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

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Abstract

This study evaluates the potential usefulness of the halogenated compounds HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116 as oceanographic transient tracers to better constrain ocean ventilation processes. We do this mainly from four aspects of the characteristics of the potential tracers: input function (including atmospheric history and historical surface saturation), seawater solubility, feasibility of measurement, and stability in seawater, of which the atmospheric history and seawater solubility have been investigated in previous work. ~~The historical surface saturation of halogenated transient tracers in the Mediterranean Sea is estimated to have been nearly constant at 94 % based on historical data.~~ For the latter two aspects, we collected seawater samples and modified an established analytical technique to the Medusa-Aqua system ~~in order~~ to simultaneously measure these compounds. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 have been measured in depth-profiles in the Mediterranean Sea for the first time, and reproducibility in the Baltic Sea. We found that t~~The~~ historical surface saturation of halogenated transient tracers in the Mediterranean Sea is estimated to have been nearly constant at 94% based on historical data. Of the investigated compounds, HCFC-142b, ~~and~~ HCFC-141b, and HFC-134a are found to currently be the most promising transient tracer in the ocean ~~currently~~. The compounds that have the greatest potential as future tracers are PFC-14 and PFC-116, ~~although~~ mainly hampered by the low solubility in seawater that creates challenging analytical conditions, (i.e., low concentration~~s) that can potentially be improved by modifying the Medusa-Aqua analytical system~~. HCFC-22 is found to be likely unstable in warm seawater, which compromises the ~~leads to low confidence in terms of its~~ potential as an oceanic transient tracer, although it is possibly useful in colder water. For compounds ~~HFC-134a,~~ HFC-125 and HFC-23, we ~~ar~~were not able to fully evaluate their potential as tracers 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 might~~can~~ not need~~longer to~~ be considered because there are alternative tracers with similar input histories that are better suited as transient tracers.

1 Introduction

~~Ocean v~~Ventilation is defined as the process that ~~time elapsed since the water parcel has left the mixed layer and been~~ transport~~ed~~ perturbations such as the concentration of trace gases from the surface mixed layer into the ocean interior. Ocean ventilation and mixing processes play significant roles in climate ~~as they are important processes to propagate perturbations on the ocean surface to the interior~~. They largely control the accumulated uptake of anthropogenic carbon (C_{ant}) at mid- and high latitudes and the deep ocean's oxygen supply. One possible method to quantitatively describe these processes are based on transient tracer measurements.

1.1 Why do we look for new transient tracers?

Transient tracers include chronological transient tracers such as dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11) and sulfur hexafluoride (SF_6), and radioactive transient tracers such as Tritium-Helium (^3H-^3He), Argon-39 (^{39}Ar), and Carbon-14 (^{14}C), although ^{39}Ar is assumed to be in steady-state and cannot be regarded as a transient racer in the true meaning of the word. They have been used as oceanic transient tracers to study ~~the~~ oceanic processes, such as ventilation, mixing, and circulation processes. CFC-12 and CFC-11 have been used since the 1980s, whereas SF_6 has only been used since the late 1990s. These compounds are ~~mostly~~ stable in seawater under most circumstances; their seawater solubility functions are well-established (Warner and Weiss, 1985; Bullister et al., 2002) and their historical atmospheric concentrations over time are known (Walker et al., 2000; Bullister, 2015). However, the industrial use~~s~~ of CFC-12 and CFC-11 w~~as~~ere phased out as a result of the implementation of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer designed to curtail the degradation of the Earth's ozone layer. Therefore, the atmospheric concentrations of CFC-12 and CFC-11 have decreased since the early 2000s and the early 1990s, respectively (Bullister, 2015), which has reduced their usefulness as ~~an~~ oceanographic transient tracer~~s~~ 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. Due to its very high global warming potential, some local restrictions on the production and use of SF_6 ~~implemented~~has been imposed since 2006. However, the concentrations of SF_6 in the atmosphere ~~continue to rise~~ is still increasing, partly due to its long atmospheric lifetime. ~~Currently,~~ CFC-12, SF_6, and CFC-11 can~~have~~ readily be~~en~~ measured onboard research vessels at a reasonable rate from one seawater sample. ~~CFC-11 has been extensively used as a transient tracer but found to has a time-history similar to that of CFC-12 and be degraded in anoxic marine waters (Bullister and Lee, 1995); the simultaneous measurement of SF_6 and CFC-11 is complicated (Bullister and Wisegarver, 2008), so that the use of CFC-11 is being reduced. Similarly,~~ 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and carbon tetrachloride (CCl_4) have previously been ~~extensively~~ used as oceanic transient tracers, but have now been largely discarded since they have been found to be degraded in warm waters (Roether et al., 2001) as well as in low oxygen waters (Wallace and Krysell, 1989; Huhn et al., 2001). 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). With the constraints of the weak signal of ^3H and the decreasing atmospheric mole fraction of CFC-12, presently only SF_6 is a relatively reliable transient tracer in the seawater timescale less than 100 years (Fig. 1). Since a combination of multiple transient tracers is needed to constrain ocean ventilation (Stöven and Tanhua, 2014; Holzer et

al., 2018), it is useful~~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) well-quantified sources and sinks, 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~~se~~ 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. The atmospheric abundances of most HCFCs, ~~and~~ HFCs, and PFCs are increasing~~, as are the concentrations of PFCs~~. Here we ~~describe~~ call 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", from the analytical instrument used to measure them. ~~With the constraints of the weak signal of ^{3}H and the decreasing atmospheric mole fraction of CFC-12, presently only SF$_6$ is a relatively reliable transient tracer in the seawater timescale less than 100 years (Fig. 1).~~ Fortunately, the different atmospheric histories of the potential alternative transient tracers (Li et al., 2019) allow us to explore one or several compounds to replace or supplement the established transient tracers (Fig. 1).

1.3 Stability of alternative tracers in seawater

Chemical reactions (including hydrolysis), adsorption to particles, and biological degradation process~~es~~ should be considered with regard to the stability of compounds in seawater. There are few studies of the stability of the Medusa tracers, and close to none o~~n~~f the stability in seawater. One indication of the stability is the ~~stable~~ chemical structure and the atmospheric lifetime~~, which is expressed as the following aspects~~. For instance, PFCs have very long atmospheric lifetimes, i.e., > 50 000 and > 10 000 years for PFC-14 and PFC-116, respectively~~.~~, and PFC-14 (CF$_4$) is stable at temperatures of at least 1200°C and the rate of hydrolysis of CF$_4$ is immeasurably small (Ravishankara et al., 1993; Cicerone, 1979). In addition, there are no indications of biological processes that can break C-F bonds, indicating that PFCs are likely to be very stable in the environment.

The contribution of the partial atmospheric lifetime with respect to oceanic uptake of selected HCFCs and HFCs to the total lifetimes is another indirect indication of the stability in seawater. Such partial atmospheric lifetimes depend on the solubility in seawater and other losses relative to their atmospheric concentration, and are always larger than their total lifetimes. Considering the low fraction of these mainly non-polar compounds in the ocean, a small loss in the ocean is insignificant for the overall budget of the compound, but can still be indicative of ~~significance for a~~the potential as a transient tracer. As ~~indicated~~ suggested from previous studies (Yvon-Lewis and Butler, 2002; Carpenter et al., 2014) using this method, HCFCs and HFCs seem to be stable in seawater, although with large uncertainties ~~associated to these estimates~~ (Sect. S1 and Table S1). Note that the partial atmospheric lifetimes with respect to oceanic uptake in Table S1 were calculated only considering the chemical degradation process.

Another route is to compare surface saturations of a tracer with unknown stability to those~~at~~ of a compound that is known to be ~~un~~stable in seawater, e.g., CFC-12. The ~~CCl$_4$ has a short lifetime in warm seawater.~~ average s~~S~~urface saturation of HCFCs ~~is~~ tends to be higher than ~~not as under-saturated as~~ those of CFC-12 ~~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 1992-2004 (ftp://ftp.cmdl.noaa.gov/hats/ocean/, last access: 20 January 2020) and the Gulf of Mexico and East Coast Carbon Cruise (GOMECC) in 2007 (https://seabass.gsfc.nasa.gov/cruise/gomecc-1, last access: 10 June 2020) (Table S2). This may suggests that HCFCs are stable enough to be more stable than CCl₄ in surface seawater and possibly suited as tracers in the ocean.

Based on these discussions, PFCs are stable, while HCFCs and HFCs are potentiallyseem to be relatively stable in the ocean when only considering the chemical degradation process and surface saturation in seawater (only for HCFCs). However, the influences of oxygen dependence and biological degradation processes in seawater have not been investigated (Yvon-Lewis and Butler, 2002). For a compilation of published information on biodegradation in freshwater and soil, see Sect. S2 and Table S32. In summary, not enough information is known on the stability of the selected HCFCs and HFCs in the ocean.

1.4 Goals of this study

This study extends the work by Li et al. (2019), with a focus on evaluating if rapid, relatively inexpensive, and accurate measurements are possible as well as (point 4) and if these compounds are conservative in the oceanic environment (point 5). We also estimate the historical surface saturation to supplement the input function and discuss differences in tracer input functions and their ability to provide additional information on ventilation. A suite of observations of transient tracers with sufficiently different input functions would support the empiric determination of Transit Time Distributions (TTDs), as reported in Stöven and Tanhua (2014). As the first step towards this, these Medusa tracers have been measured, sometimes for the first time, and the results were interpreted to identify their possible use as transient tracers in the ocean. The Mediterranean Sea was chosen for this study because of its rapid ventilation, which causes transient tracers to penetrate most of the water column. In addition, we report from sampling at a shallow station in the southSouth-western Baltic Sea.

2 Measurement system

2.1 Progress in analytical technology Measurement 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) ideally 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 measured by an Electron Capture Detector (ECD) that is normally used for CFC-12 and SF_6 (Lobert et al., 1995; Sousa and Bialkowski, 2001; 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, allowing identification and quantification simultaneously. HCFCs and HFC-134a measurements by GC-MS in seawater samples have also been reported in previous studies (Lobert et al., 1996; Ooki and Yokouchi, 2011).

2.2 The Medusa-Aqua system

The Medusa-GC-MS system (shortened as the Medusa system) for the precise and simultaneous analysis of a wide range of volatile trace gases in the atmosphere has been developed at the Scripps Institution of Oceanography (Miller et al., 2008). This system includes two traps kept at accurately controlled temperatures to trap the volatile gases. The

5 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 Advanced Global Atmospheric Gases Experiment (AGAGE) remote field stations (Prinn et al., 2018) and is unique in that it provides high accuracy measurements of more than 40

10 compounds including halocarbons, hydrocarbons and sulfur compounds involved in ozone depletion and/or climate forcing from the same sample. The measurement precisions of most halogenated compounds are less than 0.5% in 2 L ambient air. The Medusa-Aqua system, ~~as~~ developed based on the Medusa system, ~~can~~ is able to measure the majority of the 40 halogenated compounds in seawater samples.

~~2.2 Difference between Medusa-Aqua and Medusa system~~

15 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~~ purges gaseous tracers from the water samples before injecting them into the Medusa system, replacing the air sampling device of the original Medusa system. ~~The technology is based on a purge and trap~~

20 ~~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 the 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

25 standard loop for standard gases determination. 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 Baltic Sea in September 2018. Over the past years, we have

30 collected samples on a few cruises and ~~empirically~~ improved our method (Sect. S3, Figs. S1-S7, and Tables S~~4~~3-S~~6~~5).

3.1 Sample collection

Seawater samples were collected throughout the water column in three areas of the Mediterranean Sea (Fig. 3): Southern Ionian Sea (SIS), Tyrrhenian Sea (TS), and Western Mediterranean Sea (WMS) on the cruise MSM72 by the research vessel *Maria S. Merian* from March 2nd to April 3rd, 2018 along the GO-SHIP line MED-01 (Hainbucher et

al., 2020). ~~and o~~One station (10.1 °E, 54.5 °N) in the Baltic Sea was sampled on the cruise AL516 by the research vessel *Alkor* from September 12th to 22nd, 2018 (Booge, 2018). These seawater samples were collected in glass ampoules (~1.3 L) connected to the Niskin bottles via a stainless steel mounting system (Vollmer and Weiss, 2002). 5 minutes is needed 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. The ampoules were flame-sealed immediately after sampling under a flow of high purity N_2 (Air Liquide, grade 6.0, Germany) and then sent back to the laboratory in Kiel for measurement. As seen in Fig. 3, no onboard CFC-12 and SF_6 measurements (on a PT-GC-ECD) were conducted on the stations we sampled for the Medusa-Aqua system in the Mediterranean Sea, although they were measured at both adjacent~~for the nearby~~ stations~~,~~ located 15 nm ~~(nautical miles)~~ away along the cruise track~~from either direction~~.

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 support the transfer of the gases into the headspace and to enhance the purging efficiency ~~by driving the gases into the headspace~~. The stem of the ampoule is inserted vertically into the cracking chamber and is held by a ~~screw~~ nut secured by a Teflon ferrule. Then the cracking chamber is flushed with N_2 (grade 6.0) for 10 minutes to flush out ambient air completely. A blank test for the cracking chamber is made by simulating an extraction without breaking the glass ampoule. For analysis, the tip of the ampoule's stem is shattered 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 dissolved gases out of the seawater, and more importantly from the head~~-~~space.

The extraction process is started by purging the gases in the ampoule with N_2 (grade 6.0) for 20 minutes at a flow rate of 100 mL min^{-1}. Water vapor is removed from the sample by passing the gases through two Nafion dryers (N1 and N2) of 1.8 m length and one (N3) of 0.6 m length. 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 the carrier gas and subsequently detected by the MS. The mass of seawater in the ampoules was calculated as the difference between the full weight of the ampoule before measurement and the empty ampoule (including glass splinters) after rinsing with distilled water and drying in an oven.

3.3 Standard and calibration

The standard gas ~~used in the laboratory in Kiel~~ is a tertiary standard calibrated by the Scripps Institution of Oceanography (SIO) on the AGAGE relative scale "SIO-R1". For details about the propagation of the standard see Miller et al. (2008). Gravimetric calibration scales and calibrated errors of compounds in the tertiary standard are reported in Table 1. Measurements in seawater are reported on the latest SIO absolute calibration scales for HFC-125 (SIO-14), HFC-23 and PFC-14 (SIO-07)~~,~~ and other compounds (SIO-05). The tertiary calibration scale is directly used as a working standard to determine weekly calibration curves and daily drift corrections. These calibration measurements are made by multiple injections of the gas in a 10.0 mL gravimetrically calibrated sample loop. Each

injection lasts 40 seconds at a flow rate of 50-60 mL min^{-1}. The detector response~~s~~ for compounds in Table 1 are linear in the range of our measurements.

3.4 Purge efficiency, detection limit, and precision

Each sample was measured 3-6 times until none of the compounds in Table 1 could be detected in the seawater sample so that the purge efficiency for all compounds is 100%. The averaged stripping efficiencies for the first purge of seawater samples from cruise MSM72 are 92.5 ± 5.4% for CFC-12, 76.6 ± 7.9% for HCFC-22, 87.5 ± 8.3% for HCFC-141b, 83.2 ± 10.6% for HCFC-142b, 83.1 ± 7.5% for HFC-134a, and 88.9 ± 7.5% for HFC-125. The~~ir~~ detection limits ~~for measurements of all compounds by the Medusa-Aqua system~~ are ~~also shown in Table 1~~ 29.8, 13.8, 4.0, 3.2, 7.3, and 1.2 fmol kg^{-1}, respectively (Table 1), based on the signals corresponding to the blank values plus ten standard deviations.

The precision of the measurement is dependent on the size of the ampoules and the amount of tracer in the sample; the sample with a higher amount of tracer has better precisions than those with a lower amount. The precision (or reproducibility) for seawater sample measurements were determined by the relative standard deviations (RSD~~1σ~~) of the concentrations for ~~two pairs of~~ duplicate samples from the Baltic Sea (Table 1). They are 0.4%, 3.1%, 6.1%, 1.8%, 9.7%, and 2.0% for CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125, respectively. ~~The detection limits for measurements of all compounds by the Medusa-Aqua system are also shown in Table 1 based on the signals corresponding to the blank values plus ten standard deviations.~~

To quantify the reproducibility of the analytical set-up, we took seawater from the tropical Atlantic Ocean, and let it equilibrate with the atmosphere in the laboratory. The water was then sampled from Niskin bottles in the same way as during a cruise and flame sealed in ampoules, although for this experiment we used 300 mL samples. The reproducibility for CFC-12, HCFC-22, HCFC-141b, and HCFC-142b measurements from four duplicate samples are 3.7%, 2.0%, 3.5%, and 3.4%, respectively (Table 1).

For the target compounds measured by the Medusa-Aqua system from the Mediterranean Sea and Baltic Sea, ~~T~~the concentration of SF$_6$, PFC-14, and PFC-116 in most seawater samples w~~ere~~as lower than the detection limit, and HFC-23 had 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 (in pmol kg^{-1}) measured by the Medusa-Aqua system in seawater from both cruises are shown in Table S~~6~~7 with quality flags marked.

3.5 Quality control

In order to evaluate the precision and accuracy of seawater measurements by the Medusa-Aqua system, ~~T~~the observations of CFC-12 measured by the Medusa-Aqua system are compared with those in adjacent stations measured onboard by the PT-GC-ECD system in the Mediterranean Sea (Fig. 4~~8~~). We performed a two-step quality control procedure on the medusa data where, in the first step outliers were flagged as bad (flag 3 in Table S7), and in a second step we flagged data as likely bad (flag 5) where the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD, and as good (flag 2) when they are consistent (Fig. 4~~8~~). The "inconsistent" means that the misfits of CFC-12 concentrations measured by the two instruments are more than three times the standard deviations (3σ), indicating a possible issue during the sampling process. The~~is~~ two-step quality control process led to 9 samples in the

Mediterranean that meets all these criteria and have similar concentration as the PT-GC-ECD observations. For such samples, the averaged difference of CFC-12 concentrations measured by the two different instruments is 5.9 ± 4.6% at roughly the same depth by ignoring their distance differences.

3.65 Comparison of instruments measuring CFC-12

5   As mentioned in the previous section~~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. The latter~~is~~ 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, information on the performance of a similar purge and trap system set-up (Cracker-PT-GC-ECD) to

10   measure flame-sealed ampoules for CFC-12 and SF_6 is added to a comparison of the three instrument set-ups (Table 2). Compared to other systems, the Medusa-Aqua system has lower purge efficiency due to its larger sampling volume if only considering a single purge (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 Interpretation of t~~T~~ransient tracer distributions~~interpreting methods~~

4.1 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 historical surface saturations. For

20   ideal applicability, atmospheric histories of tracers should increase monotonically in the atmosphere. For older waters, and low tracer concentrations, the precision and detection limits will be limiting factors (Tanhua et al., 2008; Stöven et al., 2015). Figure 45 shows the atmospheric histories of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12, and SF_6 in the Northern Hemisphere (Bullister, 2015; Li et al., 2019).

4.2 Tracer age and the Transit Time Distribution (TTD)

25   Tracer age (or partial pressure age) is defined as the age of a water parcel based on a purely advective flow in the ocean. Figure 65 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.

30   Similar trends are found for the following tracer couples: HCFC-141b and HCFC-142b, HFC-134a and HFC-125, SF_6 and HCFC-22/HFC-23, PFC-14 and PFC-116. Assuming that all these compounds fulfill the other criteria as transient tracers, it is enough to choose one of each couple for transient tracer work (i.e., adding~~tion~~ to the other compound in the pair adds little new information).

If the relative tracer concentrations are higher than 100% in Fig. 6̶5̶, there has been a decrease in atmospheric concentrations, e.g.̲, for CFC-12. 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). Thus, 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. 6̶5̶). This indicates that the ability of CFC-12 as 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. 6̶5̶).

We used the well-established ocean ventilation model, the Transit Time Distribution (TTD) model that is based on the Green's function (Hall and Plumb, 1994) describing the propagation of tracer boundary conditions into the interior. This model is based on a one-dimensional flow model with time-invariant advective velocity and diffusivity gradient and is thus known as the one-dimensional Inverse Gaussian Transit Time Distribution (IG-TTD). The key variables are the mean age Γ and the width of the distribution Δ (Waugh et al., 2003). The Δ/Γ ratio of the TTD with a range of 0.2–1.8 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. For more details on the TTD model and mean age see Sect. S4 and Figs. S9–S10.

5 Results

5.1 Historical surface saturation in the Mediterranean Sea

The historical surface saturation of transient tracers is important to constrain the input function (together with the atmospheric history). To determine this for the Mediterranean Sea, we calculated seawater saturation in the winter mixed layer (WML) from historical cruise data. The depths of the WMLs in summer and winter are shown in Fig. 7̶6̶ for two examples of density profiles. It is the saturation during winter that is relevant for deep and intermediate water formation, and thus for the input functions, not the one in the summer mixed -̲layer. Therefore, only the WML was considered in the calculation of historical surface saturation for all cruises. The depth ranges of WMLs (Fig. S8) and the saturation for CFC-12 and SF$_6$ (Fig. 8̶7̶) were determined by profiles of temperature, potential density, and CFC-12 and SF$_6$ concentration for every historical cruise in the Mediterranean Sea from 1987 to 2018 (Schneider et al., 2014; Li and Tanhua, 2020). Since no clear trend over time could be described, we averaged the mean seawater saturation from every single cruise,̶ and determined the historical surface saturation to be 94 ± 6% and 94 ± 4% for CFC-12 and SF$_6$, respectively. For CFC-12, this is different from the situation in the North Atlantic Ocean (Tanhua et al., 2008), and could be̶i̶s̶ ̶p̶r̶o̶b̶a̶b̶l̶y̶ an indication of the different oceanographic setting̲s where the inflowing Atlantic Water (to the Mediterranean Sea) takes a long time to equilibrate with the atmosphere. The constant undersaturation through time is then mainly a function of rapid cooling during winter and entrainment of water from below, rather than a rapid change of the atmospheric concentration that can drive undersaturation that varies over time. For the following calculations of ages and evaluation of stability, the historical surface saturations are assumed to be a constant 94% for

all tracers in this study as no data exists to determine the historical surface saturation of selected HCFCs and HFCs in the Mediterranean Sea.

5.2 Observations of the Medusa tracers in the Mediterranean Sea~~seawater~~

~~The observations of CFC-12 measured by the Medusa-Aqua system are compared with those in adjacent stations measured onboard by the PT-GC-ECD system (Fig. 8). We performed a two-step quality control procedure on the medusa data where, in the first step outliers were flagged, and in a second step we flagged data where the Medusa-CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD (Fig. 8). This process led to 9 samples in the Mediterranean that meets all these criteria and have similar concentration as the PT-GC-ECD observations. For such samples, the averaged difference of CFC-12 concentrations measured by the two different instruments is 5.9 ± 4.6 %.~~ Based on the reasonable correlation between CFC-12 observations from the Medusa-Aqua system and the onboard PT-GC-ECD system (Sect. 3.5), we can move on and interpret the profiles of the Medusa tracers. Observations of CFC-12 and SF_6 from profiles 51, 83, and 105 measured by the PT-GC-ECD and those of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 from the nearby profiles 52, 84, and 106 measured by the Medusa-Aqua system are shown in Fig. 9. ~~Concentration ranges of Medusa tracers are 16.1-129.4 ppt for HCFC-22, 2.1-18.7 ppt for HCFC-141b, 5.0-29.0 ppt for HCFC-142b, 41.0-217.4 ppt for HFC-134a and 4.9-12.8 ppt for HFC-125.~~ The concentrations of Medusa tracers decreased from the surface to the intermediate layer and then increased in the deep layer, consistent with our expectations of tracer concentrations, and indicating the well-ventilated Mediterranean deep waters as interpreted by CFC-12 and SF_6 (Li and Tanhua, 2020).

5.3 Surface saturation of Medusa tracers in seawater

The s~~S~~urface saturation of~~in~~ seawater can~~ould~~ be an ~~factor~~indicator of~~that describes~~ the stability of a compound in surface seawater or the correctness of~~confidence in~~ the seawater solubility function. However, saturation is influenced by multiple parameters, such as partial pressures in the atmosphere and surface seawater, the air-sea exchange velocity, the solubility and diffusivity of the gas, bubble injection and/or vertical mixing, and the temperature dependence of these parameters (Lobert et al., 1995; Butler et al., 2016). In the Mediterranean Sea, we ~~had to~~ flagged all surface samples as suspect due to discrepancies between CFC-12 concentrations as measured by the Medusa-Aqua system and PT-GC-ECD. We, therefore, turn to the samples collected in the Baltic Sea where the seawater saturation of CFC-12 and Medusa tracers in one surface sample and two bottom samples are shown in Table 3. Note that the bottom waters (at about 23.5 meters depth) can be considered as recently ventilated as this water is ventilated on an annual bas~~i~~se. The averaged saturation for~~f~~ the Baltic seawater samples are: CFC-12 (122 ± 8%), HCFC-22 (77 ± 8%), HCFC-141b (74 ± 12%), HCFC-142b (114 ± 2%), HFC-134a (125 ± 23%), and HFC-125 ~~in seawater are 122 ± 8%, 77 ± 8%, 74 ± 12%, 114 ± 2%, 125 ± 23% and~~ (252 ± 35%~~), respectively~~.

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 for the Mediterranean samples 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 for the Mediterranean and Baltic samples (Fig. 10). The c~~C~~oncentration ~~values~~ of the Medusa tracers from the recent (usually shallow) layers are located in the upper right corner with older (usually deep) samples near the lower left in Fig. 10. In the figure, we added the atmospheric history of the Medusa tracers vs. CFC-12, ~~as well as~~ the theoretical mixing line between contemporary and pre-industrial concentrations (boundary line to 2018), as well as the theoretical mixing lines assuming an IG-TTD with $\Delta/\Gamma = 0.2–1.8$. ~~; a~~All samples will have to fall between the~~se~~ first two lines (i.e.~~,~~ the stability area) if the tracer is conservative in seawater by referring to previous methods (Huhn et al., 2001; Roether et al., 2001). Compounds where the samples fall below the "stability area" are not stable (assuming that CFC-12 is stable), and for samples above it, there are issues with too high values (see below). For instance, HCFC-22 is found in the lower part of the stability area (samples would fall on this lowest line if there were no mixing but only advection in the ocean); HCFC-141b, HFC-125, and SF_6 are well in the allowed range~~s~~; whereas HCFC-142b and HFC-134a are around or above the upper boundary.

The increased ventilation of the (western) Mediterranean Sea during the last decade tends to result in different effects on CFC-12, which is decreasing in the atmosphere, and the Medusa tracers with increasing atmospheric concentrations. This argument suggests that we could ~~expect~~ see slightly higher than expected concentrations (similar to SF_6) for the Medusa tracers. This is exactly what we see f~~r~~o~~m~~r HCFC-142b ~~and HFC-125~~ (Fig. 10). ~~In addition, w~~We ~~could~~ fou~~i~~nd that the Δ/Γ ratio determined by the CFC-12/HCFC-141b and CFC-12/HCFC-142b tracer pairs are similar ~~located closer~~ to that ~~by~~ of the CFC-12/SF_6 pair, indicating~~,~~ ~~pointing out the more~~ promising tracer pairs. The~~However, too~~ high~~er than expected~~ concentration~~s~~ of~~r~~ HFC-134a may be caused by~~associate with a few possible reasons:~~ 1) contamination during sampling or measurement in the laboratory; 2) problems with solubility functions; 3) some other issues within the measurements in the laboratory causing our ~~observations~~ measurements to be too high.

Although the assumption of time-invariant ventilation is not valid for the Mediterranean Sea, the TTD model can produce indicative results to understand the mean ages estimated from Medusa tracers (assuming $\Delta/\Gamma = 1.0$) and their comparison to those estimated from CFC-12 and SF_6, see Sects. S4-S5 and Figs. S9-S11.

6 Discussions

The results from this study ~~on stability~~ based on interior ocean observations can be ~~evaluat~~used to evaluate~~analyze~~ the stability and further determine the potential of the Medusa tracers as oceanic transient tracers, and are as such dependent on reasonably accurate ~~the confidence that the~~ measurements ~~are reasonably accurate~~. The comparison between the mean ages calculated from the Medusa tracers and CFC-12 is sensitive to the assumed shape of the TTD, and the differences in input history that make them respond differently to the time-variant ventilation of the (western) Mediterranean Sea. As a component of the input function, the historical surface saturation has been estimated to be 94%; the atmospheric histories of the Medusa tracers have been given by Li et al. (2019), which~~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 potential of the Medusa tracers as transient tracers in the ocean is summarized in Table 4 by mainly evaluating their atmospheric

history, seawater solubility, ease of measurement, and stability in seawater. ~~The more precise historical surface saturation will be a future consideration.~~

~~As a reference, we start with~~ **CFC-12**. ~~.~~ This tracer is included as a reference as it is a commonly used transient tracer ~~marked with medium/high confidence/feasibility~~. The atmospheric history of CFC-12 is well-documented (Walker et al., 2000; Bullister, 2015), and the seawater solubility function is well-established (Warner and Weiss, 1985). In addition, CFC-12 has been observed for several decades by mature analytical techniques, and its stability in warm waters, as well as poorly oxygenated waters, has been proven. However, the decreasing atmospheric history of CFC-12 limits its ability as an oceanic transient tracer - only two black stars in the column "Atmospheric concentration" since it is well-established but still not ideal for an oceanic transient tracer of recently ventilated waters.

HCFC-22. The increasing atmospheric history is well-established by a combination of the model results and observations (Li et al., 2019). The seawater solubility function has been constructed by combining the CGW (Clark–Glew–Weiss) model on the experimental freshwater solubility data and another model (poly-parameter linear free-energy relationships, pp-LFERs) on the salting-out coefficients (Li et al., 2019). The results of freshwater solubility matched those published by Deeds (2008) on measurements and the CGW model results between 298-348 K, and those published in Abraham et al. (2001) on observations and the pp-LFERs model results at 298 K and 310 K. The confidence in the seawater solubility was marked as medium due to lack of direct experimental seawater solubility data to verify the function. ~~As to measurements,~~ HCFC-22 has been measured on several cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) by GC-ECD and GC-MS instruments, and in this study by the Medusa-Aqua system. The stability was evaluated by comparison to CFC-12 observations. The clustering of HCFC-22 values in the lower range (Fig. 10) could be an indication of slow degradation in seawater, which is also supported by the weak hydrolysis of HCFC-22 in tropical and subtropical waters reported by Lobert et al. (1995). Therefore, HCFC-22 was determined to be unstable in warm waters; additional experiments are needed to evaluate ~~more measurements should be added for~~ the stability ~~analysis~~, especially in poorly oxygenated waters. In addition, HCFC-22 can be replaced by SF_6 as a transient tracer since they have similar atmospheric histories (Fig. 54 and Fig. 65). These indicate that HCFC-22 might not be suitable as a new transient tracer in the warm ocean, for instance, the Mediterranean Sea, but could be used for colder waters.

HCFC-141b. The atmospheric history is reliably reconstructed (Li et al., 2019). However, the seawater solubility function was constructed for the first time (Li et al., 2019), and the freshwater solubility only matched the data presented in Abraham et al. (2001) at the two temperatures. The low surface saturation measured in the Baltic Sea suggests that there is likely an issue with the solubility function. HCFC-141b has been previously measured on cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) and also in this study, thus we have high confidence in the ability to measure this compound. ~~As for the stability,~~ HCFC-141b is identified to be potentially stable in seawater since its concentrations are ~~likely~~ in the expected range in the interior ocean (Fig. 10)~~, assuming that the solubility function is valid~~. The input function of HCFC-141b is different enough from the traditional transient tracers to provide additional information, but since the atmospheric history started to decrease in 2017 (Li et al., 2019), the use of HCFC-141b as a transient tracer for "young" waters will be compromised. All these indicate that HCFC-141b has probably limited potential as a transient tracer in the future.

HCFC-142b. The confidence of the atmospheric history ~~and seawater solubility function~~ is similar to those of HCFC-141b for the same reasons, while the high HCFC-142b saturation of samples from the Baltic Sea supports the medium confidence of the seawater solubility function. 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 have the confidence to accurately measure this compound. We have medium confidence in our ability to estimate the stability of HCFC-142b because of ~~slightly~~ higher than the expected concentrations in the interior ocean (Fig. 10), but that could be linked to the slightly too high saturation observed. 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 a high potential to be used as a transient tracer ~~currently~~.

HFC-134a. We ~~judge that we~~ have high and medium confidences in the atmospheric history and seawater solubility function (Li et al., 2019), respectively. Although the estimated seawater solubility function was constructed based on the modeled salting-out coefficients and the experimental freshwater solubility (Li et al., 2019) that matched both the observations (Deeds, 2008) and model results (Abraham et al., 2001), we have only medium confidence in the seawater solubility function due to the lack of experimental seawater solubility data. However, the samples from the Baltic Sea suggest that the solubility function seems reasonable. HFC-134a was measured ~~in~~ by Ooki and Yokouchi (2011) by GC-MS and in this study by the Medusa-Aqua system. It could indicate contamination issues due to~~although with~~ higher than expected concentrations (see Sect. 5.4)~~, so we have medium confidence to accurately measure this compound~~. We have medium confidence~~only poor knowledge~~ in~~of~~ the stability of HFC-134a also because ~~of its~~ higher than expected concentrations (Fig. 10). The compound is not identified as unstable and Fig. 10 suggests that the HFC134a is stable (see Sect. 5.4)~~, but its stability is still largely unknown considering the issues on seawater solubility function and/or measurements~~. In addition~~Besides~~, HFC-134a can only be used ~~only~~ as a tracer for "young" waters due to its short atmospheric history. Based on all these discussions, HFC-134a has a medium~~lower~~ potential ~~than HCFC-142b but higher potential compared to HCFC-22~~ to be an oceanic transient tracer.

HFC-125. The atmospheric c~~C~~oncentrations of HFC-125 in the early 1990s ~~in the atmosphere~~ are unclear (Fig. 6~~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. This~~All these~~ leads~~s~~ to low confidence in the seawater solubility function of HFC-125. We also consider~~evaluate~~ the fe~~as~~ibility to measure HFC-125 as low since this compound has been measured ~~in this study~~ for the first time in seawater in this study, and we find almost no vertical gradient (Fig. 9), which is unexpected. Furthermore, observed HFC-125 concentrations in freshwater are inconsistent 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 in this work. ~~Besides~~Also, HFC-125 can only be a tracer for "young" water due to its short atmospheric history. Therefore, we consider that HFC-125 has ~~currently~~ low potential as a transient tracer in the ocean ~~due to the poorly constrained~~

~~solubility and stability, and possible problems in seawater measurements.~~, although ~~T~~this might be remedied by ~~constructing the~~ experimental~~ly determining the~~ seawater solubility function and solving possible measurement issues.

HFC-23. HFC-23 could not be reliably measured in our system due to unstable non-zero blanks (see Sect. 3.4). Therefore, we can~~, obviously,~~ not reliabl~~ey~~ assess the stability of HFC-23 in seawater, and we have low confidence in

5 ~~our~~the fe~~asi~~bility ~~to~~f ~~the~~ measure~~ments~~ this compound, although the blank problem might be solved by a different instrument configuration. The atmospheric history of HFC-23 has been constructed (Li et al., 2019; Simmonds et al., 2018), but we have only medium confidence as it does not start from zero (Simmonds et al., 2018) due to limited data. ~~Also, w~~We have only medium confidence in the seawater solubility function 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

10 seawater solubility function was not constructed by experimental seawater solubility data. In consequence, unknown stability and current issues with measurements lead to the~~an~~ overall assessment that HFC-23 has ~~currently~~ low potential as a transient tracer in the ocean.

PFC-14 and PFC-116. The increasing atmospheric histories of PFC-14 and PFC-116 are well~~have been~~ established (Li et al., 2019; Trudinger et al., 2016). ~~Also, t~~The seawater solubility functions have been constructed with~~in~~ medium

15 confidence for PFC-14~~; such confidence is higher than those for other compounds with medium confidence~~ as it matches both seawater measurements (Scharlin and Battino, 1995) and freshwater solubility (Clever et al., 2005; Abraham et al., 2001). In contrast, low confidence for the solubility function for PFC-116 is attributed to its freshwater solubility only matching that from Deeds (2008) but not the theoretical assessment from Abraham et al. (2001). PFC-14 and PFC-116 are very stable in the environment, but can~~no²~~t easily be measured in seawater because of the low

20 solubility (Li et al., 2019), i.e.~~,~~ low concentration in seawater. The high stability and long atmospheric histories make PFCs potentially promising transient tracers in the ocean, although ~~it is challenging to~~ measure~~ments are~~these ~~compounds~~challenging. A possibility would be to use an ECD that has~~with a~~ higher~~er~~ sensitivity for C-F bonds, but with the additional complication of co-elution on the chromatogram.

7 Conclusions and outlook

25 This study, combined with the study by Li et al. (2019), provides a method to identify and evaluate if a compound is suitable for use as a transient tracer in the ocean. Selected HCFCs, HFCs, and PFCs were ~~selected for~~ evaluat~~ed~~ion ~~as~~ for their potential ~~replacements for CFCs (~~as transient tracers~~)~~. The evaluation mainly considered four aspects: input function (including atmospheric history and historical surface saturation), seawater solubility, feasibility of measurement, and stability in seawater. We also considered how Medusa tracers with different atmospheric histories

30 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 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.

By comprehensive evaluation, we conclude that HCFC-22 is unlikely to be a transient tracer in warm waters, whereas

35 HFC-23 cannot be evaluated as a transient tracer because of the lack of ~~too much~~ information. Fortunately, these two compounds can be ~~replac~~substitut~~e~~d by SF_6 that has a similar atmospheric history. On the other hand, both HCFC-

141b and HCFC-142b show high potential as transient tracers currently. Considering their similar atmospheric histories and the decreasing atmospheric mole fraction of HCFC-141b, HCFC-142b should be further evaluated by obtaining more reliable solubility and stability information in seawater. HFC-134a and HFC-125 show medium and low potentials as transient tracers, respectively; the former because of higher than expected concentrations pointing to issues on the seawater solubility function and/or the measurements but not identified to be unstable; the latter due to the lack of information on solubility, stability, and feasibility of measurement in seawater. Considering their similar atmospheric histories, HFC-134a is a more promising candidate as a transient tracer. Last but not least, PFC-14 and PFC-116 show large potential as transient tracers once their accurate measurement in seawater is resolved. The high stability and long atmospheric history make it worthwhile to explore improved analytical methods, whether it implies using a more sensitive detector, or larger samples.

The main result from this study is that although a couple of the investigated tracers might be useful as oceanic tracers, at least under some circumstances such as cold waters, etc., none of the tracers would be fully qualified at this time. Although we have a good handle of the input function in the atmospheric history, we recognize that targeted work is needed for all compounds to better constrain the solubility. For stability, we have an idea which ones are possibly stable, but more work is needed here too (possibly laboratory experiments under controlled conditions). There are limitations in the current configuration of the analytical techniques as described, and additional efforts are needed to understand and improve the system. In summary, we are not quite yet in the position to recommend targeted observations of these tracers, but this study provides a useful summary of the current knowledge, including the new research reported on in this manuscript, to guide further, more targeted experiments and studies.

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

Data availability

Cruises data on historical surface 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 those of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 measured by the Medusa-Aqua system in seawater from cruises MSM72 and AL516 are shown in Table S76.

Author contributions

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

5 **Competing interests**

The authors declare that they have no conflict of interest.

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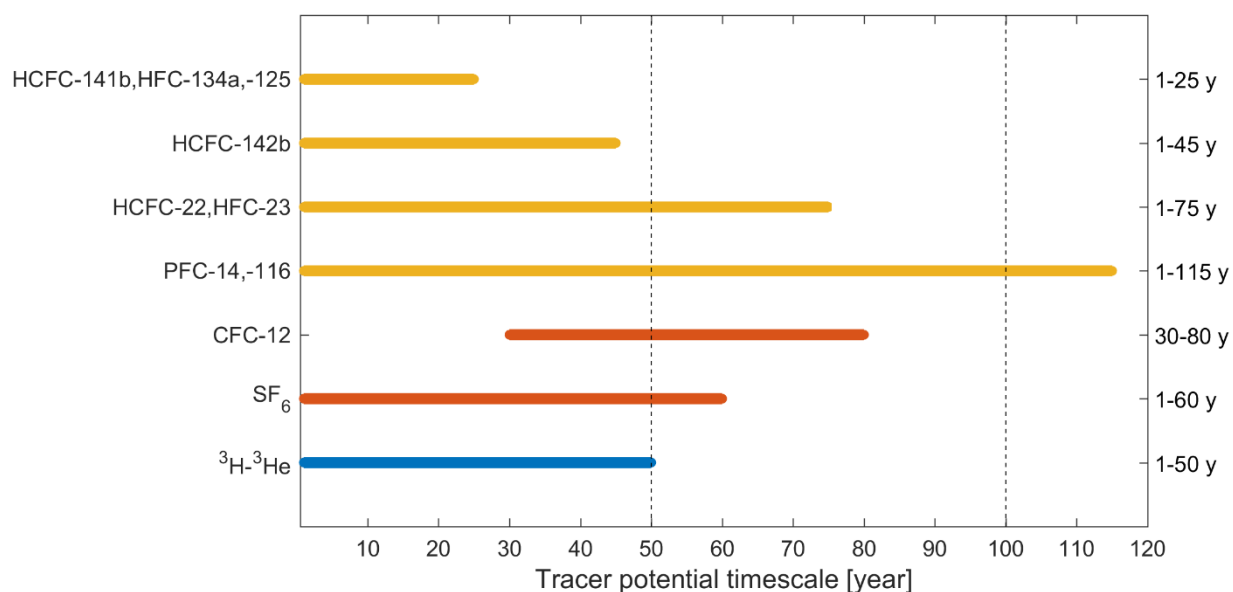
Figure 1. Seawater timescales ("tracer age ranges") of ~~halogenated compound dating using~~ potential chronological transient tracers (selected HCFCs, HFCs, and PFCs, yellow) as well as traditional chronological transient tracers (CFC-12 and SF₆, red) combined with radioisotope dating using radioactive transient tracers (^{3}H-^{3}He, blue). Tracer age ranges of chronological transient tracers are approximately estimated from Fig. 6~~5~~ (see below), while tracer age ranges of radioactive transient tracers are from Aggarwal (2013).
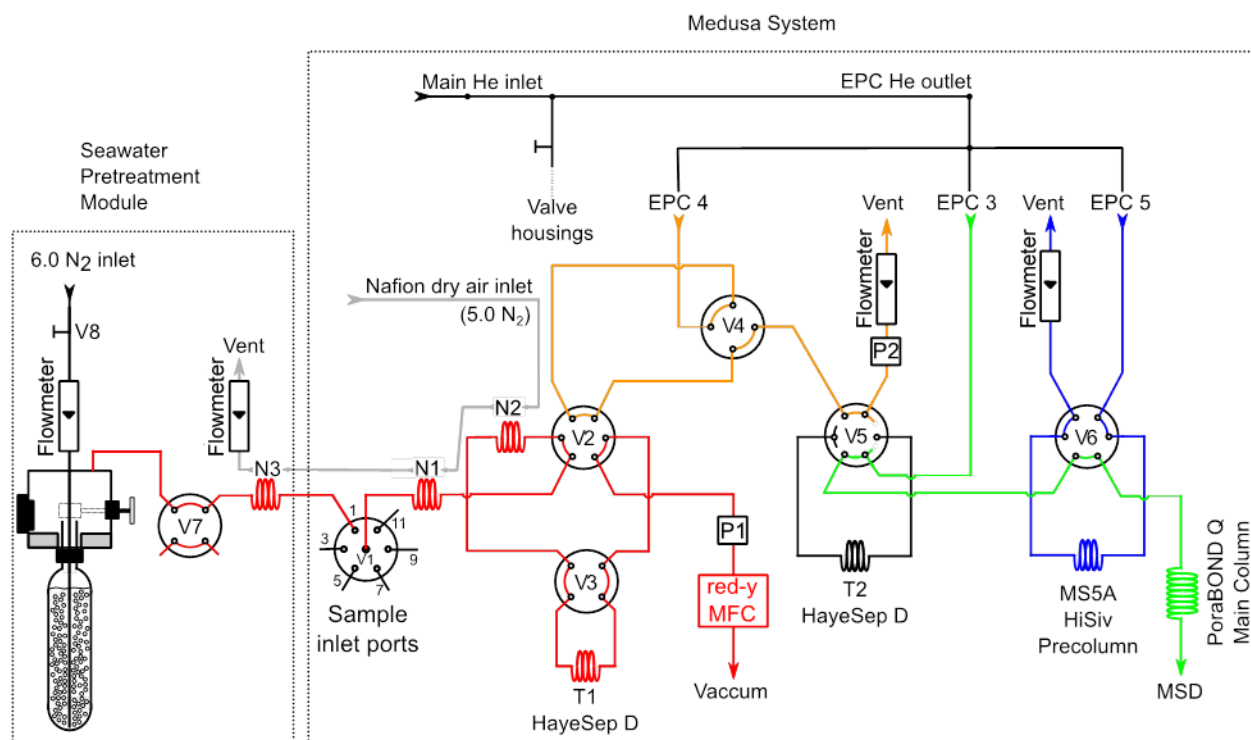
Figure 2. The Medusa-Aqua system flow scheme where. Tthe Medusa system remains identical to that given by Miller et al. (2008). The seawater pretreatment module is added to degas gaseous tracers from samples before injecting into Medusa. Electronic Pressure Controllers (EPC3, EPC4, and EPC5) supply helium throughout the system. The Mass Flow Controller (MFC) is used to measure the sample volume downstream of Trap 1 (T1), was not used in this study. The cryogenic packing materials are 200 mg of 100/120 mesh HayeSep D (HSD) for Trap 1 (T1) and 5.5 mg of HSD adsorbent for Trap 2 (T2). N1-N3 are the Nafion driers and V1-V8 are multiport valves. P1 and P2 are pressure transducers (100PSI-A-DO, All Sensor Corporation, Morgan Hill, CA).
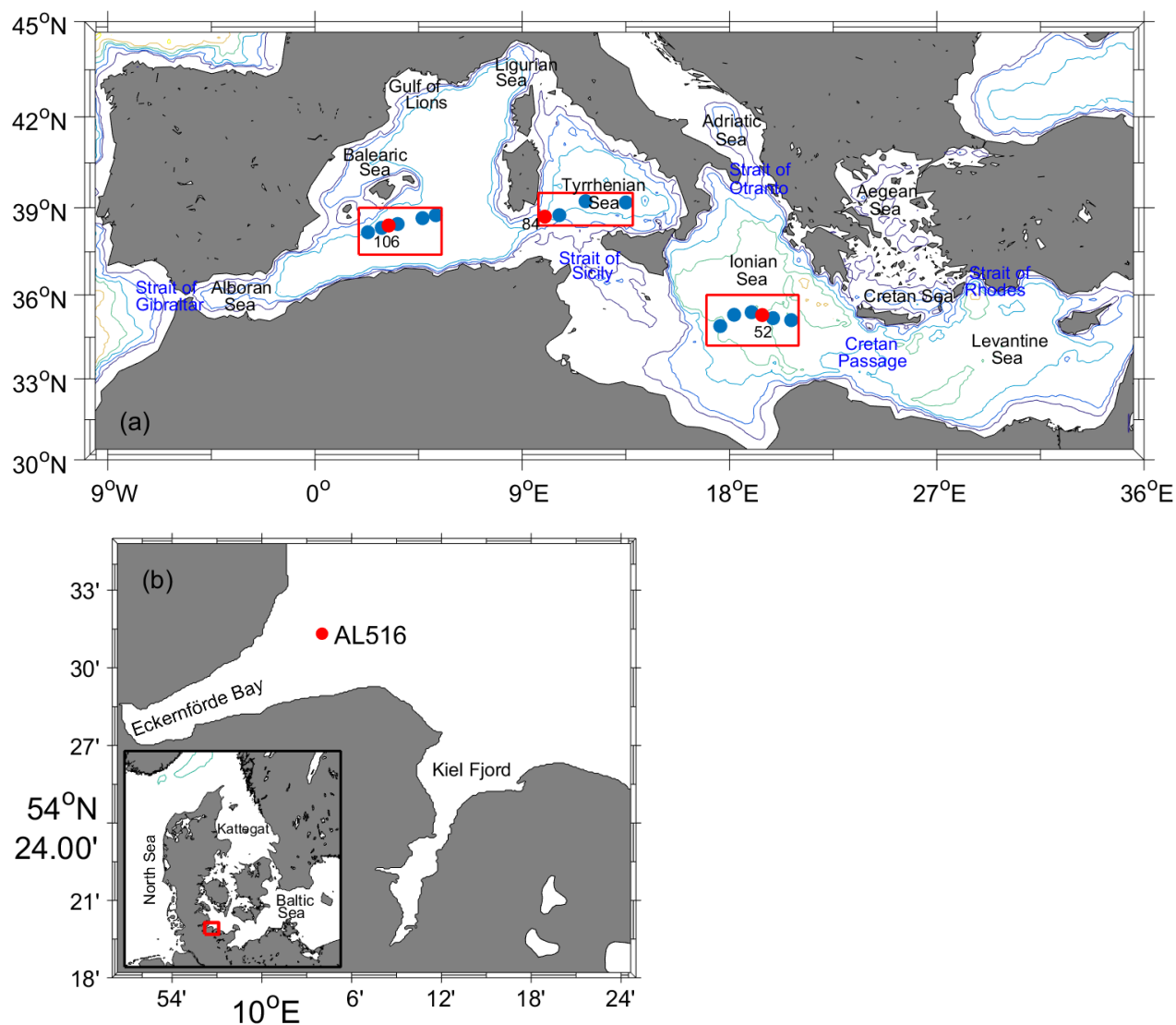
Figure 3. Locations of sampling sites from (a) cruise MSM72 in the Mediterranean Sea in three areas: ~~the~~ Southern Ionian Sea (SIS), ~~the~~ Tyrrhenian Sea (TS) and ~~the~~ Western Mediterranean Sea (WMS), and (b) cruise AL516 in the Baltic Sea. Sampling sites in red solid circles indicate samples measured by the Medusa-Aqua system for HCFCs, HFCs, PFCs, and CFC-12, blue solid circles were for CFC-12, and SF_6 measured by the PT-GC-ECD. The depth contours are 500 m, 1000 m, 2000 m, 3000 m, 4000 m, and 5000 m~~, and 6000 m~~.
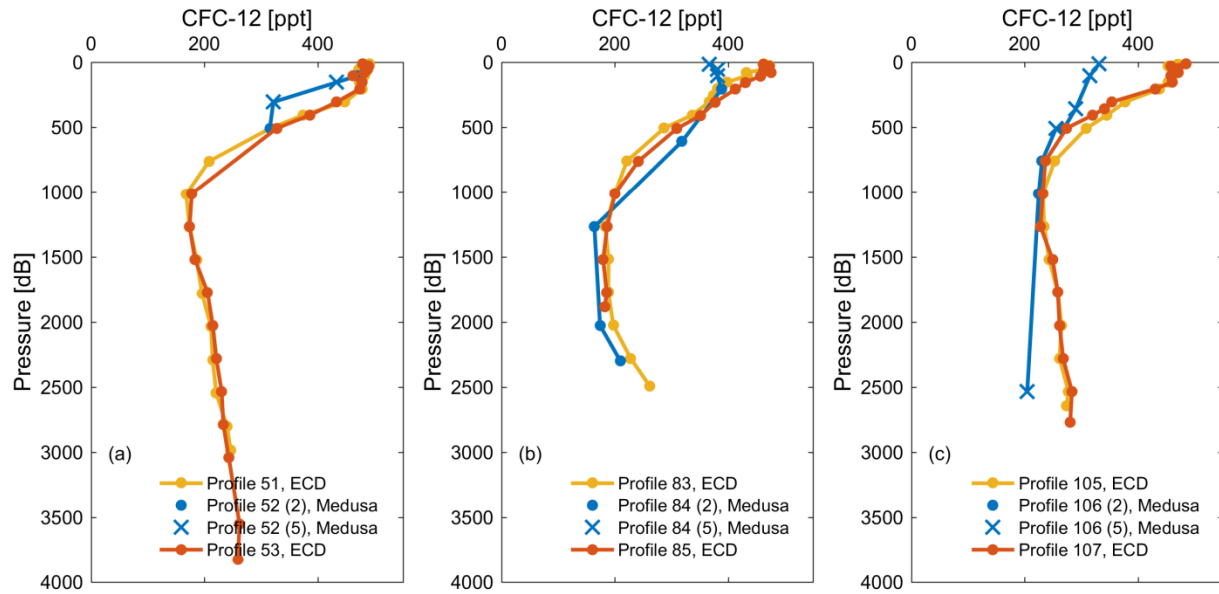
Figure 48. Comparison of CFC-12 observations from cruise MSM72 measured by the PT-GC-ECD (ECD) and the Medusa-Aqua system (Medusa) in three areas: (a) ~~the~~ Southern Ionian Sea, (b) ~~the~~ Tyrrhenian Sea, and (c) ~~the~~ Western Mediterranean Sea. Samples flagged as good (flag 2) are shown as dots, whereas for samples that are deemed inconsistent with PT-GC-ECD samples are flagged as likely bad (here we used flag 5, see text). ~~We used normal quality control routines and flagged outliers as probably bad ("3" in Table S6), which are not further considered. One more step was done to compare the Medusa-Aqua system observations with those from the PT-GC-ECD; if the Medusa CFC-12 values are inconsistent with the CFC-12 values from PT-GC-ECD measurements, they were flagged "5" in Table S6 indicating a possible issue during the sampling or measurement process; if they are consistent, they were flagged "2" representing good data.~~ In the following plots, we show all data with a quality flag of "2 (dots)" or "5 (crosses)".
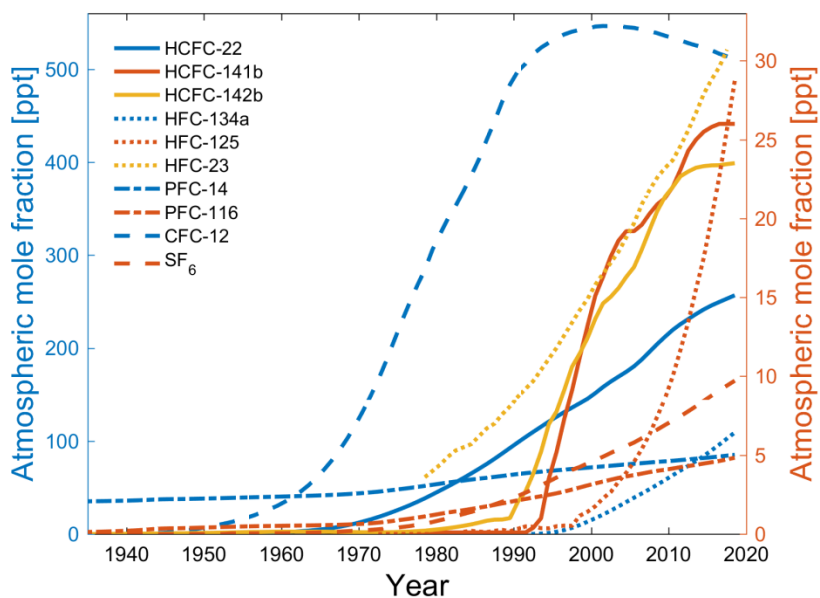
Figure 4~~5~~. Atmospheric histories of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12 and SF$_6$ in the Northern Hemisphere. HCFC-22, HFC-134a, PFC-14, and CFC-12 share the left y-axis scale; other compounds share the right y-axis scale.
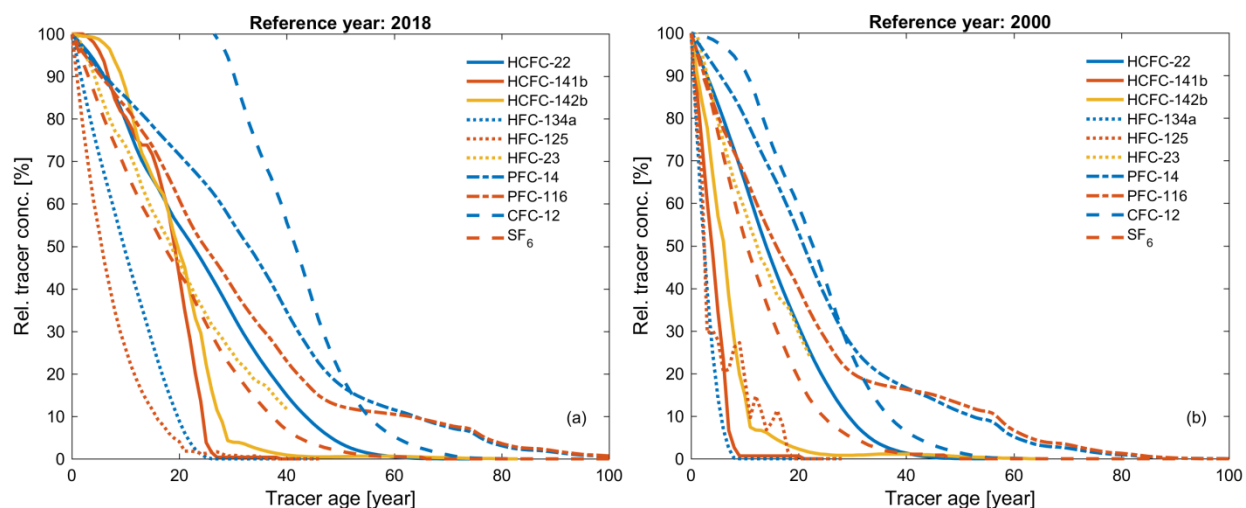
Figure ~~5~~6. Relative tracer concentrations in percent (i.e., normalized to the contemporaneous atmospheric concentrations) and corresponding tracer age for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12, and SF$_6$ in the Northern Hemisphere for two sampling years: (a) 2018 and (b) 2000.
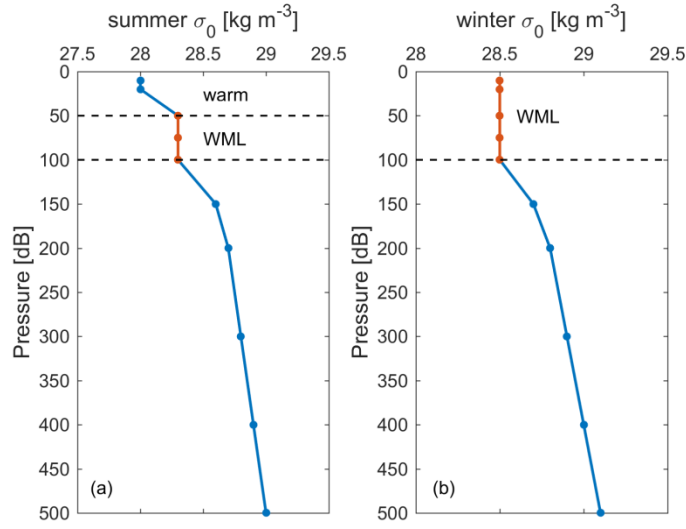
Figure 67. Example of the winter mixed layer (WML) depth (marked as red) determined in (a) summer and (b) winter in potential density (σ_0) profiles especially for historical surface saturation calculation.
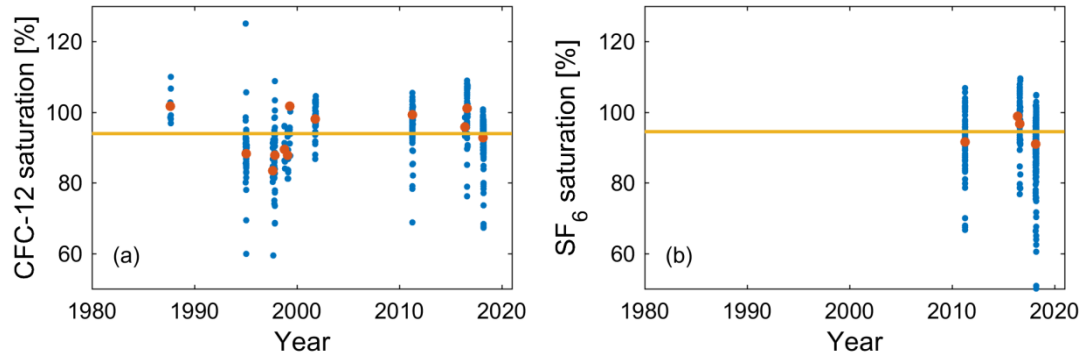
Figure 78. Historical surface saturations in winter mixed layers (blue solid circles) for (a) CFC-12 from 12 cruises in 1987-2018 and (b) SF$_6$ from 4 cruises in the Mediterranean Sea. Red solid circles denote the means of seawater saturation for each cruise and the yellow lines (94%) are the mean of averaged seawater saturation of every cruise.

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. 8̶4.
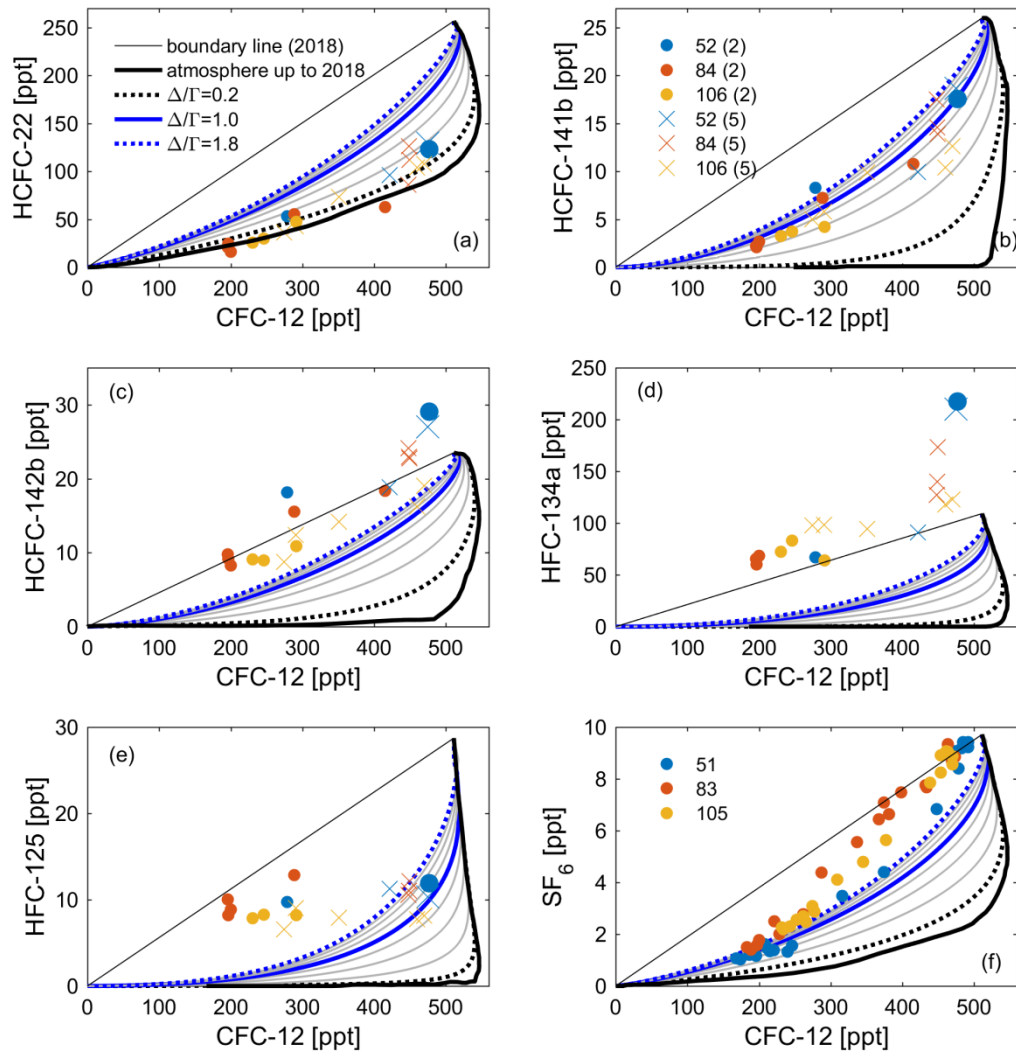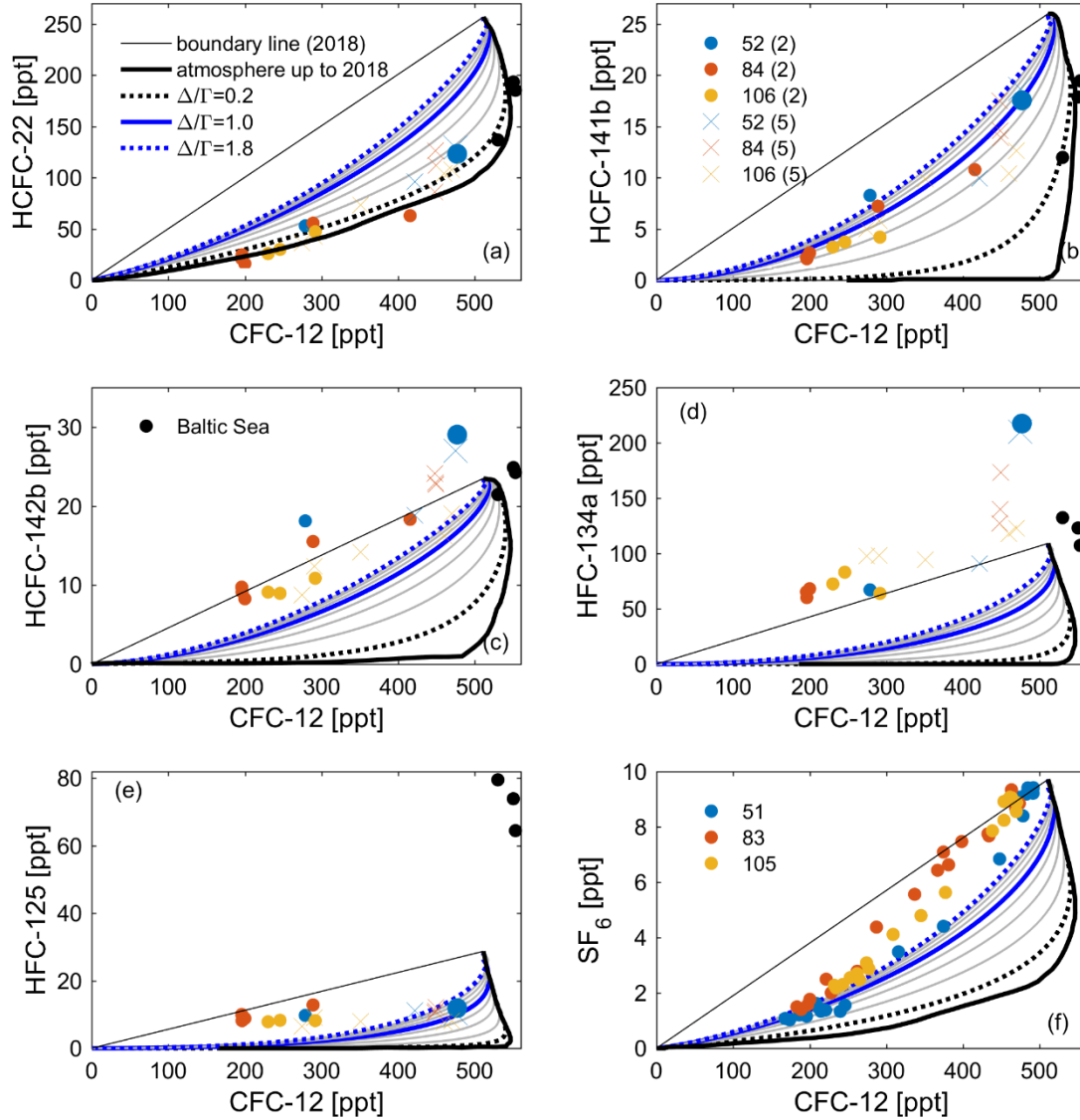
Figure 10. Observations of (a) HCFC-22, (b) HCFC-141b, (c) HCFC-142b, (d) HFC-134a and (e) HFC-125 in profiles 52, 84, and 106 measured by Medusa-Aqua system and (f) SF₆ in profiles 51, 83, and 105 measured by PT-GC-ECD plotted against the (interpolated) CFC-12 based on measurements by PT-GC-ECD in the Mediterranean Sea. Observations of tracers from cruise AL516 in the Baltic Sea have been added (black dots). The thick black line is the atmospheric history of the tracer pair ($\Delta/\Gamma = 0.0$) and the thin black line is the theoretical mixing line between contemporary and pre-industrial concentrations. The theoretical mixing lines assuming an ~~Inverse Gaussian~~ IG TTD ~~(Sect. S4 and Fig. S9)~~ with $\Delta/\Gamma = 0.2$–1.8 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~~4.

Table 1. 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] (%)	Precision [b] (%)
SF$_6$	SF$_6$	sulfur hexafluoride	SIO-05	0.37	0.548	--	--
CFC-12	CCl$_2$F$_2$	dichlorodifluoromethane	SIO-05	0.08	29.83	0.4	3.7
HCFC-22	CHClF$_2$	chlorodifluoromethane	SIO-05	0.22	13.875	3.1	2.0
HCFC-141b	CH$_3$CCl$_2$F	1,1-dichloro-1-fluoroethane	SIO-05	0.20	4.01	6.1	3.5
HCFC-142b	CH$_3$CClF$_2$	1-chloro-1,1-difluoroethane	SIO-05	0.21	3.24	1.8	3.4
HFC-134a	CH$_2$FCF$_3$	1,1,1,2-tetrafluoroethane	SIO-05	0.21	7.31	9.7	--
HFC-125	CHF$_2$CF$_3$	pentafluoroethane	SIO-14	0.23	1.219	2.0	--
HFC-23	CHF$_3$	fluoroform	SIO-07	0.49	6.71	--	--
PFC-14	CF$_4$	carbon tetrafluoride	SIO-05	0.30	0.44	--	--
PFC-116	CF$_3$CF$_3$	hexafluoroethane	SIO-07	0.32	1.41	--	--

[a] Precision (reproducibility, 1σ) of tracers in seawater was determined by ~1.3 L samples at 23.5 dbar from cruise AL516 in the Baltic Sea in September 2018; [b] Precision of tracers for four duplicate seawater samples equilibrated with the atmosphere; the 300 mL seawater samples were sampled from the tropical Atlantic Ocean.

Table 2. Comparison of instrument performance measuring CFC-12

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

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

Table 3. Seawater surface saturations (%) of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-125 in profile 30 from cruise AL516 (measured by the Medusa-Aqua system).

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

Table 4. Evaluating the possibilities of selected HCFCs, HFCs, and PFCs as transient tracers in the ocean from four aspects

Compound	Atmospheric history	Solubility in seawater	Feasibility of measurement in seawater	Stability in seawater	Possibility to be a 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 "reasonably well resolved" and three stars "well documented or resolved"; the number of black stars represents the possiability of a compound as a transient tracer through current assessments. For instance, the atmospheric history for CFC-12 got 3 stars since we know this very well, but only 2 of those are black since its atmospheric concentrations are decreasing after experiencing a continuous increase.

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