Topic Editor Decision: Reconsider after major revisions (04 Jun 2020) by Piers Chapman

Comments to the Author:

I have now received three reviews of the revised paper, two of which suggest that it needs considerable work before it can be published. In the circumstances, I ask the authors to consider carefully the comments of the reviewers and then submit a revised manuscript, as the information is certainly of considerable importance to researchers wanting to use similar tracers to investigate water movement and mixing rates. At this stage I am not sure if the work required counts as a major or minor revision, and the paper may need to be sent out again for review.

We greatly thank three referees for your constructive suggestions and comments. Below, we address all the comments and describe our responses to them one by one. In the revised manuscript, all changes from the original text are marked.

The main result from this study is that although a couple of the investigated tracers might be useful as oceanic tracers, at least under some circumstances such as cold waters, etc., none of the tracers would fully qualify at this time. Of the four basic requirements, 1) we have a good handle of the input function in the atmosphere through the work of the "atmospheric community". 2) for the solubility, we recognize that targeted work on this is needed for all compounds, 3) for stability we have an idea which ones are possibly stable, but more work is needed here too (laboratory experiments under controlled conditions could be one way), and 4) the analytical limitations in the current configuration are described, also here laboratory experiments are needed to fully understand/improve the system. In summary, we are not quite yet in the position to recommend targeted observations of these tracers, but this study provides a useful summary of the current knowledge, including the new research reported on in this manuscript, to guide further, more targeted experiments.

With this in mind, we hope that the manuscript is now acceptable for publication in Ocean Science.

os-2019-101-referee-report-1

This manuscript has improved significantly and I think now suitable for publication. I only have a few minor suggestions.

Pg 7 lines 21-25. This is material more suited for introduction and not methods section. I think could just start with statement on using TTD framework to interpret data

Response: The texts to introduce ventilation have been moved as the first paragraph in the Introduction.

Pg 13, line 28. I think more accurate to replace "considered" with "used only", as the short lifetime could be very useful if combine with age from CFC-12 or SF_6.

Response: Done.

Pg 14, last paragraph. This is a bit repetitive as just mentioned above and will then be mentioned again in conclusions. I think should be removed or used to replace text in conclusions (I like description here better than longer discussion in conclusions).

Response: The last paragraph has replaced some texts in conclusions. And the conclusion section has been rewritten.

os-2019-101-referee-report-2

Much of the interpretation of tracer ages and TTDs would not warrant publication on their own. It is the development of the methods to focus on the potential new transient tracers that would be the important contribution of this research. However, the authors have not presented enough information on the analytical techniques to convince me that the compounds can be measured at the precision and accuracy necessary to identify the compounds as useful tracers.

This manuscript is a companion piece to a previous study by these two authors (along with additional co-authors) to identify potential new anthropogenic transient tracers for studies of ocean ventilation on decadal timescales. While the first manuscript (Li et al., 2019) focused on reconstructing the atmospheric histories and estimating the solubilities in water and seawater for several halogenated compounds, this manuscript is focused on the feasibility of measuring these compounds in seawater, demonstrating whether they behave conservatively, and finally rating their potential as tracers. In my view, the key to the publication of this manuscript is to have demonstrated the capability to measure the seawater concentration of these tracers. As such, the authors should have focused on the methods necessary to produce high-quality "Medusa" tracer data. In the data presented from the Mediterranean Sea, only 9 of the 21 samples are evaluated as

good. Another 10 are given the flag of 5. The data from the Baltic Sea may be better, but the authors spend very little time on their interpretation. The remainder of the manuscript consists of hypothetical data interpretation (e.g. Fig. 5, Figs. S1 and S2) that is not worthy of publication on their own. I cannot recommend that this manuscript be published without major revisions that may include further method development. Developing the implementation of new tracers for studying the ocean is important, and I encourage the authors to understand the issues affecting their measurements. I would suggest some laboratory measurements using seawater samples equilibrated with atmospheric gases as a potential method for future studies.

Response: Many thanks for your comment. Before the Medusa-Aqua system used for the measurement of seawater samples from the Mediterranean Sea (cruise MSM72) and the Baltic Sea (cruise AL516), it has been improved. The improved processes have been added in the Supplement (Section S3, Figures S1-S7, Tables S3-S5). For data from the Baltic Sea, we only collected a few samples for analysis of reproducibility and we have interpreted them all. The results can be found in the new Table 1 and Table S4b.

The suggestion for laboratory experiments using seawater with equilibrated sea-water samples is certainly a very good idea. The main result from this study is that although a couple of the investigated tracers might be useful as oceanic tracers, at least under some circumstances such as cold waters, etc., none of the tracers would qualify at this time. Of the four basic requirements, 1) we have a good handle of the input function in the atmosphere through the work of the "atmospheric community". 2) for the solubility, we know that targeted work on this is needed for all compounds, 3) for stability we have an idea which ones are possibly stable, but more work is needed here too (laboratory experiments under controlled conditions could be one way), and 4) the analytical limitations in the current configuration is described, also here laboratory experiments are needed to fully understand/improve the system. In summary, we are not quite yet in the position to recommend targeted observations of these tracers, but the current study provides a useful summary of the current knowledge to guide further, more targeted experiments. With this in mind, we argue that the results can, and should, be published.

In addition to the major scientific issue, the manuscript has many other issues with both writing and with some of the interpretation. I have listed many of them below:

p. 1, L21 – "potential be tracers"

Response: "potential as tracers"

p. 1, L31 - The source function for bomb tritium is not well constrained for much of the ocean. It was the 3He-3H tracer pair which are used as transient tracers. On the pedantic side, ^{39}Ar is not a "transient" tracer as it's assumed to be at steady-state.

Response: "Tritium (^{3}H)" has been changed to "Tritium-Helium (^{3}H-^{3}He)", and similar change for Figure 1. For ^{39}Ar, that is obviously correct. In a previous paper (Stöven et al., 2015), we used the terms "natural radioactive transient tracers" and "chronological transient tracers" to make this distinction. Maybe not perfect as the term "transient" is still in there, but at least it is a step in the right direction. We have now made this clear in the manuscript by adding ", although ^{39}Ar is assumed to be in steady-state and cannot be regarded as a transient racer in the true meaning of the word" at the end of the sentence.

p.2, L 3 – the industrial use of CFC-12 was phased out; assign a year to the Montreal Protocol

Response: The sentence "the <u>use</u> of CFC-12 was <u>phased-out</u> as a result of the implementation of the <u>Montreal Protocol</u>" has been changed to "the <u>industrial use</u> of CFC-12 and CFC-11 were <u>phased out</u> as a result of the implementation of the <u>1987 Montreal Protocol</u> …."

p.2, L9 – Although restrictions on SF_6 may be implemented, the concentrations in the atmosphere will continue to rise for the foreseeable future due to its long atmospheric lifetime. Note that the PFCs also have high GHG potential, yet the authors conclude that they should be considered as transient tracers.

Response: SF_6 is the compound that has the highest Global Warming Potential (GWP) among halocarbons and related compounds (including CFCs, HCFCs, HFCs, Halons, PFCs, HFEs, HGs, etc.). It has a GWP of 23,507 over 100 years, while PFC-14 and PFC-116 have GWPs of 6,626 and 11,123 respectively (Hodnebrog et al., 2013). Compared to SF_6, the GWPs of PFCs are relatively lower.

The corresponding sentences "However, some local restrictions are in place for the production and use of SF_6 due to its very high global warming potential that may restrict SF_6 to be an oceanic tracer in the future." have been revised as "Due to its very high global warming potential, some local restrictions on the production and use of SF_6 implemented. However, the concentrations of SF_6 in the atmosphere continue to rise due to its long atmospheric lifetime."

p. 2, L15 – Note that CFC-11 is a Level 1 (required) measurement for the US GO-SHIP program (https://usgoship.ucsd.edu/level-1-data/). The measurements of tracers are complicated – fortunately, the Bullister and Wisegarver (2008) paper referenced by the authors describes an analytical system capable of measuring seawater concentrations of CFC-11, CFC-12, SF_6, and CCl_4 precisely and accurately aboard a research vessel.

Response: Although CFC-11 is a Level 1 required measurement for the GO-SHIP program, the application of CFC-11 as an oceanic transient tracer has been largely reduced during the past decade compared to CFC-12 and SF_6, mostly due to the complications on simultaneous observations (for one sample) in seawater. Even though Bullister and Wisegarver solved the problem, few others have used that set-up. We acknowledge that CFC-11 is, and has been, an important transient tracer.

We changed the related sentences "In addition, trichlorofluoromethane (CFC-11), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and carbon tetrachloride (CCl_4) had been extensively used as transient tracers, but have largely been discarded. CFC-11 was found to be degraded in anoxic marine waters (Bullister and Lee, 1995) and has a time-history similar to that of CFC-12. Besides, the simultaneous

measurement of SF_6 and CFC-11 is complicated. Both CFC-113 and CCl_4 have been found to be degraded in warm waters (Roether et al., 2001) as well as in low oxygen waters (Wallace and Krysell, 1989; Huhn et al., 2001)." to "CFC-11 has been extensively used as a transient tracer but found to has a time-history similar to that of CFC-12 and be degraded in anoxic marine waters; the simultaneous measurement of SF_6 and CFC-11 is complicated, so that the use of CFC-11 is being reduced. In addition, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and carbon tetrachloride (CCl_4) have been extensively used as transient tracers, but have now been largely discarded since they have been found to be degraded in warm waters (Roether et al., 2001) as well as in low oxygen waters (Wallace and Krysell, 1989; Huhn et al., 2001).".

p. 2, L20 – There should never be a 1-sentence paragraph

Response: The sentence has been added to the end of the last paragraph.

p.2, L 24 – "Well-quantified sources and sinks" instead of "known input function"

Response: "known input function" has been changed to "well-quantified sources and sinks".

p.2, L 29 - two phrases beginning with "as" makes the sentence confusing to read

Response: "As the replacements of CFCs, the atmospheric abundances of most HCFCs and HFCs are increasing, as are the concentrations of PFCs." has been changed to "The atmospheric abundances of most HCFCs and HFCs are increasing, as are the concentrations of PFCs."

P.2, L 35 - CFC-12 is difficult to use by itself as a tracer; with some caveats, it can be used as a tracer pair with e.g. SF_6. Based upon the reported blank level (0.48 fmol/kg), the utility of SF_6 extends back about 50 y instead of 100 y.

Response: We are sorry for your misunderstanding. "1-100 years" here does not mean the validation period of SF_6 but means that in this seawater timescale range only SF_6 is a relatively reliable transient tracer while ^3H-^3He and CFC-12 are with constraints. This is also the reason why we explore and evaluate the potential tracers in this range considering that tracer pairs are more validated to estimate ages.

Blank values of SF_6 are different depending on various analytical technologies. The blank value of SF_6 is 0 fmol/kg and the detection limit is 0.03 fmol/kg when measured by PT-GC-ECD (Stöven, 2011). Therefore, based upon the detection limit, blank value, and source function, the tracer potential timescale range of SF_6 was estimated as 1-60 years as shown in Figure 1.

In the revised manuscript, "timescale range of 1-100 years" has changed to "timescales less than 100 years". We note that several groups working with GC-ECD systems achieve considerable lower blank levels, although the reported blank level (0.48 fmol/kg), i.e., the detection limit mentioned in the original Table 3 (now Table 1), is relatively high value because such a value is 19 % of the maximum value of SF_6 (2.52 fmol/kg) from measurements on cruise MSM72. Therefore, the current Medusa-Aqua system is still not suitable to measure SF_6 in seawater.

p. 3, L8 – see https://www.ncbi.nlm.nih.gov/pubmed/12608868 for a marine natural product with a C-F bond.
Response: "no known marine natural products contain C-F bonds and" has been removed.

p. 3, L9 – grammar: "reasoning true for PFC-116"
Response: "This is reasoning true for PFC-116" has been removed.

p.3, L 19 – replace of with to; where is "here"?
Response: The corresponding sentences "Judged against their environmental total lifetimes, the oceanic contributions of these compounds are small enough to be neglected. But here the ocean partial lifetimes were calculated only considering the chemical degradation process." have been changed to "Judged against their environmental total lifetimes, the oceanic contributions to these compounds are small enough to be neglected. Note that the partial atmospheric lifetimes with respect to oceanic uptake in Table S1 were calculated only considering the chemical degradation process."

p. 3, L 24 – when I went to this ftp site, the data were available through 2004 and the only HCFC data were for HCFC-22
Response: You could find data for HCFC-22 and HCFC-142b from the GOMECC-1 in 2007. The corresponding text "National Oceanic and Atmospheric Administration (NOAA) cruises in 1992-2008 (ftp://ftp.cmdl.noaa.gov/hats/ocean/, last access: 20 January 2020)." has been changed to "National

Oceanic and Atmospheric Administration (NOAA) cruises in 1992-2004 (ftp://ftp.cmdl.noaa.gov/hats/ocean/, last access: 20 January 2020) and the Gulf of Mexico and East Coast Carbon Cruise (GOMECC) in 2007 (https://seabass.gsfc.nasa.gov/cruise/gomecc-1, last access: 10 June 2020)."

p. 3, L27+ - If these studies of degradation in soils have no relevance for CFC-12 in the seawater, why should they have relevance for the Medusa tracers? This contributes nothing to this manuscript.

Response: Although these studies focused on biodegradation in freshwater and soils, these are the only biodegradation information related to the Medusa tracers we could find in the related environment. Anyway, the paragraph related to the biodegradation of Medusa tracers and the original Table 2 have been moved to Supplement (Section S2 and Table S2).

p. 3, L. 36 – "not enough information…"

Response: "no enough information" has been changed to "not enough information".

p.4, L 13 – grammar: "…rendering transient tracers to penetrate…"

Response: "rendering" has been changed to "which causes".

p. 4, L14 – TTDs assume a time-invariant circulation. In other words, they should not be expected to produce useful information (i.e. Sec. 5.5 is just a data exercise)

Response: Although the assumption of time-invariant ventilation is not valid for the Mediterranean Sea, the TTD model can produce indicative results to understand the mean ages estimated from Medusa tracers (assuming $\Delta/\Gamma =1.0$) and their comparison to those estimated from CFC-12 and SF$_6$. Based on this, we have moved Section 5.5 and Figure 11 to the Supplement as Section S5 and Figure S11.

p.4, L 25 – Lobert et al., 1995 only reported HCFC-22; Beyer et al., 2014 only report CFC-1301. How are these relevant specifically to HFC-134a and HFC-125?

Response: Please see Table B1 in Beyer et al., (2014) for the information of HFC-134a and HFC-125. The original publication (Sousa and Bialkowski, 2001) reported HFC-134a and HFC-125 has also been added in the revised manuscript.

p.4, L 27-28 – citation for the precision of MS vs. ECD?

Response: The sentence "The MS as a detector is becoming increasingly popular since the sensitivity is approaching that of an ECD." has been replaced by "HCFCs and HFC-134a measurements by GC-MS in seawater samples have also been reported in previous studies (Lobert et al., 1996; Ooki and Yokouchi, 2011)."

p. 4, L 28-29 – The last sentence in this paragraph seems to be misplaced.

Response: The last sentence has been removed.

p. 4, L 30 – Shortened not shorted

Response: "shorted" has been changed to "shortened".

p. 4, L 32 – An important component of the Medusa system is the trapping system – I wouldn't say the system is "based" upon it.

Response: "This system is based on trapping of the volatile gases on two traps kept at accurately controlled temperatures" has been changed to "This system includes two traps kept at accurately controlled temperatures to trap the volatile gases".

p. 5, L 28 – This is the first mention of the samples from the Baltic in the manuscript. It seems like a late addition.

Response: In fact, the Baltic Sea samples were first mentioned on L21 on this page (in Section 3 not only Section 3.1). Samples took from here were only for reproducibility. But now we added a sentence on sampling in the Baltic Sea in Section 1.4: "In addition, we report from sampling at a shallow station in the south-west Baltic Sea.", which is the last sentence of the paragraph.

5, L 32 – I doubt that the glass ampoule was closed with a screw.

Response: Followings are the photo and the schematic figure of the stainless-steel mounting system for sampling onboard. The left end was first connected to the outlet of the Niskin bottle. After seawater flushing the glass ampoule three times, the right end was closed with a screw. In order to avoid

misunderstanding, "After <u>removing and closing the ampoule with a screw</u>, the ampoule was flame-sealed as soon as possible under…" has been changed to "The ampoules were flame-sealed immediately after <u>sampling</u> under…".
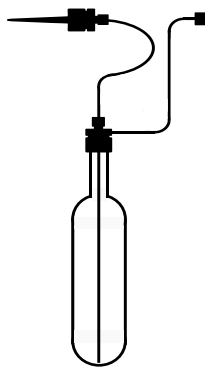
p. 6, L 10 – Is the difference in bubble size noticeable over the depth of the ampoule?

I could understand placing the purge tube near the bottom of the ampoule to increase the physical stirring of the entire water sample. In addition, the bubbles are primarily responsible for stripping the compounds out of the sample – exchange across the gas-water interface would be extremely slow.

Response: It depends on the contact state of the purge tube with the ampoule bottom. Bubble sizes are usually similar over the depth of the ampoule, except for the nitrogen-seawater interface where the bubbles may be connected as a big one and then disappear.

p. 6 and Fig. 2 – The manuscript and/or figure caption need more details. For example, I assume N1, N2 and N3 are the Nafion driers mentioned in the text. If the Methods section is the major component of the paper, elaborate.

Response: For the manuscript, "When introduced into the Medusa, two Nafion dryers of 1.8 m length and one Nafion dryer of 0.6 m length are used to remove water vapor from the samples" has been changed to "Water vapor is removed from the sample by passing the gases through two Nafion dryers <u>(N1 and N2)</u> of 1.8 m length and one <u>(N3)</u> of 0.6 m length".

We also added more descriptions at the end of Figure 2 caption: "N1-N3 are the Nafion driers and V1-V8 are multiport valves. P1 and P2 are pressure transducers (100PSI-A-DO, All Sensor Corporation, Morgan Hill, CA)."

p. 6, L13 – In this method, approximately 2 L of gas is used to purge 1.3 L of sample. In comparison, the Bullister and Wisegarver CFC/SF$_6$ system purges a 200-cc sample with approximately a liter of UHP N2. It's not surprising that it takes multiple purges.

Response: We also tried to purge a ~1.3 L sample with approximately 6 L of N$_2$ for a single purge. It still needs another 1-2 purges to complete the whole purge process. One of the reasons is the larger solubility of the slightly higher polarity of the (most) of the compounds in this study.

p. 6, L 33 – What is the "stripping efficiency" for the first purge? i.e. how much of the total tracer remains in solution?

Response: "The averaged stripping efficiencies for the first purge of seawater samples from cruise MSM72 are 92.5 ± 5.4 % for CFC-12, 76.6 ± 7.9 % for HCFC-22, 87.5 ± 8.3 % for HCFC-141b, 83.2 ± 10.6 % for HCFC-142b, 83.1 ± 7.5 % for HFC-134a, and 88.9 ± 7.5 % for HFC-125.", which has been added in the revised manuscript.

p. 7, L3 – Clarify what is meant by "noises"

Response: The "noise" here means the one in "signal-to-noise". In order to avoid misunderstanding, "The detection limits… based on the signals corresponding to <u>the blank values or noises plus ten standard deviations</u>." has been changed to "The detection limits… based on the signals corresponding to <u>the blank values plus ten standard deviations</u>.".

p. 7, L16 – "Larger" rather than "bigger"; a single purge

Response: "due to <u>using a bigger</u> sampling volume if only considering <u>purge once</u>" has been changed to "due to <u>its larger</u> sampling volume if only considering <u>a single purge</u>".

p. 7 L 18 – Are the blanks additive? Since each analysis of a single purge has an error associated with it, don't those errors add up (or at least the square root of the sum of the blanks squared)?

Response: Good question. It depends on if the blank is in the Medusa system itself, in which case they do add up, or if it is associated with blank values from the ampoule and cracker, in which case they don't add up. In our case, it is only HFC-23 that falls in the second category. For other Medusa tracers, it is already the total uncertainty considered since the precision was calculated as the reproducibility of two measurements at the same depth, which has included the multiple purge errors.

p. 8, L 6 – monotonically

Response: The sentence "Atmospheric histories of tracers should be monotonic increasing in the atmosphere for ideal applicability" has been changed to "For ideal applicability, atmospheric histories of tracers should increase monotonically in the atmosphere".

p. 8, L8 - Why does the HFC-125 source function start in the mid-1990s? In Li et al. (2019) there is a reconstructed atmospheric concentration prior to that.

Response: The reconstructed atmospheric history of HFC-125 started from the 1970s in Li et al. (2019), but atmospheric mole fractions of HFC-125 before 1990 were very close to zero so that they do not show well in Figure 4.

p. 8, L25 – What sets the maximum useful age? Blank level? Source function?

Response: The maximum useful age is decided by the detection limit, blank value (i.e. the quantification limit), and source function.

p. 8, L31 – I'm not sure what evaluated to be transient tracers means. I would probably say demonstrated to be useful (and that includes easily measured).

Response: The sentence "As CFC-12 is limited to be used as a tracer in the upper ocean, PFCs will obtain more attention if they are evaluated to be transient tracers in the ocean." has been removed.

p. 9 first paragraph – If both figures referred to in a paragraph are in the supplemental material, then perhaps that is where the paragraph belongs as well.

Response: The paragraph has been moved to Supplement as part of Section S4.

Section 5.1 – The authors stress the importance of the WML for determining the long-term average saturation, then never return to this concept. I'm not sure why this is here, since they evaluate the Medusa tracers by their surface saturation (Section 5.3)

Response: We are sorry for your misunderstanding. In Section 5.1, we addressed the WML and estimated the historical surface saturation of CFC-12 and SF_6 in the WML from 1987 to 2018. Such saturation value 94 % was also used for Medusa tracers for following calculations of their tracer age and mean age. While in Section 5.3, only surface saturation of Medusa tracers from cruises in 2018, not the historical one, was described. In order to make it clearer, we have changed "For the following calculations…" to "For the following calculations of ages and evaluation of stability…" for the last sentence in Section 5.1.

In fact, the result of the "historical surface saturation" of transient tracers (i.e. CFC-12 and SF_6) in the Mediterranean Sea is a useful number for other studies working on ventilation times in the Mediterranean Sea. This is thus relevant to report on by its own right.

p. 9, L 13 – Examples of density profiles – rather than exemplary

Response: "two exemplary density profiles" has been changed to "two examples of density profiles".

p. 9, L 23 – Takes a long time or has a long time or has been isolated from the atmosphere for a long time?

Response: "where the inflowing Atlantic Water (to the Mediterranean Sea) has a long time to equilibrate with the atmosphere" has been changed to "where the inflowing Atlantic Water (to the Mediterranean Sea) takes a long time to equilibrate with the atmosphere."

p.9, L29 – "generally comparable" is meaningless. The authors should plot CFC-12 (MS) vs. CFC-12 (ECD), and let the reviewer decide if they are comparable.

Response: "generally comparable with" has been changed to "compared with". Note that the comparison is given in Figure 8.

p. 9, L31 – Is 5.9% an absolute difference? This is much larger than the precision of the measurements. How are data flagged as "good"? Note that only 9 of 21 samples are classified as "good".

5.9 % is the average value of the following 18 errors in Table A1 (below) ignoring pressure differences and distance differences of closed stations.

Table A1. Misfit of CFC-12 observations (ppt) measured by Medusa-Aqua system and PT-GC-ECD at closed stations

Medusa-Aqua system		PT-GC-ECD			PT-GC-ECD		
Profile 52		Profile 51			Profile 53		
pressure	CFC-12	pressure	CFC-12	Error52-51	pressure	CFC-12	Error52-53
103.86	470.4	103.4	482.5	2.5%	104.4	462.3	1.7%
508.79	315.5	508.4	315.8	0.1%	507.3	327.7	3.8%
Profile 84		Profile 83			Profile 85		
pressure	CFC-12	pressure	CFC-12	Error84-83	pressure	CFC-12	Error84-85
206.2	388.8	203.4	381.1	2.0%	207.2	413.1	6.1%
1266.5	164.0	1265.0	183.1	11.0%	1264.5	186.5	12.9%
2025.9	174.0	2023.9	197.4	12.6%			
2298.7	209.8	2279.1	228.1	8.3%			
Profile 106		Profile 105			Profile 107		
pressure	CFC-12	pressure	CFC-12	Error106-105	pressure	CFC-12	Error106-107
507.6	269.3	507.9	308.8	13.7%	5073	274.0	1.7%
759.8	230.5	759.6	252.7	9.2%	7594	236.4	2.5%
1012.0	224.8	1012.6	232.2	3.2%	1012.3	231.9	3.1%

We added descriptions before 5.9 %: "We performed a two-step quality control procedure on the medusa data where, in the first step outliers were flagged, and in a second step we flagged data where the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD (Fig. 8). This process led to 9 samples in the Mediterranean that meets all these criteria and have similar concentration as the PT-GC-ECD observations.". Part of the text now in Section 5.2 was moved from Section 5.3.

Data flagged as "good" or "2" are data for sampling sites that measured CFC-12 by Medusa-Aqua system matched the one by PT-GC-ECD, see description in caption of Figure 8.

Section 5.2 – This section is entitled "Observations of Medusa Tracers in Seawater" yet the Medusa tracers are never discussed. The final sentence points to Fig. 9.

At the end of the paragraph in Section 5.2, we added sentences "Concentration ranges of Medusa tracers are 16.1-129.4 ppt for HCFC-22, 2.1-18.7 ppt for HCFC-141b, 5.0-29.0 ppt for HCFC-

142b, 41.0-217.4 ppt for HFC-134a and 4.9-12.8 ppt for HFC-125. The concentrations of Medusa tracers decreased from the surface to the intermediate layer and then increased in the deep layer, consistent with the well-ventilated Mediterranean deep waters.".

p. 10, L 5 – In Section 5.3, the authors wrote that there is too much variability in the surface saturation to be useful.

Response: We did not write just that, we are trying to tell readers that surface saturation is influenced by many factors. More measurements are needed to better discuss the results of surface saturation. Note that all near-surface sampling points are flagged "5", a fact that, although described, was not clear enough described. We have now removed the discussion of surface saturation for the Mediterranean samples.

p. 10, L7 – Do not forget bubble injection and/or vertical mixing

Response: "bubble injection and/or vertical mixing" has been added.

p. 10, L10 – If the Medusa Aqua measurements of CFC-12 are 20 % too low at the surface of the Mediterranean Sea, how can the reviewer have confidence in any of the other tracer measurements? Unless the authors can provide a reasonable explanation for this discrepancy for CFC-12, the remainder of the data are suspect in my opinion. Likewise, the surface CFC-12 saturations of 122% in the Baltic Sea also seem unreasonable. Since data from only one station in the Baltic Sea is reported, I assume that the uncertainties in the surface saturation are an indication of the precision of the Medusa tracer measurements. These are also not very reassuring for the most part (except for HCFC-142b at 2 %).

The manuscript would greatly benefit from measurements of the Medusa tracers in the laboratory under controlled settings. I need to be convinced that Medusa Aqua a reliably measure the tracer concentration under laboratory conditions in order to have confidence in the reported measurements from the Mediterranean and Baltic Seas.

Response: Since all surface samples from the Mediterranean Sea have been flagged as "5", we should not have discussed the surface saturation of Medusa tracers in the Mediterranean Sea in the first place. This has nows been removed from the original Table 5 (now Table 3). We now focus on samples from the Baltic Sea where we have surface saturation of Medusa tracers in one surface sample and two bottom samples. Note that the bottom waters (at about 23.5 meters depth) can be considered as recently ventilated as this water is ventilated on an annual base.

We agree that the reviewer's suggestion to work with a number of seawater samples in a controlled laboratory environment would be the best solution, and something we will try to realize in the future. We suggest that the information in the current article is useful for reporting on the initial field observations to better guide future work, in addition to be (in our opinion) relevant results by its own right.

p. 10, L 25 – grammar: easy to soluble

Response: It has been changed to "ease of solubility".

p. 11, L 21 – Why not take the approach of finding an IG-TTD with a delta/gamma ratio that matches CFC-12 and SF$_6$ together (instead of assuming the ratio is 1), and then applying this IG-TTD to the Medusa tracers?

Response: In Figure 10f, the Δ/Γ ratio for most sampling sites, especially the surface ones, are over 1.8. Due to the time-variant ventilation, and possibly the influence of more than one major water mass (leading to a bi-modal shape of the TTD), we were not able to find any suitable D/G based on IG-TTD for the Mediterranean Sea based on the CFC-12/SF$_6$ tracer couple. But from Figure 10, we could find that the D/G ratio determined by CFC-12/HCFC-141b and CFC-12/HCFC-142b tracer pairs located closer to that by CFC-12/SF$_6$, pointing out the more promising tracer pairs. This is also another expression of your suggested method.

p. 11, L 30 – The discussion of solubilities should have been in Li et al. (2019)

Response: Section 5.5 has been removed.

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Difficult to follow text, but a worthwhile effort. Would like to see some added discussion into what next steps will be / should be taken

This is a worthwhile study, and I think it should see the light of day (i.e. be published) after some work on presentation. The authors pursue the potential of synthetic compounds that are regularly measured/monitored in the atmosphere as new tracers for quantifying ocean ventilation timescales. New tracers are needed as the most commonly used tracers, the chlorofluorocarbons, are now decreasing in the atmosphere, and their replacement/complement, Sulfur Hexafluoride, is much more difficult to measure and is likely to suffer from regulatory limits in the near future as well. To evaluate alternate synthetic tracers (almost too many to list), the authors used the analytical equipment built to quantify their atmospheric abundances by adapting/attaching a sparging apparatus to the intake. This allowed the authors to evaluate a number of potential tracers in terms of measurement feasibility, likely stability in seawater, and known solubility.

One issue of presentation has to do with the discussion. HFC-125 is easily quantifiable with the Ampule-Medusa system, and based on one solubility estimate, may be stable in seawater. Rather than discount the tracer (p. 15, lines 35 onward), one would ordinarily recommend that empirical (laboratory) studies of HFC-125 solubility (a la Warner and Weiss, 1998) in seawater be performed. With known solubility, then, HFC-125's stability can be addressed. (The lower mean ages from TTDs are not a hindrance, newer tracers will be expected to yield younger ages). The authors don't discuss anything about possible next steps towards pursuing the promising tracers.

Response: The empirical laboratory studies of HFC-125 solubility would be one of the next steps. The possible next steps have been added in the rewritten Section 7 (Conclusions and outlook).

Figure 1 can be improved by dropping ^{39}Ar and ^{14}C – allowing the distinction between the anthropogenic gases to be easier to see. Tritium-helium might be a good addition.

Response: We thank the reviewer for the suggestion and have now removed ^{39}Ar and ^{14}C from that figure which allows us to scale up the x-axis for better visibility.

The same perspective could be applied to PFC-14 and PFC-16. Although Aqua-Medusa is not sensitive enough for these gases, perhaps they could be pursued with an electron-capture detector? ECDs love C-

F bonds, after all. Looking at Table 5, one concludes that PFC-14 and PFC-16 are too hard to measure, but one wonders if that's true using 'traditional' purge-trap GC-ECD techniques.

Response: We found previous publications that PFC-14 (CF_4) analyzed by Gas Chromatography (GC) detector (Varian Model 90P) (Cosgrove and Walkley, 1981) and gas-solid chromatography (Smith et al., 1981). But we have not found any publications where PFCs were measured by PT-GC-ECD in seawater, which could be tried in the near future.

The discussion would benefit, greatly, with some discussion of what to do next, is what I'm saying. The second author, in particular, is a known leader in developing custom analytical system for aquatic trace gases. It is disappointing to have that expertise not weighing in on the potential of PFCs as future tracers. The bottom line is that Aqua-Medusa's utility on in oceanography is limited by its poor sensitivity (relative to ECDs). This lower sensitivity requires a water budget (5 liters, by my estimation) that is simply not sustainable on regular oceanographic cruises.

Response: Measurement of PFCs should be first resolved. We have rewritten the conclusion and outlook section.

My recommendation is that a few hard passes through the text are required before the paper is ready for publication. The figure and analyses all make sense. The text is confusing and hard to follow, and the conclusions rely too much on "applicability within Aqua-Medusa" of these tracers, rather than on the perspective of "applicability within oceanography". I applaud the intent of the effort and am happy to review a draft that is easier to follow.

Response: We thank the topic editor who helped us went through the text. The conclusion and outlook section have been rewritten. We also did the language check several times.

References

Cosgrove, B. A., and Walkley, J.: Solubilities of Gases in H_2O and D_2O, J. Chromatogr. A, 216, 7, https://doi.org/10.1016/S0021-9673(00)82344-4, 1981.

Hodnebrog, Ø., Etminan, M., Fuglestvedt, J. S., Marston, G., Myhre, G., Nielsen, C. J., Shine, K. P., and Wallington, T. J.: Global warming potentials and radiative efficiencies of halocarbons and related compounds: A comprehensive review, Rev. Geophys., 51, 300–378, https://doi.org/10.1002/rog.20013, 2013.

Smith, R. A., Porter, E. G., and Miller, K. W.: The solubility of anesthetic gases in lipid bilayers, Biochimica et Biophysica Acta (BBA)-Biomembranes, 645, 327-338, https://doi.org/10.1016/0005-2736(81)90204-2, 1981.

Stöven, T.: Ventilation processes of the Mediterranean Sea based on CFC-12 and SF_6 measurements, Master thesis, 116 pp., 2011.

Stöven, T., Tanhua, T., Hoppema, M., and Bullister, J. L.: Perspectives of transient tracer applications and limiting cases, Ocean Sci., 11, 699–718, https://doi.org/10.5194/os-11-699-2015, 2015.

Medusa-Aqua system: simultaneous measurement and evaluation of novel potential halogenated transient tracers HCFCs, HFCs and PFCs in the ocean

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Abstract

This study evaluates the potential usefulness of the halogenated compounds HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116 as oceanographic transient tracers to better constrain ocean ventilation processes. We do this mainly from four aspects of the characteristics of the potential tracers: input function (including atmospheric history and historical surface saturation), seawater solubility, feasibility of measurement and stability in seawater, of which t. The atmospheric history and seawater solubilityformer two aspects have been investigated in previous work. The historical surface saturation of halogenated transient tracers in the Mediterranean Sea is estimated to have been nearly constant at 94 % based on historical data. For the latter two aspects, we collected seawater samples and modified an established analytical technique to the Medusa-Aqua system in order to simultaneously measure these compounds. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 have been measured in depth-profiles in the Mediterranean Sea for the first time. Of the investigated compounds, HCFC-142b and HCFC-141b are found to currently be the most promising transient tracer in the ocean currently. The compounds that have the greatest potential as future tracers are PFC-14 and PFC-116, although the low solubility in seawater creates challenging analytical conditions (i.e. low concentration) that can potentially be improved by modifying the Medusa-Aqua analytical system. HCFC-22 is found to be likely unstable in warm seawater, which leads to its low confidence in terms of its potential as an oceanic transient tracer, although it is possibly useful in colder water. For compounds HFC-134a, HFC-125 and HFC-23, we are not able to fully evaluate their potential asbe tracers fully due to the inconclusive results, especially on their solubility and stability in seawater, but also with regard to potential analytical challenges. On the other hand, HFC-125, HFC-23, and HCFC-22 can no longer be considered as transient tracers because there are alternative tracers with similar input histories that are better suited as transient tracers. With the exception of providing the information on potential alternative oceanic transient tracers, this study also provides a more general method on how to evaluate the feasibility of a compound to be a transient tracer in the ocean.

1 Introduction

Ventilation is defined as the time elapsed since thea water parcel has left the mixed layer and beenis transported to the ocean interior. Ocean ventilation and mixing processes play significant roles in climate as they are important processes to propagate perturbations on the ocean surface to the interior. They, largely controlling the accumulatedive uptake of

~~anthropogenic carbon (C_ant) at mid- and high latitudes and~~ the deep ocean's oxygen supply. One possible method~~In order~~ to quantitatively describe these processes are based on transient tracer measurements~~.~~

1.1 Why do we look for new transient tracers?

Transient tracers include~~consist of~~ chronological transient tracers~~,~~ such as dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11) and sulfur hexafluoride (SF_6), and radioactive transient tracers~~,~~ such as Tritium-Helium (^3H-^3He), Argon-39 (^{39}Ar) and Carbon-14 (^{14}C), although ^{39}Ar is assumed to be in steady-state and cannot be regarded as a transient racer in the true meaning of the word. They have been used as oceanic transient tracers to study the oceanic processes, such as ventilation, mixing and circulation processes. CFC-12 and CFC-11 ha~~ve~~s been used since the 1980s, whereas SF_6 has only been used since the late 1990s. ~~Both~~These compounds are mostly stable in seawater; their seawater solubility functions are well-established (Warner and Weiss, 1985; Bullister et al., 2002) and their historical atmospheric concentrations over time are known (Walker et al., 2000; Bullister, 2015). However, the industrial use of CFC-12 and CFC-11 was phased -out as a result of the implementation of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer designed to curtail the degradation of the Earth's ozone layer. Therefore, the atmospheric concentrations of CFC-12 and CFC-11 ha~~ve been~~s decreased since the early 2000s and the early 1990s (Bullister, 2015), which has reduced their~~its~~ usefulness as an oceanographic transient tracer for recently ventilated water masses. Consequently, SF_6 has been added to the suite of commonly measured oceanic transient tracers (Tanhua et al., 2004; Bullister et al., 2006) as it is an inert gas whose atmospheric abundance is increasing. ~~However, some local restrictions are in place for the production and use of SF_6 d~~Due to its very high global warming potential, some local restrictions on the production and use of SF_6 implemented~~that may restrict SF_6 to be an oceanic tracer in the future~~. However, the concentrations of SF_6 in the atmosphere continue to rise due to its long atmospheric lifetime. Currently,~~Both~~ CFC-12 and SF_6 have readily measured onboard a research vessel at a reasonable rate from one seawater sample. CFC-11 has been extensively used as a transient tracer but ~~was~~found to ha~~s~~ a time-history similar to that of CFC-12 and be degraded in anoxic marine waters (Bullister and Lee, 1995); ~~and has a time-history similar to that of CFC-12. Besides,~~ the simultaneous measurement of SF_6 and CFC-11 is complicated (Bullister and Wisegarver, 2008), so that the use of CFC-11 is being reduced. Similarly~~In addition, trichlorofluoromethane (CFC-11),~~ 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)~~,~~ and carbon tetrachloride (CCl_4) ha~~ve~~d been extensively used ~~as transient tracers,~~ but have now been largely ~~been~~discarded since they~~.~~ ~~Both CFC-113 and CCl_4~~ have been found to be degraded in warm waters (Roether et al., 2001) as well as in low oxygen waters (Wallace and Krysell, 1989; Huhn et al., 2001). ~~Similarly, t~~The radioactive isotope ^{39}Ar is in many ways an ideal tracer for ocean circulation for older water masses, but its use has been impeded by difficult analytics. However, recent technological advancements have increased the feasibility of oceanic ^{39}Ar observations (Lu et al., 2014; Ebser et al., 2018). ~~In addition, trichlorofluoromethane (CFC-11), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and carbon tetrachloride (CCl_4) had been extensively used as transient tracers, but have largely been discarded. CFC-11 was found to be degraded in anoxic marine waters (Bullister and Lee, 1995) and has a time-history similar to that of CFC-12. Besides, the simultaneous measurement of SF_6 and CFC-11 is complicated. Both CFC-113 and CCl_4 have been found to be degraded in warm waters (Roether et al., 2001) as well as in low oxygen waters.~~ Since a combination of multiple transient tracers is needed to constrain ocean

ventilation, it is necessary to explore novel transient tracers with monotonically changing input functions for a better understanding of ventilation and mixing processes in the ocean.

1.2 Potential alternative transient tracers

There are a few general requirements for a transient tracer: 1) ~~known input function~~well-quantified sources and sinks,

5   2) no (or well known) natural background, 3) large dynamic range, 4) feasible measurement techniques and 5) non-reactive and stable in seawater. In the previous work (Li et al., 2019), we focused on points 1, 2 and 3 for the potential alternative oceanographic transient tracers: hydrochlorofluorocarbons (HCFCs) such as HCFC-22, HCFC-141b and HCFC-142b, hydrofluorocarbons (HFCs) such as HFC-134a, HFC-125 and HFC-23 and perfluorocarbons (PFCs) such as PFC-14 (CF_4) and PFC-116. ~~As the replacements of CFCs, t~~The atmospheric abundances of most HCFCs and HFCs

10   are increasing, as are the concentrations of PFCs. Here we describe~~use the terminology for~~ the potential chronological transient tracers HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116 as the "Medusa tracers"~~, CFC-12 and SF₆ as traditional chronological transient tracers and ³H, ³⁹Ar and ¹⁴C as radioactive transient tracers. For the radioactive transient tracers, the half-lives of the three tracer nuclides have different orders of magnitude, allowing them to cover a wide range of ages ("seawater timescales", Fig. 1). However, w~~With the

15   constraints of the weak signal of ^3H and the decreasing atmospheric mole fraction of CFC-12, presently only SF_6 is a relatively reliable transient tracer in the seawater timescale ~~range of 1~~less than 100 years (Fig. 1). Fortunately, the different atmospheric histories of the potential alternative transient tracers (Li et al., 2019) allow us to ~~find~~explore one or several compounds to replace or supplement the established transient tracers (Fig. 1).

1.3 Stability of alternative tracers in seawater

20   Chemical reactions (including hydrolysis), adsorption to particles and biological degradation process should be considered with regard to~~for~~ the stability of compounds in seawater. There are few studies of the stability of the Medusa tracers, and close to none of the stability in seawater. One indication of the stability is the stable chemical structure, which is expressed as the following aspects. For instance, PFCs have very long atmospheric lifetimes, i.e. > 50 000 and > 10 000 years for PFC-14 and PFC-116, respectively. PFC-14 (CF_4) ~~is thought to be stable and inert in the ocean~~

25   ~~(Ravishankara et al., 1993; Cicerone, 1979) since CF₄~~ is stable at temperatures of at least 1200°C and the rate of hydrolysis of CF_4 is immeasurably small (Ravishankara et al., 1993; Cicerone, 1979). In addition, ~~Furthermore, no known marine natural products contain C-F bonds and~~ there are no indications of biological processes that can break C-F bonds, indicating that~~. This is reasoning true for PFC-116 and other~~ PFCs ~~that~~ are likely to be very stable in the environment. ~~On the other hand, we are not aware of any publications that directly discuss the stability of the other~~

30   ~~compounds in seawater. Therefore, their stabilities are inferred from other studies with slightly different perspectives and environmental foci.~~

~~One example is t~~The contribution of the ~~oceanic~~ partial atmospheric lifetime with respect to oceanic uptake of selected HCFCs and HFCs to the total lifetimes is another indirect indication of the stability in seawater. Such partial atmospheric lifetimes depend on the solubility in seawater and other losses relative to their atmospheric concentration,

35   and are always larger than their total lifetimes. Considering the low fraction of these mainly non-polar compounds in the ocean, a small loss in the ocean is insignificant for the overall budget of the compound, but can still be of

3

significance for a potential transient tracer. As ~~far as we know~~ indicated from previous studies (Yvon-Lewis and Butler, 2002; Carpenter et al., 2014) using this method, HCFCs and HFCs ~~are~~ seem to be~~relatively~~ stable in seawater, although with large uncertainties associated to these estimates ~~and their ocean partial lifetimes (i.e. partial atmospheric lifetimes with respect to oceanic uptake) range from thousands to millions of years~~ (Sect. S1 and Table S1). ~~Judged against their environmental total lifetimes, the oceanic contributions of these compounds are small enough to be neglected. But here~~ Note that the ~~ocean~~ partial atmospheric lifetimes with respect to oceanic uptake in Table S1 were calculated only considering the chemical degradation process.

Another route is to compare surface saturations of a tracer with unknown stability to th~~e one~~at of a compound that is known to be unstable in seawater. CCl₄ has a short lifetime in warm seawater. Surface saturation of HCFCs is not as under-saturated as those of CCl₄ (Butler et al., 2016) by the comparison of their saturations in various oceans based on the results from the National Oceanic and Atmospheric Administration (NOAA) cruises in 1992-200~~4~~8 (ftp://ftp.cmdl.noaa.gov/hats/ocean/, last access: 20 January 2020) and the Gulf of Mexico and East Coast Carbon Cruise (GOMECC) in 2007 (https://seabass.gsfc.nasa.gov/cruise/gomecc-1, last access: 10 June 2020). This suggests that HCFCs are more stable than CCl₄ in surface seawater and possibly suited as~~to be~~ tracers in the ocean.

~~We also utilized published information on biodegradation of compounds in freshwater or soil, although a compound can be degraded in the freshwater or soil but can still be stable in seawater, such as CFC-12. Chang and Criddle (1995), Oremland (1996), and Streger et al. (1999) observed the aerobic bacterial degradations of selected HCFCs and HFC-134a in very high oxygen concentrations and substrate levels (Table 2), and these aerobic microorganisms are common inhabitants of soil and aquatic systems. Although rapid removal in the soil can be an indication of non-conservative behavior in the ocean, the lifetime of a compound in soil or freshwater can be considerably shorter than the one in open ocean waters with few particles.~~

Based on these discussions, PFCs are stable, while HCFCs and HFCs seem to be relatively stable in the ocean when only considering the chemical degradation process and surface saturation in seawater (only for HCFCs). However, the influences of oxygen dependence and biological degradation processes in seawater have not been investigated (Yvon-Lewis and Butler, 2002). For a compilation of published information on biodegradation in freshwater and soil, see Sect. S2 and Table S2. In summary, not enough information is known on the stability of the selected HCFCs and HFCs in the ocean.

1.4 Goals~~Purpose~~ of this study

~~In order to explore the possibility of the use of the targeted compounds as oceanic transient tracers, their atmospheric histories and seawater solubility have already been reported by Li et al. (2019).~~ This study is an extend~~sion~~s of th~~at~~e work by Li et al. (2019), with a~~the~~ focus on ~~the~~ evaluati~~on~~ng ~~of the usefulness of these halogenated compounds as oceanographic transient tracers. Based on observations of these tracers in the Mediterranean Sea, we mainly address points 4 and 5 of the general requirements in this study, i.e. discuss~~ if rapid, relatively inexpensive and accurate measurements are possible (point 4) and if these compounds are conservative in the oceanic environment (point 5). We also estimate the historical surface saturation to supplement the input function and discuss ~~the~~ differences in tracer input functions ~~of the tracers,~~ and the~~ir~~ ability to provide additional information on ventilation. A suite of observations of transient tracers with sufficiently different input functions would support the empiric determination of Transit Time

Distributions (TTDs), as reported in Stöven and Tanhua (2014). As the first step towards this, these Medusa tracers have been measured, sometimes for the first time, and the results interpreted ~~based on the Inverse Gaussian Transit Time Distribution (IG TTD) concept~~ to identify their possib~~ility~~le use as transient tracers in the ocean. The Mediterranean Sea was chosen for this study because of its rapid ventilation, which causes~~rendering~~ transient tracers to penetrate most of the water column. In addition, we report from sampling at a shallow station in the south-west Baltic Sea. ~~However, on the down-side, the time-variant ventilation and the contribution of several deep-water sources make the TTD concept difficult for the Mediterranean Sea.~~

2 Medusa-Aqua system

2.1 Progress in analytical technology of selected HCFCs, HFCs and PFCs

Measurement of halogenated compounds is often performed by "gas-solvent extraction" techniques, e.g. purge-and-trap where an inert gas is bubbled through a seawater sample to move the analytes from the sample into a cold trap for pre-concentration. By desorbing the content of the trap, the sample can then be injected into a gas chromatograph (GC) for separation and detection. This is a well-established technique that has been used successfully for CFCs and SF_6 (Bullister and Weiss, 1988; Bullister and Wisegarver, 2008) achieving accuracies in the order of 1 % (Bullister and Tanhua, 2010). However, several HCFCs and HFCs (i.e. HCFC-22, HFC-134a, and HFC-125) have low responses and large uncertainties when they are measur~~detect~~ed by an Electron Capture Detector (ECD) that is normally used for CFC-12 and SF_6 (Lobert et al., 1995; Beyer et al., 2014; Sousa and Bialkowski, 2001). One alternative is to use a mass spectrometer (MS) for detection that has the advantage of scanning for unique masses for different compounds, allowing~~i.e.~~ identification and quantification simultaneously. ~~The MS as a detector is becoming increasingly popular since the sensitivity is approaching that of an ECD. A further complication is that the HCFCs tend to be more soluble, making it more difficult to quantitatively purge all of the tracers from a water sample.~~ HCFCs and HFC-134a measurements by GC-MS in seawater samples have also been reported in previous studies (Lobert et al., 1996; Ooki and Yokouchi, 2011).

The Medusa-GC-MS system (shorte~~ne~~d as the Medusa system) for the precise and simultaneous analysis of a wide range of volatile trace gases has been developed at the Scripps Institution of Oceanography (Miller et al., 2008). This system include~~is based on trapping of the volatile gases on~~ two traps kept at accurately controlled temperatures to trap the volatile gases. The packing material of the traps and the temperature during the trapping stage are designed in a way that allows for the fractionation of the compounds on two traps. In this way, interferences from atmospheric permanent gases can be avoided and hard-to-measure gases like PFC-14 (CF_4) can be measured. This analytical system was designed to automatically and continuously measure air samples at ~~the~~ Advanced Global Atmospheric Gases Experiment (AGAGE) remote field stations (Prinn et al., 2018) and is unique in that it provides high accuracy measurements of more than 40 compounds including halocarbons, hydrocarbons and sulfur compounds involved in ozone depletion and/or climate forcing from the same sample. The measurement precisions of most halogenated compounds are less than 0.5 % in 2 L ambient air. The Medusa-Aqua system as developed based on the Medusa system can measure the majority of the 40 halogenated compounds in seawater samples.

2.2 Difference between Medusa-Aqua and Medusa system

The Medusa-Aqua system consists of a Medusa system (Miller et al., 2008) and a seawater sample pretreatment system (Fig. 2). The Medusa system consists of a cryogenic pre-concentration unit, named Medusa, an Agilent 6890N gas chromatograph (GC) and an Agilent 5975B quadrupole mass spectrometer (MS). The seawater sample pretreatment

5 system was developed to degas ~~the samples from~~ gaseous tracers from samples before injecting into the Medusa system, replacing the air sampling device of the original Medusa system. The technology is based on a purge-and-trap technology where the Medusa serves as the trap unit prior to the chromatographic separation of the sample for detection in the MS.

The main difference between Medusa and Medusa-Aqua system is that the former uses an air-pump module as the gas

10 sample pretreatment system and the sample volume is determined by an integrating mass flow controller (MFC), while the latter uses a purge module as the seawater sample pretreatment system and a gravimetrically calibrated standard loop for standard gases. For the injection of water samples to the system, we use the Ampoule-Cracker-System, as designed by Vollmer and Weiss (2002) and then modified by Stöven (2011).

3 Sampling and Measurement

15 Here we describe the sampling and measurement methods for samples collected from cruise MSM72 to the Mediterranean Sea in March and cruise AL516 to the Baltic Sea in September 2018. Over the past years, we have collected samples on a few cruises and empirically improved our method (Sect. S3, Figs. S1-S7 and Tables S3-S5).

3.1 Sample collection

~~The seawater samples were sampled and flame-sealed in ~1.3 L ampoules at sea and subsequently measured in the~~

20 ~~laboratory.~~ Seawater samples were collected throughout the water column in three areas of the Mediterranean Sea (Fig. 3): Southern Ionian Sea (SIS), Tyrrhenian Sea (TS) and Western Mediterranean Sea (WMS) on the cruise MSM72 by the research vessel *Maria S. Merian* from March 2nd to April 3rd, 2018 along the GO-SHIP line MED-01 (Hainbucher et al., 2019) and one station (10.1 °E, 54.5 °N) in the Baltic Sea on the cruise AL516 by the research vessel *Alkor* from September 12th to 22nd, 2018 (Booge, 2018). These seawater samples were collected in glass ampoules (~1.3 L)~~by~~

25 connected to the Niskin bottles via a stainless steel mounting system (Vollmer and Weiss, 2002). ~~Around~~ 5 minutes is needed~~spent~~ for the seawater to fill up a whole glass ampoule and the sampling process lasted for 15 minutes to allow for the seawater to flush the whole ampoule volume three times. ~~After removing and closing the ampoule with a screw,~~ ~~t~~The ampoule~~s~~ ~~w~~w~~ere~~as flame-sealed ~~as soon as possible~~immediately after sampling under a flow of high purity N$_2$ (Air Liquide, grade 6.0, Germany) and then sent back to the laboratory in Kiel for measurement. As seen in Fig. 3, no

30 onboard CFC-12 and SF$_6$ measurements (on a PT-GC-ECD) were conducted on the stations we sampled for the Medusa-Aqua system in the Mediterranean Sea, although they were measured for the nearby ~~. The distance between~~ stations, ~~on this cruise was~~ 15 nm (nautical miles) away from either direction~~, and normally we sampled for chemistry on every second station~~.

3.2 Gas extraction, separation, and detection

The flow scheme for the Medusa-Aqua system is shown in Fig. 2. Before measurement, each ampoule sample was immersed in a warm water bath at 65 °C overnight to enhance the purging efficiency by driving the gases into the headspace. The stem of the ampoule is inserted vertically ~~up~~ into the cracking chamber and is held by a screw-nut

5 ~~with~~secured by a ~~nylon~~ Teflon ferrule. Then the cracking chamber is flushed with N_2 (grade 6.0) for 10 minutes to flush out ambient air completely. A blank test for the cracking chamber is made by simulating an extraction without breaking the glass ampoule. For analysis, the tip of the ampoule's stem is shattered ~~into pieces~~ inside the enclosed cracking chamber by rotating the cracking paddle. A straight purge tube is then inserted down into the ampoule until touching the ampoule bottom for finer bubbles. These bubbles will help strip the ~~compounds~~ dissolved gases out of

10 the seawater, and more importantly from the head-space~~enhance the purge efficiencies for the dissolved gases~~.

The extraction process is started by purging the gases in the ampoule with N_2 (grade 6.0) for 20 minutes at a flow rate of 100 mL min^{-1}. Water vapor is removed from the sample by passing the gases through~~When introduced into the Medusa,~~ two Nafion dryers (N1 and N2) of 1.8 m length and one (N3)~~Nafion dryer~~ of 0.6 m length~~are used to remove water vapor from the samples~~. The counter-flow rate of Nafion dryer gas (N_2, grade 5.0) was set to 120 mL min^{-1}.

15 After the purge gas is injected into Medusa, the following path is the same as described by Miller et al. (2008). The tracer gases are separated on the main column with helium (Air Liquide, grade 6.0, Germany) as the~~a~~ carrier gas and subsequently detected by the MS. The mass of seawater in the ampoules was calculated as the difference between the full weight of the ampoule before measurement and the empty ampoule (including glass splinters) after rinsing with distilled water and drying in an oven~~for around 96 h~~.

3.3 Standard and calibration

The standard gas used in the laboratory in Kiel is a tertiary standard calibrated by the Scripps Institution of Oceanography (SIO) on the AGAGE relative scale "SIO-R1". For details about the propagation of the standard see Miller et al. (2008). Gravimetric calibration scales and calibrated errors of compounds in the tertiary standard are reported in Table 1~~3~~. Measurements in seawater are reported on the latest SIO absolute calibration scales for HFC-125

25 (SIO-14), HFC-23 and PFC-1~~1~~4 (SIO-07) and other compounds (SIO-05). The tertiary calibration scale is directly used as ~~propagated to~~ a working standard ~~used~~ to determine weekly calibration curves and daily drift corrections. These calibration measurements are made by multiple injections of the gas in a 10.0 mL gravimetrically calibrated sample loop. Each injection lasts 40 seconds at a flow rate of 50-60 mL min^{-1}. The detector response~~s~~ for compounds in Table 1~~3~~ are linear in the range of our measurements.

3.4 Purge efficiency, detection limit, and precision

Each sample was measured 3-6 times until none of the compounds in Table 1~~3~~ could be detected in the seawater sample so that the purge efficiency for all compounds is 100 %. The averaged stripping efficiencies for the first purge of seawater samples from cruise MSM72 are 92.5 ± 5.4 % for CFC-12, 76.6 ± 7.9 % for HCFC-22, 87.5 ± 8.3 % for HCFC-141b, 83.2 ± 10.6 % for HCFC-142b, 83.1 ± 7.5 % for HFC-134a, and 88.9 ± 7.5 % for HFC-125. The precision

35 of the measurement is dependent on the size of the ampoules and ~~sampling concentration (i.e.~~ the amount of tracer in the sample~~)~~; the sample~~s~~ with a higher amount of tracer ha~~s~~ve better precisions than those with a lower amount. The

precision (or reproducibility) for seawater sample measurements were determined by the relative standard deviations (1σ) of the concentrations for two pairs of duplicate samples (Table 1~~3~~). The detection limits for measurements of all compounds by the Medusa-Aqua system are also shown in Table 1~~3~~ based on the signals corresponding to the blank values ~~or noises~~ plus ten standard deviations.

5 The concentrations of SF$_6$, PFC-14, and PFC-116 in most seawater samples were~~are~~ lower than the detection limit, and HFC-23 ha~~s~~d unstable and non-zero blank values in all measurements, preventing us from evaluating those results. The observations of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 measured by the Medusa-Aqua system in seawater from ~~the~~both cruises ~~MSM72~~ are shown in Table S6~~1~~ with quality flags marked.

3.5 Comparison of instruments measuring CFC-12

10 In order to explore the precision and accuracy of seawater measurements by the Medusa-Aqua system, CFC-12 was measured by both the Medusa-Aqua system and a purge and trap GC-ECD instrument (Syringe-PT-GC-ECD) used onboard the cruise MSM72. This is a mature system to measure CFC-12, SF$_6$ and SF$_5$CF$_3$ (Stöven, 2011; Stöven and Tanhua, 2014; Stöven et al., 2016; Bullister and Wisegarver, 2008). For comparison, information on the performance of a similar purge and trap system set-up (Cracker-PT-GC-ECD) to measure flame-sealed ampoules for CFC-12 and

15 SF$_6$ is added to a~~. A detailed~~ comparison of the three instrument set-ups ~~is shown in~~ (Table 2~~4~~). Compared to other systems, the Medusa-Aqua system has lower purge efficiency due to its larger~~using a bigger~~ sampling volume if only considering a single purge ~~once~~ (although we used multiple purge cycles to increase the purge efficiency and reduce the uncertainty); has lower precision than that of the Syringe-PT-GC-ECD but higher than that of the Cracker-PT-GC-ECD system; ~~and~~ can measure more compounds.

20 **4 Transient tracer interpreting methods**

~~**4.1 Ocean ventilation and transit time distribution (TTD) model**~~

~~Ventilation is defined as the time elapsed since a water parcel left the mixed layer and is transported to the ocean interior. Ocean ventilation and mixing processes play significant roles in climate as they are important processes to propagate perturbations on the ocean surface to the interior, largely controlling the accumulative uptake of~~

25 ~~anthropogenic carbon (C$_{ant}$) at mid- and high latitudes and oxygen supply. In order to quantitatively describe these processes, we used a conceptual but well-established ocean ventilation model, the Transit Time Distribution (TTD) model that is based on the Green's function $G(t,r)$ described the propagation of tracer boundary conditions into the interior (Hall and Plumb, 1994). As shown in Eq. (1), $c(t_s,r)$ describe the concentration of a transient tracer at year t_s and location r. The boundary concentration $c_0(t_s,r)$ is the concentration at source year $(t_s - t)$ related to the input~~

30 ~~function of a tracer, whereas the exponential term $(e^{-\lambda t})$ describes the decay rate of radioactive transient tracers. This function is based on a steady and one-dimensional flow model with time-invariant advective velocity and diffusivity gradient. One commonly used solution to Eq. (1) is the one-dimensional Inverse Gaussian Transit Time Distribution (IG-TTD), simplified and expressed as Eq. (2). $G(t)$ is defined based on the mean age Γ, the width of the distribution Δ and the time range t (Waugh et al., 2003).~~

$$c(t_s, r) = \int_0^\infty c_0(t_s - t)e^{-\lambda t} \cdot G(t,r)dt \qquad (1)$$

$$G(t) = \sqrt{\frac{\Gamma^3}{4\pi\Delta^2 t^3}} \cdot \exp\left(\frac{-\Gamma(t-\Gamma)^2}{4\Delta^2 t}\right) \qquad (2)$$

The Δ/Γ ratio of the TTD corresponds to the proportion of advective transport and eddy diffusive characteristics of the mixing processes for a water parcel; the higher the Δ/Γ ratio, the more dominant the diffusion and vice-versa.

4.12 Time range, tracer age, mean age and Transient Time Distribution

Time range. The time range where a tracer can be used as a transient tracer is defined by its input function. For
chronological transient tracers, the input functions are described by their atmospheric histories and historicalseawater
surface saturations. For ideal applicability, aAtmospheric histories of tracers should be monotonic increaseing
monotonically in the atmosphere for ideal applicability. Figure 4 shows the atmospheric histories of HCFC-22, HCFC-
141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12 and SF$_6$ in the Northern Hemisphere
(Bullister, 2015; Li et al., 2019).

4.2 Tracer age

Tracer age. Tracer age is defined as the age of a water parcel based on a purely advective flow in the ocean, i.e. Δ/Γ
equals zero in the IG TTD concept. Each tracer has a specific time and application range related to possible age
information. Figure 5 shows the relation between the relative tracer concentrations in percent, i.e. normalized to the
contemporaneous atmospheric concentrations, and the corresponding tracer ages for 10 transient tracers in two
different sampling years 2018 and 2000, which highlights tracer similarities and the specific application range for each
tracer.

Relatively sSimilar trends of relative tracer concentrations (Fig. 5) are found for the following tracer couples: HCFC-
141b and HCFC-142b, HFC-134a and HFC-125, SF$_6$ and HCFC-22/HFC-23, PFC-14 and PFC-116. Assuming that all
these compounds fulfill the other criteria as transient tracers, it is enough to choose one of each couple for transient
tracer work (i.e. addition to the other compound in the pair adds little new information)could be chosen for further
studies depending on their relative tracer concentrations.
The specific application ranges of tracer ages for tracers can be found in Fig. 5 with the compiled results shown in Fig.
1. In Fig. 5, iIf the relative tracer concentrations are over higher than 100 % in Fig. 5,then there has been a decrease in
atmospheric concentrations, such as the tracer age range of 0-30 years for e.g. for CFC-12 (Fig. 5a) produced by the
decreasing atmospheric mole fractions (Fig. 4). When the atmospheric history of a compound is not monotonically
changing, the equilibrium atmospheric mole fraction (and ultimately the age associated with that mole fraction)
calculated from its concentration in the ocean is not unique, reducing its potential as a transient tracer (Li et al., 2019).
Thuserefore, the tracer age range is a function of the sampling year. For instance, the useful tracer age range of CFC-
12 is 30-80 years and 1-60 years for sampling in 2018 and 2000, respectively (Fig. 5). This indicates that the ability of
CFC-12 asto be a transient tracer for recently ventilated water is decreasing with time, but CFC-12 still provides
important time information for intermediate and deep water layers with moderate ventilation timescales. It is worth

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pointing out that PFCs have a longer tracer age range compared to other compounds, even CFC-12, among the chronological transient tracers (Fig. 5). ~~As CFC-12 is limited to be used as a tracer in the upper ocean, PFCs will obtain more attention if they are evaluated to be transient tracers in the ocean.~~

~~**Mean age and Transient Time Distribution (TTD).** The mean age, calculated as the average of the TTD, can be~~
5   ~~used as an estimate of the age of a water parcel based on a combination of advective and mixing flow in the ocean.~~
~~Assuming an IG-TTD, the theoretical tracer concentrations $c(t_s, r)$ for a range of Δ/Γ ratios (0.2-1.8) based on Eqs.~~
~~(1) and (2) have been calculated for the Medusa tracers (Fig. S1). Figure S2 shows the mean age matrices of $\Delta/\Gamma = 1.0$ (the blue lines in Fig. S1) for each Medusa tracer and describes the expected tracer concentration as a function of~~
~~different mean ages and sampling years. More complicated or different TTDs than the IG-TTD can also be assumed,~~
10 ~~and if the observed concentrations match the theoretical tracer concentrations for a range of tracers with different input~~
~~functions it is an indication that the assumption is valid.~~

5 Results

5.1 Historical surface~~awater~~ saturation in the Mediterranean Sea

The historical surface saturation of transient tracers is ~~an~~ important ~~factor to illustrate ventilation~~to constrain the input
15 function (together with the atmospheric history). To determine this for the Mediterranean Sea, we calculated seawater saturation in the winter mixed layer (WML) from historical cruise~~s~~ data. The depths of the WMLs in summer and winter are shown in Fig. 6 for two ex~~a~~empl~~es~~~~ary~~ of density profiles. It is ~~T~~the ~~seawater~~ saturation ~~in the warm surface is often higher than the one~~ during winter~~, which~~ that is ~~the~~ relevant ~~saturation level~~ for deep and intermediate water formation, and thus for the input functions, not the one in the summer mixed-layer. Therefore, only the WML was
20 considered in the calculation of historical surface~~awater~~ saturation for all cruises. The depth ranges of WMLs (Fig. S8~~3~~) and the saturation ~~level~~ for CFC-12 and SF_6 (Fig. 7) were determined by profiles of temperature, potential density, and CFC-12 concentration~~s~~ for ~~each~~ every historical cruise ~~that we have access to~~ in the Mediterranean Sea from 1987 to 2018 (Schneider et al., 2014; Li and Tanhua, 2020). Since no clear trend over time could be described, we~~By~~ averag~~ed~~~~ing~~ the mean seawater saturation from every single cruise, and determined the historical surface saturation
25 ~~level is determined~~ to be 94 ± 6 % and 94 ± 4 % for CFC-12 and SF_6, respectively. ~~These historical seawater saturations do not show a clear trend over time.~~ For CFC-12, this is different from~~than~~ the situation in the North Atlantic Ocean (Tanhua et al., 2008), and is probably an indication of the different oceanographic setting where the inflowing Atlantic Water (to the Mediterranean Sea) ~~h~~takes a long time to equilibrate with the atmosphere.

For the following calculations of ages and evaluation of stability, the historical surface~~awater~~ saturations are assumed
30 to be a constant 94 % ~~(overtime)~~ for all tracers in this study as no data exists to determine the historical surface~~awater~~ saturation of selected HCFCs and HFCs in the Mediterranean Sea. ~~The historical seawater saturation and the atmospheric concentration histories of all compounds together describe their input functions.~~

5.2 Observations of the Medusa tracers in seawater

The observations of CFC-12 measured by the Medusa-Aqua system are ~~generally~~ comparab~~le~~d with those in adjacent
35 stations measured onboard by the PT-GC-ECD system (Fig. 8). We performed a two-step quality control procedure on

the medusa data where, in the first step outliers were flagged, and in a second step we flagged data where the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD (Fig. 8). This process led to 9 samples in the Mediterranean that meets all these criteria and have similar concentration as the PT-GC-ECD observations. For such samples, tThe averaged difference of CFC-12 concentrations measured by the two different instruments is 5.9 ± 4.6 % focusing on only the data with quality flagged "good". Based on the reasonable correlation between CFC-12 observations from the Medusa-Aqua system and the onboard PT-GC-ECD system, we can move on and interpret the profiles of the Medusa-only compounds (i.e. Medusa tracers). As shown in Fig. 9, the oObservations of CFC-12 and SF$_6$ from profiles 51, 83 and 105 measured by the PT-GC-ECD and thoseobservations of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 from the nearby profiles 52, 84 and 106 measured by the Medusa-Aqua system are shown in Fig. 9were presented for comparison. CConcentration ranges of Medusa tracers are 16.1-129.4 ppt for HCFC-22, 2.1-18.7 ppt for HCFC-141b, 5.0-29.0 ppt for HCFC-142b, 41.0-217.4 ppt for HFC-134a and 4.9-12.8 ppt for HFC-125. The sconcentrations of Medusa tracers decreased from the surface to the intermediate layer and then increased in the deep layer, consistent with the well-ventilated Mediterranean deep waters.

5.3 Surface saturation of Medusa tracers in seawater

Surface saturation in seawater could be a factor that describesto analyze the stability of a compound in surface seawater or confidence in theof seawater solubility function. However, saturationIt is influenced by multiple parameters, such as partial pressures in the atmosphere and surface seawater, the air-sea exchange velocity, the solubility and diffusivity of the gas, bubble injection and/or vertical mixing, and the temperature dependence of these parameters (Lobert et al., 1995; Butler et al., 2016).

In the Mediterranean Sea, the averaged saturations of SF$_6$ and CFC-12 measured by the PT-GC-ECD are 94.5 ± 4 % and 91.5 ± 1 %, respectively (Table 5), which is close to the ones estimated from historical seawater saturation (see Sect. 5.1). The surface saturation of CFC-12 measured by the Medusa-Aqua system is ~20 % lower than the adjacent ones by the PT-GC-ECD. The averaged surface saturations of HCFC-22, HCFC-141b and HFC-125 measured by the Medusa-Aqua system are 43 ± 1 %, 52 ± 4 % and 37 ± 10 %, which are lower than expected. The averaged saturation of HCFC-142b measured by the Medusa-Aqua system is 90 ± 11 %, whereas the averaged saturation of HFC-134a is 139 ± 34 %. There are a few possible reasons for the lower than expected saturations: 1) problems in measurements/sampling; 2) poorly defined solubility functions; 3) degradation in seawater. Degradation is not likely for CFC-12, which is known to be stable in flame-sealed glass ampoules. Based on these, we conclude that there is an, to us not defined, issue with sampling or measurement of these surface samples. Since we have the benefit of "reference" measurements from a proven technique (the PT-GC-ECD system) in the Mediterranean Sea, we flagged data where the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD (Fig. 8). we had to flag all surface samples as suspect due to discrepancies between CFC-12 concentrations as measured by Medusa-Aqua system and PT-GC-ECD. We, therefore, turn to the samples collected i

In the Baltic Sea where the seawater saturation of CFC-12 and Medusa tracers in one surface sample and two bottom samples are shown in Table 3. Note that the bottom waters (at about 23.5 meters depth) can be considered as recently ventilated as this water is ventilated on an annual base. T, the averaged seawater surface saturation of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 in seawater are 122 ± 8 %, 77 ± 8 %, 74 ± 12 %, 114 ± 2 %,

125 ± 23 % and 252 ± 35 %, respectively ~~(Table 5)~~. ~~These higher and more realistic surface saturation levels also indicate that a sampling or measurement issue might be responsible for the compounds with low saturations, such as HCFC-22, HCFC-141b and HFC-125, in the Mediterranean Sea. But in the Baltic Sea, the lower saturation of HCFC-22 may attribute to degradation considering its higher partial pressures in the atmosphere than in the surface seawater (increasing atmospheric history) and easy to soluble in seawater; the lower saturation of HCFC-141b might be due to degradation and/or lower partial pressures in the atmosphere than in the surface seawater (decreasing atmospheric history) and high solubility in seawater. For HFC-125, the very low saturations in the Mediterranean Sea and very high saturations in the Baltic Sea are probably a result of issues in the seawater solubility function and/or measurement.~~

5.4 Stability based on interior ocean observations

In order to validate the stability of HCFCs and HFCs, the concentrations of CFC-12 from the adjacent PT-GC-ECD measurements are vertically interpolated by a piecewise cubic hermite interpolating method on potential density surfaces and averaged by the arithmetic mean of the interpolated profiles (Tanhua et al., 2010; Schneider et al., 2014). Then the concentrations of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 and SF$_6$ (measured by the PT-GC-ECD) are plotted against the (interpolated) CFC-12 (Fig. 10). Concentration value~~s~~ of Medusa tracers from~~in~~ the recent (usually shallow) layers are located in the upper right corner with older (usually deep) samples near the lower left in Fig. 10~~and vice versa~~. In the figure, we added the atmospheric history of the Medusa tracers vs. CFC-12 as well as the theoretical mixing line between contemporary ~~concentrations~~ and pre-industrial concentrations; all samples will have to fall between these two lines (i.e. the stability area) if the tracer is conservative in seawater. Compounds where the samples fall below the "stability area" are not stable (assuming that CFC-12 is stable), and ~~for~~the samples above it, there are issues with too high values (see below). For instance, HCFC-22 is found in the lower part of the stability area (samples would fall on this lowest line if there were no mixing but only advection in the ocean); HCFC-141b, HFC-125, and SF$_6$ are well in the allowed range; whereas HCFC-142b and HFC-134a are around or above the upper boundary.

The increased ventilation of the (western) Mediterranean Sea during the last decade tends to result in~~have~~ ~~very~~ different effects on CFC-12, which ~~that~~ is decreasing in the atmosphere, and the Medusa tracers ~~that are mostly~~with increasing atmospheric concentrations. This argument suggests that we could expect higher than expected concentrations (similar to~~as~~ SF$_6$ ~~presented~~) for the Medusa tracers. This is exactly what we see from HCFC-142b and HFC-125 (Fig. 10). In addition, we could find that the Δ/Γ ratio determined by CFC-12/HCFC-141b and CFC-12/HCFC-142b tracer pairs located closer to that by CFC-12/SF$_6$, pointing out the more promising tracer pairs. However, too high concentrations for HFC-134a may associate with a few possible reasons: 1) contamination ~~of the samples~~ during sampling ~~process~~ or measurement in the laboratory; 2) ~~a~~ problem~~s~~ with~~in~~ solubility functions; ~~and~~ 3) some other issues within the measurements in the laboratory causing our observations to be high. Although the assumption of time-invariant ventilation is not valid for the Mediterranean Sea, the TTD model can produce indicative results to understand the mean ages estimated from Medusa tracers (assuming Δ/Γ =1.0) and their comparison to those estimated from CFC-12 and SF$_6$, see Sects. S4-S5 and Figs. S9-S11.

6 Discussions

The results from this study on ~~surface saturation in seawater,~~ stability based on interior ocean observations ~~and mean age in relation to CFC-12 are summarized in Table 6. These results~~ can be evaluated to analyze the stability and further determine the potential of the Medusa tracers as oceanic transient tracers, and are as such dependent on the confidence that the measurements are reasonably accurate. The comparison between the mean ages calculated from the Medusa tracers and CFC-12 is sensitive to the assumed shape of the TTD, and the differences in input history that make them respond~~sensitive in a~~ differently ~~way in relation~~ to the time-variant ventilation of the (western) Mediterranean Sea. As a component of the input function, the historical surface saturation has been estimated to be 94 %; the atmospheric histories of the Medusa tracers have been given by Li et al. (2019), who also used indirect methods to estimate the solubility functions. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 can be measured by the Medusa-Aqua system. Based on the combined results from Li et al. (2019) and this study, ~~the evaluation of~~ the potential of the Medusa tracers as transient tracers in the ocean is summarized in Table 4~~7~~ by mainly evaluating their ~~confidence or feasibility of~~ atmospheric history, seawater solubility, ease of measurement and stability in seawater. The more precise historical surface saturation will be a future consideration.

As a reference, we start with CFC-12, ~~that is~~ a commonly used transient tracer marked with medium/high confidence/ feasibility. The atmospheric history of CFC-12 is well-documented (Walker et al., 2000; Bullister, 2015), and the seawater solubility function is well-established (Warner and Weiss, 1985). In addition, CFC-12 has been observed for several decades by mature analytical techniques, and its~~the~~ stability~~ies~~ in warm waters, as well as poorly oxygenated waters, has~~ve~~ been proven. However, the decreasing atmospheric history of CFC-12 limits its ability as an oceanic transient tracer.

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HCFC-22. The increasing atmospheric history is well-established by a combination of the model results and observations (Li et al., 2019). The seawater solubility function has been constructed by combining the CGW (Clark–Glew–Weiss) model on the experimental freshwater solubility data and another model (poly-parameter linear free-energy relationships, pp-LFERs) on the salting-out coefficients (Li et al., 2019). The results of freshwater solubility matched those ~~ones~~ published ~~by~~in Deeds (2008) on measurements and the CGW model ~~fitted~~ results ~~in~~ between 298-348 K, and those ~~ones~~ published in Abraham et al. (2001) on observations and the pp-LFERs model results at 298 K and 310 K. The confidence ~~us, our ability to estimate~~in the seawater solubility was marked as medium ~~confidence~~ due to lack of ~~ing the~~direct experimental seawater solubility ~~empirical~~ data to verify the function. As to measurements, HCFC-22 has been measured on several cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) by GC-ECD and GC-MS instruments and in this study by the Medusa-Aqua system. The stability was evaluated by ~~analyzing the surface saturations in seawater,~~comparison to CFC-12 observations~~, and comparison to mean ages estimated from CFC-12/SF$_6$~~. The ~~surface saturation was lower than expected probably due to degradation (see Sect. 5.3), which may support that HCFC-22 is unstable in surface seawater. Similarly, the~~clustering of HCFC-22 values in the lower range (Fig. 10) could be an indication of slow degradation in ~~warm~~ seawater, which ~~wa~~is also supported by the weak hydrolysis of HCFC-22 in tropical and subtropical waters reported by Lobert et al. (1995). ~~The mean ages estimated from HCFC-22 were found to be higher (i.e. indicating low concentrations) than those estimated from CFC-12 and SF$_6$, supporting non-conservative behavior.~~Therefore, HCFC-22 was determined to be unstable in warm waters; more measurements should be added for the stability analysis, especially in poorly oxygenated ~~and cold~~ waters. In addition, HCFC-22 can be replaced by SF$_6$ as a transient tracer since they have similar atmospheric histories (Fig. 4 and Fig. 5). These ~~all~~ indicate that HCFC-22 ~~seems~~might not suitable ~~as~~to be a ~~potential~~ new transient tracer in the warm ocean, for instance, the Mediterranean Sea, but could be used for colder waters.

HCFC-141b. The atmospheric history ~~(high confidence)~~ ~~wa~~is ~~well~~reliably reconstructed (Li et al., 2019). However, the seawater solubility function ~~(low confidence)~~ was constructed for the first time (Li et al., 2019) and the freshwater solubility only matched data ~~the ones~~ in Abraham et al. (2001) at the two temperatures. HCFC-141b has been previously measured on cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) and also in this study, thus we have high confidence in the ability ~~f~~to~~r~~ measure~~ment~~ this compound. As for the stability, HCFC-141b ~~wa~~is identified to be potentially stable in seawater ~~(medium confidence)~~ since its concentrations are likely in the ~~the~~expected range ~~of likely ones~~ in the interior ocean (Fig. 10), assuming that the solubility function is valid~~, and the observed mean ages are similar to those estimated from both CFC-12 and SF$_6$ (Fig. 11). However, the low surface saturation points to the possibility of degradation (see Sect. 5.3).~~The input function of HCFC-141b is different enough from the traditional transient tracers to provide additional information, but since the atmospheric history started to decrease in 2017 (Li et al., 2019), the use of HCFC-141b as a transient tracer for "young" waters will be compromised~~become complicated~~. All these indicate that HCFC-141b has ~~a~~probably limited ~~ability~~potential as a transient tracer in the future.

HCFC-142b. The confidence of the atmospheric history and seawater solubility function is similar to those of HCFC-141b for the same reasons. HCFC-142b has been measured on some cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) and also in this study, rendering us to ~~determine that it is highly feasible~~have the confidence to accurately measure this compound. We have medium confidence in our ability to estimate the stability of HCFC-142b because of slightly higher than the expected concentrations in the interior ocean (Fig. 10)~~, lower than expected mean ages~~

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particularly in the Atlantic Water Layer (Fig. 11), and its surface saturation similar to the ones of CFC-12/SF₆ in seawater. The input function of HCFC-142b is different from those of most other tracers (only similar to that of HCFC-141b but with a longer time range). Consequently, HCFC-142b has ~~currently good~~ high potential to be used as a transient tracer currently.

5 **HFC-134a**. We judge that we have high and medium confidences in the atmospheric history and seawater solubility function (Li et al., 2019), respectively. Although the estimated seawater solubility function was constructed based on the modeled salting-out coefficients and the experimental freshwater solubility (Li et al., 2019) that matched both the observations (Deeds, 2008) and model results (Abraham et al., 2001), we have only ~~consider~~ medium confidence in the seawater solubility function due to the lack of experimental seawater solubility data. HFC-134a was measured in

10 Ooki and Yokouchi (2011) by GC-MS and in this study by the Medusa-Aqua system although with higher than expected concentrations (see Sect. 5.4), so we ~~consider~~ have medium ~~feasibility~~ confidence ~~f~~tor accurately measure this compound~~ments in this study due to higher than expected concentrations (see Sect. 5.4)~~. We have only poor knowledge of~~n~~ the stability of HFC-134a because its~~since~~ higher than expected ~~surface saturation (Table 5) and~~ concentrations (Fig. 10)~~, as well as lower than expected mean ages (Fig. 11) don't suggest degradation. ~~, and t~~The

15 compound is not identified as ~~to be~~ unstable (see Sect. 5.4), but its~~the~~ stability ~~of HFC-134a~~ is still largely unknown considering the issues on seawater solubility function and/or measurements. Besides, HFC-134a can be used only ~~be considered~~ as a tracer for "young" waters due to its short atmospheric history. Based on all these discussions, HFC-134a has ~~a~~ lower po~~ssibility~~tential than HCFC-142b but ~~a~~ higher ~~possibility than~~potential compared to HCFC-22 to be an oceanic transient tracer.

20 **HFC-125**. Concentrations of HFC-125 ~~has unclear atmospheric concentrations~~ in the early 1990s in the atmosphere are unclear (Fig. 5)~~,~~ possibly related to uncertainties in the reconstruction, although this only marginally influences its ability as a transient tracer. Overall, we consider the knowledge of its reconstructed atmospheric history to be of high confidence (Li et al., 2019). Three seawater solubility functions of HFC-125 can be constructed (Li et al., 2019), although only two of them were considered; function 1 is supported by freshwater solubility results from Deeds (2008)

25 as well as stability analysis based on comparison to CFC-12 in this study (Fig. 10), whereas the observations and model results from Abraham et al. (2001) supported function 3. ~~Besides, we found under-saturated waters in the Mediterranean Sea but over-saturated waters in the Baltic Sea for HFC-125 (Table 5).~~ All these lead to low confidence in the seawater solubility function of HFC-125 ~~to be poorly constrained, and we mark it to be of low confidence~~. We also evaluate the feasibility to measure HFC-125 as low since this compound has been measured in this study for the

30 first time in seawater ~~in this study so that we can't compare the results with other studies~~, and we find almost no vertical gradient (Fig. 9), which is ~~different from~~ unexpected. Furthermore, observed HFC-125 concentrations in freshwater are inconsistent ~~with the ones in previous studies~~ as indicated by three freshwater solubility functions (Li et al., 2019), which suggests unresolved issues with its measurements in water. Due to the poorly defined solubility and difficulties in measurement, it is difficult to assess the stability of HFC-125 ~~(low confidence)~~ in this work. Besides~~The low mean

35 ages compared to the ones estimated from CFC-12 and SF₆ (Fig. 11) do not support HFC-125 to be a tracer, and in any case,~~ ,~~ HFC-125 can only be a tracer for "young" water due to its short atmospheric history. Therefore, we consider that HFC-125 has~~ve~~ currently low potential as a transient tracer in the ocean due to the poorly constrained solubility

and stability, and possible problems in seawater measurements ~~and the lower than expected mean ages~~. This might be remedied by constructing the experimental seawater solubility function and solving possible measurement issues.

HFC-23. HFC-23 could not be reliably measured in our system due to unstable~~a~~ non-zero blank~~s~~ (see Sect. 3.4~~5~~). Therefore, we can, obviously, not reliable assess the stability of HFC-23 in seawater, and we have low confidence in~~for~~ the feasibility of the measurements, although the blank problem might be solved by a different instrument configuration ~~of the instrument~~. The atmospheric history of HFC-23 has been constructed (Li et al., 2019; Simmonds et al., 2018), but we have only medium confidence as it does not start from zero (Simmonds et al., 2018) due to limited data. Also, we have only medium confidence in ~~Our ability to estimate~~ the seawater solubility function ~~was marked as medium confidence~~ for the same reason as for HFC-134a. That is, the freshwater solubility function matched results from Deeds (2008) and Abraham et al. (2001) but the seawater solubility function was not constructed by experimental seawater solubility data. In consequence, unknown stability and current issues with measurements lead to an overall assessment that HFC-23 has ~~a~~ currently low potential as a transient tracer in the ocean ~~at this moment~~.

PFC-14 and PFC-116. The increasing atmospheric histories of PFC-14 and PFC-116 ~~(high confidence)~~ have been established (Li et al., 2019; Trudinger et al., 2016). Also, the seawater solubility functions ~~were~~ have been constructed in ~~, although we have only~~ medium ~~and low~~ confidence~~s~~ for PFC-14 ~~and PFC-116, respectively~~; the~~such~~ confidence ~~for PFC-14~~ is higher than th~~ose~~ ~~ones~~ for other compounds with medium confidence as it~~by~~ matche~~sd~~ both~~several~~ seawater measurements (Scharlin and Battino, 1995) and freshwater solubility (Clever et al., 2005; Abraham et al., 2001). In contrast, ~~whereas the~~ low confidence for the solubility function for PFC-116 wa~~is~~ attributed to its freshwater solubility only match~~ inged~~ th~~ate one~~ from Deeds (2008) but not the ~~and absent supporting~~ theoretical assessment from Abraham et al. (2001). PFC-14 and PFC-116 are very stable in the environment, but can't easily be measured in seawater because of the low solubility (Li et al., 2019), i.e. low concentration in seawater. The high stability and long atmospheric histories make PFCs potentially promising transient tracers in the ocean, although it is~~with a~~ challenging~~e~~ to measure these compounds. A possibility would be to use an ECD with higher sensitivity for C-F bonds, but with the additional complication of co-elution on the chromatogram.

~~Based on all the above discussions, HCFC-22 is unlikely to be a transient tracer in warm waters. HFC-23 can't be identified as a transient tracer because of lacking too much information on the four aspects. On the other hand, these two compounds can be replaced by SF₆ that has similar atmospheric histories (Fig. 4 and Fig. 5). Since SF₆ is a mature transient tracer, we will no longer consider the possibility of HCFC-22 and HFC-23 as transient tracers. HCFC-141b and HCFC-142b are able to be transient tracers currently. Considering their similar atmospheric history and the decreasing atmospheric history of HCFC-141b, HCFC-142b can be further evaluated as a transient tracer by obtaining more reliable solubility and stability information in seawater. HFC-134a and HFC-125 can't be identified as transient tracers; the former because of higher than expected concentrations pointing to issues on the seawater solubility function and/or the measurements; the latter due to the lack of information on solubility, stability, and feasibility of measurement in seawater. Considering the similar atmospheric histories of HFC-134a and HFC-125, HFC-134a is a more promising candidate as a transient tracer. Last but not least, PFC-14 and PFC-116 are able to be transient tracers in the future (medium confidence) once the measurement of the seawater sample is resolved. Currently, HCFC-142b and HCFC-141b are better choices as transient tracers.~~

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7 Conclusions and outlook

This study, combined with the study by Li et al. (2019), provides a method to identify and evaluate if a compound is suitable for~~to be~~ use~~d~~ as a transient tracer in the ocean. ~~As the replacements of CFCs, promising (in terms of being potential transient tracers)~~ HCFCs, HFCs and PFCs were selected for~~to be~~ evaluat~~ioned~~ as potential replacements for CFCs (as transient tracers). The evaluation mainly considered four aspects: input function (including atmospheric history and historical surface saturation), seawater solubility, feasibility of measurement and stability in seawater. We also considered how Medusa tracers with different atmospheric histor~~ies~~y complement each other when constraining ocean ventilation, whereas tracers with similar input functions provide little additional information. For these purposes, we modified an existing analytical system ~~to the Medusa Aqua system~~ for seawater measurements and observed the seawater concentrations of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125. Unfortunately, the poorly soluble PFCs could not be successfully measured with our current analytical system.

~~The atmospheric histories, combined with historical seawater saturations, form the input functions. The atmospheric histories have been reconstructed in our last study (Li et al., 2019), and the historical seawater saturation in the Mediterranean Sea was determined to be a constant 94 % based on historical tracer observations.~~

~~The seawater solubility functions have been constructed by Li et al. (2019) by combining experimental freshwater solubility data and a model on the salting-out effect. However, the results from this study identify questions for some of the evaluated compounds, in particular for HFC-125, so that seawater solubility functions constructed based on experimental seawater solubility data are needed.~~

~~Measurements of CFC-12 by the Medusa Aqua system were compared to observations by an onboard, well-described analytical system. Based on the reasonable correlation between CFC-12 observations from the two systems, we interpreted the observations of the Medusa tracers for further analysis of the surface saturation, stability and mean age. We conclude that HCFC-141b, HCFC-142b, and possibly HFC-125, are probably stable in seawater, whereas there are indications of slow degradation of HCFC-22 in warm seawater. We were not able to estimate the stability of HFC-134a. Although not evaluated based on observations in this study, there are strong indications that the PFCs are stable in seawater.~~

~~By comprehensive evaluation of these aspects, HCFC-142b and HCFC-141b are found to currently be the most promising novel oceanic transient tracers since they fulfill several essential requirements by virtue of well-documented atmospheric history, established seawater solubility, feasible measurements, and inertness in seawater. However, more information on seawater solubility and stability (especially biodegradation) is needed to further assess their ability as transient tracers in seawater. Furthermore, HCFC-142b and HCFC-141b will likely only work as transient tracers for the next few years/decades considering their restrictions on production and consumption imposed by the Montreal Protocol, and their (upcoming) decreasing atmospheric mole fractions (Li et al., 2019).~~

~~The compounds that have the greatest potential as oceanic transient tracers in the future are PFC-14 and PFC-116 because of their high stability in seawater, the long and well-document atmospheric concentration histories and well-constructed seawater solubility functions (Li et al., 2019). This view is also supported by the work of Deeds et al. (2008). The challenge is how to measure the PFCs accurately due to their low concentrations in seawater. Possible ways forward are to modify the Medusa system according to Arnold et al. (2012) to improve the sensitivity for PFC-~~

14 (CF$_4$) and try field measurements using the vacuum sparge method by Law et al. (1994) to improve the speed of gas extraction.

For other tracers, HFC-134a needs to be further evaluated as a transient tracer by adding more reliable information on stability and solubility in seawater and feasibility in measurement, whereas HCFC-22, HFC-125 and HFC-23 could no longer be considered as oceanic transient tracers due to one or more reasons, such as unconstrained solubility function, unstable in seawater, difficult to be measured and can be replaced by mature or better tracers that own the similar atmospheric history.

By comprehensive evaluation, we conclude thatased on all the above discussions HCFC-22 is unlikely to be a transient tracer in warm waters., whereas HFC-23 canno'̶t be identifiedevaluated as a transient tracer because of the lack ofing too much information on the four aspects. On the other handFortunately, these two compounds can be replaced by SF$_6$ that has a similar atmospheric historyies (Fig. 4 and Fig. 5). Since SF$_6$ is a mature transient tracer, we will no longer consider the possibility of HCFC-22 and HFC-23 as transient tracers. On the other hand, both HCFC-141b and HCFC-142b show high potential asare able to be transient tracers currently. Considering their similar atmospheric historiesy and the decreasing atmospheric mole fractionhistory of HCFC-141b, HCFC-142b shouldean be further evaluated as a transient tracer by obtaining more reliable solubility and stability information in seawater. HFC-134a and HFC-125 show low potentialcan't be identified as transient tracers; the former because of higher than expected concentrations pointing to issues on the seawater solubility function and/or the measurements; the latter due to the lack of information on solubility, stability, and feasibility of measurement in seawater. Considering their similar atmospheric histories of HFC-134a and HFC-125, HFC-134a is a more promising candidate as a transient tracer. Last but not least, PFC-14 and PFC-116 show large potential asare able to be transient tracers in the future (medium confidence) once their accurate measurement inof the seawater sample is resolved. Currently, HCFC-142b and HCFC-141b are better choices as transient tracers.The high stability and long atmospheric history make it worthwhile to explore improved analytical methods, whether it implies using a more sensitive detector, or larger samples.

Future work will be further evaluating the potential transient tracers identified in this study. The next steps include experiments in controlled laboratory conditions with the aim to constructing the seawater solubility functions and exploring the stability of the compounds, in particular for warm and/or oxygen-depleted seawater; work on improving the measurement capacity for PFC-14 and PFC-116 by modifying the Medusa system according to Arnold et al. (2012) or possibly using a more sensitive detector (i.e. ECD). The reliability and reproducibility of the measurements for routine use should be improved, possibly by using the vacuum-sparge method by Law et al. (1994) that would speed up the gas extraction and reduce the number of purge cycles needed.

Data availability

Cruises data on worked for historical surfaceawater saturation of CFC-12 and SF$_6$ in the Mediterranean Sea (Sect. 5.1) are from https://www.nodc.noaa.gov/ocads/oceans/Coastal/Meteor_Med_Sea.html. Observations of CFC-12 and SF$_6$ measured by the PT-GC-ECD and thoseobservations of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 measured by the Medusa-Aqua system in seawater from cruises MSM72 and AL516 are shown in Table S61.

Author contributions

TT conducted the sampling from cruise MSM72. PL developed the instrument and carried out the measurements. PL interpreted the data and analyzed the results based on the discussion with TT. PL wrote the paper with contributions from TT.

5 **Competing interests**

The authors declare that they have no conflict of interest.

Acknowledgments

Figure 1. Seawater timescales ("tracer age ranges") of halogenated compounds dating using potential chronological transient tracers (selected HCFCs, HFCs, and PFCs, yelloworange) as well as traditional chronological transient tracers (CFC-12 and SF$_6$, red) combined with radioisotope dating using radioactive transient tracers (^{3}H-^{3}He, ^{39}Ar, and ^{14}C, blue). Tracer age ranges of chronological transient tracers are approximately estimated from Fig. 5 (see below), while tracer age ranges of radioactive transient tracers are from Aggarwal (2013).
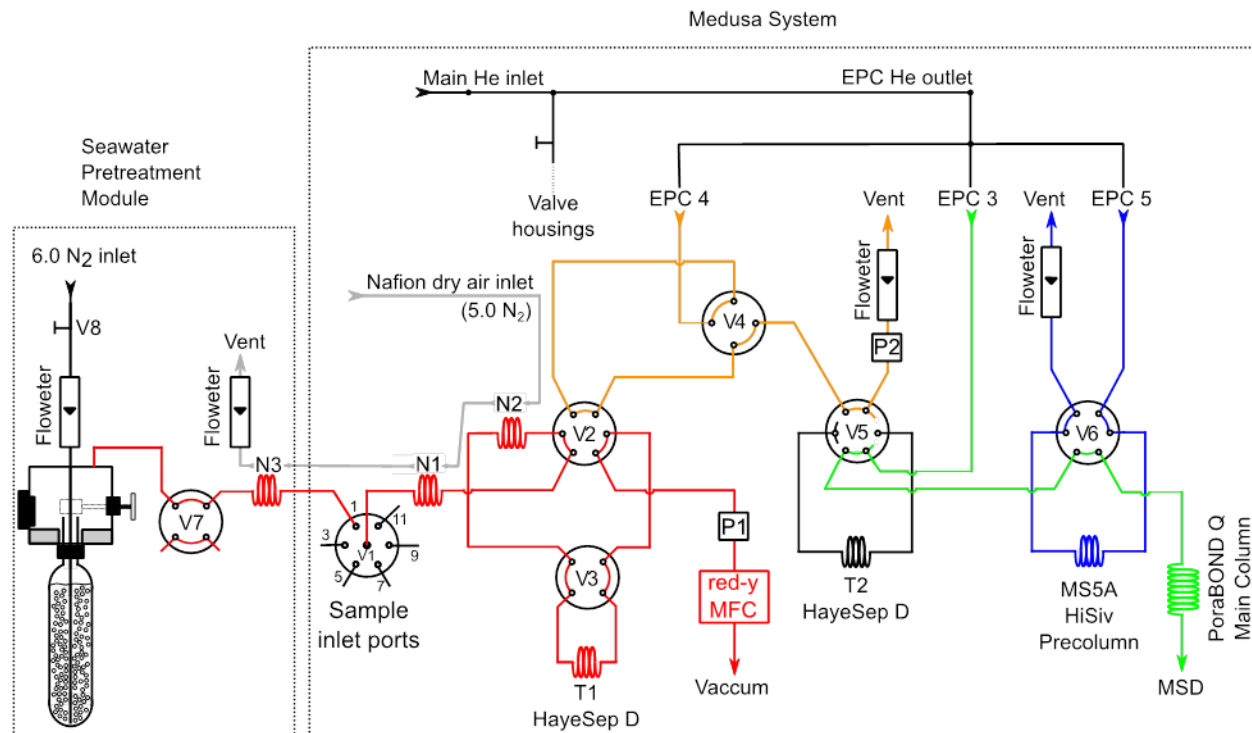
Figure 2. Medusa-Aqua system flow scheme. The Medusa system remains identical to that given by Miller et al. (2008). The seawater pretreatment module is added to degas ~~the samples from~~ gaseous tracers from samples before injecting into Medusa. Electronic Pressure Controllers (EPC3, EPC4, and EPC5) supply helium throughout the system. The Mass Flow Controller (MFC) ~~is~~ used to measure the sample volume downstream of Trap 1 (T1), was ~~but~~ not used in this study. The cryogenic packing materials are 200 mg of 100/120 mesh HayeSep D (HSD) for Trap 1 (T1) and 5.5 mg of HSD adsorbent for Trap 2 (T2). N1-N3 are the Nafion driers and V1-V8 are multiport valves. P1 and P2 are pressure transducers (100PSI-A-DO, All Sensor Corporation, Morgan Hill, CA).
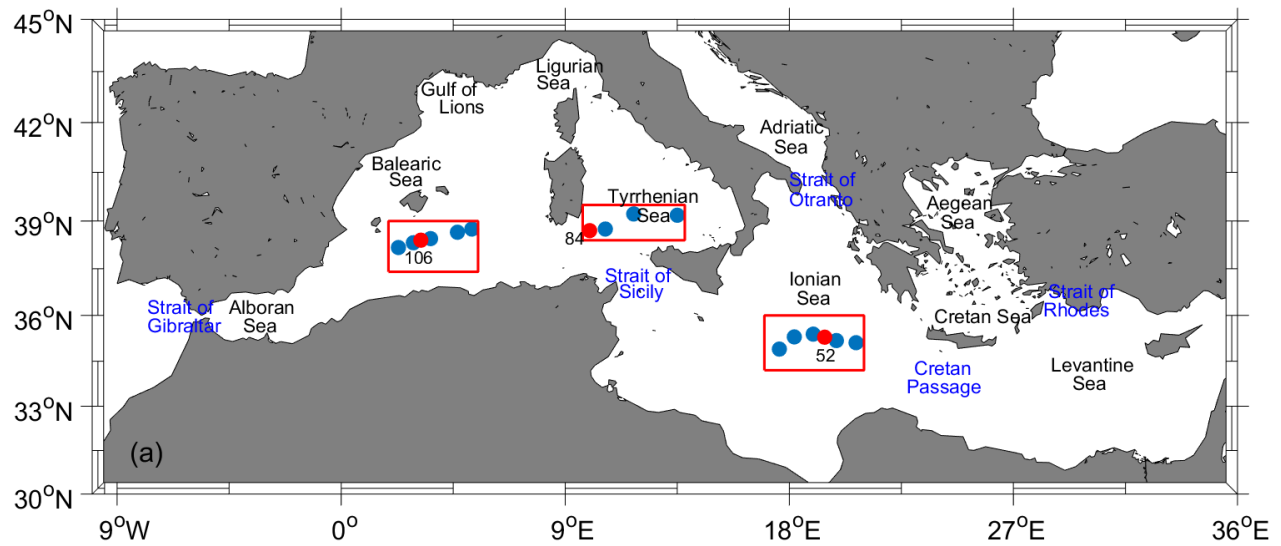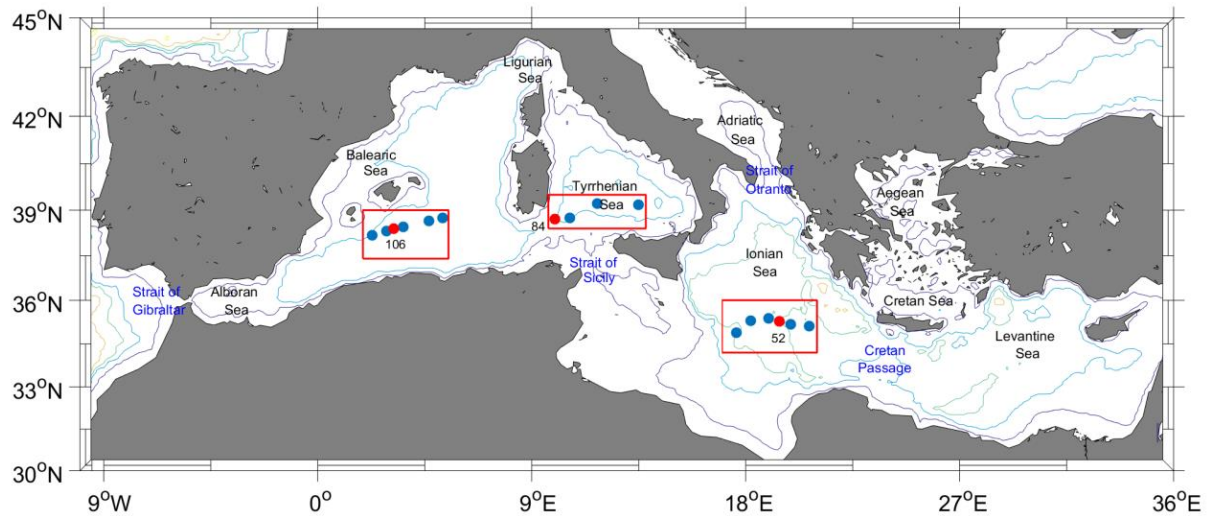
Figure 3. ~~Locations of S~~sampling sites ~~distributed~~ from (a) cruise MSM72 in the Mediterranean Sea ~~from the cruise MSM72~~ in three areas: the Southern Ionian Sea (SIS), the Tyrrhenian Sea (TS) and the Western Mediterranean Sea (WMS), and (b) cruise
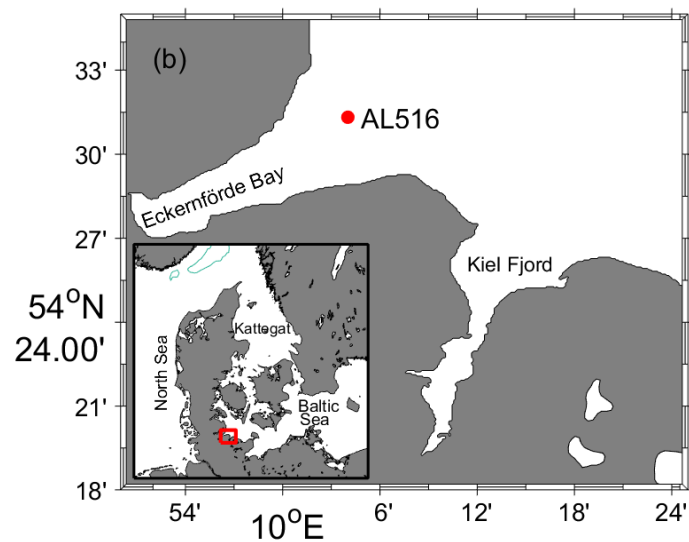
. Sampling sites in red solid circles indicate samples measured by the Medusa-Aqua system for HCFCs, HFCs, PFCs and CFC-12, ~~and the ones in~~ blue solid circles were for CFC-12 and SF_6 measured by the PT-GC-ECD. The depth contours are 500 m, 2000 m, 3000 m, 4000 m, 5000 m, and 6000 m.
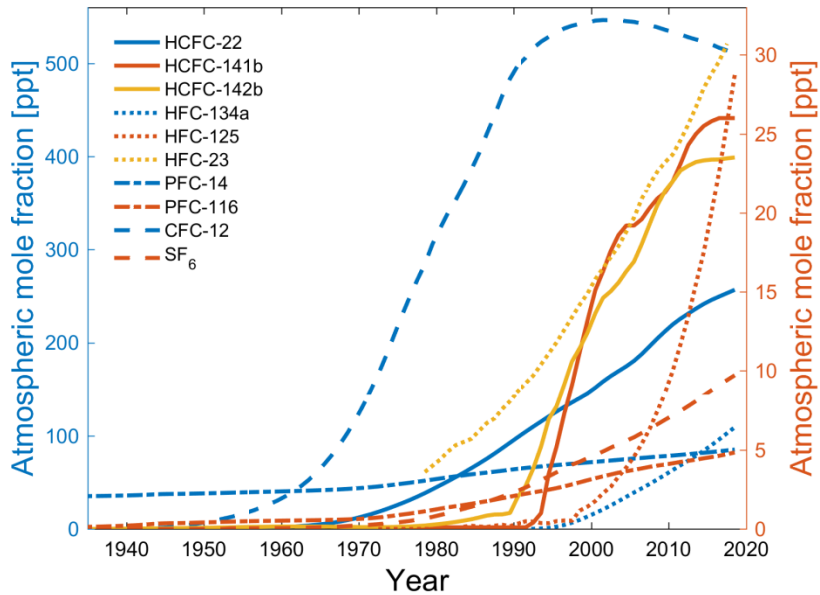
Figure 4. Atmospheric histories of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12 and SF_6 in the Northern Hemisphere. HCFC-22, HFC-134a, PFC-14, and CFC-12 share the left y-axis scale; other compounds share the right y-axis scale.
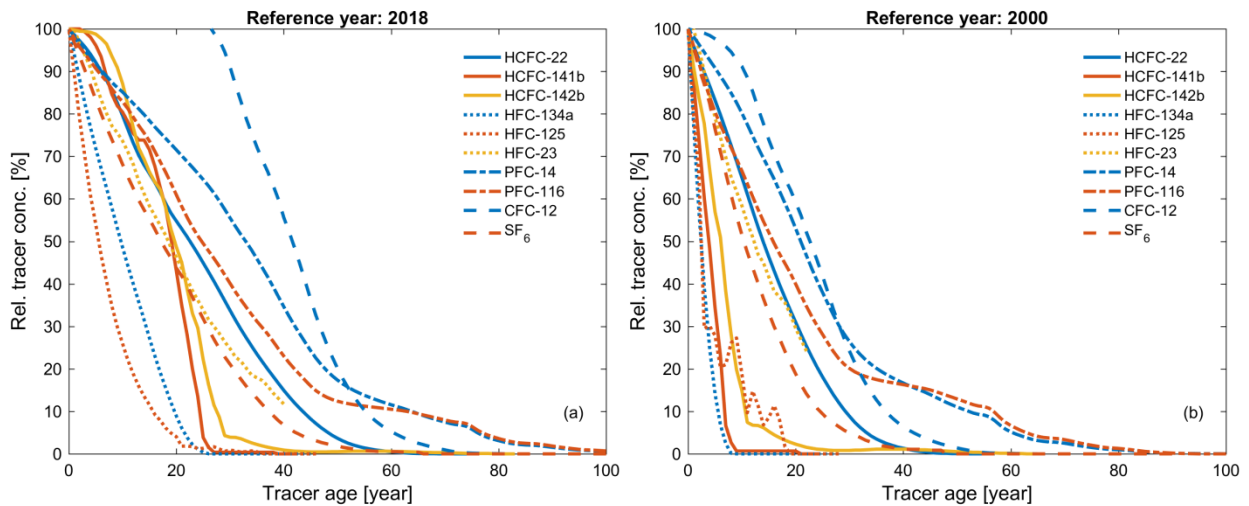
Figure 5. Relative tracer concentrations in percent (i.e. normalized to the contemporaneous atmospheric concentrations) and corresponding tracer age for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12, and SF_6 in the Northern Hemisphere for two sampling years. ~~Reference year~~: (a) 2018 and (b) 2000.
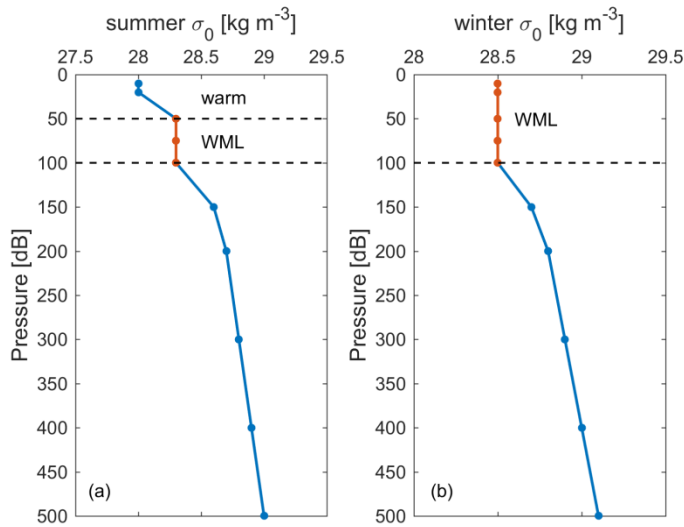
Figure 6. Example of the winter mixed layer (WML) depth (marked as red) determined in (a) summer and (b) winter in potential density (σ_0) profiles especially for historical surfaceawater saturation calculation.
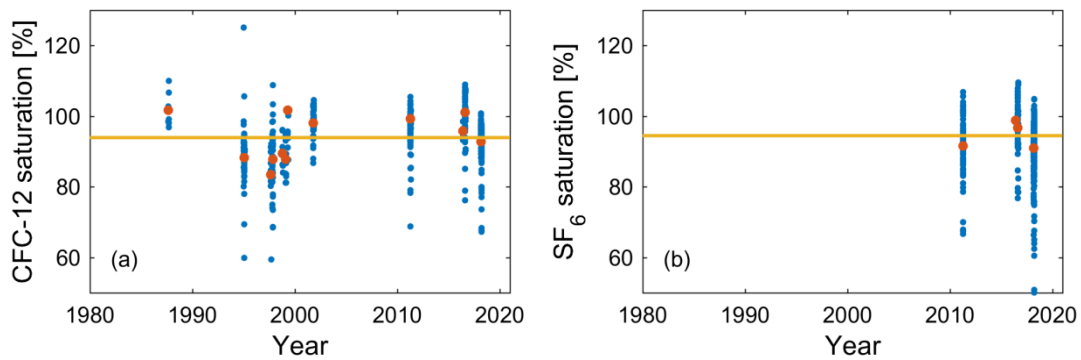
Figure 7. Historical surfaceawater saturations in winter mixed layers (blue solid circles) for (a) CFC-12 from 12 cruises in 1987-2018 and (b) SF$_6$ from 4 cruises in the Mediterranean Sea. In addition to the data from Schneider et al. (2014), data from the cruises CRELEV2016 and TALPro2016 in 2016 and MSM72 in 2018(Li and Tanhua, 2020) were added. Red solid circles denote the means of seawater saturation for each cruise and the . Orangeyellow lines (94 %) are the mean of averaged seawater saturation of everyeach cruise.
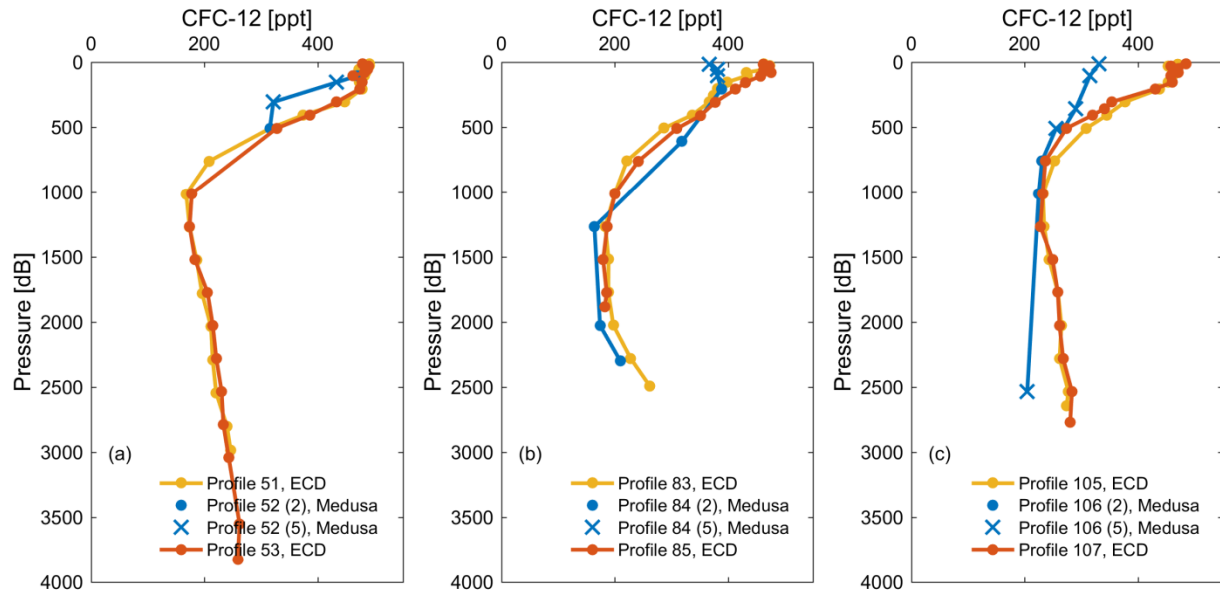
Figure 8. Comparison of CFC-12 observations from cruise MSM72 measured by the PT-GC-ECD (ECD) and the Medusa-Aqua system (Medusa) in three areas: (a) the Southern Ionian Sea, (b) the Tyrrhenian Sea and (c) the Western Mediterranean Sea. We used normal quality control routines and flagged outliers as probably bad ("3" in Table S6~~1~~), which are not further considered. One more step was done to compare the Medusa-Aqua system observations with th~~ose~~ _from the_ PT-GC-ECD ~~ones~~; if the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD measurements, _they were_~~it was~~ flagged "5" in Table S6~~1~~ indicating a possible issue during the sampling or measurement process; if they are consistent, _they were_~~it was~~ flagged "2" representing good data. In the following plots, we show all data with a quality flag of "2 (dots)" or "5 (crosses)".
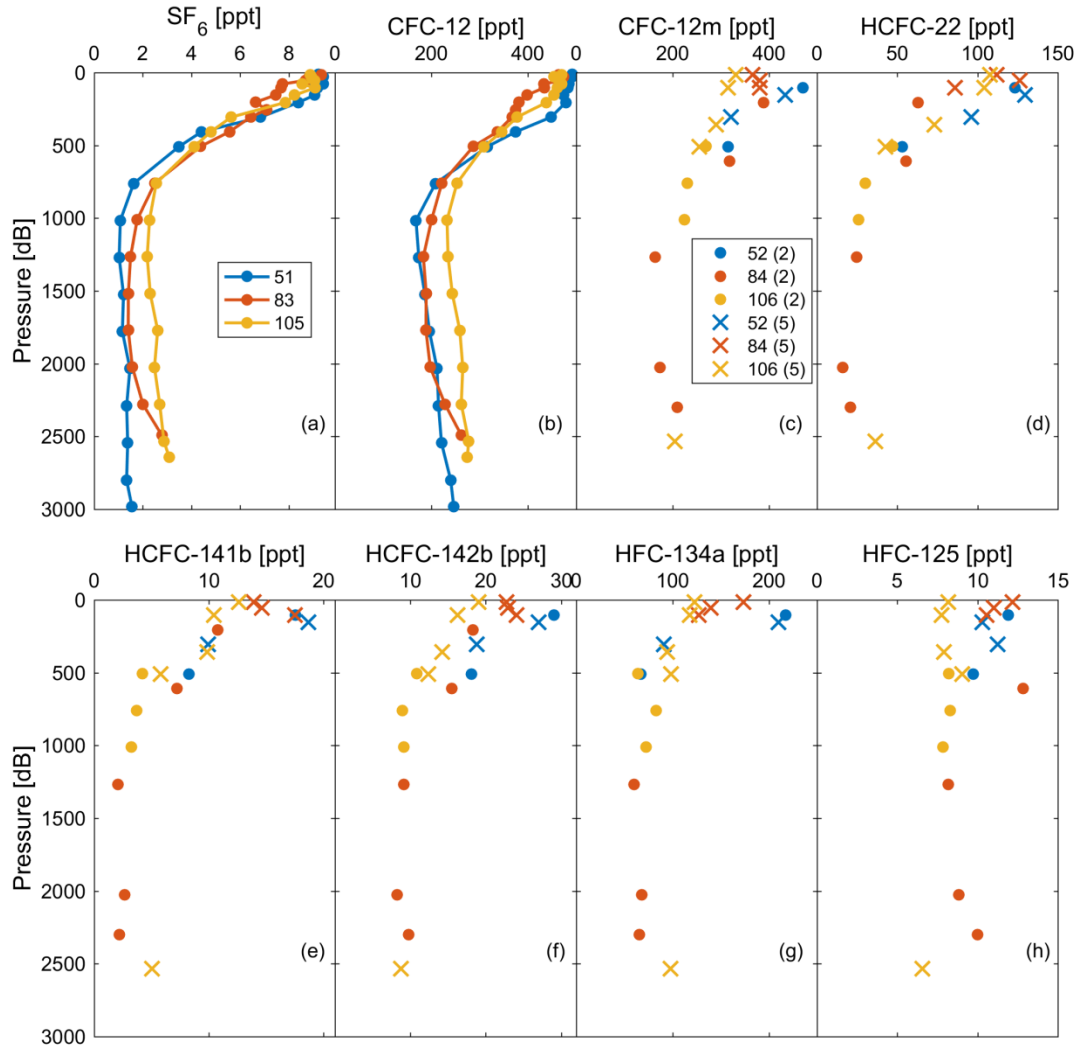
Figure 9. Observations of (a) SF₆ and (b) CFC-12 in profiles 51, 83 and 105 measured by the PT-GC-ECD and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.
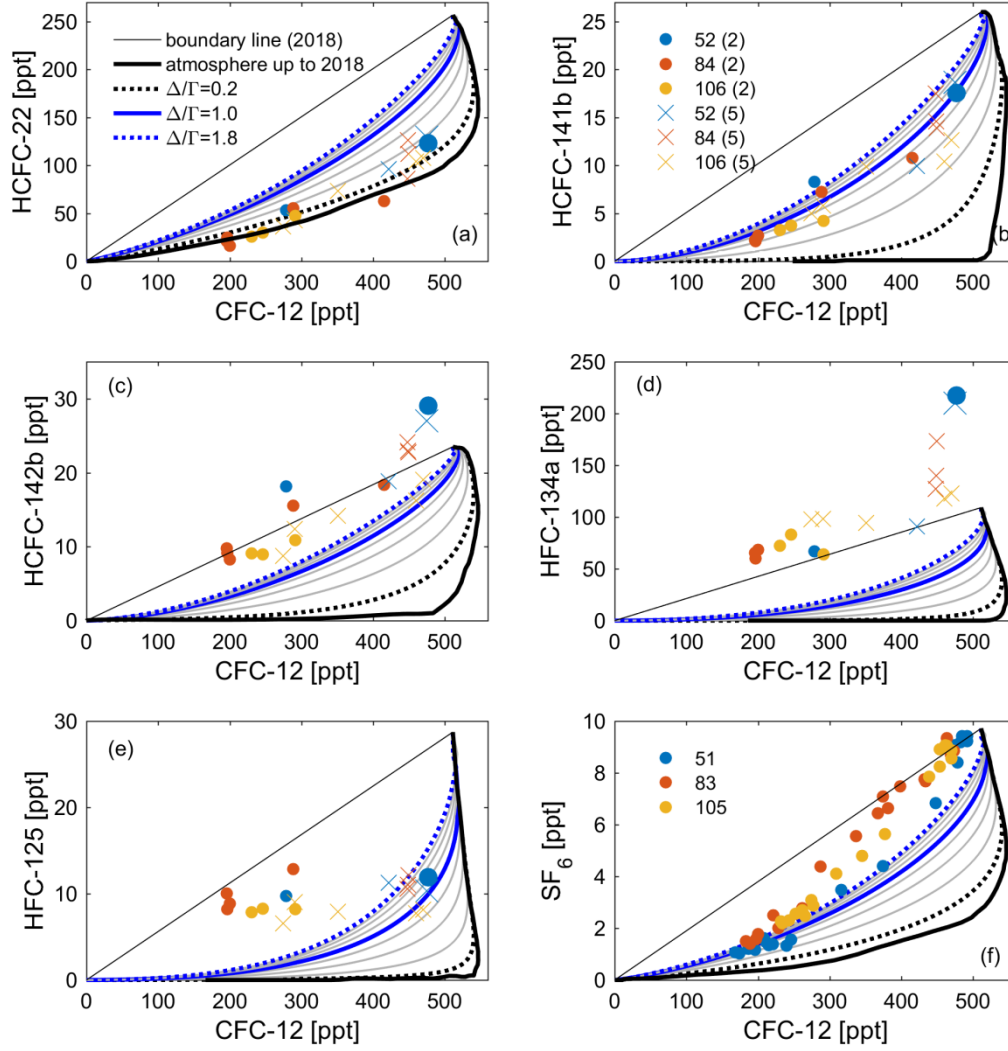
Figure 10. Observations of (a) HCFC-22, (b) HCFC-141b, (c) HCFC-142b, (d) HFC-134a and (e) HFC-125 in profiles 52, 84 and 106 measured by ~~the~~ Medusa-Aqua system and (f) SF$_6$ in profiles 51, 83 and 105 measured by ~~the~~ PT-GC-ECD plotted against the (interpolated) CFC-12 based on measurements by ~~the~~ PT-GC-ECD. The thick black line is the atmospheric history of the tracer pair ($\Delta/\Gamma = 0.0$) and the thin black line is the theoretical mixing line between contemporary ~~concentrations~~ and pre-industrial concentrations. The theoretical mixing lines assuming an Inverse Gaussian TTD (Sect. S4 and Fig. S9) with $\Delta/\Gamma = 0.2-1.8$ ~~based on IG TTD~~ have also been added. The values of the top two points of profile 52 are marked with a bigger size to identify the samples in shallow layers. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.

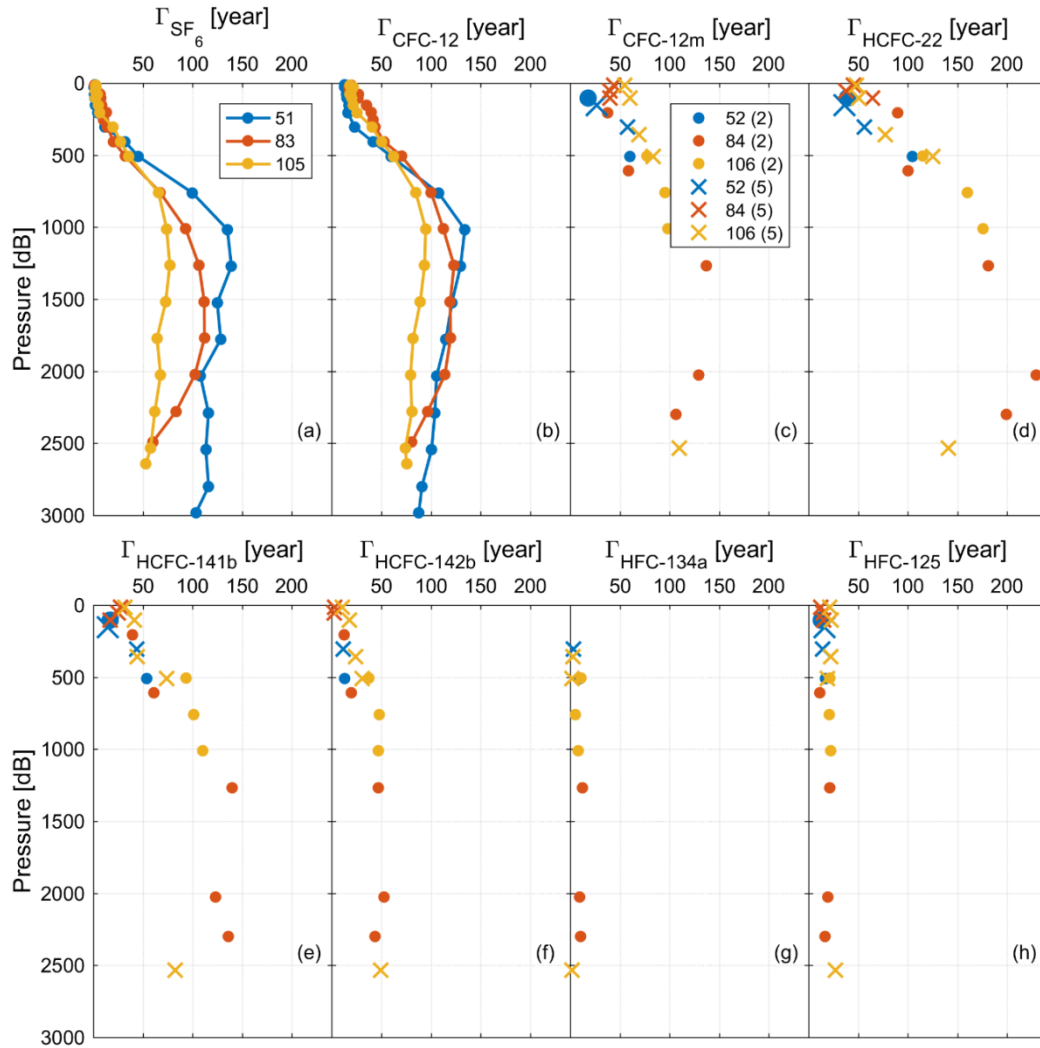**Figure 11**. Mean age estimated from (a) SF₆ and (b) CFC-12 in profiles 51, 83 and 105 and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 based on Δ/*Γ* = 1.0 of IG-TTD. The values of the top two points of profile 52 are marked with a bigger size. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.

Table 1. Total lifetimes, ocean partial lifetimes and ocean contributions for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116

Species	Total lifetime [a] (years)	Ocean partial lifetimes [b] (years) (Yvon-Lewis and Butler, 2002)	Ocean contributions [c] (%)
HCFC-22	11.9	1,174	1
HCFC-141b	9.4	9,190	0.1
HCFC-142b	18	122,200	0.01
HFC-134a	14	5,909	0.2
HFC-125	31	10,650	0.3
HFC-23	228		
PFC-14	>50,000	low solubility	
PFC-116	>10,000	low solubility	

[a] Total lifetime includes tropospheric OH and Cl atom reaction and photolysis loss, stratospheric loss due to reaction (OH and O(^{1}D)) and photolysis, and ocean and soil uptake as noted in the table, data from SPARC (2013); [b] Lifetimes with respect to oceanic uptake. [c] Based on the calculation method in Huhn et al. (2001).

Table 2. Review on biodegradation of selected HCFCs and HFCs in freshwater or soil

Microorganisms or culture	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-125	HFC-23	References
Methanotrophic bacterium *Methylosinus trichosporium OB3b(pure culture)*		√ [a]	x [b]	x			(Streger et al., 1999)
Mixed methanotrophic culture (MM1) with many heterotrophs	√		√	√			(Chang and Criddle, 1995)
Cell suspensions of M. capsulatus, methanotrophs in natural assemblages	√						(Oremland, 1996)
Methanotrophic mixed culture ENV2040		x	x				(Streger et al., 1999)
Unidentified methanotroph ENV2041		x	x	x			(Streger et al., 1999)
Propane oxidizing bacteria, *M. vaccae JOB5*	x	√ (0.1 µmol h^{-1})	√	x	x	x	(Streger et al., 1999)
Methylococcus capsulatus (Bath)	√						(Matheson et al., 1997)
Aerobic condition closed bottle tests		x		x	x		(Berends et al., 1999)
Anoxic sediments		√					(Oremland, 1996)
Landfill soil	√ [e]	x		x			(Scheutz et al., 2004)
Anaerobic conditions in sewage sludge and aquifer sediment slurries	x	x	x	x			(Balsiger et al., 2005)

[a] √: Biodegradation in freshwater/soil; [b] x: No biodegradation in freshwater/soil; [e] In the oxidative zone

Table 1~~3~~. Selected Medusa-Aqua analytes, calibration scales and errors in standard gas, detection limits and precision of seawater measurements

Industrial name (abbreviation)	Chemical formula	Full name	Standard scale	Calibrated errors of the standard gas (%)	Detection limit (fmol kg^{-1})	Precision [a] (%)
SF$_6$	SF$_6$	sulfur hexafluoride	SIO-05	0.37	0.48	--
CFC-12	CCl$_2$F$_2$	dichlorodifluoromethane	SIO-05	0.08	29.83	0.4
HCFC-22	CHClF$_2$	chlorodifluoromethane	SIO-05	0.22	13.75	3.1
HCFC-141b	CH$_3$CCl$_2$F	1,1-dichloro-1-fluoroethane	SIO-05	0.20	4.01	6.1
HCFC-142b	CH$_3$CClF$_2$	1-chloro-1,1-difluoroethane	SIO-05	0.21	3.24	1.8
HFC-134a	CH$_2$FCF$_3$	1,1,1,2-tetrafluoroethane	SIO-05	0.21	7.31	9.7
HFC-125	CHF$_2$CF$_3$	pentafluoroethane	SIO-14	0.23	1.19	2.0
HFC-23	CHF$_3$	fluoroform	SIO-07	0.49	6.71	--
PFC-14	CF$_4$	carbon tetrafluoride	SIO-05	0.30	0.44	--
PFC-116	CF$_3$CF$_3$	hexafluoroethane	SIO-07	0.32	1.41	--

[a] Precision (reproducibility, 1σ) of tracers in seawater was determined by samples at 23.5 dbar from cruise AL516 in the Baltic Sea in September 2018.

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Table 2~~4~~. Comparison of instrument performance measuring CFC-12

System	Medusa-Aqua system	PT-GC-ECD	PT-GC-ECD
Instrument	Cracker-Medusa-GC-MS	Syringe-PT-GC-ECD	Cracker-PT-GC-ECD
Workplace	Laboratory in Kiel	Onboard	Laboratory in Kiel
Purge efficiency (%)	99.5 ± 0.5 [a]	99.2 ± 3.6 [b]	99.6 ± 0.1 [c]
Precision (%)	0.4	0.3	1.4
Sampling volume (L)	~1.3	~0.3	~0.3
Measured compound	CFCs, HCFCs, HFCs, PFCs, etc.	CFC-12, SF$_6$, SF$_5$CF$_3$	CFC-12, SF$_6$, SF$_5$CF$_3$

[a] After purging three times; [b] After purging once; [c] After purging twice.

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Table 3~~5~~. Seawater surface saturations (%) of ~~SF$_6$ and CFC-12 in profiles 83 and 105 from cruise MSM72 (measured onboard with the PT-GC-ECD system) and~~ CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 ~~in profiles 84 and 106 from cruise MSM72 and~~ in profile 30 from cruise AL516 (measured by~~in the laboratory in Kiel with the~~ Medusa-Aqua system).

Profile	Pressure (dbar)	CFC-12	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-125
30	1.6	132	68	61	115	150	287
30	23.5	118	79	84	112	105	218
30	23.5	117	83	77	115	120	250

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Table 6. Evaluating the stability of selected HCFCs and HFCs based on seawater measurements in relation to observations of CFC-12

Compound	Surface saturation	Location in the stability area	Mean age in relation to CFC-12
HCFC-22	Low	Low	High
HCFC-141b	Low	Within area	Slightly high
HCFC-142b	As expected	Slightly high	Low
HFC-134a	High	High	Low
HFC-125	Low and high *	Within area	Low

5 * HFC-125 has low saturations in the Mediterranean Sea but high saturations in the Baltic Sea.

Table 47. Evaluating the possibilities of selected HCFCs, HFCs and PFCs as transient tracers in the ocean from four aspects

Compound	Atmospheric history	Solubility in seawater	Feasibility ofCan be measuremented in seawater	Stability in seawater	Possibility to be transient tracer
CFC-12	*** [a]	***	***	***	***
HCFC-22	***	**	***	**	**
HCFC-141b	***	*	***	**	**
HCFC-142b	***	*	***	**	**
HFC-134a	***	**	**	*	*
HFC-125	***	*	*	*	*
HFC-23	**	**	*	*	*
PFC-14	***	**	*	***	**
PFC-116	***	*	*	***	**

[a] The total number of (black and red) stars represent current knowledge: one star means "largely unknown", two stars "reasonablye well resolved" and three stars "well documented or resolved"; the number of black stars represents the ability of a compound as a transient tracer through current assessments: one, two and three stars mean the ability to be low, medium and high. After the two steps, the comprehensive evaluation of the information is determined to be low, medium and high confidence or feasibility (see Sect. 6). For instance, HFCF-141b has three stars and two black stars for "atmospheric history" since that is well-known, but the ability of HCFC-141b is only medium well suited as a new transient tracer considering the decreasing atmospheric history.

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References

Abraham, M. H., Gola, J. M., Cometto-Muñiz, J. E., and Cain, W. S.: Solvation properties of refrigerants, and the estimation of their water-solvent and gas-solvent partitions, Fluid Phase Equilib., 180, 41–58, https://doi.org/10.1016/S0378-3812(00)00511-2, 2001.

Aggarwal, P. K.: Isotope Methods for Dating Old Groundwater, edited by: Suckow, A., Aggarwal, P., and Araguas-Araguas, L., International Atomic Energy Agency, Vienna, 357 pp., 2013.

Arnold, T., Mühle, J., Salameh, P. K., Harth, C. M., Ivy, D. J., and Weiss, R. F.: Automated Measurement of Nitrogen Trifluoride in Ambient Air, Anal. Chem., 84, 4798–4804, https://doi.org/10.1021/ac300373e, 2012.

Balsiger, C., Holliger, C., and Höhener, P.: Reductive dechlorination of chlorofluorocarbons and hydrochlorofluorocarbons in sewage sludge and aquifer sediment microcosms, Chemosphere, 61, 361–373, https://doi.org/10.1016/j.chemosphere.2005.02.087, 2005.

Berends, A., De Rooij, C., Shin-Ya, S., and Thompson, R.: Biodegradation and ecotoxicity of HFCs and HCFCs, Arch. Environ. Contam. Toxicol., 36, 146–151, https://doi.org/10.1007/s002449900454, 1999.

Beyer, M., van der Raaij, R., Morgenstern, U., and Jackson, B.: Potential groundwater age tracer found: Halon-1301 (CF_3Br), as previously identified as CFC-13 (CF_3Cl), Water Resour. Res., 50, 7318–7331, https://doi.org/10.1002/2014WR015818, 2014.

Booge, D.: FS Alkor Cruise Report, Cruise AL516, 2018.

Bullister, J., and Weiss, R.: Determination of CCl_3F and CCl_2F_2 in seawater and air, Deep Sea Res. Part A. Oceanogr. Res. Pap., 35, 839–853, https://doi.org/10.1016/0198-0149(88)90033-7, 1988.

Bullister, J., and Tanhua, T.: Sampling and measurement of chlorofluorocarbon and sulfur hexafluoride in seawater, GO-SHIP (Unesco/IOC), Report, 1–11, 2010.

Bullister, J. L., and Lee, B. S.: Chlorofluorocarbon-11 removal in anoxic marine waters, Geophys. Res. Lett., 22, 1893–1896, https://doi.org/10.1029/95GL01517, 1995.

Bullister, J. L., Wisegarver, D. P., and Menzia, F. A.: The solubility of sulfur hexafluoride in water and seawater, Deep-Sea Res. Pt. I, 49, 175–187, https://doi.org/10.1016/S0967-0637(01)00051-6, 2002.

Bullister, J. L., Wisegarver, D. P., and Sonnerup, R. E.: Sulfur hexafluoride as a transient tracer in the North Pacific Ocean, Geophys. Res. Lett., 33, L18603, https://doi.org/10.1029/2006GL026514, 2006.

Bullister, J. L., and Wisegarver, D. P.: The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater, Deep-Sea Res. Pt. I, 55, 1063–1074, https://doi.org/10.1016/j.dsr.2008.03.014, 2008.

Bullister, J. L.: Atmospheric Histories (1765-2015) for CFC-11, CFC-12, CFC-113, CCl_4, SF_6 and N_2O, NDP-095, 1–23, https://doi.org/10.3334/CDIAC/otg.CFC_ATM_Hist_2015, 2015.

Butler, J. H., Yvon-Lewis, S. A., Lobert, J. M., King, D. B., Montzka, S. A., Bullister, J. L., Koropalov, V., Elkins, J. W., Hall, B. D., and Hu, L.: A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl_4) to the ocean, Atmos. Chem. Phys., 16, 10899–10910, https://doi.org/10.5194/acp-16-10899-2016, 2016.

Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A.: Scientific Assessment of Ozone Depletion: 2014, World Meteorological Organization Geneva, 1.1–5.58, 2014.

Chang, W.-k., and Criddle, C. S.: Biotransformation of HCFC-22, HCFC-142b, HCFC-123, and HFC-134a by methanotrophic mixed culture MM1, Biodegradation, 6, 1–9, https://doi.org/10.1007/BF00702293, 1995.

Cicerone, R. J.: Atmospheric carbon tetrafluoride: A nearly inert gas, Science, 206, 59–61, https://doi.org/10.1126/science.206.4414.59, 1979.

Clever, H. L., Battino, R., Clever, H. L., Jaselskis, B., Clever, H. L., Yampol'skii, Y. P., Jaselskis, B., Scharlin, P., and Young, C. L.: IUPAC-NIST Solubility Data Series. 80. Gaseous Fluorides of Boron, Nitrogen, Sulfur, Carbon, and Silicon and Solid Xenon Fluorides in all Solvents, J. Phys. Chem. Ref. Data, 34, 201–438, https://doi.org/10.1063/1.1794762, 2005.

Deeds, D. A.: The Natural Geochemistry of Tetrafluoromethane and Sulfur Hexafluoride : Studies of Ancient Mojave Desert Groundwaters, North Pacific Seawaters and the Summit Emissions of Kilauea Volcano, PhD thesis, 2008.

Deeds, D. A., Mühle, J., and Weiss, R. F.: Tetrafluoromethane in the deep North Pacific Ocean, Geophys. Res. Lett., 35, L14606, https://doi.org/10.1029/2008gl034355, 2008.

Ebser, S., Kersting, A., Stöven, T., Feng, Z., Ringena, L., Schmidt, M., Tanhua, T., Aeschbach, W., and Oberthaler, M. K.: [39]Ar dating with small samples provides new key constraints on ocean ventilation, Nat. Commun., 9, 5046, https://doi.org/10.1038/s41467-018-07465-7, 2018.

Hainbucher, D., Álvarez, M., Astray, B., Bachi, G., Cardin, V., Celentano, P., Chaikakis, S., Montero, M. C., Civitarese, G., Hassoun, A. E. R., Fajar, N. M., Fripiat, F., Gerke, L., Gogou, A., Guallart, E., Gülk, B., Lange, N., Rochner, A., Santinelli, C., Schroeder, K., Steinhoff, T., Tanhua, T., Urbini, L., Velaoras, D., Wolf, F., and Welsch, A.: Variability and Trends in Physical and Biogeochemical Parameters of the Mediterranean Sea, Cruise No. MSM72, March 02,

2018 - April 03, 2018, Iraklion (Greece) - Cádiz (Spain), MED-SHIP2, in, MARIA S. MERIAN-Berichte, Gutachterpanel Forschungsschiffe, Bremen, 2019.

Hall, T. M., and Plumb, R. A.: Age as a diagnostic of stratospheric transport, J. Geophy. Res.: Atmos., 99, 1059–1070, https://doi.org/10.1029/93JD03192, 1994.

5   Huhn, O., Roether, W., Beining, P., and Rose, H.: Validity limits of carbon tetrachloride as an ocean tracer, Deep-Sea Res. Pt. I, 48, 2025–2049, https://doi.org/10.1016/S0967-0637(01)00004-8, 2001.

Law, C., Watson, A., and Liddicoat, M.: Automated vacuum analysis of sulphur hexafluoride in seawater: derivation of the atmospheric trend (1970–1993) and potential as a transient tracer, Mar. Chem., 48, 57–69, https://doi.org/10.1016/0304-4203(94)90062-0, 1994.

10   Li, P., Mühle, J., Montzka, S. A., Oram, D. E., Miller, B. R., Weiss, R. F., Fraser, P. J., and Tanhua, T.: Atmospheric histories, growth rates and solubilities in seawater and other natural waters of the potential transient tracers HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116, Ocean Sci., 15, 33–60, https://doi.org/10.5194/os-15-33-2019, 2019.

Li, P., and Tanhua, T.: Recent changes in deep ventilation of the Mediterranean Sea; evidence from long-term transient
15   tracer observations, Frontiers in Marine Science, 7, 594, https://doi.org/10.3389/fmars.2020.00594, 2020.

Lobert, J. M., Baring, T. J., Butler, J. H., Montzka, S. A., Myers, R. C., Elkins, J. W., Brown, R. H., Baker, D. J., and Rasmussen, J. L.: OAXTC 92: Ocean/atmosphere exchange of trace compounds 1992, 1–43, 1995.

Lobert, J. M., Butler, J. H., Geller, L. S., Yvon, S. A., Montzka, S. A., Myers, R. C., Clarke, A. D., and Elkins, J. W.: Blast 94: Bromine latitudinal air/sea transect 1994, 1–39, 1996.

20   Lu, Z. T., Schlosser, P., Smethie Jr, W. M., Sturchio, N. C., Fischer, T. P., Kennedy, B. M., Purtschert, R., Severinghaus, J. P., Solomon, D. K., Tanhua, T., and Yokochi, R.: Tracer applications of noble gas radionuclides in the geosciences, Earth-Sci. Rev., 138, 196–214, https://doi.org/10.1016/j.earscirev.2013.09.002, 2014.

Matheson, L. J., Jahnke, L. L., and Oremland, R. S.: Inhibition of methane oxidation by Methylococcus capsulatus with hydrochlorofluorocarbons and fluorinated methanes, Appl. Environ. Microbiol., 63, 2952–2956, 1997.

25   Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., and Simmonds, P. G.: Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80, 1536–1545, https://doi.org/10.1021/ac702084k, 2008.

Ooki, A., and Yokouchi, Y.: Determination of Henry's law constant of halocarbons in seawater and analysis of sea-to-air flux of iodoethane (C_2H_5I) in the Indian and Southern oceans based on partial pressure measurements, Geochem.
30   J., 45, e1–e7, https://doi.org/10.2343/geochemj.1.0122, 2011.

Oremland, R. S.: Microbiology of Atmospheric Trace Gases, 306 pp., 1996.

Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., and Hermansen, O.: History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE), Earth Syst. Sci. Data, 10, 985–1018, https://doi.org/10.5194/essd-10-985-
35   2018, 2018.

Ravishankara, A., Solomon, S., Turnipseed, A. A., and Warren, R.: Atmospheric lifetimes of long-lived halogenated species, Science, 194–199, https://doi.org/10.1126/science.259.5092.194, 1993.

Roether, W., Klein, B., and Bulsiewicz, K.: Apparent loss of CFC-113 in the upper ocean, J. Geophys. Res.: Oceans, 106, 2679–2688, https://doi.org/0148-0227/01/1999JC000079, 2001.

40   Scharlin, P., and Battino, R.: Solubility of CCl_2F_2, $CClF_3$, CF_4, and CH_4 in Water and Seawater at 288.15-303.15 K and 101.325 kPa, J. Chem. Eng. Data, 40, 167–169, https://doi.org/10.1021/je00017a036, 1995.

Scheutz, C., Mosbæk, H., and Kjeldsen, P.: Attenuation of methane and volatile organic compounds in landfill soil covers, J. Environ. Qual., 33, 61–71, https://doi.org/10.2134/jeq2004.6100, 2004.

Schneider, A., Tanhua, T., Roether, W., and Steinfeldt, R.: Changes in ventilation of the Mediterranean Sea during the
45   past 25 year, Ocean Sci., 10, 1–16, https://doi.org/10.5194/os-10-1-2014, 2014.

Simmonds, P. G., Rigby, M., McCulloch, A., Vollmer, M. K., Henne, S., Mühle, J., O'Doherty, S., Manning, A. J., Krummel, P. B., Fraser, P. J., Young, D., Weiss, R. F., Salameh, P. K., Harth, C. M., Reimann, S., Trudinger, C. M., Steele, P., Wang, R. H. J., Ivy, D. J., Prinn, R. G., Mitrevski, B., and Etheridge, D. M.: Recent increases in the atmospheric growth rate and emissions of HFC-23 (CHF_3) and the link to HCFC-22 ($CHClF_2$) production, Atmos.
50   Chem. Phys., 2018, 4153–4169, https://doi.org/10.5194/acp-18-4153-2018, 2018.

Sousa, S. R., and Bialkowski, S. E.: Comparison of gas chromatography detection limits and relative responses of common alternative fluorocarbons using electron capture, atomic emission, and mass spectrometry detection, Anal. Chim. Acta, 433, 181-186, https://doi.org/10.1016/S0003-2670(01)00789-9, 2001.

SPARC: Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, AGU Fall
55   Meeting Abstracts, 2013, 1.1–6.21.

Stöven, T.: Ventilation processes of the Mediterranean Sea based on CFC-12 and SF_6 measurements, Master thesis, 116 pp., 2011.

Stöven, T., and Tanhua, T.: Ventilation of the Mediterranean Sea constrained by multiple transient tracer measurements, Ocean Sci., 10, 439–457, https://doi.org/10.5194/os-10-439-2014, 2014.

Stöven, T., Tanhua, T., Hoppema, M., and von Appen, W. J.: Transient tracer distributions in the Fram Strait in 2012 and inferred anthropogenic carbon content and transport, Ocean Sci., 12, 319–333, https://doi.org/10.5194/os-12-319-2016, 2016.

Streger, S. H., Condee, C. W., Togna, A. P., and DeFlaun, M. F.: Degradation of hydrohalocarbons and brominated compounds by methane-and propane-oxidizing bacteria, Environ. Sci. Technol., 33, 4477–4482, https://doi.org/10.1021/es9907459, 1999.

Tanhua, T., Anders Olsson, K., and Fogelqvist, E.: A first study of SF_6 as a transient tracer in the Southern Ocean, Deep-Sea Res. Pt. II, 51, 2683–2699, https://doi.org/10.1016/j.dsr2.2001.02.001, 2004.

Tanhua, T., Waugh, D. W., and Wallace, D. W. R.: Use of SF_6 to estimate anthropogenic CO_2 in the upper ocean, J. Geophy. Res., 113, C04037, https://doi.org/10.1029/2007jc004416, 2008.

Tanhua, T., Van Heuven, S., Key, R. M., Velo, A., Olsen, A., and Schirnick, C.: Quality control procedures and methods of the CARINA database, Earth Syst. Sci. Data, 2, 35–49, https://doi.org/10.5194/essd-2-35-2010, 2010.

Trudinger, C. M., Fraser, P. J., Etheridge, D. M., Sturges, W. T., Vollmer, M. K., Rigby, M., Martinerie, P., Mühle, J., Worton, D. R., and Krummel, P. B.: Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1800 inferred from ice core, firn, air archive and in situ measurements, Atmos. Chem. Phys., 16, 11733–11754, https://doi.org/10.5194/acp-16-11733-2016, 2016.

Vollmer, M. K., and Weiss, R. F.: Simultaneous determination of sulfur hexafluoride and three chlorofluorocarbons in water and air, Mar. Chem., 78, 137–148, https://doi.org/10.1016/S0304-4203(02)00015-4, 2002.

Walker, S. J., Weiss, R. F., and Salameh, P. K.: Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11 CFC-12, CFC-113, and carbon tetrachloride, J. Geophy. Res., 105, 14285–14296, https://doi.org/10.1029/1999jc900273, 2000.

Wallace, D. W. R., and Krysell, M.: Hydrolysis of Carbon Tetrachloride, Science, 246, 1638–1639, https://doi.org/10.1126/science.1638-a, 1989.

Warner, M. J., and Weiss, R. F.: Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, Deep Sea Res. Part A. Oceanogr. Res. Pap., 32, 1485–1497, https://doi.org/10.1016/0198-0149(85)90099-8, 1985.

Waugh, D. W., Hall, T. M., and Haine, T. W.: Relationships among tracer ages, J. Geophys. Res.: Oceans, 108, 3138, https://doi.org/10.1029/2002JC001325, 2003.

Yvon-Lewis, S., Liu, Y., Hu, L., and O'Hern, J.: Selected CFC and HCFC Tracers Observed During the Gulf of Mexico East Coast Carbon (GOMECC) Cruise, AGU Fall Meeting Abstracts, 2008, 1–65.

Yvon-Lewis, S. A., and Butler, J. H.: Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, J. Geophy. Res.: Atmos., 107, 4414, https://doi.org/10.1029/2001JD001267, 2002.