Interactive Comment on "Medusa-Aqua system: simultaneous measurement and evaluation of novel potential halogenated transient tracers HCFCs, HFCs and PFCs in the ocean" *by* Pingyang Li and Toste Tanhua

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We thank two anonymous referees for your constructive suggestions and comments. Below, we address all the comments and describe our responses to them where we refer to the revised manuscript (Italic) by listing the pages or sections of changes. In the following Revised Manuscript and Supplement, all changes from the original text are marked.

Anonymous Referee #1

MAJOR COMMENTS

Comment: 1. I think the overall conclusions of the study need to be more clearly presented. I like Table 5, and accompanying discussion in Section 6, as a summary of the analysis/paper, but the Introduction, and Conclusions are less clear. I think someone just reading these (as a lot of people will do before reading the whole paper) will come away a bit confused. I don't have any specific suggestions, but I think some rewriting is required so it is clearer which tracers are definitely not suitable, and which are (and maybe a third category of tracers where not sure and more measurements/tests needed).

As part of this I think you need to clarify what is meant (or remove usage) in the highlights by "most possible" and "most potential" tracers. I think I understand what is meant but only after reading the paper in detail.

Response: Thank you very much for your comment. All the "most possible" and "most potential" have been removed. We have rewritten the Introduction and Conclusion, see the Revised Manuscript. Of the investigated halogenated compounds, HCFC-142b and HCFC-141b are found to be the most promising transient tracers currently and PFC-14 and PFC-116 for the future (medium confidence). HCFC-22 is not suitable as a transient tracer in warm waters but possible for cold waters. We are not able to evaluate the potential of HFC-134, HFC-125, and HFC-23 as tracers fully due to lacking information on their solubility and stability in seawater and with potential analytical challenges. But we could no longer consider HCFC-22, HFC-125 and HFC-23 as tracers since they could be replaced by mature or better transient tracers based on the similar atmospheric history.

Comment: 2. As written the manuscript seems to suggest that a conserved tracer is only useful as a transient tracer if it is linearly increasing, and can then be used to estimate the mean age. However, a tracer with nonlinear history can still be used as a transient tracer, and be used to help constrain the TTD (especially if multiple tracers are available). For example, a linear and quadratically increase can be used in combination to estimate both the mean and the width. Also, the fact that the atmospheric concentration of the tracers is essentially zero at differing times in the past (e.g.

HFC-125 in late 1990s, HCFC-142b in late 1980s, and HCFC-22 in late 1960s) might be very useful for containing aspects of the TTD, even if can't estimate the mean age from each tracer. The authors make a few references to determining more complex TTDs as in Stoven and Tanhua, but even if you still assume IG TTD multiple tracers could be used to estimate both parameters of the IG.

It might be asking too much for detailed multi-tracer analysis in this paper, but even if this is the case I think the possibility of a multi-tracer analysis that does not aim solely at estimating the mean age needs to be discussed. I would encourage the authors to think if there are more appropriate approaches than just estimate the mean age assuming D/G=1, and whether this may change conclusions on whether a tracer is useful.

Response: Many thanks for your comment. Of course, we could try more methods. However, there are still too many unknowns in the calculation involving new tracers with uncertain stability, and sometimes atmospheric history will make it impossible to be applied by some methods. Besides, these methods may lead to a bigger bias based on limited measurements. Actually, we did try some based on current observations, but the time-variant ventilation in the Mediterranean Sea made our attempts fail. Therefore, we would like to try these methods after we obtain more observations. Since our main purpose in this study is to solve our primary task – evaluating the usefulness of the new tracers, it will be future work to explore more appropriate approaches based on multi-tracers rather than only TTDs.

Comment: 3. The description of how the mean age is estimated from each tracer needs to be clearer. I don't find the description on top of page 7 and figs 4 and 5 very helpful, and if I wasn't already familiar with the approach would be confused. Related to this the text "mean age of HCFC-141b" (and other such usages throughout the manuscript) needs to be replaced with "mean age estimated from HCFC-141b". This may seem like petty semantics, but it is important to be clear that you are trying to estimate the same mean age from different tracers and not a tracer dependent quantity (as written it implies the latter). I think a paragraph where you clearly describe how you estimate the mean age from measurements of a given tracer, and then define your terminology, will help.

Actually, what are the take-home points from figures 4 and 5? I understand what is shown but I don't know what I am meant to take home from them (and if the purpose is to describe the calculation of the mean age, I don't think it works). Note, I find figures like fig 5 nice to look at but difficult to interpret/read off values.

Response: Thanks for your comment. Considering two referees commented on the original Figures 4 and 5, the two figures have been moved to Supplement as Figures S1 and S2. All "*mean age of*" in the manuscript has been changed to "*mean age (estimated) from*". Actually, the concept of TTD and Equations (1) and (2) are used to calculate the mean age. Through the TTD, we obtained the mean age look-up figures (Fig. S1 and S2) based on the input functions of tracers, sampling year, theoretical tracer concentrations in seawater, and assumed or determined Δ/Γ ratio. When the observed tracer concentrations match the theoretical ones, the mean age can be determined by looking up in the mean age look-up figures. The method to estimate the mean age from a given tracer based on observations can be found in the subsection (named "Mean age and Transient Time Distribution") of Sect. 4.2 in the Revised Manuscript.

Comment: 4. The shorter atmospheric history is given as a possible cause of the young estimates of mean age from HCFC-142b, HFC-134a, and HFC-25 (pg 13, line 21), but what does this not cause a similar bias for HCFC-141b?

Can the differences in mean age estimates be linked to the location of points in figure 12? I think fig 12 and 13 need to be linked together better than they currently are.

Would it help to include curves for different Delta/Gamma in figure 12 (thick curve is Delta/Gamma=0, and could add curves for a couple of values D/G)? This might show whether data consistent with different values of D/G.

Response: Thanks for your comment. The reasons for the young estimates of mean age from some tracers have been rewritten as uncertainty in the TTD ratio that will affect tracers with different input function differently, and/or uncertainty in the solubility function or analytical error and so on. For more details, see the second paragraph of Sect. 5.5 in the Revised Manuscript.

In order to better link the differences in mean age estimates in original Fig. 13 (now Fig. 11) to the location of points in Fig. 12 (now Fig. 10), Fig. 10 and 11 have been updated with the values of the top two points of profile 52 marked with a bigger size. As seen in Fig. 10, concentrations in the shallow layers are more located in the upper right corner and vice-versa.

In Fig. 10, curves of Δ/Γ ratios from 0.2 to 1.8 have been added. Thus curves of Δ/Γ = 0.0−1.8 have been plotted. Besides, SF_6 concentrations from profiles 51, 83 and 105 again CFC-12 concentrations have also been added for comparison (Fig. 10f). Here both SF_6 and CFC-12 were measured by the PT-GC-ECD. Obviously, the data is not consistent with different values of Δ/Γ. The reason for assuming Δ/Γ=1 see the first paragraph of Sect. 5.5 in the Revised Manuscript.

Figures 10 and 11, their captions and related contents in Sect. 5.4 and 5.5 have been revised, see the Revised Manuscript.

MINOR COMMENTS

Comment: Pg 6, line 5: This description of fig 3 needs to be earlier when fig 3 is first mentioned. Also, I think what is meant by relative tracer concentration should be in the caption.

Response: The description of the original Fig. 3 (now Fig. 5) has been moved upwards, see the first paragraph of subsection (named "Tracer age") of Sect. 4.2 in the Revised Manuscript. We also added the meaning of relative tracer concentrations in the caption of Fig. 5.

Comment: Pg 6, line 23: The sentence "… the calculated age is mean age considered both advection …" does not make sense.

Comment: Pg 12, lines 27-34 are repetitive.

Response: The related sentences have been removed.

Comment: Pg 13, line 15. Remove "1" from "1IG".

Response: "*assumption of a 1IG-TTD*" has been changed to "*assumption of an IG-TTD*".

Comment: Pg 15, line 1: "one star as no as some higher …" does not make sense.

Response: The sentence "*Our ability to estimate the stability of HCFC-142b only got one star as no as some higher than expected concentration points to another issue (see Sect. 5.4) though its seawater surface saturation was similar to the ones of SF_6 and CFC-12*" has been rewritten as "*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 particularly in the Atlantic Water Layer (Fig. 11), and its surface saturation similar to the ones of CFC-12/SF_6 in seawater*".

Anonymous Referee #2

GENERAL COMMENTS

Comment: I have reviewed the manuscript "Medusa-Aqua system . . . ", by Pingyang Li and Toste Tanhua and, while I find it appropriate for publication, it needs considerable modification before that. The authors describe a promising approach for continuing our ability to date ocean water masses with transient tracers as their emission histories evolve and new methods for their analysis emerge. The community faces a significant challenge in monitoring these gases in the ocean and interpreting results, as they are sequentially phased out and their atmospheric histories are no longer monotonic. Tracers useful today may not be useful tomorrow, so it is important that analytical and interpretive skills improve overtime as well. This paper describes such an improvement and demonstrates its capabilities with verification in the field.

However, the manuscript is loosely written in some parts and wordier than it needs to be. The authors need to seek out and eliminate redundant statements and tighten up the language where they can. I also worry about the organization and think it would be best to start with the instrument description, show the data, then interpret and explain it. Because of its organization, the manuscript tends to bounce the reader around rather than build a case from observations. Part of me wants to suggest that the authors write two papers – one about the method and results and one about the value of the tracers. But I think they can get this into one if it is better organized and tightened up.

Some of the figures are excellent and appropriate, while others have too much information and are not useful. The overall important message is that applying this new technology allows for the measurement of new transient tracers that will likely be useful over the next decade in understanding ocean transport. Going too far beyond that is superfluous and should be avoided.

Response: Thank you very much for your comment. As suggested, the sequence of the original Sect. 3, 4 and 2 have been changed to Sect. 2, 3 and 4, that is, the interpreted method has been followed with the instrument description. The original Figures 4 and 5 have been moved to the Supplement as Figures S1 and S2. A new Table 1 (total lifetimes, ocean partial lifetimes and ocean contributions for tracers) and Table 6 (evaluating the stability of selected HCFCs and HFCs based on seawater measurements in relation to observations of CFC-12) have been added. The sequence of figures and tables has also been revised correspondingly. Besides, we have eliminated redundant statements and tighten up the language carefully.

SOME SPECIFIC SUGGESTIONS

PAGE 1

Comment: The abstract overall could be shortened. Summary statements are better in the abstract than explanations, which are in the text.

Response: Highlights (Summary statements) have been removed. The main points in the Highlights have been added in the abstract and the abstract has been shortened, see the Revised Manuscript.

Comment: Line 14 – Can these two compounds be put into the sentence above? The way it's worded, it's not clear what the difference between "possible" and "potential" is.

Response: The two sentences on "possible" and "potential" in the Highlights (Summary statements) have been removed.

Comment: Line 13 – replace "be the most possible" with "have the greatest potential as"

Response: "be the most possible" has been changed to "be the most promising"

Comment: Line 18 – delete "the" after "as"

Line 32 – "most potential" is awkward. Try "the compounds that have the greatest potential as tracers in the future are . . ."

Response: Done as suggested.

PAGE 2

Comment: Line 8 – Place "and" before SF_6 and add "has been used" after SF_6; replace they with both

Line 9 – replace "as are" with "and"

Line 10 – Add "are known" after "time"

Lines 13, 14 – Replace "to be" with "as"

Response: Done as suggested.

Comment: Line 27 – "solubility" is not a part of the "input history"

Response: "*(including known solubility in seawater)*" has been removed.

PAGE 3

Comment: Line 7 – Hydrolysis is not a significant mechanism for destroying CCl_4 in seawater, but in some locations microbial degradation in low oxygen waters is.

Response: "*CFC-113 was found to be lost in warm upper waters (Roether et al., 2001) and CCl_4 was found to hydrolysis in warm waters and low oxygen regions (Wallace and Krysell, 1989; Huhn et al., 2001)*" has been changed to "*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)*".

Comment: Lines 9-11 – Awkward sentence; please revise.

Response: "*However, with the constraints of the weak signal of ^{3}H and the decreasing atmospheric history of CFC-12, only SF_6 can be the relatively reliable transient tracer in the timescale range of 1-100 years despite local restrictions were in place*" has been changed to "*However, with the constraints of the weak signal of 3H and the decreasing atmospheric mole fraction of CFC-12, only SF6 is a relatively reliable transient tracer in the seawater timescale range of 1-100 years (Fig. 1)*".

Comment: Line 22 – Add "ing" to "discuss"

Line 32 – replace "as" with "and"

Response: Done as suggested.

Comment: Lines 23-24 – Awkward sentence

Response: "*Therefore their stability is presented from several other perspectives that we could find from previous studies*" has been changed to "*Therefore, their stabilities are inferred from other studies with slightly different perspectives and environmental foci*".

Comment: Lines 24-25 – Incomplete sentence

Response: "*Considering the total fraction of a compound in the ocean (as compared to the atmosphere), a small loss in the ocean is insignificant for the overall budget of the compound, but can still be important for a potential transient tracer*" has been changed to "*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 significance for a potential transient tracer*".

Comment: Lines 33-37 – Consider tabulating these numbers instead of putting them into text.

Response: The new Table 1 has been added on page 26 in the Revised Manuscript. The sequence of other tables has also been revised correspondingly. The related descriptions have been changed in the second paragraph of Sect. 1.3 in the Revised Manuscript.

PAGE 4

Comment: Line 2 – Add "s" to "enter"

Response: The related sentence has been removed.

Line 11 – delete "a"; add "s" to "tracer"

Line 22 – delete the last sentence

Line 27 – delete "would"

Response: Done as suggested.

Comment: Lines 4, 5 – Hydrolysis is only one mechanism; low hydrolysis does not rule out other possible chemical or biological removal mechanisms. Revise or delete the sentence.

Response: The sentence "*This means that oceanic chemical degradation processes alone are possibly not significant sinks for selected HCFCs and HFCs, although further research on this is needed*." has been removed.

Comment: Line 24 – change "target" to "targeted" (?) The first sentence here is a little awkward; perhaps it can be improved.

Response: "*In order to explore if the target halogenated compounds can be used as oceanic alternative transient tracers, their atmospheric histories and seawater solubility have already been reported by Li et al. (2019)*" has been changed to "*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)*".

Comment: Lines 30-36 – This structure for the paper feels awkward. Would it be better to describe the instrument first, show some results from it, and then go into the modeling and descriptions of how the data can be used? I think the paper would be easier on the reader if that approach were taken.

Response: As suggested, the sequence of original Sect. 3, 4 and 2 have been changed to Sect. 2, 3 and 4, that is, the modeling and interpreted method has been followed with the instrument description.

PAGES 5-7

Comment: Section 2.2 is a good background but seems to meander. Can it be condensed and still deliver what is needed for the reader to interpret the data that are later presented?

Response: Many thanks for your comments. The original Sect. 2.2 (now Sect. 4.2) is not only background information (time range and tracer/mean age definitions) but also the interpreted results (tracer similarities and the specific application range shown in Fig. 5) based on atmospheric histories and seawater solubility of HCFCs, HFCs and PFCs. The shortened Sect. 4.2 can be found in the Revised Manuscript.

PAGE 5

Comment: Line 22 – Add "ally" to "monotonic"

Response: The related sentence has been removed.

PAGE 10

Comment: Line 10 – add "s" to "standard", delete "measurements", replace "done" with "measured" or "analyzed"

Response: The related sentence has been removed.

PAGE 11

Comment: Line 1 – delete "effective"

Lines 5-8 – This could probably be deleted with no impact on the paper.

Line 10 – add "s" to "depth"

Line 21 – replace “to” with “than”

Response: Done as suggested.

Comment: Line 9 – change “was” to “were”

Response: “*Seawater saturations in the winter mixed layer was calculated from historical cruises data*” has been changed to “*we calculated seawater saturation in the winter mixed layer (WML) from historical cruises data*”.

Comment: Line 20 – Sentence is awkward.

Response: “*Neither the historical seawater saturation of CFC-12 or SF_6 does show a clear trend over time*” has been changed to “*These historical seawater saturations do not show a clear trend over time*”.

PAGES 12, 13

Comment: Section 5.3 – These low values for surface saturations seem like a serious concern for the capability of the Medusa-Aqua system. Although loss during transport of samples is possible with some compounds, it is not likely for CFC-12. I hope this is not a “show-stopper”, meaning that the Medusa-Aqua system is not capable of quantitatively analyzing these compounds from seawater. The authors need to do a better job of explaining this so as not to mislead the reader about the capabilities of this system. If it has issues, what do they suggest for improving it?

Response: Section 5.3 has been rewritten by adding more observations from the Baltic Sea to describe the reasons for the low surface saturations. For details, see the Sect. 5.3 in the Revised Manuscript.

Comment: Section 5.4 – It’s always difficult to follow the description of a figure while reading the text and this section is no exception. I would prefer such a description to appear in the figure caption and then for the authors to use the text simply to state what the figure means. That lets the reader get on with the story and not get bogged down looking back and forth.

Response: The caption and the related description in the text (Sect. 5.4) of the original Fig. 12 (now Fig. 10) has been changed. The captions of figures and texts related to this question have also been revised in the Revised Manuscript.

Comment: Section 5.5 – This discussion seems to meander about. It is not clear and it’s hard to follow. It takes several readings to get to what the authors are trying to say. What exactly are the points the authors are trying to make? I recommend they state those points and use the figure references (parenthetically) to support them. Such an approach would be good for all three of these sections.

Response: Thanks for your comments. We have deleted some sentences and stated points by using the figure references (parenthetically) to support them, see the Sect. 5.3, 5.4 and 5.5 in the Revised Manuscript.

PAGE 14

Comment: Section 6 – This section, too, meanders. Here and elsewhere (e.g., previous sections), the authors get into trouble when they start describing the content of figures (or in some cases tables) in the text. The authors would do well to consider referring to figures and tables only parenthetically, then using the text to make their important points,

i.e., treat the figures much as they do references to other papers. Figure descriptions and explanations should go into the figure captions, thus freeing the authors (and readers) to engage solely in scientific meaning in the text. The idea is that text and figures should be able to stand alone. When this is done, it makes for a much easier read and quicker understanding.

Response: "in Sect. xx", "in Fig. xx" and "in Table xx" have been changed to "(see Sect. xx)", "(Fig. xx)" and "(Table xx)" in Sect. 6 and previous sections.

Comment: Line 12 and elsewhere – The reference to the number of stars is mentioned in the text without reference to their meaning. This is another example of not keeping the text and figures independently coherent. The reader should not have to refer to a figure to understand what is being said in the text, and *vice versa*.

Response: The number of stars has been replaced with the low, medium and high confidence/feasibility in Sect. 6. More footnotes have been added for the original Table 5 (now Table 7) to explain the stars inside the table.

Comment: Line 16 – Should HCFC-12 be HCFC-22?

Response: "HCFC-12" has been changed to "HCFC-22".

Comment: Lines 24-26 – This reminds me that here and in the "highlights" section at the beginning of the paper, the authors refer to "potential" and "possible" as different things, but do not state how they define that difference. They may want to drop this distinction or else provide definitions for the terms.

Response: All sentences related "most possible" and "most potential" has been removed.

PAGE 15

Comment: Line 15 – delete "and concentration". Also, this sentence is a bit awkward

Response: "*Our ability in estimating the stability of HFC-134a only got one star due to higher than the expected seawater surface saturation and concentration, but also not identified to be unstable, see Sect. 5.3 and 5.4*" has been changed to "*We have only poor knowledge on stability of HFC-134a since higher than expected surface saturation (Table 5) and concentration (Fig. 10), as well as lower than expected mean ages (Fig. 11) don't suggest degradation, and the compound is not identified to be unstable (see Sect. 5.4), but the stability of HFC-134a is still largely unknown considering the issues on seawater solubility function and/or measurements*".

Comment: Line 29 – "estimating" should be "estimate"

Response: All "ability to estimating" has been changed to "ability to estimate".

PAGE 16

Comment: Line 3 – "estimating" should be "estimate"

Response: All "ability to estimating" has been changed to "ability to estimate".

Comment: Section 7 – This section needs to be more succinct. It's very important that readers can understand immediately what the paper found. Statements about how things were done are not necessary for the conclusion, only the findings.

Response: Section 7 has been shortened, see the Revised Manuscript.

FIGURES AND TABLES

Comment: Figure 3 – For the purposes of this paper, I don't believe it is necessary to show the same plot three times with different reference years. I recommend choosing one as an example to make the point that each gas has a different history that is recorded differently in the ocean.

Figure 4 – As it stands, this figure is useless. There is little to be obtained from this plethora of minuscule plots. I think the authors are trying to make the point that for any one of these gases there is some uncertainty as to their age distributions in the ocean. They can do that with one plot and a nice caption supporting it.

Figure 5 – I'm not sure this figure adds anything. If there is a point the authors are trying to make with this figure, they should do so clearly and, as for Figure 4 use one plot (maybe two, depending upon the point they are trying to make) and a clear description in the caption.

All other figures are valuable and I believe necessary to the paper.

Response: From Fig. 3 (now Fig. 5), we compared the difference of relative tracer concentrations of CFC-12 in two reference years 2018 and 2000, so we suggest to keep the original Fig. 3a and Fig. 3c (now Fig. 5a and Fig. 5b).

The original Fig. 4 and 5 are combined to form the mean age look-up figure for each tracer, which has been moved to the Supplement as Fig. S1 and S2.

Comment: The tables are all useful in the manuscript. In Table 2, it would be good to note whether the reproducibility is expressed as one or two sigmas or if another approach is used. Tables 4 and 5 support the text, but, as noted above, the text in the manuscript needs to draw out the meaning of what these tables contain in a way that is readily understood by the reader.

Response: As suggested, we added a new Table 1 (ocean partial lifetimes and ocean contributions for tracers).

For the original Table 2 (now Table 3), the reproducibility is expressed as one sigma. The footnote "Precision (reproducibility)" has been changed to "Precision (reproducibility, 1σ)".

The original Table 4 (now Table 5) added more surface saturations in seawater from the Baltic Sea.

A new Table 6 (evaluating the stability of tracers based on seawater measurements in relation to observations of CFC-12) has been added.

The original Table 5 (now Table 7) has been revised by adding red stars and rewriting the footnote, see the Revised Manuscript.

Comment: FINAL NOTE: Finally, I would appreciate it if the authors would have someone else in their institute go through the final version of the next draft and catch typos, grammatical errors, etc. Independent eyes are always useful for finding things that authors miss simply because they've worked the text so many times.

Response: Many thanks for your kind reminder. Some colleagues have helped us check the language carefully.

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: atmospheric history, seawater solubility, feasibility of measurement and stability in seawater. The former two aspects have been investigated in previous work. In this study, 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. 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 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 evaluate their potential be 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

1.1 Why do we look for new transient tracers?

Transient tracers consist of chronological transient tracers, such as dichlorodifluoromethane (CFC-12) and sulfur hexafluoride (SF_6), and radioactive transient tracers, such as Tritium (^3H), Argon-39 (^{39}Ar) and Carbon-14 (^{14}C). They have been used as oceanic transient tracers to study the oceanic processes, such as ventilation, mixing and circulation processes. CFC-12 has been used since the 1980s, whereas SF_6 has only been used since the 1990s. Both

Deleted: Highlights¶
<#>A method to evaluate the utility of a compound to be an oceanic transient tracer is provided.¶
<#>The Medusa-Aqua system to simultaneous measure selected CFCs, HCFCs, HFCs and PFCs in seawater is described.¶
<#>HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 were measured in the Mediterranean Sea for the first time.¶
<#>HCFC-141b was found to be the most possible oceanic transient tracers.¶
<#>PFC-14 and PFC-116 were found to be the most potential oceanic transient tracers.¶

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compounds are 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 use of CFC-12 was phased-out as a result of the implementation of the Montreal Protocol on Substances that Deplete the Ozone Layer designed to curtail the degradation of the Earth's ozone layer. Therefore, the atmospheric concentration of CFC-12 has been decreased since the early 2000s (Bullister, 2015), which has reduced 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 due to its very high global warming potential that may restrict SF_6 to be an oceanic tracer in the future. Both CFC-12 and SF_6 are readily measured onboard a research vessel at a reasonable rate. Similarly, 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 (Wallace and Krysell, 1989; Huhn et al., 2001).

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, 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, the atmospheric abundances of most HCFCs and HFCs are increasing, as are the concentrations of PFCs. Here we 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 SF_6 as traditional chronological transient tracers and ^{3}H, ^{39}Ar and ^{14}C 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, with the constraints of the weak signal of ^{3}H and the decreasing atmospheric mole fraction of CFC-12, only SF_6 is a relatively reliable transient tracer in the seawater timescale range of 1-100 years (Fig. 1). Fortunately, the different atmospheric

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histories of the potential alternative transient tracers (Li et al., 2019) allow us to find one or several compounds to replace or supplement the established transient tracers.

1.3 Stability of alternative tracers in seawater

Chemical reactions (including hydrolysis), adsorption to particles and biological degradation process should be considered for the stability of compounds in seawater. 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 (Ravishankara et al., 1993; Cicerone, 1979) since CF_4 is stable at temperatures of at least 1200°C and the rate of hydrolysis of CF_4 is immeasurably small. Furthermore, no known marine natural products contain C-F bonds and there are no indications of biological processes that can break C-F bonds. 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 compounds in seawater. Therefore, their stabilities are inferred from other studies with slightly different perspectives and environmental foci.

One example is the contribution of the oceanic partial lifetime of selected HCFCs and HFCs to the 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 significance for a potential transient tracer. As far as we know from previous studies (Yvon-Lewis and Butler, 2002; Carpenter et al., 2014), HCFCs and HFCs are relatively stable in seawater and their ocean partial lifetimes (i.e. partial atmospheric lifetimes with respect to oceanic uptake) range from thousands to millions of years (Table 1). 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.

Another route is to compare surface saturations of a tracer with unknown stability to the one of a compound that is known to be unstable in seawater. Surface saturation of HCFCs is not as under-saturated as those of CCl_4 (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 1992-2008 (ftp://ftp.cmdl.noaa.gov/hats/ocean/, last access: 20 January 2020). This suggests that HCFCs are more stable than CCl_4 in surface seawater and possibly suited 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, HCFCs seem to be relatively stable in the ocean when only considering the chemical degradation process and surface saturation in seawater. However, the influence of oxygen dependence and biological degradation processes in seawater have not been investigated (Yvon-Lewis and Butler, 2002). In summary, no enough information is known on the stability of the selected HCFCs and HFCs in the ocean.

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1.4 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 extension of that work with the focus on the evaluation 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 and if these compounds are conservative in the oceanic environment. We also discuss the differences in input functions of the tracers, and the 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 interpreted based on the Inverse Gaussian Transit Time Distribution (IG-TTD) concept to identify their possibility as transient tracers in the ocean. The Mediterranean Sea was chosen for this study because of its rapid ventilation, rendering transient tracers to penetrate most of the water column. 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 detected by an Electron Capture Detector (ECD) that is normally used for CFC-12 and SF_6 (Lobert et al., 1995; Beyer et al., 2014). One alternative is to use a mass spectrometer (MS) for detection that has the advantage of scanning for unique masses for different compounds, 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.

The Medusa-GC-MS system (shorted 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 is based on trapping of the volatile gases on two traps kept at accurately controlled temperatures. 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

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(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 the majority of the 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 system was developed to degas the samples from gaseous tracers 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 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

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 western Baltic Sea in September 2018. Over the past years, we have collected samples on a few cruises and empirically improved our method.

3.1 Sample collection

The seawater samples were sampled and flame-sealed in ~1.3 L ampoules at sea and subsequently measured in the laboratory. Seawater samples were collected 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 by connected to the Niskin bottles via a stainless steel mounting system (Vollmer and Weiss, 2002). Around 5 minutes is 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, the ampoule was flame-sealed as soon as possible 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 onboard CFC-12 and SF_6 measurements were conducted on

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the stations we sampled for the Medusa-Aqua system in the Mediterranean Sea. The distance between stations on this cruise was 15 nm (nautical miles), 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 with nylon ferrule. Then the cracking chamber is flushed with N_2 for 10 minutes to flush out ambient air. 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 out of the seawater and 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}. 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. The counter-flow rate of Nafion dryer gas (N_2, grade 5.0) was set to 120 mL min^{-1}. 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 a carrier gas, and 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 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 3. Measurements in seawater are reported on the latest SIO absolute calibration scales for HFC-125 (SIO-14), HFC-23 and PF-114 (SIO-07) and other compounds (SIO-05). The tertiary calibration scale is propagated to a working standard used to determine weekly calibration curves and daily drift corrections. These calibration measurements are made by multiple injections of 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 responses for compounds in Table 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 3 could be detected in the seawater sample so that the purge efficiency for all compounds is 100 %. The precision of the measurement is dependent on the size of ampoules and sampling concentration (i.e. the amount of tracer); the samples with a higher amount of tracer have better precisions than those with a lower amount. The precision (or reproducibility) for seawater sample

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The cracked ampoules (with glass sprinters) were weighed right after removing them from the cracking device. Then they were emptied and rinsed with distilled water. The glass splinters were sorted back into the ampoules. The ampoule, as well as glass splinters, was together put into an electro-thermal drying oven for around 96 h. Finally, the ampoules were weighed again to quantify the masses of the seawater samples.¶
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measurements were determined by the relative standard deviations (1σ) of the concentrations for two pairs of duplicate samples (Table 3). The detection limits for measurements of all compounds by the Medusa-Aqua system are also shown in Table 3 based on the signals corresponding to the blank values or noises plus ten standard deviations.

The concentrations of SF_6, PFC-14, and PFC-116 in most seawater samples are lower than the detection limit, and HFC-23 has 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 cruise MSM72 are shown in Table S1 with quality flags marked.

3.5 Comparison of instruments measuring CFC-12

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_5CF_3 (Stöven, 2011; Stöven and Tanhua, 2014; Stöven et al., 2016; Bullister and Wisegarver, 2008). For comparison, a similar purge and trap system set-up (Cracker-PT-GC-ECD) to measure flame-sealed ampoules is added. A detailed comparison of the three instruments is shown in Table 4. Compared to other systems, the Medusa-Aqua system has lower purge efficiency due to using a bigger sampling volume if only considering 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.

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 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 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).

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

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

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.

4.2 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 seawater surface saturations. Atmospheric histories of tracers should be monotonic increasing 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).

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 similar trends of relative tracer concentrations (Fig. 5) are found for the following 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, one of each couple 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, if the relative tracer concentrations are over 100 % then there has been a decrease in atmospheric concentrations, such as the tracer age range of 0-30 years 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). Therefore, 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 to 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 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.

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Mean age and Transient Time Distribution (TTD). The mean age, calculated as the average of the TTD, can be 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 Δ/Γ = 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, 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 seawater saturation in the Mediterranean Sea

The historical saturation of transient tracers is an important factor to illustrate ventilation. To determine this for the Mediterranean Sea, we calculated seawater saturation in the winter mixed layer (WML) from historical cruises data. The depths of the WMLs in summer and winter are shown in Fig. 6 for two exemplary density profiles. The seawater saturation in the warm surface is often higher than the one during winter, which is the relevant saturation level for deep and intermediate water formation, and thus for the input functions. Therefore, only the WML was considered in the calculation of historical seawater saturation for all cruises. The depth ranges of WMLs (Fig. S3) and the saturation level for CFC-12 and SF_6 (Fig. 7) were determined by profiles of temperature, potential density, and CFC-12 concentrations for each historical cruise that we have access to in the Mediterranean Sea from 1987 to 2018 (Schneider et al., 2014; Li and Tanhua, in preparation). By averaging the mean seawater saturation from every single cruise, the saturation 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 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) has a long time to equilibrate with the atmosphere.

For the following calculations, the historical seawater saturations are assumed to be a constant 94 % (overtime) for all tracers in this study as no data exists to determine the historical seawater 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 comparable with those in adjacent stations measured onboard by the PT-GC-ECD system (Fig. 8). The 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 observations of CFC-12 and SF_6 from profiles 51, 83 and 105 measured by the PT-GC-ECD

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As seen in Fig. 5, the mean age distributions of the IG-TTD for the tracers are different depending on their atmospheric concentration histories (Fig. 2), part of the input functions. Such a suite of transient tracers with sufficiently different input functions could support the empiric determination of more complex TTDs, as reported in Stöven and Tanhua (2014). As the first step, these Medusa tracers have been measured, sometimes for the first time, in this study and interpreted based on the IG-TTD concept to identify their possibility to be transient tracers in the ocean.¶

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and observations 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 were presented for comparison.

5.3 Surface saturation of Medusa tracers in seawater

Surface saturation in seawater could be a factor to analyze the stability of a compound in surface seawater or confidence of seawater solubility function. It 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, 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).

In the Baltic Sea, the averaged seawater surface saturation of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 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). Concentrations in the shallow layers are more located in the upper right corner and vice-versa. In the figure, we added the atmospheric history of the Medusa

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tracers vs. CFC-12 as well as the theoretical mixing line between contemporary concentrations and pre-industrial; 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 below the "stability area" are not stable (assuming that CFC-12 is stable), and the samples above 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 have very different effects on CFC-12 that is decreasing in the atmosphere, and the Medusa tracers that are mostly increasing concentrations. This argument suggests that we could expect higher than expected concentrations (as SF_6 presented) for the Medusa tracers. This is exactly what we see from HCFC-142b and HFC-125 (Fig. 10). 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 in solubility functions and 3) some other issues within the measurements in the laboratory causing our observations to be high.

5.5 Comparison of mean age estimates

In order to compare the mean ages estimated from HCFCs and HFCs with the ones estimated from CFC-12 and SF_6, we calculated the mean ages of these tracers (Fig. 11). Here we assumed the Δ/Γ ratio of IG-TTD to be 1.0 and the saturation of all traces to be 94 % (see Sect. 5.1). However, the TTD of the Mediterranean Sea is complicated by the variable ventilation and the influence of different source regions for interior water, see Stöven and Tanhua (2014), so that the assumption of an IG-TTD with Δ/Γ = 1.0 can be questioned, but still serves as an initial assumption to evaluate the new tracers. Note that the mean ages calculated from CFC-12 and SF_6 are not identical, although we have high confidence in these data. Therefore, we can be sure that the assumptions made on the TTD are not entirely correct but a reasonable starting point for the purpose of this study.

The mean age estimated from HCFC-141b is similar to (slightly higher than) those from CFC-12 and SF_6, whereas the mean age estimated from HCFC-22 is higher but the mean ages from HCFC-142b, HFC-134a and HFC-125 significantly lower (than the ones estimated from CFC-12 and SF_6). If the mean age is lower than expected, it implies that the concentration is probably higher than expected (Fig. 10), and vice-versa. There are different possible explanations for the difference in mean ages. One obvious explanation is uncertainty in the Δ/Γ ratio of TTD that will affect tracers with different input functions differently. Other possible explanation includes uncertainty in the solubility function or analytical error, see discussions below.

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

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the Medusa tracers and CFC-12 is sensitive to the assumed shape of the TTD, and the difference in input history that makes them sensitive in a different way in relation to the time-variant ventilation of the (western) Mediterranean Sea.

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 7 by mainly evaluating the confidence or feasibility of atmospheric history, seawater solubility, ease of measurement and stability in seawater.

As a reference, we start with CFC-12 that is a commonly used transient tracer marked with 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 the stabilities in warm waters, as well as poorly oxygenated waters, have been proven.

HCFC-22. The increasing atmospheric history (high confidence) 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 the ones published in Deeds (2008) on measurements and the CGW model fitted results in 298-348 K, and the ones published in Abraham et al. (2001) on observations and the pp-LFERs model results at 298 K and 310 K. Thus, our ability to estimate the seawater solubility was marked as medium confidence due to lacking the experimental seawater solubility empirical data to verify the function. As to measurement, 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 (high feasibility). 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 was also supported by the weak hydrolysis of HCFC-22 in tropical and subtropical waters (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 not suitable to be a potential new transient tracer in the warm ocean, for instance, the Mediterranean Sea, but could possibly be used for colder waters.

HCFC-141b. The atmospheric history (high confidence) was well 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 the ones in Abraham et al. (2001) at the two temperatures. HCFC-141b has been measured on cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) and also in this study, thus we have high confidence in the

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ability for measurement. As for the stability, HCFC-141b was identified to be potentially stable in seawater (medium confidence) since its concentrations are in the 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 become complicated. All these indicate that HCFC-141b has a probably limited ability 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 to 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 particularly in the Atlantic Water Layer (Fig. 11), and its surface saturation similar to the ones of CFC-12/SF_6 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 potential to be used as a transient tracer.

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 consider medium confidence in the seawater solubility function due to the lack of experimental seawater solubility data. HFC-134a was measured in Ooki and Yokouchi (2011) by GC-MS and in this study by the Medusa-Aqua system, so we consider medium feasibility for measurements in this study due to higher than expected concentrations (see Sect. 5.4). We have only poor knowledge on stability of HFC-134a since higher than expected surface saturation (Table 5) and concentration (Fig. 10), as well as lower than expected mean ages (Fig. 11) don't suggest degradation, and the compound is not identified to be unstable (see Sect. 5.4), but the stability of HFC-134a is still largely unknown considering the issues on seawater solubility function and/or measurements. Besides, HFC-134a can 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 possibility than HCFC-142b but a higher possibility than HCFC-22 to be an oceanic transient tracer.

HFC-125. HFC-125 has unclear atmospheric concentrations in the early 1990s (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) 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 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

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HFC-125 as low since this compound has been measured for the 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 expected. 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. The low mean ages compared to the ones estimated from CFC-12 and SF_6 (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 have currently low potential as a transient tracer in the ocean due to the poorly constrained solubility and stability, 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 a non-zero blank (see Sect. 3.5). Therefore, we can, obviously, not reliable assess the stability of HFC-23 in seawater, and we have low confidence for the feasibility of the measurements, although the blank problem might possibly be solved by a different 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. 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 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 constructed, although we have only medium and low confidences for PFC-14 and PFC-116, respectively; the confidence for PFC-14 is higher than the ones for other compounds with medium confidence by matched several seawater measurements (Scharlin and Battino, 1995) and freshwater solubility (Clever et al., 2005; Abraham et al., 2001), whereas the low confidence for PFC-116 was attributed to its freshwater solubility only matched the one from Deeds (2008) 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 with a challenge to measure these compounds.

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 SF_6 that has similar atmospheric histories (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. 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

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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.

7 Conclusions

This study, combined with the study by Li et al. (2019), provides a method to identify and evaluate if a compound is suitable to be used 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 to be evaluated. The evaluation mainly considered four aspects: atmospheric history, seawater solubility, feasibility of measurement and stability in seawater. We also considered how Medusa tracers with different atmospheric history 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

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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.

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This study is considered as the first step for exploring the novel alternative transient tracers in the ocean.
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Data availability

Cruises data worked for historical seawater 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 observations of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 measured by the Medusa-Aqua system in seawater from cruise MSM72 are shown in Table S1.

Author contributions

TT conducted the sampling. 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.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgments

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GEOMAR Innovationsfonds Technologie-Seed-Funding (Transient Tracers 70090/03) and the China/Germany Joint Research Programme (Programm des Projektbezogenen Personenaustauschs, PPP, D1820) supported by the Deutscher Akademischer Austausch Dienst (DAAD) in Germany. The authors also gratefully acknowledge support through the scholarship program from the China Scholarship Council (CSC).

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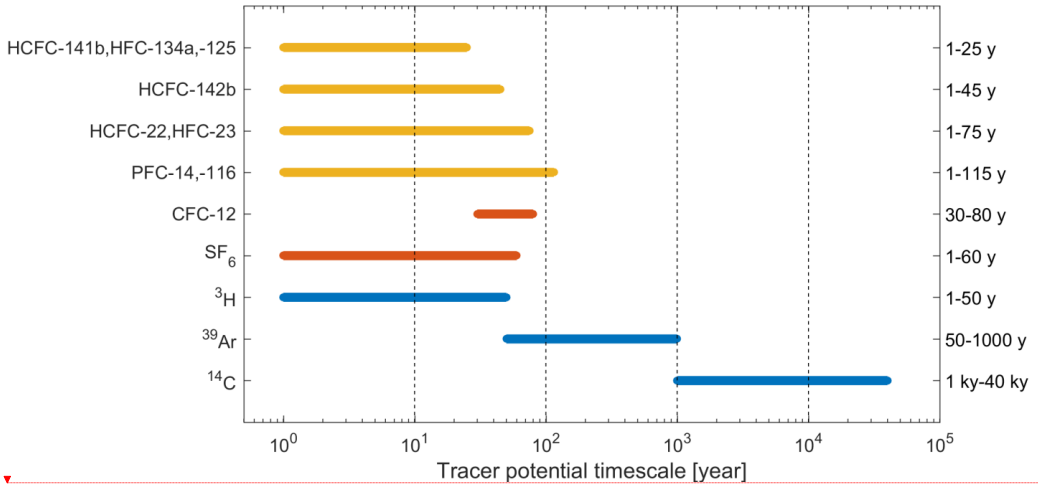

Figure 1. Seawater timescales ("tracer age ranges") of halogenated compounds dating using potential chronological transient tracers (selected HCFCs, HFCs, and PFCs, orange) as well as traditional chronological transient tracers (CFC-12 and SF_6, red) combined with radioisotope dating using radioactive transient tracers (^3H, ^{39}Ar, and ^{14}C, blue). Tracer age ranges of chronological transient tracers are estimated from Fig. 5 (see below), while tracer age ranges of radioactive transient tracers are from Aggarwal (2013).

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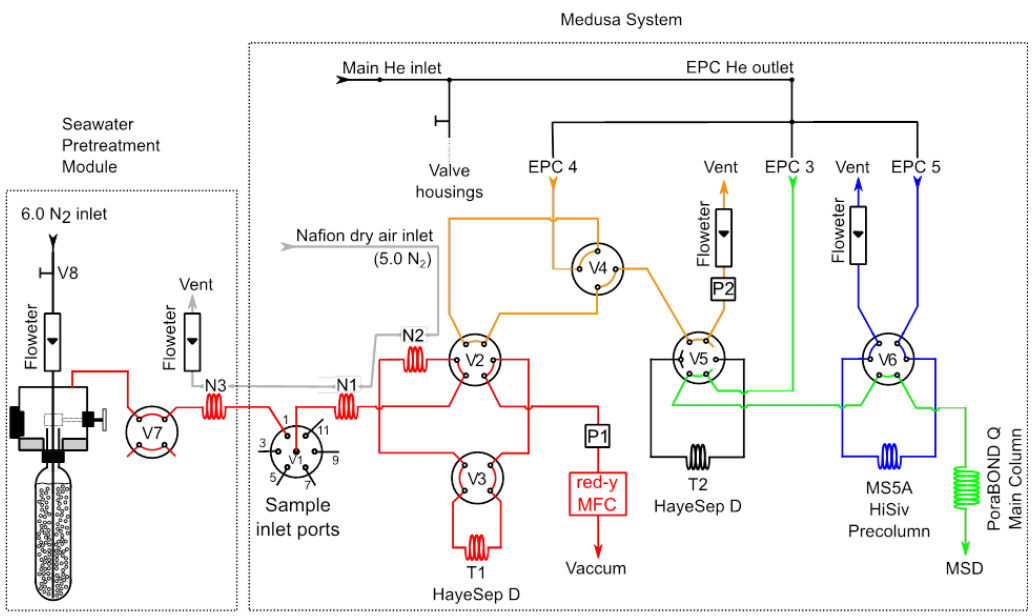

Figure 2. Medusa-Aqua system flow scheme. The Medusa system remains identical to that given by Miller et al. (2008). The seawater pretreatment module is added to degas the samples from gaseous tracers before injecting into Medusa. Electronic Pressure Controllers (EPC3, EPC4, and EPC5) supply helium throughout the system. The Mass Flow Controller (MFC) is used to measure the sample volume downstream of Trap 1 (T1) 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).

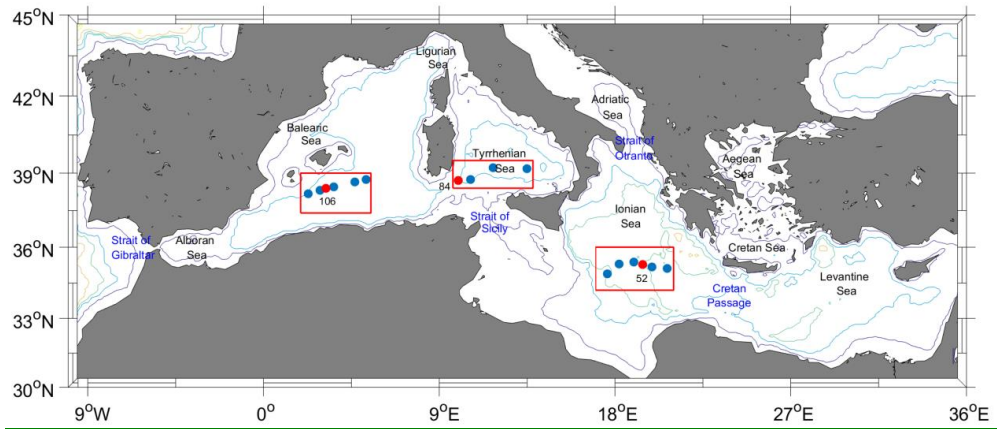

Figure 3. Sampling sites distributed in the Mediterranean Sea from the cruise MSM72 in three areas: the Southern Ionian Sea (SIS), the Tyrrhenian Sea (TS) and the Western Mediterranean Sea (WMS). Sampling sites in red solid circles indicate samples measured by the Medusa-Aqua system for HCFCs, HFCs, PFCs and CFC-12, and the ones in blue solid circles were for CFC12 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.

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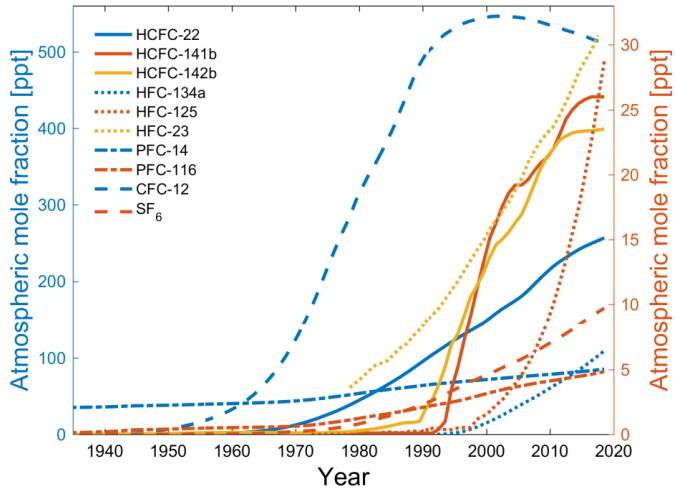

Figure 4. Atmospheric histories of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12 and SF_6 in the Northern Hemisphere. HCFC-22, HFC-134a, PFC-14, and CFC-12 share the left y-axis scale; other compounds share the right y-axis scale.

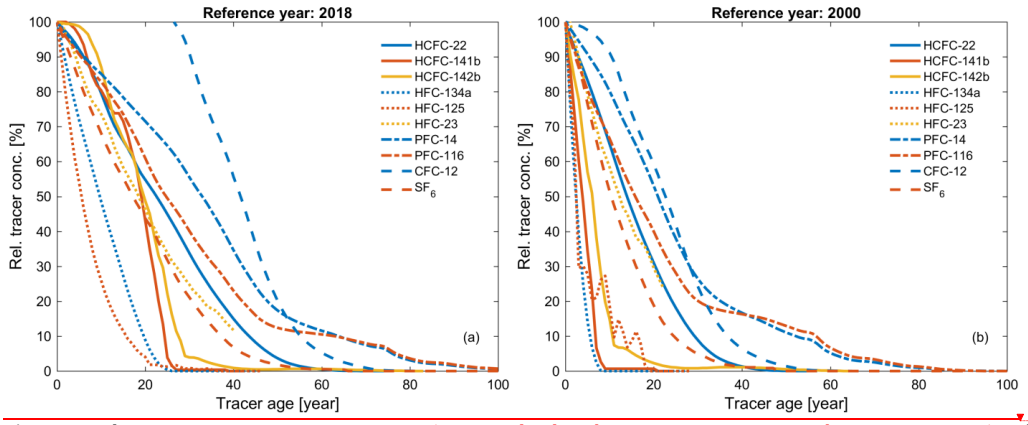

Figure 5. Relative tracer concentrations in percent (i.e. normalized to the contemporaneous atmospheric concentrations) and corresponding tracer age for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12, and SF_6 in the Northern Hemisphere. Reference year: (a) 2018 and (b) 2000.

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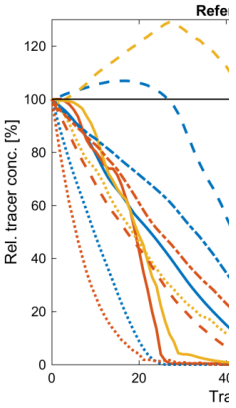

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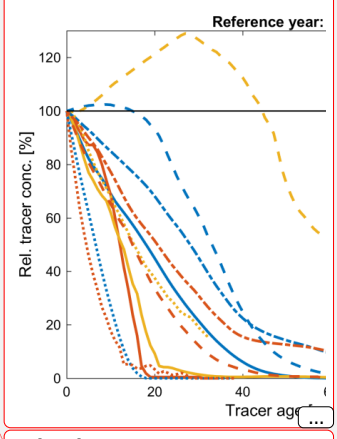

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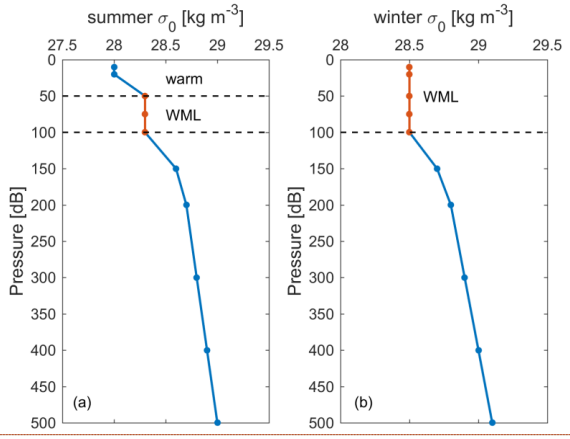


Figure 6. Example of the winter mixed layer (WML) depth (marked as red) determined in summer and winter in potential density (σ_0) profiles especially for historical seawater saturation calculation.

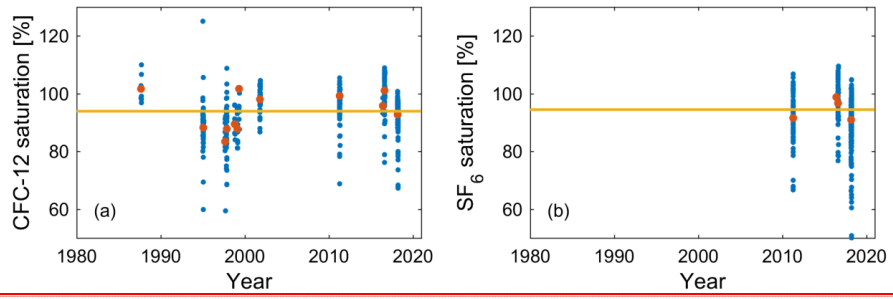
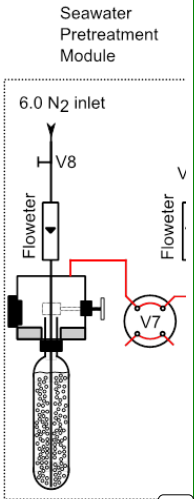


Figure 7. Historical seawater saturations in winter mixed layers (blue solid circles) for (a) CFC-12 from 12 cruises in 1987-2018 and (b) SF_6 from 4 cruises in the Mediterranean Sea. In addition to the data from Schneider et al. (2014), data from the cruises CRELEV2016 and TALPro2016 in 2016 and MSM72 in 2018 (Li and Tanhua, in preparation) were added. Red solid circles denote the means of seawater saturation for each cruise. Orange lines (94 %) are the means of averaged seawater saturation of each cruise.



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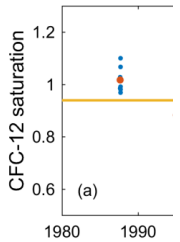

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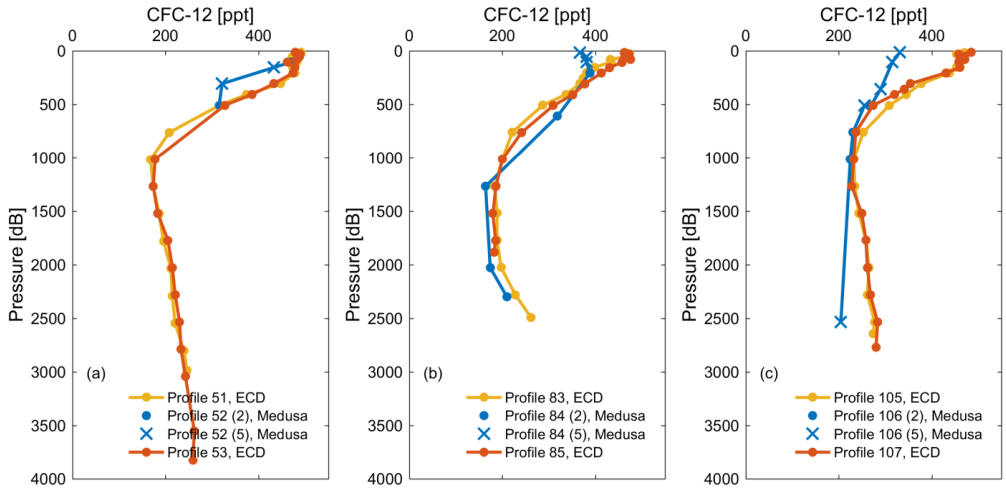

Figure 8. Comparison of CFC-12 observations from cruise MSM72 measured by the onboard PT-GC-ECD (ECD) and the Medusa-Aqua system (Medusa) in three areas: (a) the Southern Ionian Sea, (b) the Tyrrhenian Sea and (c) the Western Mediterranean Sea. We used normal quality control routines and flagged outliers as probably bad ("3" in Table S1), which are not further considered. One more step was done to compare the Medusa-Aqua system observations with the PT-GC-ECD ones: if the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD measurements, it was flagged "5" in Table S1, indicating a possible issue during the sampling or measurement process; if they are consistent, 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)".

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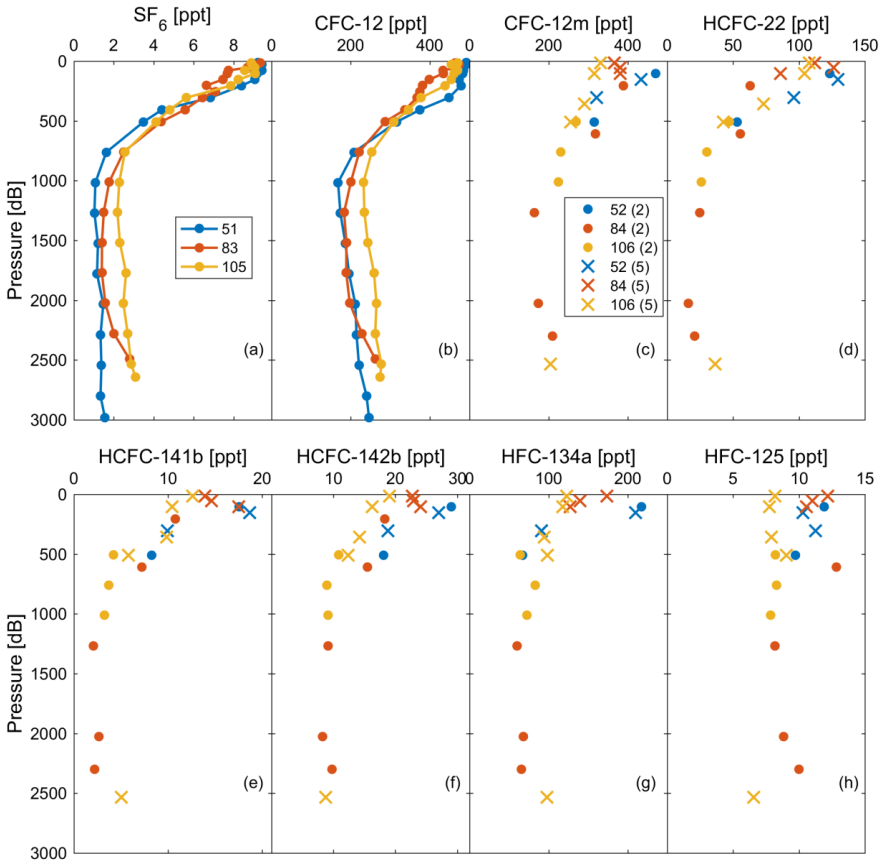

Figure 9. Observations of (a) SF_6 and (b) CFC-12 in profiles 51, 83 and 105 measured by the PT-GC-ECD and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.

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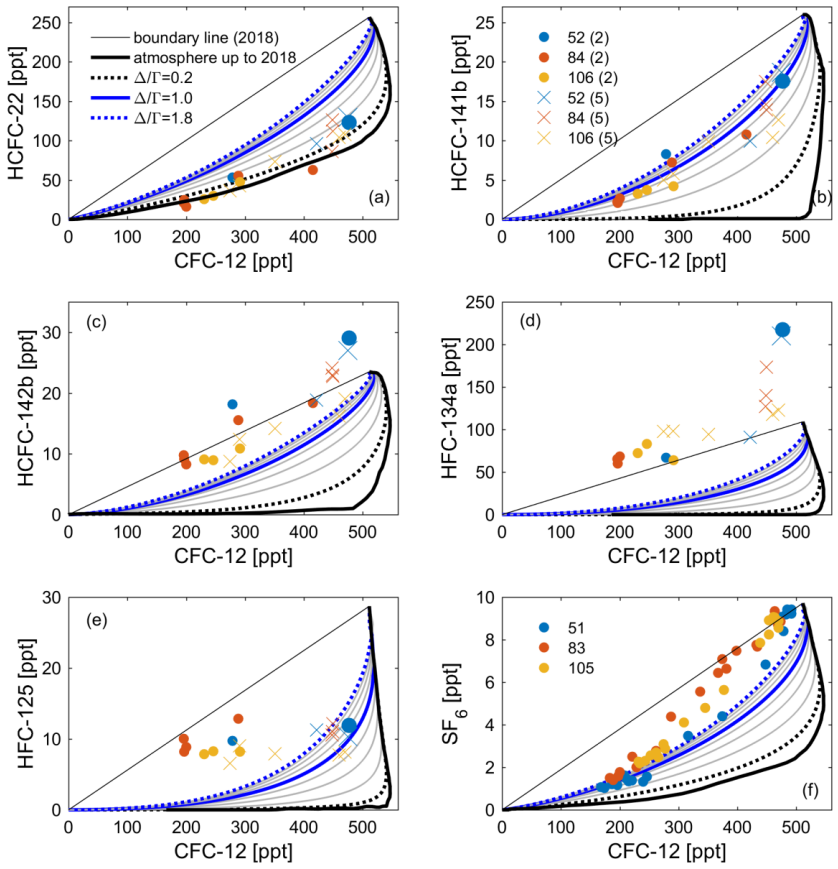

Figure 10. Observations of (a) HCFC-22, (b) HCFC-141b, (c) HCFC-142b, (d) HFC-134a and (e) HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system and (f) SF_6 in profiles 51, 83 and 105 measured by the PT-GC-ECD plotted against the (interpolated) CFC-12 based on measurements by the PT-GC-ECD. The thick black line is the atmospheric history of the tracer pair (Δ/Γ = 0.0) and the thin black line is the theoretical mixing line between contemporary concentrations and pre-industrial. The lines with Δ/Γ = 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.

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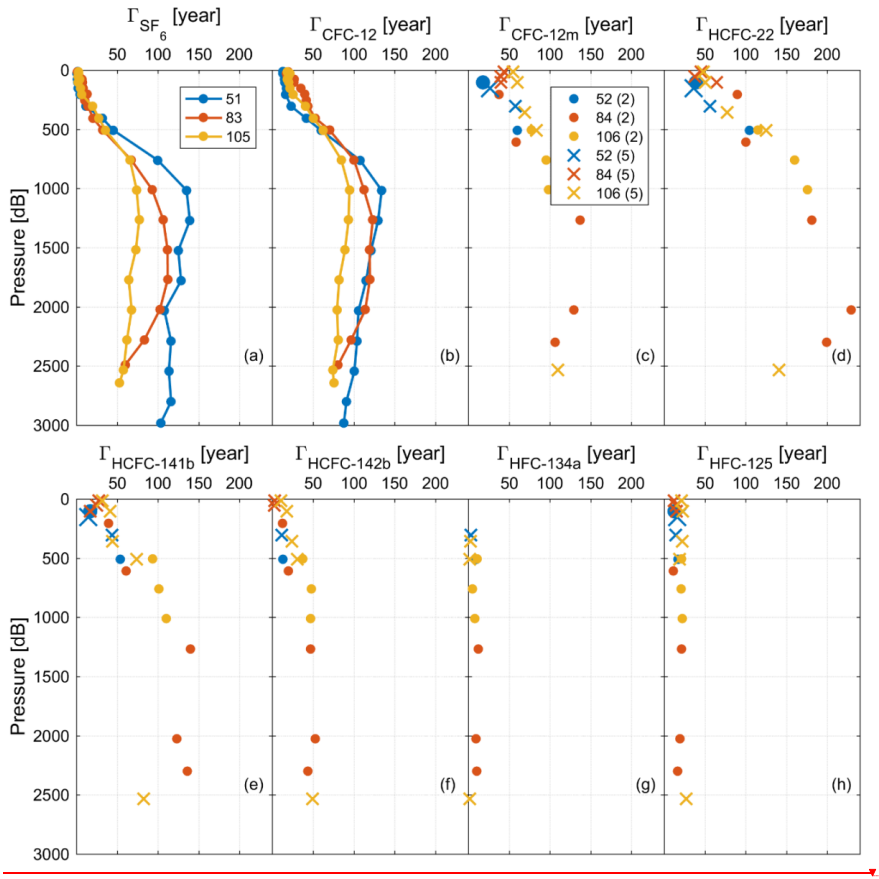

Figure 11. Mean age estimated from (a) SF_6 and (b) CFC-12 in profiles 51, 83 and 105 and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 based on Δ/Γ = 1.0 of IG-TTD. The values of the top two points of profile 52 are marked with a bigger size. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.

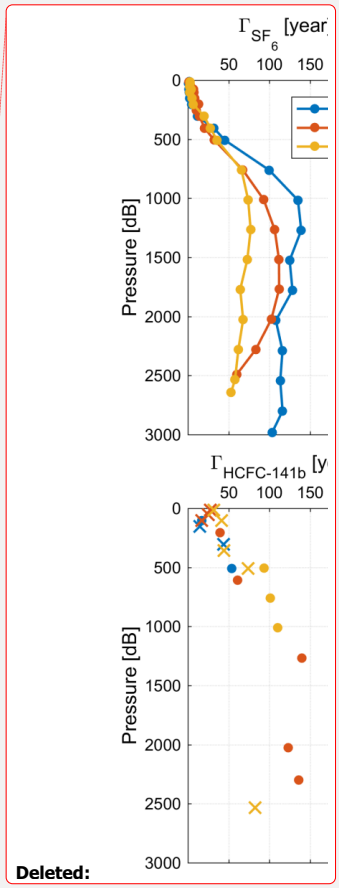

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Table 1. Total lifetimes, ocean partial lifetimes and ocean contributions for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116

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 $O(^1D)$) 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			(DeFlaun et al., 1992) (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	√ [c]	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; [c] In the oxidative zone

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Table 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_2F_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_3CCl_2F	1,1-dichloro-1-fluoroethane	SIO-05	0.20	4.01	6.1
HCFC-142b	CH_3CClF_2	1-chloro-1,1-difluoroethane	SIO-05	0.21	3.24	1.8
HFC-134a	CH_2FCF_3	1,1,1,2-tetrafluoroethane	SIO-05	0.21	7.31	9.7
HFC-125	CHF_2CF_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_3CF_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.

Table 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_5CF_3	CFC-12, SF_6, SF_5CF_3

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

Table 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 in the laboratory in Kiel with the Medusa-Aqua system).

	PT-GC-ECD				Medusa-Aqua system							
	Profile	Pressure (dbar)	SF_6	CFC-12	Profile	Pressure (dbar)	CFC-12	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-125
MSM72	83	13.4	97	91	84	14.7	72	44	54	97	163	44
	105	14.3	92	92	106	14.0	65	42	49	82	115	30
AL516					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

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 [a]	Within area	Low

[a] HFC-125 has low saturations in the Mediterranean Sea but high saturations in the Baltic Sea.

Table 7. Evaluating the possibilities of selected HCFCs, HFCs and PFCs as transient tracers in the ocean from four aspects

Compound	Atmospheric history	Solubility in seawater	Can be measured 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 "reasonable 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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Supplement of

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

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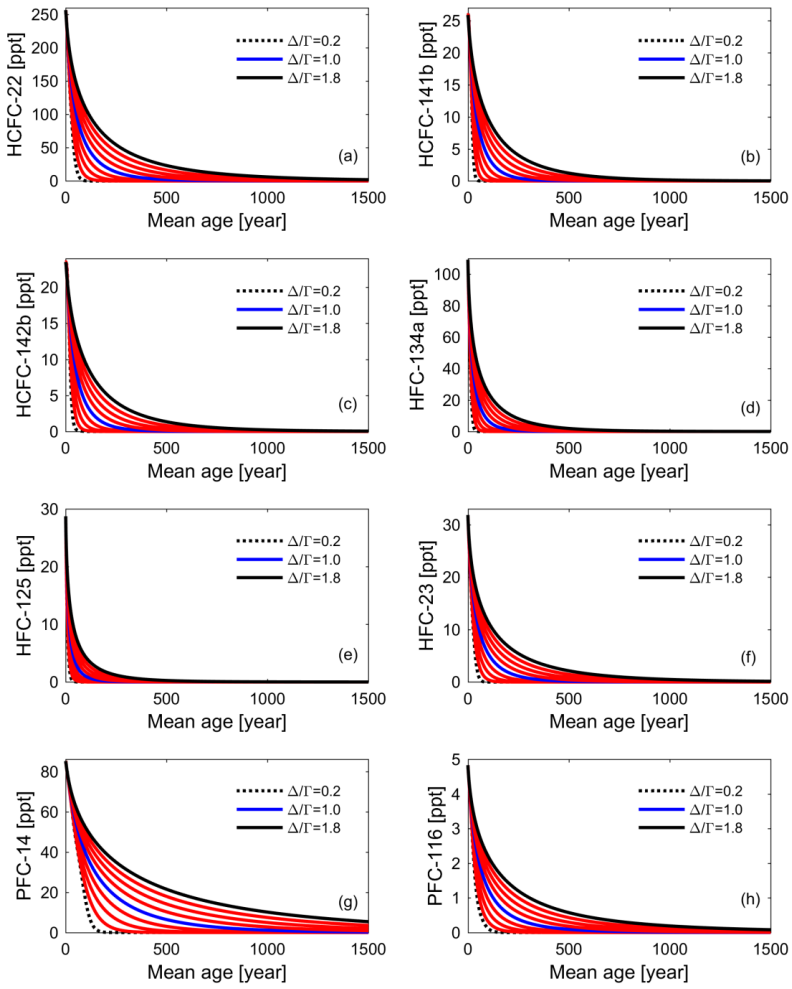
Content

Figure S1. Transient tracer concentrations (ppt, parts per trillion) of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116 vs. mean age for different Δ/Γ ratios (a range of 0.2-1.8) in the Northern Hemisphere. The unity ratio of 1.0 is shown as a blue line.

Figure S2. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116 CFC-12 and SF_6: concentrations (ppt) in different sampling year (t_s) and mean age ($\boldsymbol{\Gamma}$) in the Northern Hemisphere with $\Delta/\boldsymbol{\Gamma}$ = 1.0 based on the IG-TTD with 100 % saturation.

Figure S3. Profiles of temperature, potential density and concentrations of CFC-12 for each historical cruise in the Mediterranean Sea to determine the depth ranges of winter mixed layers.

Table S1. Bottle data of SF_6 and CFC-12 in profiles 51, 53, 83, 85, 105 and 107 measured by the PT-GC-ECD and CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system from cruise MSM72 (see the Excel file)



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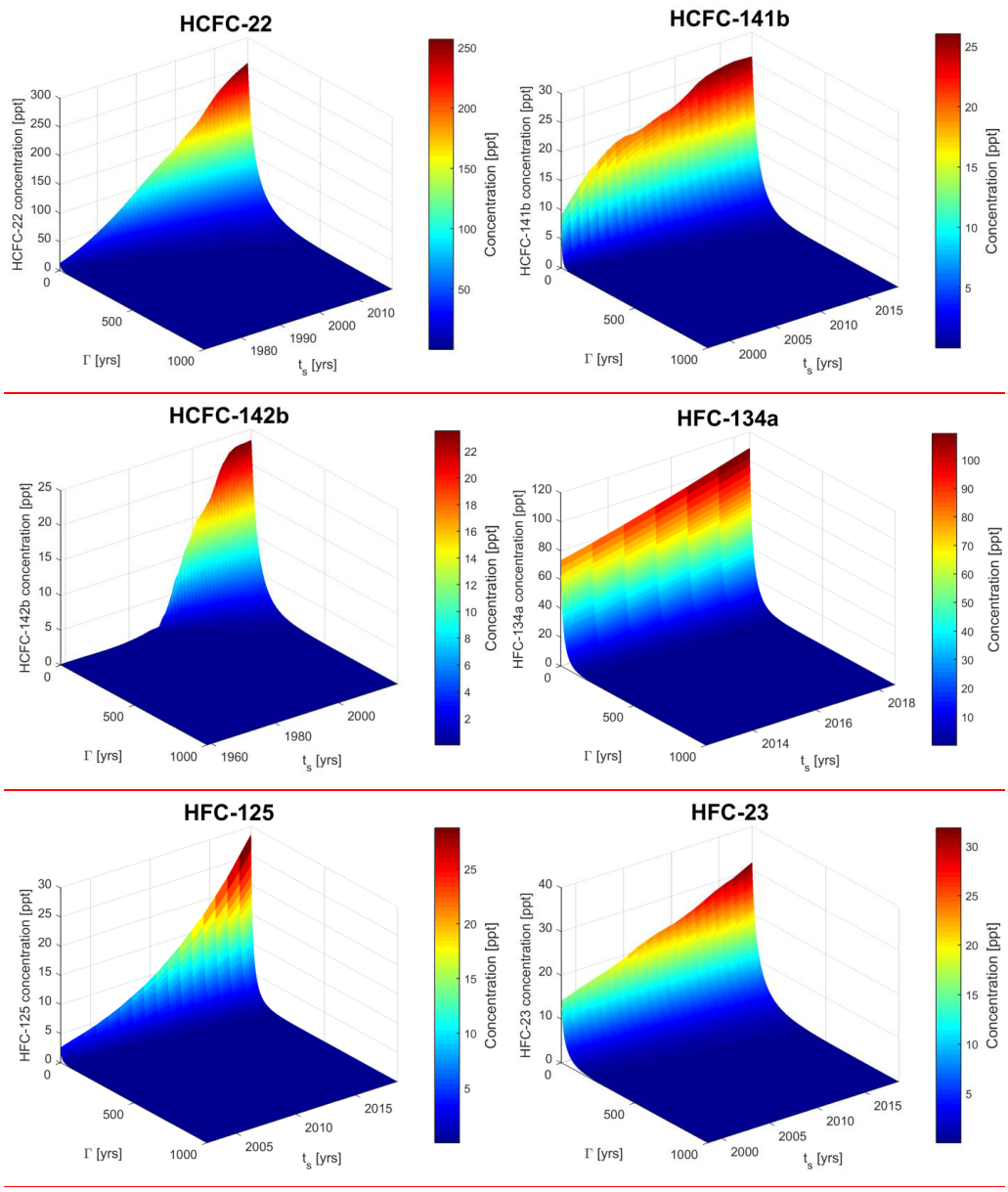
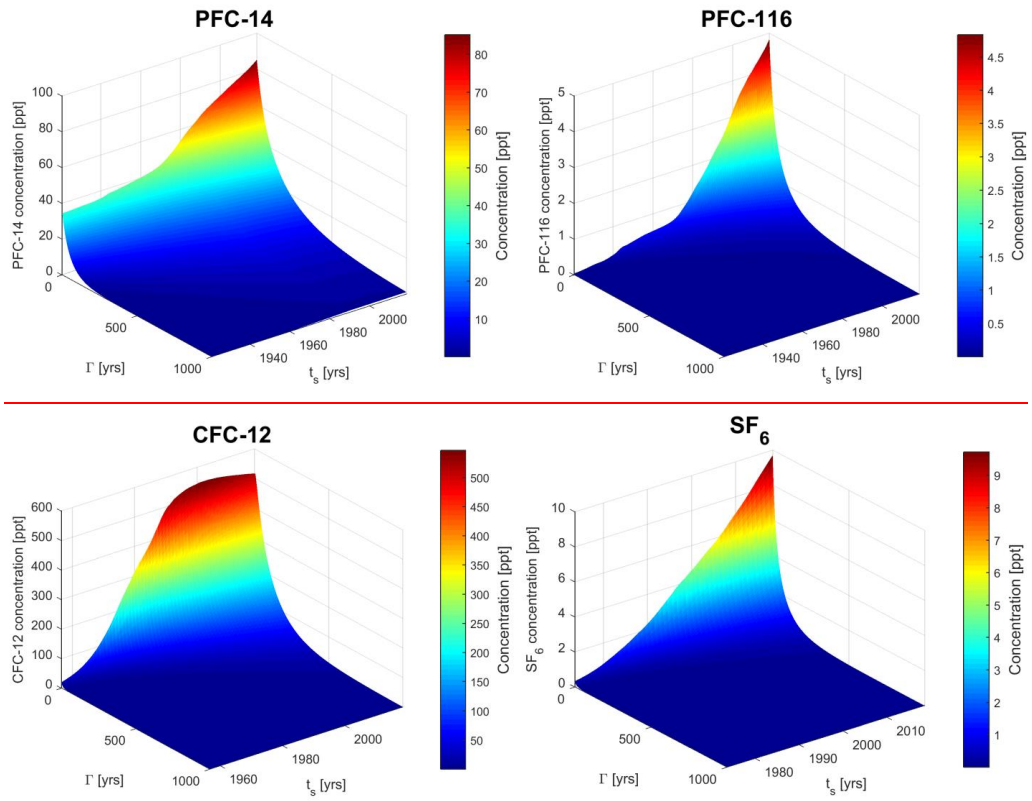

HCFC-22
HCFC-22 concentration [ppt]
Γ [yrs]
t_s [yrs]
Concentration [ppt]
HCFC-141b
HCFC-141b concentration [ppt]
HCFC-142b
HCFC-142b concentration [ppt]
HFC-134a
HFC-134a concentration [ppt]
HFC-125
HFC-125 concentration [ppt]
HFC-23
HFC-23 concentration [ppt]



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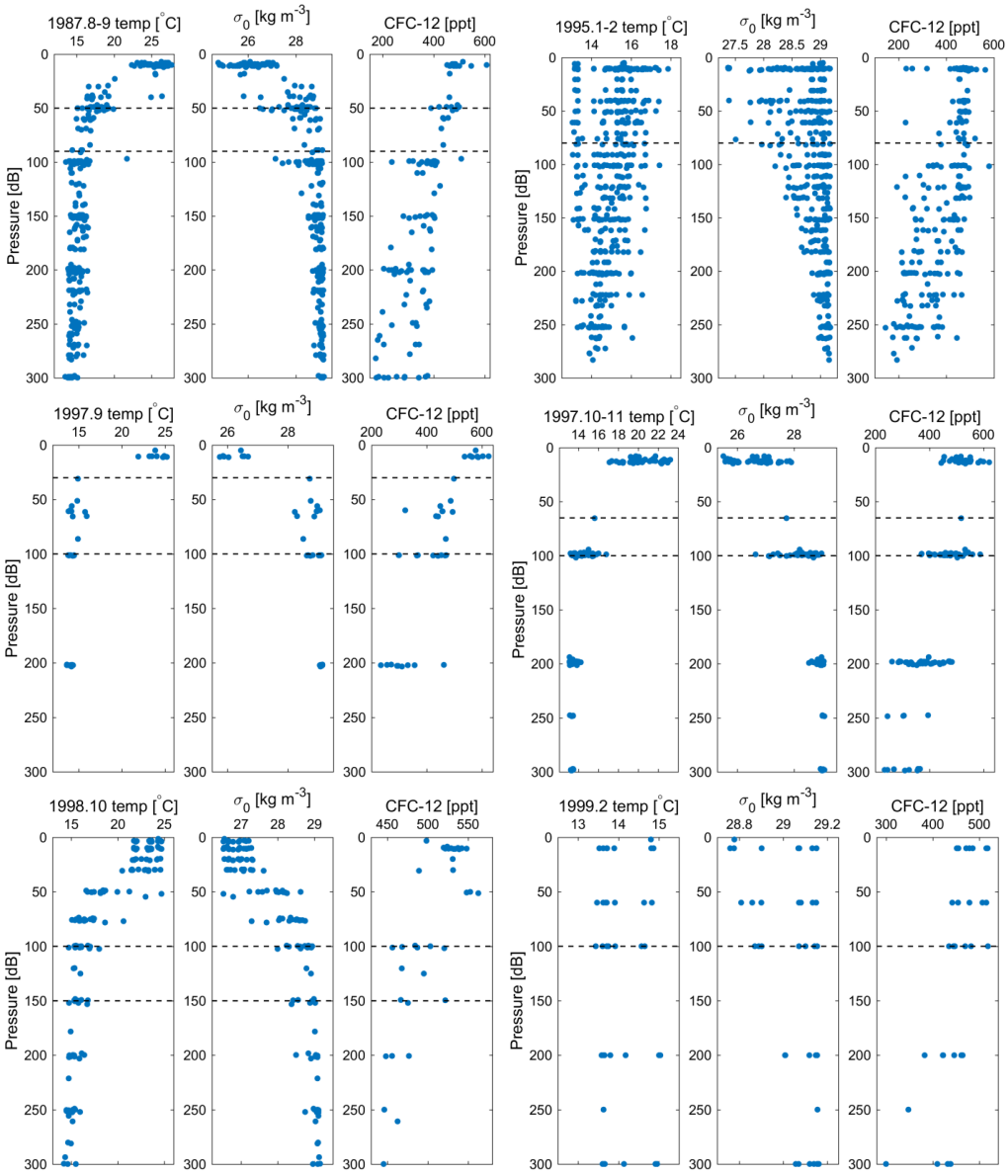
1987.8-9 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1995.1-2 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1997.9 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1997.10-11 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1998.10 temp [°C]
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CFC-12 [ppt]
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σ0 [kg m-3]
CFC-12 [ppt]
Pressure [dB]

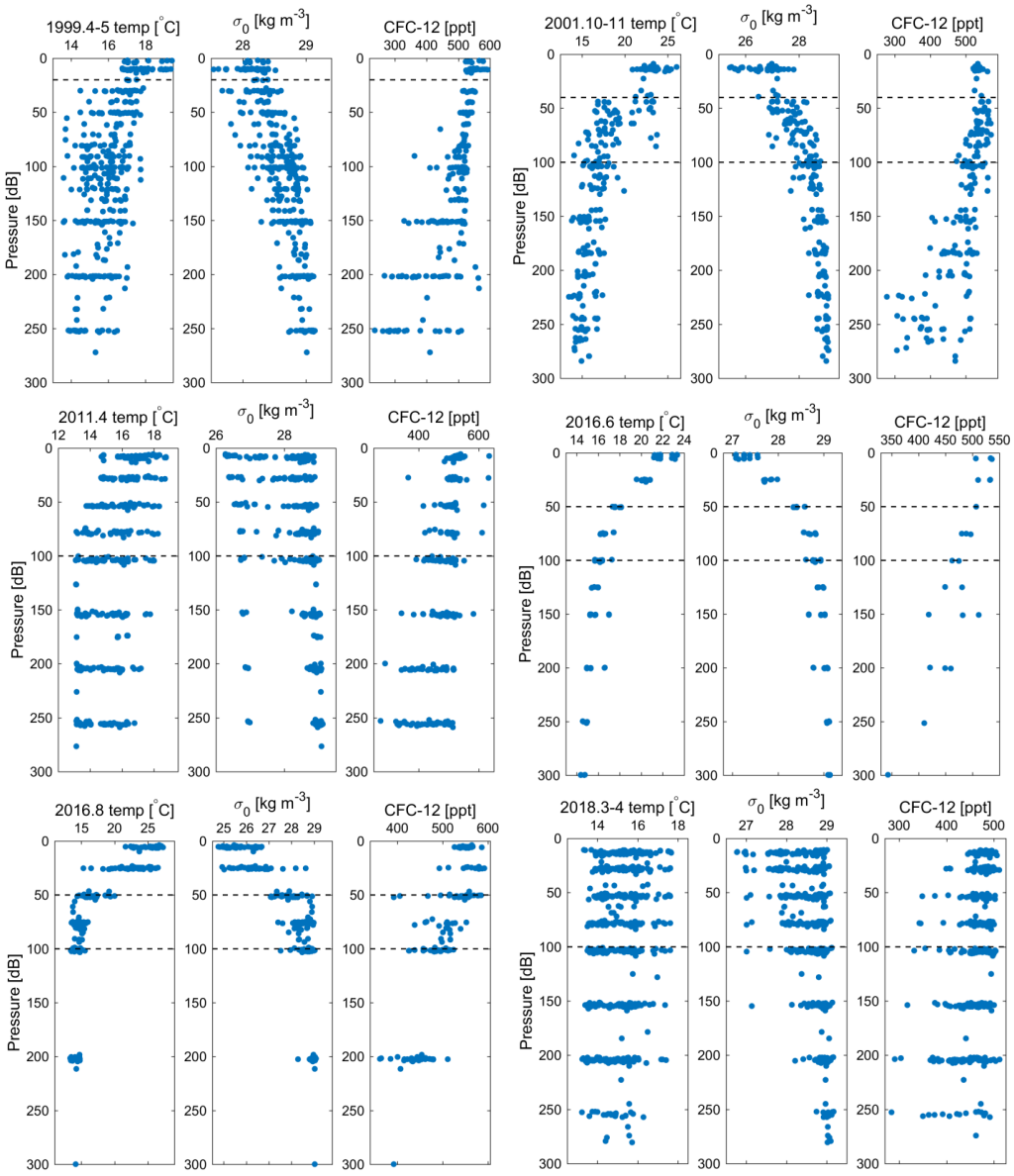

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Table S1. Bottle data of SF_6 and CFC-12 in profiles 51, 53, 83, 85, 105 and 107 measured by the PT-GC-ECD and CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system from cruise MSM72 (see the Excel file) [a]

[a] Meaning of the quality flag, this is modified from the WOCE flagging system (https://cchdo.github.io/hdo-assets/documentation/manuals/pdf/90_1/chap4.pdf, last access: 20 January 2020) only in that we added flag "5" for the purpose of this study

Quality flag number	Meaning
2	Normal data; data for sampling sites that measured CFC-12 by Medusa-Aqua system matched the one by PT-GC-ECD
3	Questionable data: may not fit the profile or some other doubts
4	Problem data definitely
5	Data for sampling sites that measured CFC-12 by Medusa-Aqua system doesn't match the one by PT-GC-ECD; data quality between 2 and 3
6	Mean of two or more measurements
9	Missing (null) data

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