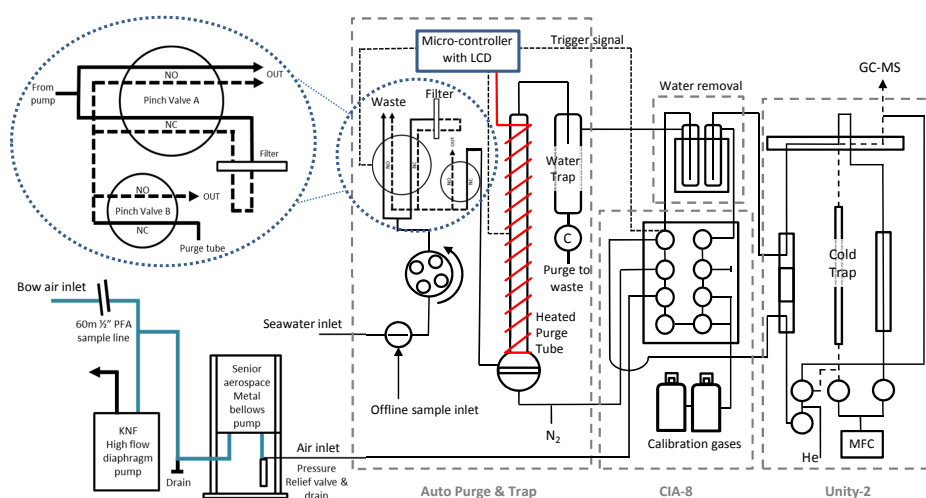


Fig. 1.

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