

## Review of Li & Tanhua (OS-2019-101, revised)

This version of the manuscript is much improved in focus. Many of my previous concerns have been addressed. However, my major issue is with the quality of the reported measurements from the Aqua-Medusa system. As a proof of concept that this instrument can detect the proposed tracers in the water column, I think the manuscript is fine. However, I have low confidence in the quality of the data - primarily based upon the inability to accurately measure CFC-12. The decision on which data are good (quality flag = 2) seems to be based on an undefined cutoff for consistency with the CFC-12 concentrations measured using the standard PT-ECD instrumentation. The assumption follows that the accuracy issue is due to the sampling or extraction, such that good CFC-12 concentrations are a necessary and sufficient condition for the other measured Medusa concentrations to also be good. I would prefer an explanation, supported by data, for the "bad" CFC-12 data. As Tanhua is aware, it is possible to measure one compound accurately but still have issues with other compounds using a PT-ECD system. Without confidence in the accuracy of the tracer data, I find the interpretation of the data to be interesting but not convincing. In my opinion, laboratory experiments conducted using seawater equilibrated with ambient air, sampled into glass ampoules and analyzed in the same manner as the samples from the Mediterranean and Baltic Sea, would greatly improve my confidence in their water column measurements. If I return to their list of five requirements for a transient tracer, I am not convinced of #4 and cannot therefore evaluate #5.

Other specific comments – both editorial and scientific – are listed below.

p. 1, Line 29 - Ventilation is usually defined as a process, not a time (e.g. the process that transports water and climatically important trace gases from the surface mixed layer into the ocean interior).

p. 2, line 12 – add the word “respectively” for clarity

p.2, line 16+- grammar (“have been” or “might be” imposed); will continue to rise?; “have readily measured”

p. 2, line 19 – None of the US tracer groups have stopped measuring CFC-11. It is clear that the Tanhua group has stopped measuring it. I’d just leave out the discussion entirely. In addition, Lee & Bullister found evidence for the degradation of CFC-11 in permanently anoxic waters (e.g. the Black Sea), but not in the waters of the ODZs in the open ocean.

p. 22, line 27 – citation for the need for multiple tracers?

p. 3, line 8 – stable and stability are repetitive. Be more clear about what is meant by stable chemical structure. Long atmospheric lifetimes are indicative that a compound is probably stable to processes such as UV degradation of bonds even in the stratosphere.

p.3, line 20 – “with” not “to”

p 3, line 23+ - As the authors point out, a comparison of the surface saturations with CCl<sub>4</sub> only suggest that the medusa tracers are perhaps more conservative than CCl<sub>4</sub>. That does not mean they are conservative. A better comparison would be to CFC-12 which is known to be conservative.

p.4, line 26 – Clarify that Medusa was developed and utilized to measure volatile gases in the atmosphere.

p. 5, line 16 – “empirically” implies that improvements were made without any logical thought.

p. 5, line 29 – I suggest “measured at both adjacent stations located 15 nm away along the cruise track”

p. 5, line 32 – Heating decreases the solubility - this results in the gases leaving solution into the headspace over a long period of time, but also increases the fractionation between the purging gas bubbles and the sample.

p. 6, line 32 – the precisions seem reasonable (Table 1). Are they based upon only one duplicate pair of ampoules? (A separate comment on Table 1 is that the number of significant figures seems rather high for the detection limits given the precision)

p. 7, line 10 – sentence needs an “and” for the final phrase

p. 7, line 13 – Interpretation of Transient Tracer Distributions ?

p. 7, line 16 – At the older end of the time range, the detection limit and precision are also important.

p. 7, line 21 – Others publications refer to the tracer age as the partial pressure age to distinguish it from other possible ages defined by the tracers.

p. 8, line 14 – add “and SF6 concentrations”

p. 8, line 19+ - I thought Atlantic Water entered the Mediterranean Sea at the surface. It is not clear to me why it should take a long time to equilibrate with the atmosphere. The typical reasons for undersaturation are entrainment of waters from below the mixed layer or cooling of the surface layer, with n=both processes occurring at rates faster than gas exchange can re-establish equilibrium.

p. 8, line 27+ - I suggest the authors apply more rigor to the QC process. What is the definition of “inconsistent”? Greater than 3 x precision difference? As presented, it seems arbitrary. Are there correlations between the concentrations of CFC-12 and the Medusa tracers in the samples labeled as 5 that could help identify the issues?

When I plot the Aqua Medusa tracers vs the Aqua Medusa CFC-12, there is significant overlap between good (flag=2) and bad (flag=5) data for HCFC141a and HCFC142b (i.e. the concentration ratios are consistent). There is less correlation for the other medusa tracers.

p. 8, line 34 – The data in the supplemental spreadsheet (Table S6) are reported in concentration units. These values are for the partial pressures. You should make this explicit in the manuscript.

p.9, line 2 – consistent with your expectations of tracer concentrations in the deep waters.

p. 9, line 4 – This sentence needs to be re-written for clarity. Proximity to equilibrium with the atmosphere is not a factor – perhaps an indicator?

p. 9, line 12 – annual basis

p. 9, line 13 - Why are the CFC-12 saturations so high in the Baltic Sea? Why do the saturations of the other gases vary so greatly? Without some explanation, I have little confidence in the data quality. Entrainment and surface warming would affect all of the tracers equally.

P. 9-10 – If the 1-G TTD was representative of the processes controlling the distributions of the tracers in the Mediterranean Sea, all of the data plotted in the panels of Fig. 10 should fall along the same  $\Delta/\Gamma$  line. Even the  $\text{SF}_6$  - CFC-12 data fall into the region of  $\Delta/\Gamma > 1.8$ .

I agree with some of what the authors conclude about the feasibility of using these tracers in future oceanographic studies. The real issue for me is whether the ampoule sampling combined with the Aqua-Medusa system is capable of being utilized for these measurements. This is where I would focus my efforts in the future.