

# 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. Of the investigated compounds, HCFC-142b and HCFC-141b are found to be the most promising transient tracer in the ocean currently. The compounds that have the greatest potential as future tracers are PFC-14 and PFC-116, although the low solubility in seawater creates challenging analytical conditions (i.e. low concentration) that can potentially be improved by modifying the Medusa-Aqua analytical system. HCFC-22 is found to be likely unstable in warm seawater, which leads to low confidence in terms of its potential as an oceanic transient tracer, although it is possibly useful in colder water. For compounds HFC-134a, HFC-125 and HFC-23, we are not able to fully evaluate their potential 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 can no longer be considered because there are alternative tracers with similar input histories that are better suited as transient tracers.

## 1 Introduction

Ventilation is defined as the time elapsed since the water parcel has left the mixed layer and been transported to the ocean interior. Ocean ventilation and mixing processes play significant roles in climate as they are important processes to propagate perturbations on the ocean surface to the interior. They largely control the accumulated uptake of anthropogenic carbon ( $C_{\text{ant}}$ ) 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<sub>6</sub>), and radioactive transient tracers such as Tritium-Helium (<sup>3</sup>H-<sup>3</sup>He), Argon-39 (<sup>39</sup>Ar) and Carbon-14 (<sup>14</sup>C), although <sup>39</sup>Ar is assumed to be in steady-state and cannot be regarded as a transient tracer 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<sub>6</sub> has only been used since the late 1990s. These compounds are mostly stable in seawater; their seawater solubility functions are well-established (Warner and Weiss, 1985; Bullister et al., 2002) and their historical atmospheric concentrations over time are known (Walker et al., 2000; Bullister, 2015). However, the industrial use of CFC-12 and CFC-11 was phased out as a result of the implementation of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer designed to curtail the degradation of the Earth's ozone layer. Therefore, the atmospheric concentrations of CFC-12 and CFC-11 have decreased since the early 2000s and the early 1990s (Bullister, 2015), which has reduced their usefulness as an oceanographic transient tracer for recently ventilated water masses. Consequently, SF<sub>6</sub> 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<sub>6</sub> implemented. However, the concentrations of SF<sub>6</sub> in the atmosphere continue to rise due to its long atmospheric lifetime. Currently, CFC-12 and SF<sub>6</sub> have readily measured onboard a research vessel at a reasonable rate from one seawater sample. CFC-11 has been extensively used as a transient tracer but found to have 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<sub>6</sub> 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<sub>4</sub>) have been extensively used 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 <sup>39</sup>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 <sup>39</sup>Ar observations (Lu et al., 2014; Ebser et al., 2018). 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) 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 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<sub>4</sub>) and PFC-116. The atmospheric abundances of most HCFCs and HFCs are increasing, as are the concentrations of PFCs. Here we describe 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". With the constraints of the weak signal of <sup>3</sup>H

and the decreasing atmospheric mole fraction of CFC-12, presently only SF<sub>6</sub> 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).

### 5 1.3 Stability of alternative tracers in seawater

Chemical reactions (including hydrolysis), adsorption to particles and biological degradation process 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 of the stability in seawater. One indication of the stability is the stable chemical structure, which is expressed as the following aspects. For instance, PFCs have very long atmospheric lifetimes, i.e. > 50 000 and > 10 000 years for PFC-14 and PFC-116, respectively. PFC-14 (CF<sub>4</sub>) is stable at temperatures of at least 1200°C and the rate of hydrolysis of CF<sub>4</sub> 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 of significance for a potential transient tracer. As indicated 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 that of a compound that is known to be unstable in seawater. CCl<sub>4</sub> has a short lifetime in warm seawater. Surface saturation of HCFCs is not as under-saturated as those of CCl<sub>4</sub> (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). This suggests that HCFCs are more stable than CCl<sub>4</sub> in surface seawater and possibly suited as tracers in the ocean.

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

## 1.4 Goals 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 (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 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 south-west Baltic 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<sub>6</sub> (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 measured by an Electron Capture Detector (ECD) that is normally used for CFC-12 and SF<sub>6</sub> (Lobert et al., 1995; Beyer et al., 2014; Sousa and Bialkowski, 2001). One alternative is to use a mass spectrometer (MS) for detection that has the advantage of scanning for unique masses for different compounds, allowing 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). The Medusa-GC-MS system (shortened 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 includes two traps kept at accurately controlled temperatures to trap the volatile gases. The packing material of the traps and the temperature during the trapping stage are designed in a way that allows for the fractionation of the compounds on two traps. In this way, interferences from atmospheric permanent gases can be avoided and hard-to-measure gases like PFC-14 (CF<sub>4</sub>) 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 compounds including halocarbons, hydrocarbons and sulfur compounds involved in ozone depletion and/or climate forcing from the same sample. The measurement precisions of most halogenated compounds are less than 0.5 % in 2 L ambient air. The Medusa-Aqua system as developed based on the Medusa system can measure the majority of the 40 halogenated compounds in seawater samples.

## 2.2 Difference between Medusa-Aqua and Medusa system

The Medusa-Aqua system consists of a Medusa system (Miller et al., 2008) and a seawater sample pretreatment system (Fig. 2). The Medusa system consists of a cryogenic pre-concentration unit, named Medusa, an Agilent 6890N gas chromatograph (GC) and an Agilent 5975B quadrupole mass spectrometer (MS). The seawater sample pretreatment system was developed to degas gaseous tracers from samples before injecting into the Medusa system, replacing the air sampling device of the original Medusa system. The technology is based on a purge-and-trap technology where the Medusa serves as the trap unit prior to the chromatographic separation of the sample for detection in the MS.

The main difference between Medusa and Medusa-Aqua system is that the former uses an air-pump module as the gas 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 Baltic Sea in September 2018. Over the past years, we have collected samples on a few cruises and empirically improved our method (Sect. S3, Figs. S1-S7 and Tables S3-S5).

### 3.1 Sample collection

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 2<sup>nd</sup> to April 3<sup>rd</sup>, 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 12<sup>th</sup> to 22<sup>nd</sup>, 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<sub>2</sub> (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<sub>6</sub> measurements (on a PT-GC-ECD) were conducted on the stations we sampled for the Medusa-Aqua system in the Mediterranean Sea, although they were measured for the nearby stations, 15 nm (nautical miles) away 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 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<sub>2</sub> (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<sub>2</sub> (grade 6.0) for 20 minutes at a flow rate of 100 mL min<sup>-1</sup>. 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<sub>2</sub>, grade 5.0) was set to 120 mL min<sup>-1</sup>. 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<sup>-1</sup>. The detector response 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 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 (1σ) of the concentrations for two pairs of duplicate samples (Table 1). 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. The concentrations of SF<sub>6</sub>, PFC-14, and PFC-116 in most seawater samples were 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 measured by the Medusa-Aqua system in seawater from both cruises are shown in Table S6 with quality flags marked.

### 3.5 Comparison of instruments measuring CFC-12

5 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<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> (Stöven, 2011; Stöven and Tanhua, 2014; Stöven et al., 2016; Bullister and Wisegarver, 2008). For comparison, information on the performance of a similar purge and trap system set-up (Cracker-PT-GC-ECD) to measure flame-sealed ampoules for CFC-12 and SF<sub>6</sub> 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; can measure more compounds.

## 4 Transient tracer interpreting methods

### 15 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 ideal applicability, atmospheric histories of tracers should increase monotonically in the atmosphere. 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<sub>6</sub> in the Northern Hemisphere (Bullister, 2015; Li et al., 2019).

### 4.2 Tracer age

Tracer age is defined as the age of a water parcel based on a purely advective flow in the ocean. 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.

Similar trends are found for the following tracer couples: HCFC-141b and HCFC-142b, HFC-134a and HFC-125, SF<sub>6</sub> and HCFC-22/HFC-23, PFC-14 and PFC-116. Assuming that all these compounds fulfill the other criteria as transient tracers, it is enough to choose one of each couple for transient tracer work (i.e. addition to the other compound in the pair adds little new information).

30 If the relative tracer concentrations are higher than 100 % in Fig. 5, 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. 5). 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. 5).

## 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. 6 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<sub>6</sub> (Fig. 7) were determined by profiles of temperature, potential density, and CFC-12 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  $94 \pm 6 \%$  and  $94 \pm 4 \%$  for CFC-12 and SF<sub>6</sub>, respectively. For CFC-12, this is different from 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) takes a long time to equilibrate with the atmosphere. 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 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  $5.9 \pm 4.6 \%$ . 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 tracers. Observations of CFC-12 and SF<sub>6</sub> 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 the well-ventilated Mediterranean deep waters.

### 5.3 Surface saturation of Medusa tracers in seawater

5 Surface saturation in seawater could be a factor that describes the stability of a compound in surface seawater or 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 flag all surface samples as suspect due to discrepancies between CFC-12 concentrations as measured by Medusa-Aqua system and PT-GC-ECD. We, therefore, turn to the samples collected in the Baltic Sea where the seawater saturation of CFC-12 and Medusa tracers in one surface sample and two bottom samples are shown in Table 3. Note that the bottom waters (at about 23.5 meters depth) can be considered as recently ventilated as this water is ventilated on an annual base. The averaged saturation of CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 in seawater are  $122 \pm 8 \%$ ,  $77 \pm 8 \%$ ,  $74 \pm 12 \%$ ,  $114 \pm 2 \%$ ,  $125 \pm 23 \%$  and  $252 \pm 35 \%$ , respectively.

### 15 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<sub>6</sub> (measured by the PT-GC-ECD) are plotted against the (interpolated) CFC-12 (Fig. 10). Concentration values of 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; all samples will have to fall between these two lines (i.e. the stability area) if the tracer is conservative in seawater. Compounds where the samples fall below the “stability area” are not stable (assuming that CFC-12 is stable), and for 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<sub>6</sub> are well in the allowed range; whereas HCFC-142b and HFC-134a are around or above the upper boundary.

The increased ventilation of the (western) Mediterranean Sea during the last decade tends to result in 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 higher than expected concentrations (similar to SF<sub>6</sub>) for the Medusa tracers. This is exactly what we see from HCFC-142b and HFC-125 (Fig. 10). In addition, we could find that the  $\Delta/\Gamma$  ratio determined by CFC-12/HCFC-141b and CFC-12/HCFC-142b tracer pairs located closer to that by CFC-12/SF<sub>6</sub>, pointing out the more promising tracer pairs. However, too high concentrations for HFC-134a may 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 to be high.

Although the assumption of time-invariant ventilation is not valid for the Mediterranean Sea, the TTD model can produce indicative results to understand the mean ages estimated from Medusa tracers (assuming  $\Delta/T = 1.0$ ) and their comparison to those estimated from CFC-12 and SF<sub>6</sub>, see Sects. S4-S5 and Figs. S9-S11.

## 6 Discussions

5 The results from this study on stability based on interior ocean observations can be evaluated to analyze the stability and further determine the potential of the Medusa tracers as oceanic transient tracers, and are as such dependent on the confidence that the measurements are reasonably accurate. The comparison between the mean ages calculated from the Medusa tracers and CFC-12 is sensitive to the assumed shape of the TTD, and the differences in input history that make them respond differently to the time-variant ventilation of the (western) Mediterranean Sea. As a component of  
10 the input function, the historical surface saturation has been estimated to be 94 %; the atmospheric histories of the Medusa tracers have been given by Li et al. (2019), who also used indirect methods to estimate the solubility functions. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 can be measured by the Medusa-Aqua system. Based on the combined results from Li et al. (2019) and this study, the 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  
15 measurement and stability in seawater. The more precise historical surface saturation will be a future consideration. As a reference, we start with CFC-12, 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  
20 oxygenated waters, has been proven. However, the decreasing atmospheric history of CFC-12 limits its ability as an oceanic transient tracer.

**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-  
25 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;  
30 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; more measurements should be added for the stability analysis, especially in poorly  
35 oxygenated waters. In addition, HCFC-22 can be replaced by SF<sub>6</sub> as a transient tracer since they have similar

atmospheric histories (Fig. 4 and Fig. 5). These indicate that HCFC-22 might not 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 data in Abraham et al. (2001) at the two temperatures. HCFC-141b has been previously measured on cruises (Lobert et al., 1996; Yvon-Lewis et al., 2008) and also in this study, thus we have high confidence in the ability 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. 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). 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 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. HFC-134a was measured in Ooki and Yokouchi (2011) by GC-MS and in this study by the Medusa-Aqua system although with higher than expected concentrations (see Sect. 5.4), so we have medium confidence to accurately measure this compound. We have only poor knowledge of the stability of HFC-134a because its higher than expected concentrations (Fig. 10). The compound is not identified as unstable (see Sect. 5.4), but its stability is still largely unknown considering the issues on seawater solubility function and/or measurements. Besides, HFC-134a can be used only as a tracer for “young” waters due to its short atmospheric history. Based on all these discussions, HFC-134a has lower potential than HCFC-142b but higher potential compared to HCFC-22 to be an oceanic transient tracer.

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

also evaluate the feasibility to measure HFC-125 as low since this compound has been measured in this study for the first time in seawater, 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, 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. This might be remedied by constructing the experimental seawater solubility function and solving possible measurement issues.

**HFC-23.** HFC-23 could not be reliably measured in our system due to unstable non-zero blanks (see Sect. 3.4). Therefore, we can, obviously, not reliably assess the stability of HFC-23 in seawater, and we have low confidence in the feasibility of the measurements, 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, 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 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 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 have been established (Li et al., 2019; Trudinger et al., 2016). Also, the seawater solubility functions have been constructed in medium 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't easily be measured in seawater because of the low solubility (Li et al., 2019), i.e. low concentration in seawater. The high stability and long atmospheric histories make PFCs potentially promising transient tracers in the ocean, although it is challenging to measure these compounds. A possibility would be to use an ECD with higher sensitivity for C-F bonds, but with the additional complication of co-elution on the chromatogram.

## 7 Conclusions and outlook

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

5 By comprehensive evaluation, we conclude that HCFC-22 is unlikely to be a transient tracer in warm waters, whereas HFC-23 cannot be evaluated as a transient tracer because of the lack of too much information. Fortunately, these two compounds can be replaced by SF<sub>6</sub> 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  
10 reliable solubility and stability information in seawater. HFC-134a and HFC-125 show low potential as transient tracers; the former because of higher than expected concentrations pointing to issues on the seawater solubility function and/or the measurements; the latter due to the lack of information on solubility, stability, and feasibility of measurement in seawater. Considering their similar atmospheric histories, HFC-134a is a more promising candidate as a transient  
15 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.

Future work will be further evaluating the potential transient tracers identified in this study. The next steps include experiments in controlled laboratory conditions with the aim to constructing the seawater solubility functions and exploring the stability of the compounds, in particular for warm and/or oxygen-depleted seawater; work on improving  
20 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**

25 Cruises data on historical surface saturation of CFC-12 and SF<sub>6</sub> in the Mediterranean Sea (Sect. 5.1) are from [https://www.nodc.noaa.gov/ocads/oceans/Coastal/Meteor\\_Med\\_Sea.html](https://www.nodc.noaa.gov/ocads/oceans/Coastal/Meteor_Med_Sea.html). Observations of CFC-12 and SF<sub>6</sub> 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 S6.

### **Author contributions**

30 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.

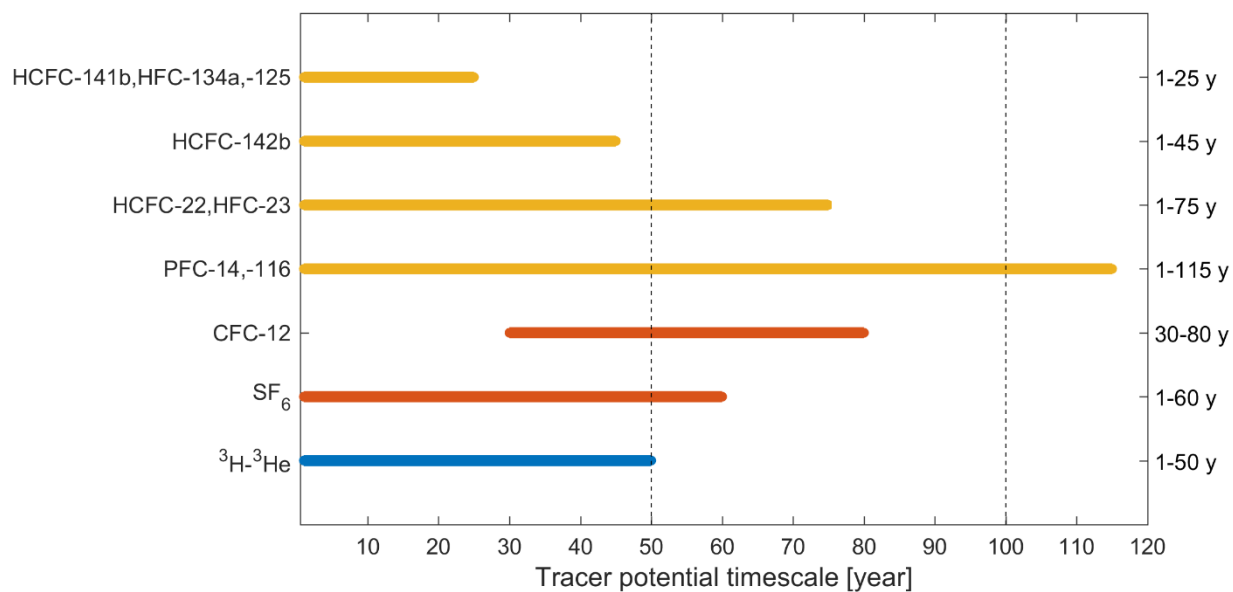
## **Competing interests**

The authors declare that they have no conflict of interest.

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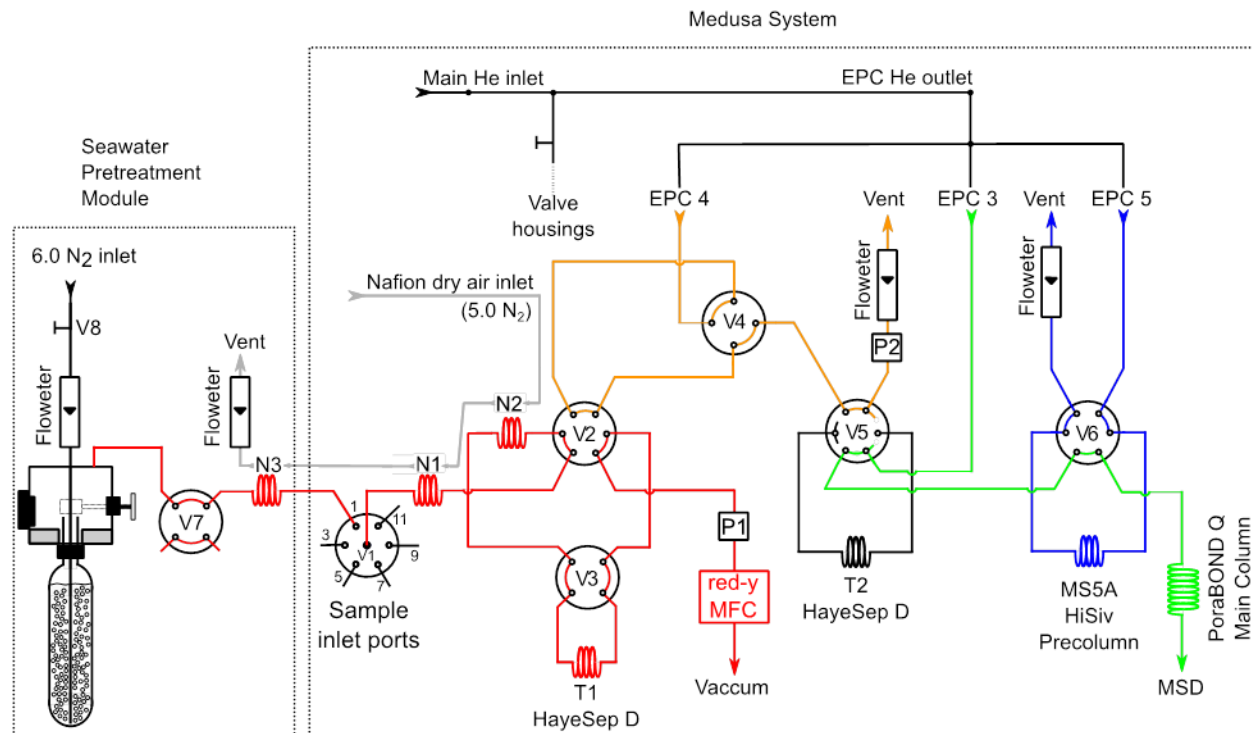
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**Figure 1.** Seawater timescales (“tracer age ranges”) of halogenated compound dating using potential chronological transient tracers (selected HCFCs, HFCs, and PFCs, yellow) as well as traditional chronological transient tracers (CFC-12 and SF<sub>6</sub>, red) combined with radioisotope dating using radioactive transient tracers (<sup>3</sup>H-<sup>3</sup>He, blue). Tracer age ranges of chronological transient tracers are approximately estimated from Fig. 5 (see below), while tracer age ranges of radioactive transient tracers are from Aggarwal (2013).

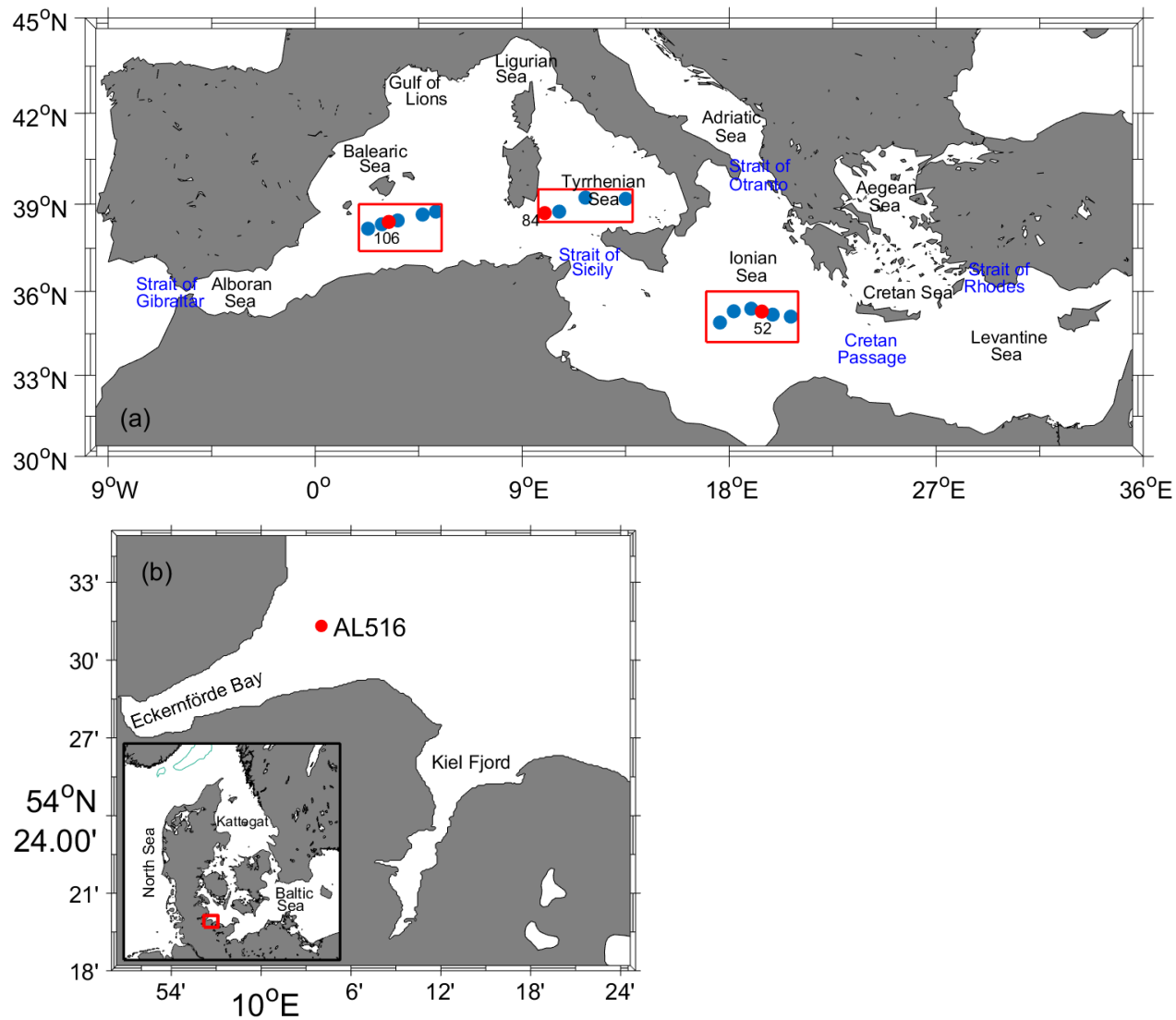
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**Figure 2.** Medusa-Aqua system flow scheme. The Medusa system remains identical to that given by Miller et al. (2008). The seawater pretreatment module is added to degas gaseous tracers from samples before injecting into Medusa. Electronic Pressure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

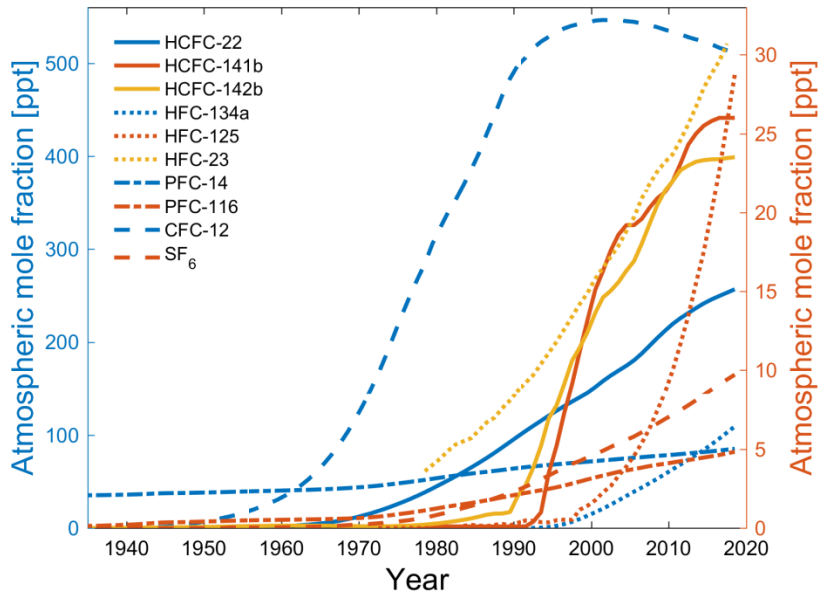
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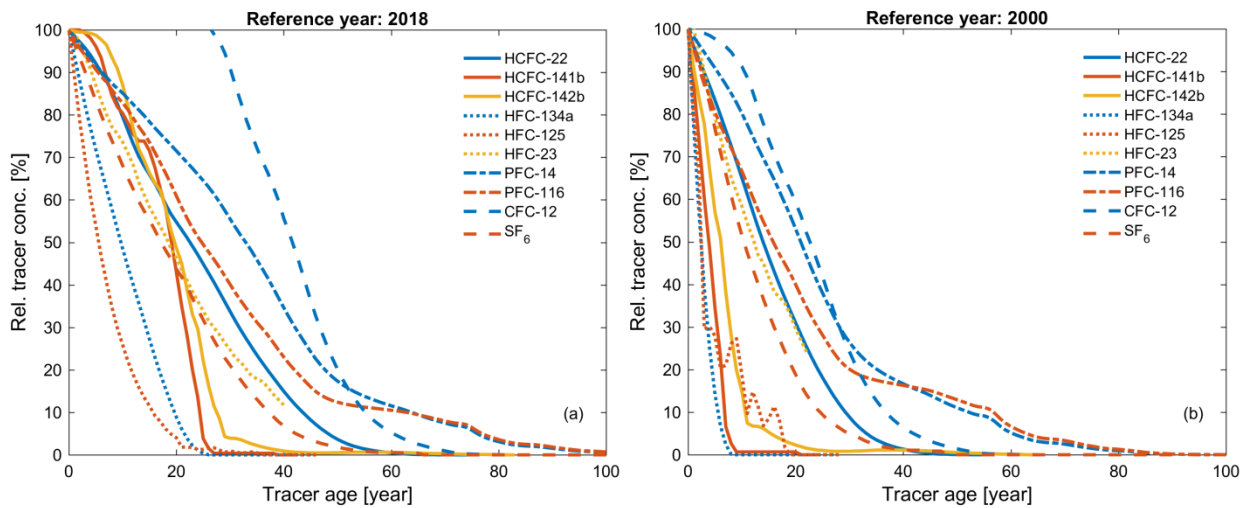
**Figure 3.** Locations of sampling sites from (a) cruise MSM72 in the Mediterranean Sea in three areas: the Southern Ionian Sea (SIS), the Tyrrhenian Sea (TS) and the Western Mediterranean Sea (WMS), and (b) cruise AL516 in the Baltic Sea. Sampling sites in red solid circles indicate samples measured by the Medusa-Aqua system for HCFCs, HFCs, PFCs and CFC-12, blue solid circles were for CFC-12 and SF<sub>6</sub> 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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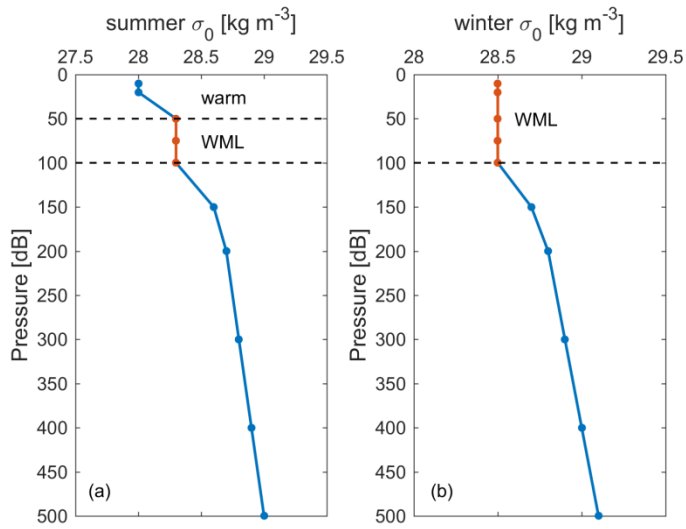
**Figure 4.** Atmospheric histories of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12 and SF<sub>6</sub> in the Northern Hemisphere. HCFC-22, HFC-134a, PFC-14, and CFC-12 share the left y-axis scale; other compounds share the right y-axis scale.

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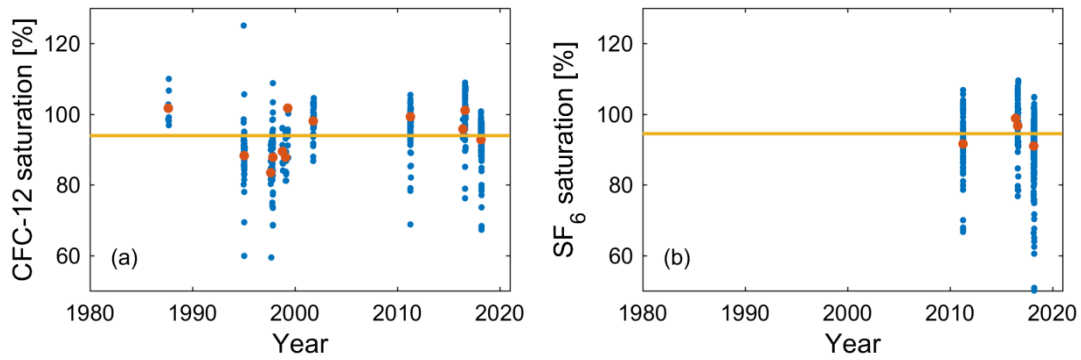


**Figure 5.** Relative tracer concentrations in percent (i.e. normalized to the contemporaneous atmospheric concentrations) and corresponding tracer age for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116, CFC-12, and SF<sub>6</sub> in the Northern Hemisphere for two sampling years: (a) 2018 and (b) 2000.

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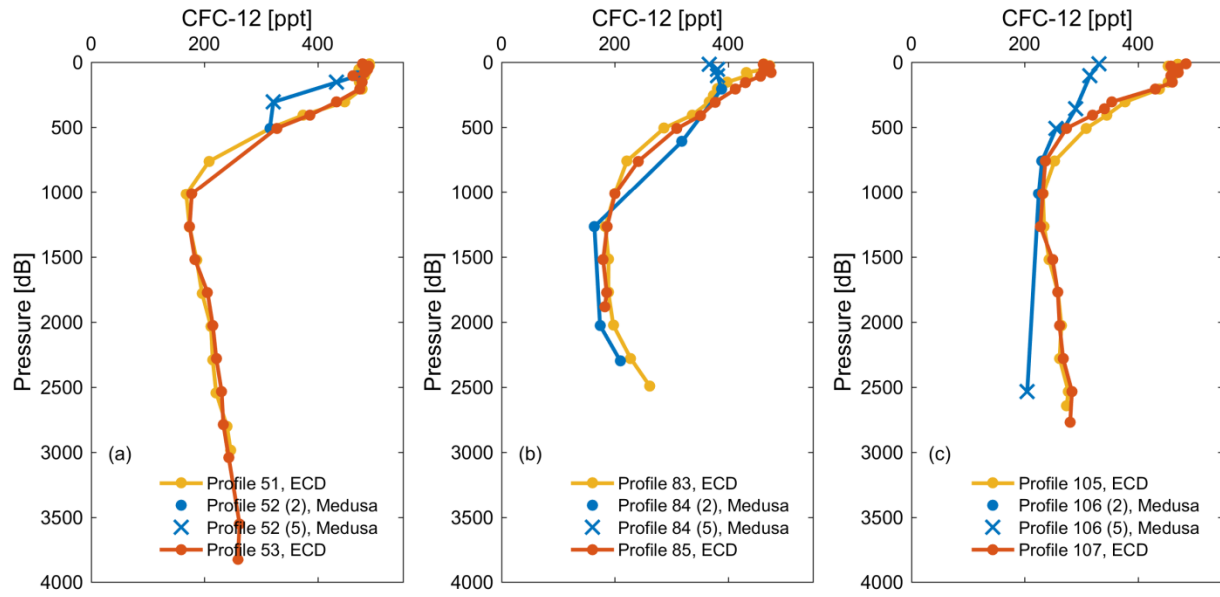


**Figure 6.** Example of the winter mixed layer (WML) depth (marked as red) determined in (a) summer and (b) winter in potential density ( $\sigma_0$ ) profiles especially for historical surface saturation calculation.

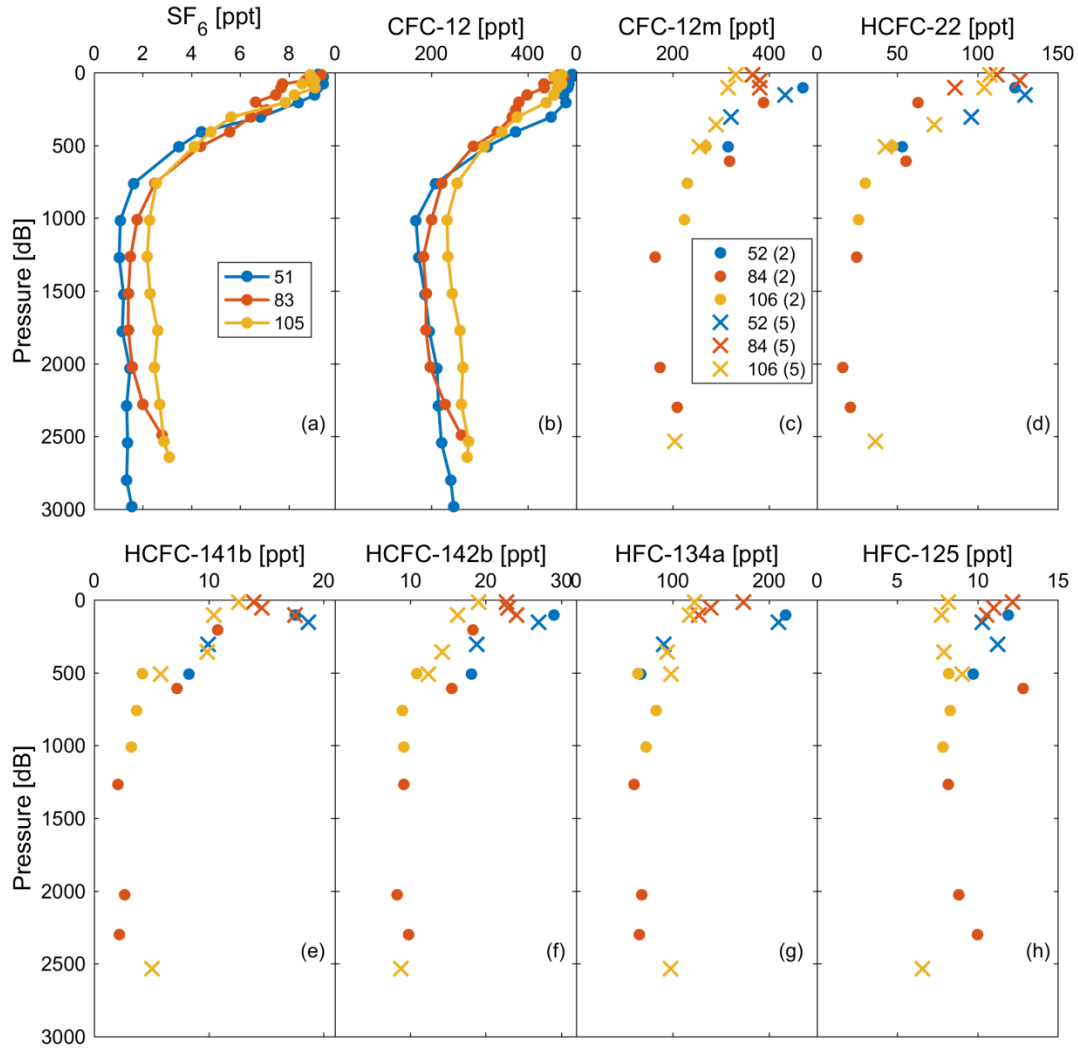


**Figure 7.** Historical surface saturations in winter mixed layers (blue solid circles) for (a) CFC-12 from 12 cruises in 1987-2018 and (b) SF<sub>6</sub> from 4 cruises in the Mediterranean Sea. Red solid circles denote the means of seawater saturation for each cruise and the yellow lines (94 %) are the mean of averaged seawater saturation of every cruise.

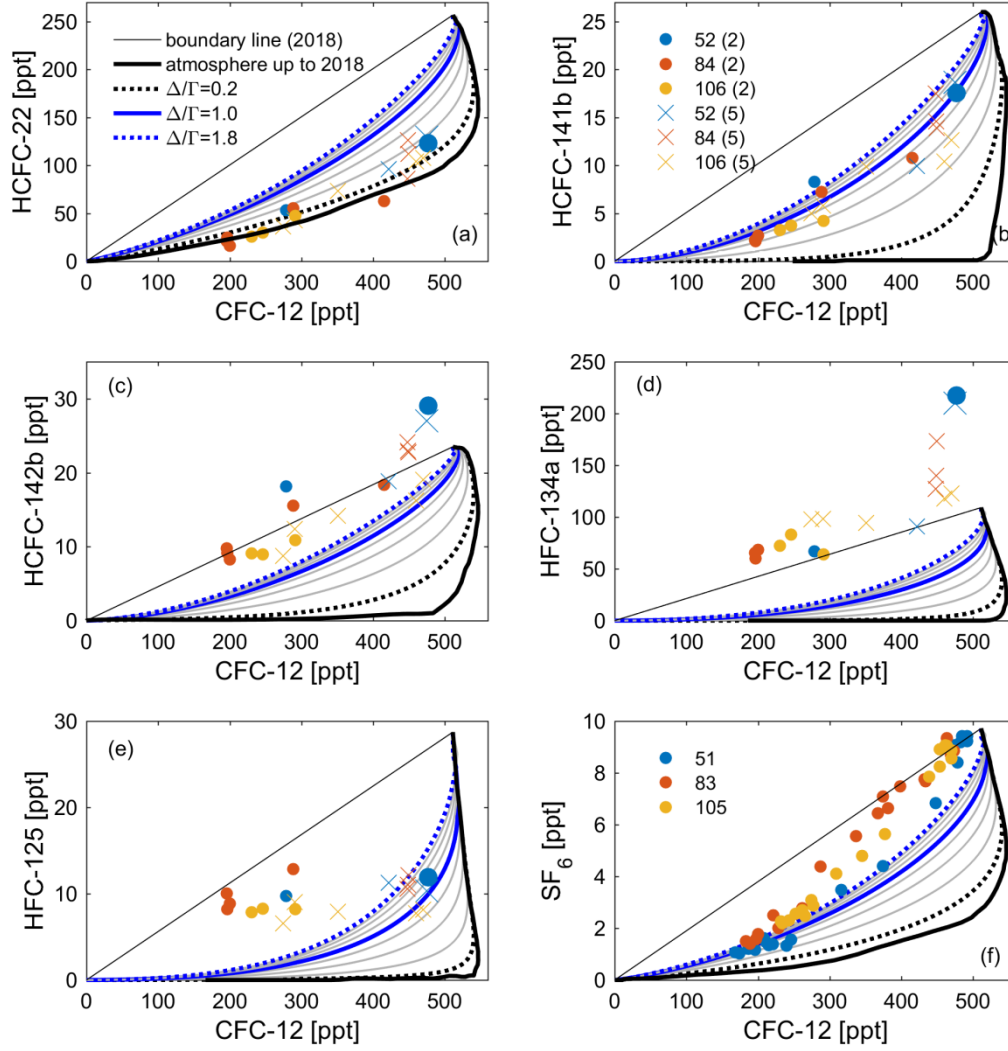
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**Figure 8.** Comparison of CFC-12 observations from cruise MSM72 measured by the PT-GC-ECD (ECD) and the Medusa-Aqua system (Medusa) in three areas: (a) the Southern Ionian Sea, (b) the Tyrrhenian Sea and (c) the Western Mediterranean Sea. We used normal quality control routines and flagged outliers as probably bad (“3” in Table S6), 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 9.** Observations of (a) SF<sub>6</sub> and (b) CFC-12 in profiles 51, 83 and 105 measured by the PT-GC-ECD and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 measured by the Medusa-Aqua system. For the explanation of (2), (5), dots and crosses, refer to Fig. 8.



**Figure 10.** Observations of (a) HCFC-22, (b) HCFC-141b, (c) HCFC-142b, (d) HFC-134a and (e) HFC-125 in profiles 52, 84 and 106 measured by Medusa-Aqua system and (f) SF<sub>6</sub> in profiles 51, 83 and 105 measured by PT-GC-ECD plotted against the (interpolated) CFC-12 based on measurements by PT-GC-ECD. The thick black line is the atmospheric history of the tracer pair ( $\Delta/\Gamma = 0.0$ ) and the thin black line is the theoretical mixing line between contemporary and pre-industrial concentrations. The theoretical mixing lines assuming an Inverse Gaussian TTD (Sect. S4 and Fig. S9) with  $\Delta/\Gamma = 0.2$ –1.8 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.

**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 <sup>-1</sup> )	Precision <sup>a</sup> (%)
SF <sub>6</sub>	SF <sub>6</sub>	sulfur hexafluoride	SIO-05	0.37	0.48	--
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	dichlorodifluoromethane	SIO-05	0.08	29.83	0.4
HCFC-22	CHClF <sub>2</sub>	chlorodifluoromethane	SIO-05	0.22	13.75	3.1
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	1,1-dichloro-1-fluoroethane	SIO-05	0.20	4.01	6.1
HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	1-chloro-1,1-difluoroethane	SIO-05	0.21	3.24	1.8
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	1,1,1,2-tetrafluoroethane	SIO-05	0.21	7.31	9.7
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	pentafluoroethane	SIO-14	0.23	1.19	2.0
HFC-23	CHF <sub>3</sub>	fluoroform	SIO-07	0.49	6.71	--
PFC-14	CF <sub>4</sub>	carbon tetrafluoride	SIO-05	0.30	0.44	--
PFC-116	CF <sub>3</sub> CF <sub>3</sub>	hexafluoroethane	SIO-07	0.32	1.41	--

5 <sup>a</sup> Precision (reproducibility, 1 $\sigma$ ) of tracers in seawater was determined by samples at 23.5 dbar from cruise AL516 in the Baltic Sea in September 2018.

**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 $\pm$ 0.5 <sup>a</sup>	99.2 $\pm$ 3.6 <sup>b</sup>	99.6 $\pm$ 0.1 <sup>c</sup>
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 <sub>6</sub> , SF <sub>5</sub> CF <sub>3</sub>	CFC-12, SF <sub>6</sub> , SF <sub>5</sub> CF <sub>3</sub>

<sup>a</sup> After purging three times; <sup>b</sup> After purging once; <sup>c</sup> After purging twice.

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**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 Medusa-Aqua system).

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

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**Table 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 transient tracer
CFC-12	*** <sup>a</sup>	***	***	***	***
HCFC-22	***	**	***	**	**
HCFC-141b	***	*	***	**	**
HCFC-142b	***	*	***	**	**
HFC-134a	***	**	**	*	*
HFC-125	***	*	*	*	*
HFC-23	**	**	*	*	*
PFC-14	***	**	*	***	**
PFC-116	***	*	*	***	**

<sup>a</sup> 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 ability of a compound as a transient tracer through current assessments.



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