Contents

Section S1. Stability of HCFCs and HFCs from the perspective of the partial atmospheric lifetime with respect to oceanic uptake

As indicated from previous studies (Yvon-Lewis and Butler, 2002; Carpenter et al., 2014), HCFCs and HFCs seem to be stable in seawater resulted from that their partial atmospheric lifetimes with respect to oceanic uptake ranged from thousands to millions of years (Table S1). Judged against their environmental total lifetimes, the oceanic contributions to these compounds are small enough to be neglected.

Table S1. Total lifetimes, partial atmospheric lifetimes with respect to oceanic uptake and ocean contributions for HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116

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

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

Table S2. Average surface saturation (%) of CFC-12, HCFC-22, and HCFC-142b from cruises BLAST III, GasEx98, PHASE1, and GOMECC

Cruise name	Sampling year	CFC-12	HCFC-22	HCFC-142b
BLAST III [a]	1996	-3.0 ± 10.4	21.6 ± 74.2	
GasEx98 [a]	1998	0.3 ± 5.8	7.6 ± 21.0	
PHASE1 [a]	2004	-22.8 ± 114.0	1.5 ± 6.7	
GOMECC [b]	2007	-0.4 ± 8.6	6.8 ± 108.7	6.0 ± 13.2

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

Section S2. Summary on biodegradation of selected HCFCs and HFCs in freshwater or soil

We used published information on biodegradation of compounds in freshwater or soil, which is the only biodegradation information related to the selected HCFCs and HFCs we could find in the seawater-related environment, although a compound can be degraded in the freshwater or soil but can still be stable in seawater, such as CFC-12. Chang and Criddle (1995), Oremland (1996), and Streger et al. (1999) observed the aerobic bacterial degradations of selected HCFCs and HFC-134a in very high oxygen concentrations and substrate levels (Table S3), and these aerobic microorganisms are common inhabitants of soil and aquatic systems. Although rapid removal in the soil can be an indication of non-conservative behavior in the ocean, the lifetime of a compound in soil or freshwater can be considerably shorter than in open ocean waters with few particles.

Table S3. Summary on biodegradation of selected HCFCs and HFCs in freshwater or soil

Microorganisms or culture	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-125	HFC-23	References
Methanotrophic bacterium *Methylosinus trichosporium OB3b (pure culture)*		√ [a]	x [b]	x			(DeFlaun et al., 1992) (Streger et al., 1999)
Mixed methanotrophic culture (MM1) with many heterotrophs	√		√	√			(Chang and Criddle, 1995)
Cell suspensions of M. capsulatus, methanotrophs in natural assemblages	√						(Oremland, 1996)
Methanotrophic mixed culture ENV2040		x	x				(Streger et al., 1999)
Unidentified methanotroph ENV2041		x	x	x			(Streger et al., 1999)
Propane-oxidizing bacteria, *M. vaccae JOB5*	x	√ (0.1 μmol h^{-1})	√	x	x	x	(Streger et al., 1999)
Methylococcus capsulatus (Bath)	√						(Matheson et al., 1997)
Aerobic condition closed bottle tests		x		x	x		(Berends et al., 1999)
Anoxic sediments		√					(Oremland, 1996)
Landfill soil	√ [c]	x		x			(Scheutz et al., 2004)
Anaerobic conditions in sewage sludge and aquifer sediment slurries	x	x	x	x			(Balsiger et al., 2005)

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

Section S3. Measurement of potential new tracers in seawater

Here is the supplementary information for the measurement of potential new tracers in seawater. Before the Medusa-Aqua system used for measurement of seawater samples from cruises MSM72 and AL516, it has been improved by updating carrier gases, the standard gas, and the quantitative tool of the standard gas (Fig. S1 and Table S4). Measurement reproducibility of compounds from different cruises can be found in Table S5. Phase I-V showed the data from different cruises and corresponded to the information in Table S4.

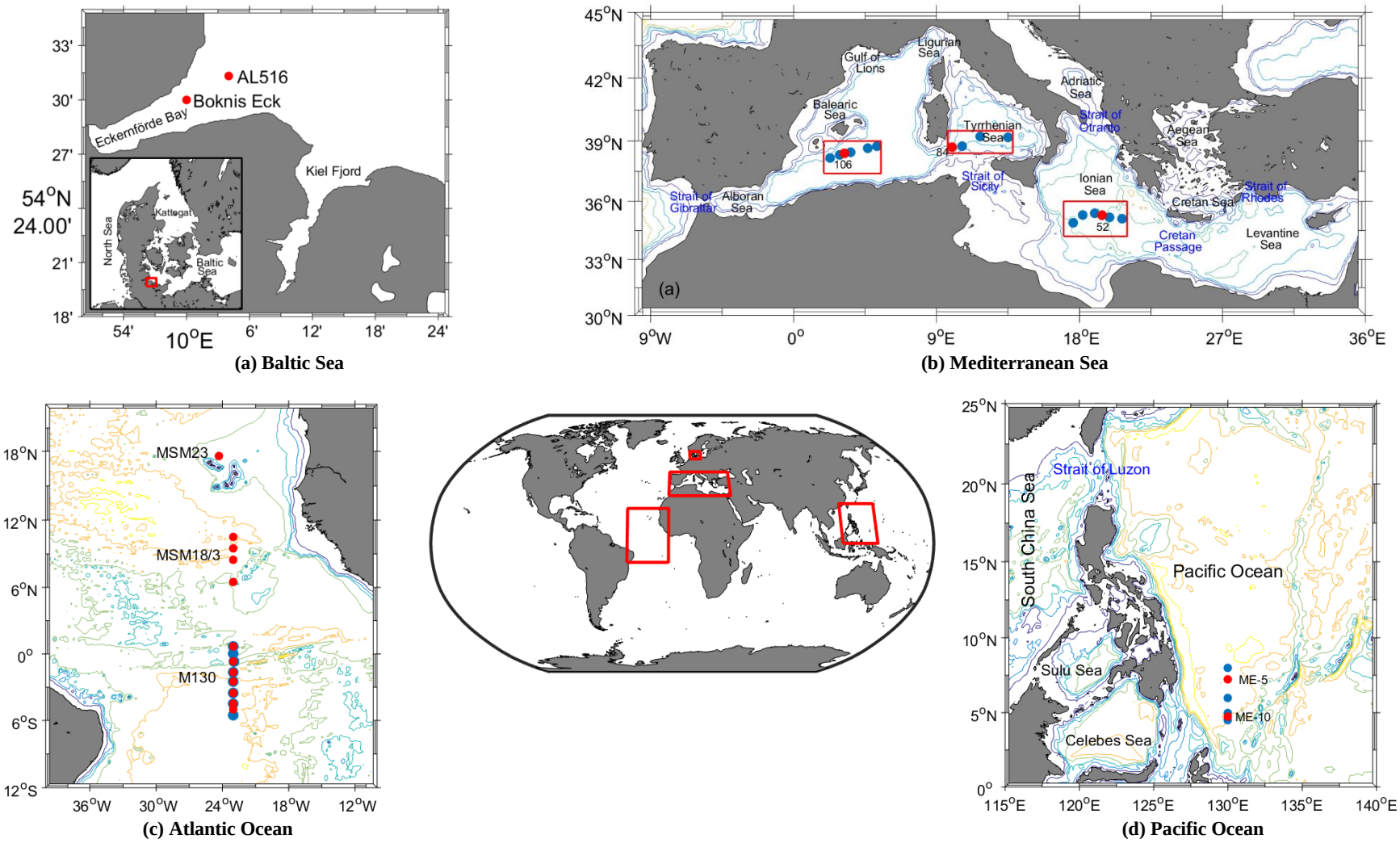


Figure S1. Locations of sampling sites from (a) cruises KBP524 (Boknis Eck) and AL516 in the Baltic Sea; (b) cruise MSM72 in the Mediterranean Sea; (c) cruises MSM23, MSM18/3, and M130 in the Atlantic Ocean; (d) cruise NORC2017-09 in the Pacific Ocean. Sampling sites in red solid circles indicate samples measured by the Medusa-Aqua system for HCFCs, HFCs, PFCs and CFC-12, blue solid circles were for CFC12 and SF_6 measured by the PT-GC-ECD. The depth contours are 500 m, 2000 m, 3000 m, 4000 m, 5000 m, and 6000 m.

Table S4. Improvement of the Medusa-Aqua system

Phase	Cruise name	Measured time	Sampling time	Area	Longitude (E)	Latitude (N)	Research Vessel	Carrier gas	Standard gas	MFC or std loop [a]	Sampling size (L)	Purpose
I	MSM18/3	2017.02-04	2011.06	Atlantic Ocean	-23.0	10.5, 9.5	Maria S. Merian	5.0 He, 5.0 N_2	natair [b]	MFC	~1.3	First seawater sample measurement
II	M130	2017.05-07	2016.09	Atlantic Ocean	-23.0	0.67, -0.67, -1.67, -2.5, -3.5, -4.5, -5.0, -5.5	Meteor	5.0 He, 5.0 N_2	natair	std loop	~1.3	Tested standard loop
III	KBP524	2017.11	2017.11	Baltic Sea	10.04	54.53	Littorina	6.0 He, 6.0 N_2	natair	MFC	~0.3	Updated carrier gases
IV	MSM18/3	2018.03	2011.06	Atlantic Ocean	-23.0	8.5, 6.5	Maria S. Merian	6.0 He, 6.0 N_2	Tanhua-2[c]	MFC	~1.3	Updated standard gas
	MSM23	2018.04	2012.12	Atlantic Ocean	-24.3	17.6	Maria S. Merian	6.0 He, 6.0 N_2	Tanhua-2	MFC	~1.3	
V	MSM72	2018.07	2018.03	Mediterranean Sea	(19.4, 35.3), (3.2, 38.4)	(9.98, 38.7),	Maria S. Merian	6.0 He, 6.0 N_2	Tanhua-2	std loop	~1.3	Updated the quantitative tool of standard gas
	NORC2017-09	2018.07-08	2017.10	Pacific Ocean	130	7.25, 4.75	Kexue	6.0 He, 6.0 N_2	Tanhua-2	std loop	~1.3	
	AL516	2018.10	2018.09	Baltic Sea	(10.067, 54.522)		Alkor	6.0 He, 6.0 N_2	Tanhua-2	std loop	~1.3	

[a] Standard gas is quantitated by the MFC (Mass Flow Controller) or the standard loop.

[b] natair (Natürliche Luft, PRÜFGAS, UN 1956, DEUSTE Steininger GmbH) calibrated by a tertiary standard (named "Tanhua_221") from SIO is used as the working standard. For the tracer gases in concern, CFCs, HCFCs, and PFCs are found in the natair, and CFC-12, SF_6, HCFCs, HFC-134a and PFC-14 are found in the tertiary standard.

[c] a new tertiary standard gas including CFCs, HCFCs and PFCs. The two tertiary standard gases can be propagated to the same primary standard by the AGAGE relative scale "SIO-R1".

Table S5. Measurement reproducibility [a] (Relative Standard Deviation, RSD) of concentrations for compounds from

(a) Cruise M130 on two profiles (1104 and 1106) at ~10 m (5.0 He, 5.0 N_2, ~1.3 L ampoule, calibrated natair)

Reproducibility	CFC-12
1104, -5.0 N (%)	0.34
1106, -5.5 N (%)	1.4

(b) Cruise AL516 at 23.5 m (6.0 He, 6.0 N_2, ~1.3 L ampoule, Tanhua-2)

Reproducibility	CFC-12	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-125
RSD (%)	0.36	3.1	6.1	1.8	9.7	2.0

[a] Reproducibility (or precision) for seawater sample measurements were determined by the relative standard deviations (1σ) of the concentrations for two pairs of duplicate samples.

Table S6. Historical cruises from the Atlantic Ocean used in this study for CFC-12 comparison in Figs. S2-S5.

Year	Expocode	Start Date	End Date	Cruise	CFC-12/SF_6	PI
2006	06MT20060606	2006.06.06	2006.07.09	M68/2	CFC-12	P. Brandt
2008	06MT20081031	2008.10.31	2008.12.06	MSM10/1	CFC-12	M. Visbeck
2009	06MT200910.26	2009.10.26	2009.11.23	M80/1	CFC-12	P. Brandt
2009	06MT20091126	2009.11.26	2009.12.22	M80/2	CFC-12, SF_6	D. Wallace
2010	06MT20101014	2010.10.14	2010.11.13	M83/1	CFC-12	T. Tanhua
2011	06M220110622	2011.06.22	2011.07.21	MSM18/3	CFC-12m	A. Körtzinger
2012	06M220121126	2012.11.26	2012.12.20	MSM23	CFC-12m	M. Visbeck
2013	06MT20130525	2013.05.25	2013.06.28	M97	CFC-12	T. Tanhua
2014	06MT20140317	2014.03.17	2014.04.16	M105	CFC-12	T. Tanhua
2016	06MT20160930	2016.08.25	2016.09.30	M130	CFC-12(m), SF_6	T. Stöven

Phase I: MSM18/3 (10.5°N and 9.5°N)

(5.0 He, 5.0 N_2, natair, MFC, ~1.3L, first seawater sample measurement)

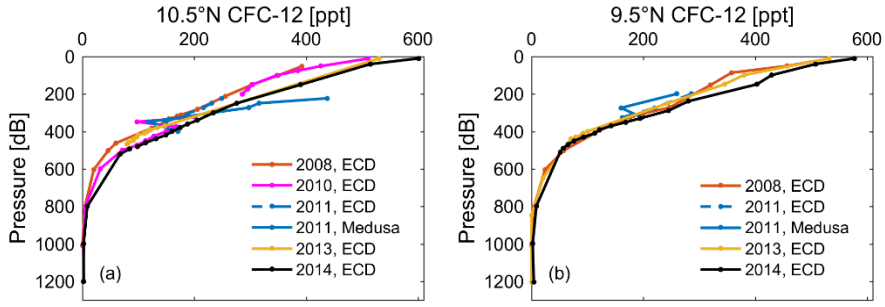


Figure S2. Comparison of observed concentrations (ppt) of CFC-12 measured by PT-GC-ECD from historical cruises in Table S6 and by Medusa-GC-MS from cruise MSM18/3 (10.5°N and 9.5°N).

Phase II: M130

(5.0 He, 5.0 N_2, natair, std loop, ~1.3L, tested standard loop)

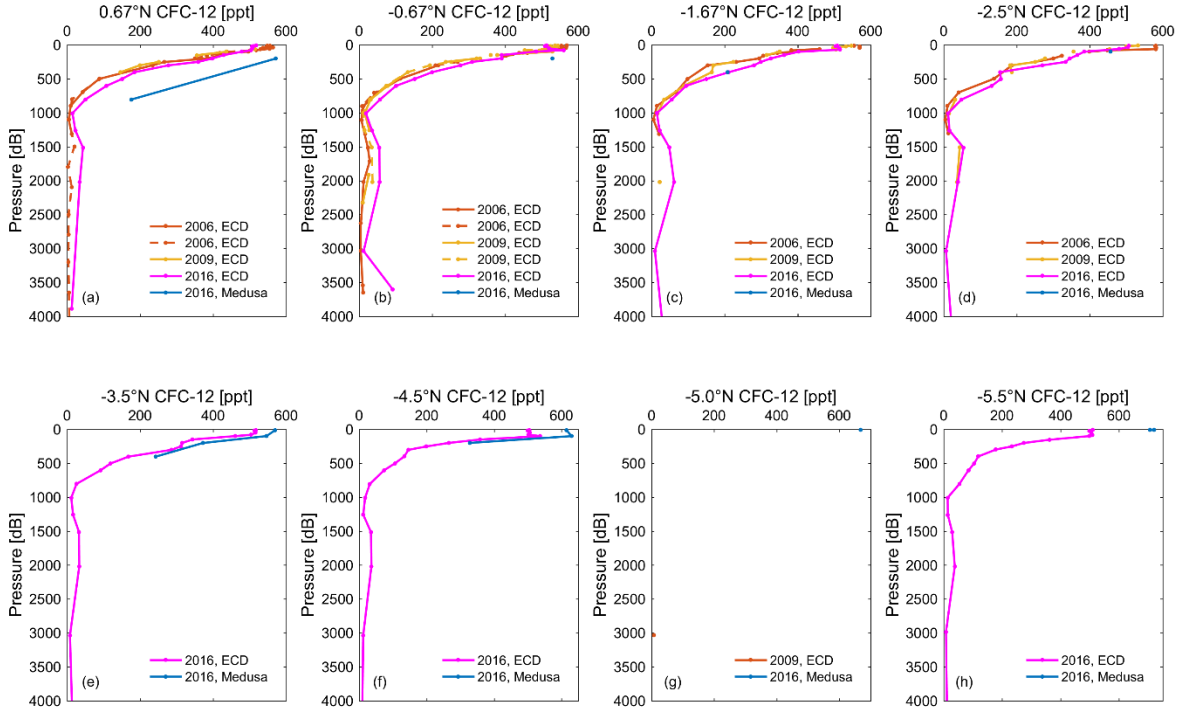


Figure S3. Comparison of observed concentrations (ppt) of CFC-12 measured by PT-GC-ECD from historical cruises in Table S6 and current cruise and by Medusa-GC-MS from cruise M130.

Phase IV: MSM18/3 (8.5°N and 6.5°N) and MSM23

(6.0 He, 6.0 N_2, Tanhua-2, MFC, ~1.3L, updated standard gas)

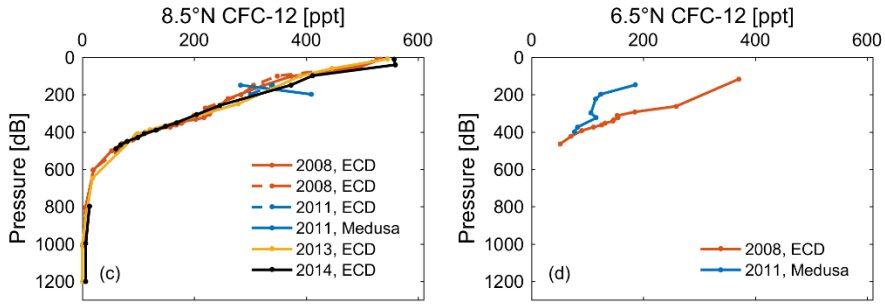


Figure S4. Comparison of observed concentrations (ppt) of CFC-12 measured by PT-GC-ECD from historical cruises in Table S6 and by Medusa-GC-MS from cruise MSM18/3 (8.5°N and 6.5°N).

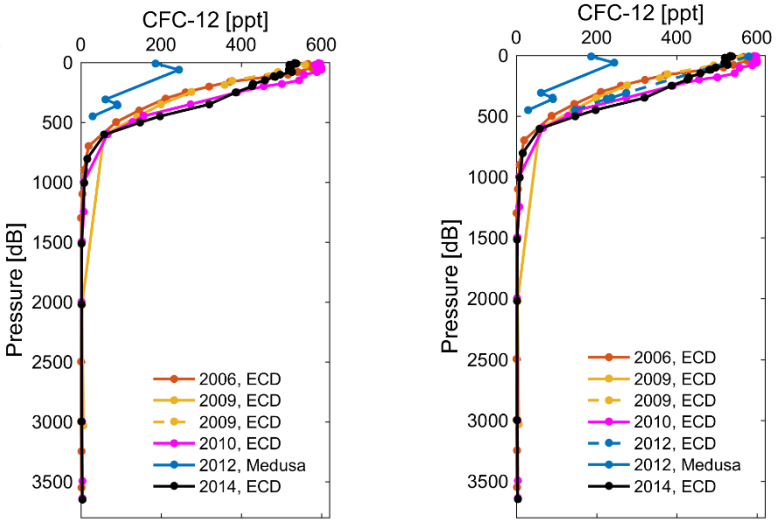


Figure S5. Comparison of observed concentrations (ppt) of CFC-12 measured by PT-GC-ECD from historical cruises in Table S6 and by Medusa-GC-MS from cruise MSM23.

Phase V: MSM72, NORC2017-09 and AL516

(6.0 He, 6.0 N_2, Tanhua-2, std loop, ~1.3L, updated the quantitative tool of standard gas)

For cruise NORC2017-09, except for CFC-12 and HCFC-142b, all other compounds were polluted in the sampling processes.

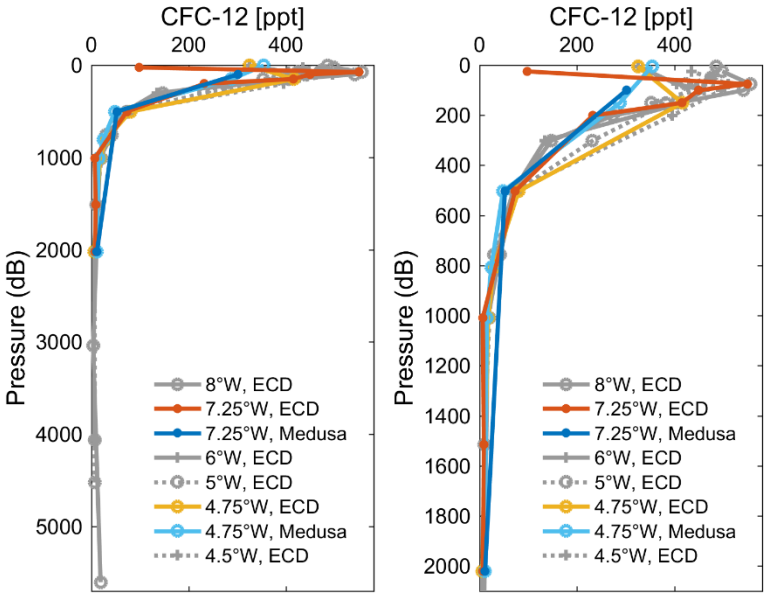


Figure S6. CFC-12 observations (ppt) measured by PT-GC-ECD (ECD) and Medusa-GC-MS (Medusa) from cruise NORC2017-09. Two plots are the same with the only difference (a) Pressure 0-6000 dbar, (b) Pressure 0-2000 dbar.

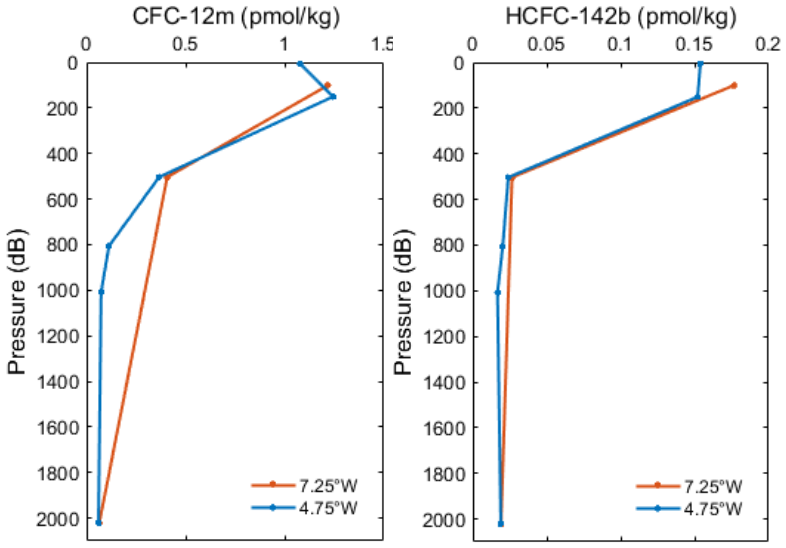
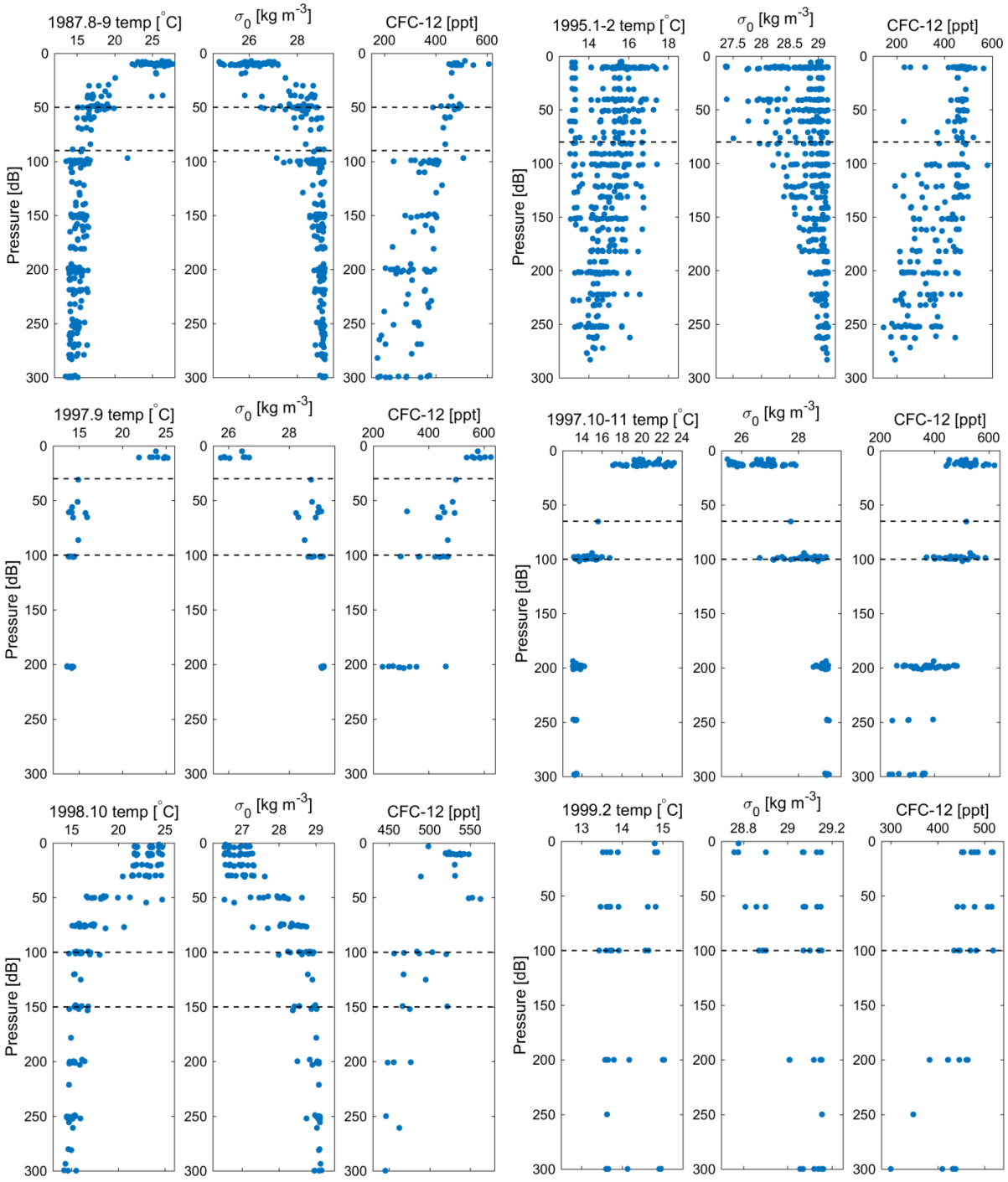


Figure S7. Observations (pmol/kg) of CFC-12 and HCFC-142b measured by Medusa-GC-MS from cruise NORC-201709.


1987.8-9 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1995.1-2 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1997.9 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1997.10-11 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1998.10 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
1999.2 temp [°C]
σ0 [kg m-3]
CFC-12 [ppt]
Pressure [dB]

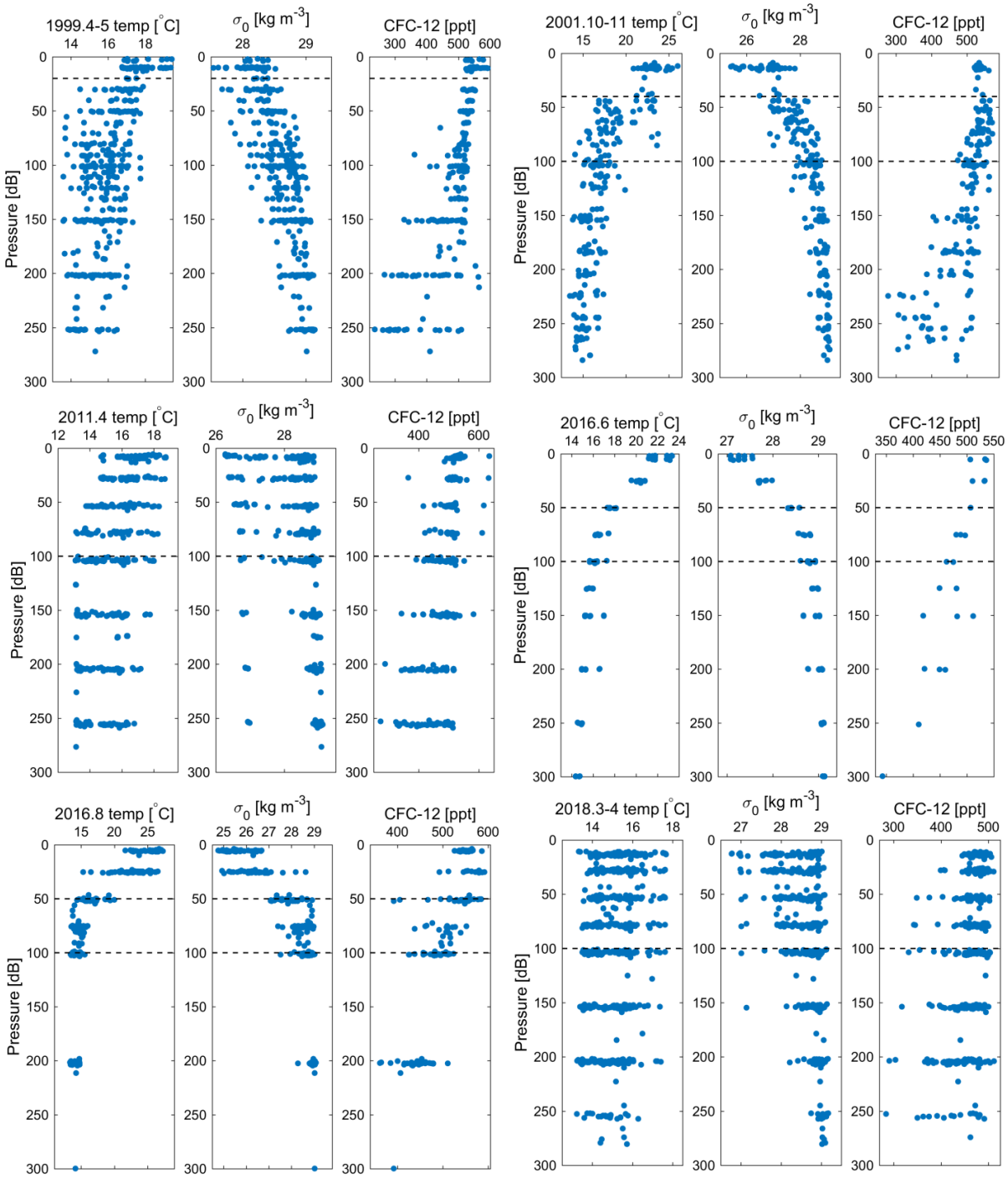


Figure S8. Profiles of temperature, potential density and concentrations of CFC-12 for each historical cruise in the Mediterranean Sea to determine the depth ranges of winter mixed layers.

Section S4. Transit Time Distribution (TTD) and mean age

We used a conceptual but well-established ocean ventilation model, the Transit Time Distribution (TTD) model that is based on the Green's function $G(t,r)$ describing the propagation of tracer boundary conditions into the interior (Hall and Plumb, 1994). As shown in Eq. (S1), $c(t_s,r)$ describe the concentration of a transient tracer at year t_s and location r. The boundary concentration $c_0(t_s,r)$ is the concentration at source year $(t_s - t)$ related to the tracer input function, while the exponential term $(e^{-\lambda t})$ describes the decay rate of radioactive transient tracers. This function is based on a steady and one-dimensional flow model with time-invariant advective velocity and diffusivity gradient. One commonly used solution to Eq. (S1) is the one-dimensional Inverse Gaussian Transit Time Distribution (IG-TTD), simplified and expressed as Eq. (S2). $G(t)$ is defined based on the mean age Γ, the width of the distribution Δ and the time range t (Waugh et al., 2003).

$$c(t_s,r) = \int_0^\infty c_0(t_s - t)e^{-\lambda t} \cdot G(t,r)dt \quad \text{(S1)}$$

$$G(t) = \sqrt{\frac{\Gamma^3}{4\pi\Delta^2 t^3}} \cdot \exp\left(\frac{-\Gamma(t-\Gamma)^2}{4\Delta^2 t}\right) \quad \text{(S2)}$$

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

The mean age, calculated as the average of the TTD, can be used as an estimate of the age of a water parcel based on a combination of advective and mixing flow in the ocean. Assuming an IG-TTD, the theoretical tracer concentrations $c(t_s,r)$ for a range of Δ/Γ ratios (0.2-1.8) based on Eqs. (S1) and (S2) have been calculated for the Medusa tracers (Fig. S9). Figure S10 shows the mean age matrices of Δ/Γ = 1.0 (the blue lines in Fig. S9) for each Medusa tracer and describes the expected tracer concentration as a function of different mean ages and sampling years. More complicated or different TTDs than the IG-TTD can also be assumed, and if the observed concentrations match the theoretical tracer concentrations for a range of tracers with different input functions it is an indication that the assumption is valid.

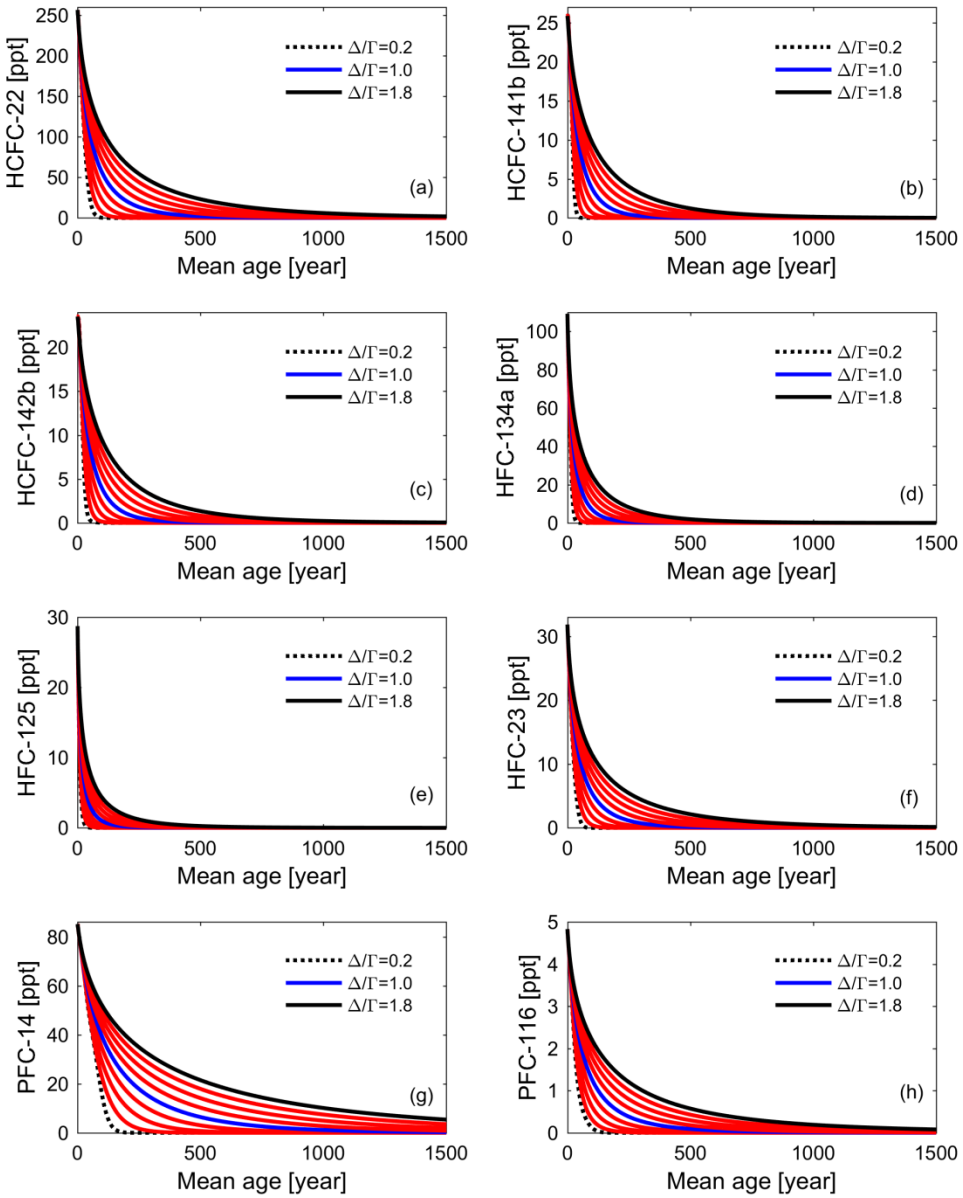
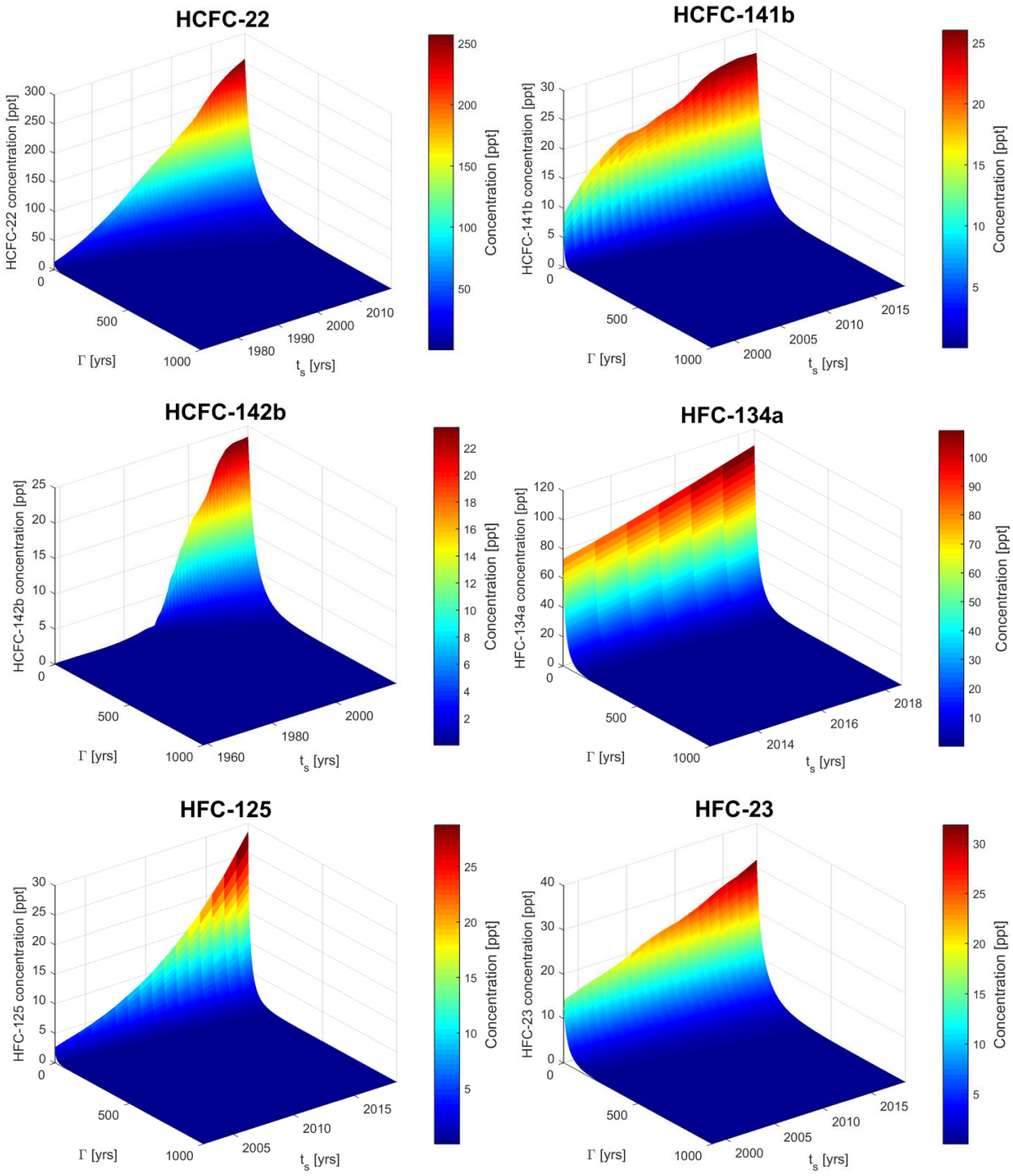


Figure S9. Transient tracer concentrations (ppt, parts per trillion) of HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116 vs. mean age for different Δ/Γ ratios (a range of 0.2-1.8) in the Northern Hemisphere. The unity ratio of 1.0 is shown as a blue line.


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

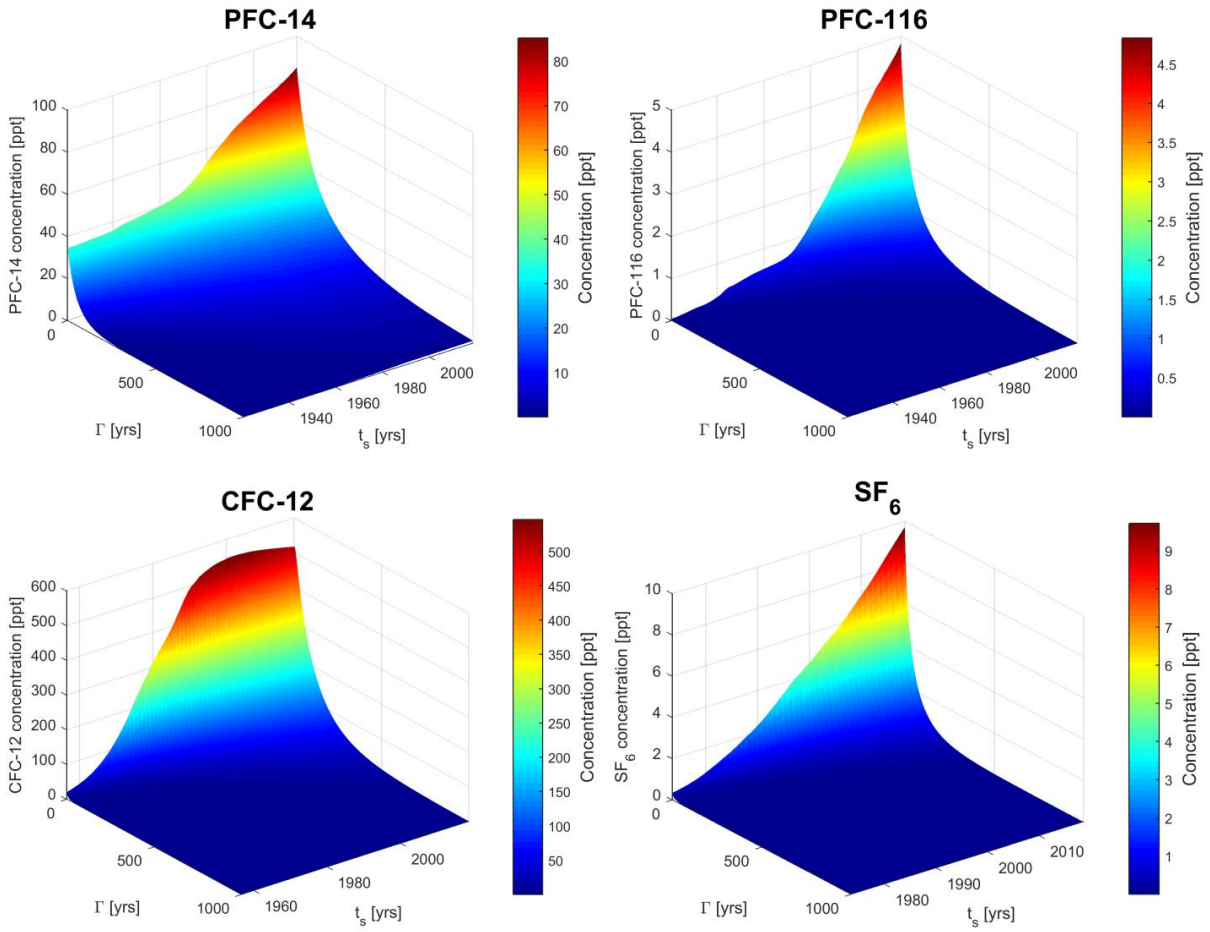


Figure S10. HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14, PFC-116 CFC-12 and SF_6: concentrations (ppt) in different sampling year (t_s) and mean age (**Γ**) in the Northern Hemisphere with **Δ/Γ** = 1.0 based on the IG-TTD with 100 % saturation.

Section S5. Comparison of mean age estimates

In order to compare the mean ages estimated from HCFCs and HFCs with those estimated from CFC-12 and SF_6, we calculated the mean ages of these tracers (Fig. S11) based on the method described in Sect. S4 and Figs. S9-S10. Here we assumed the Δ/Γ ratio of IG-TTD to be 1.0 and the saturation of all traces to be 94 % (see Sect. 5.1). However, the TTD of the Mediterranean Sea is complicated by the variable ventilation and the influence of different source regions for interior water, see Stöven and Tanhua (2014). While the assumption of an IG-TTD with Δ/Γ = 1.0 can be questioned, it can still serve as an initial assumption to evaluate the new tracers. Note that the mean ages calculated from CFC-12 and SF_6 are not identical, although we have high confidence in these data. Therefore, even though the assumptions made on the TTD are not entirely correct, they are a reasonable starting point for the goal of this study.

The mean age estimated from HCFC-141b is similar to (slightly higher than) those from CFC-12 and SF_6, whereas the mean age estimated from HCFC-22 is higher while the mean ages from HCFC-142b, HFC-134a and HFC-125 are significantly lower. If the mean age is lower than expected, it implies that the concentration is probably higher than expected (Fig. 10) and vice-versa. There are different possible explanations for the difference in mean ages. One obvious explanation is uncertainty in the Δ/Γ ratio of TTD that will affect tracers with different input functions differently. Other possible explanations include uncertainty in the solubility function (Li et al., 2019) or analytical error.

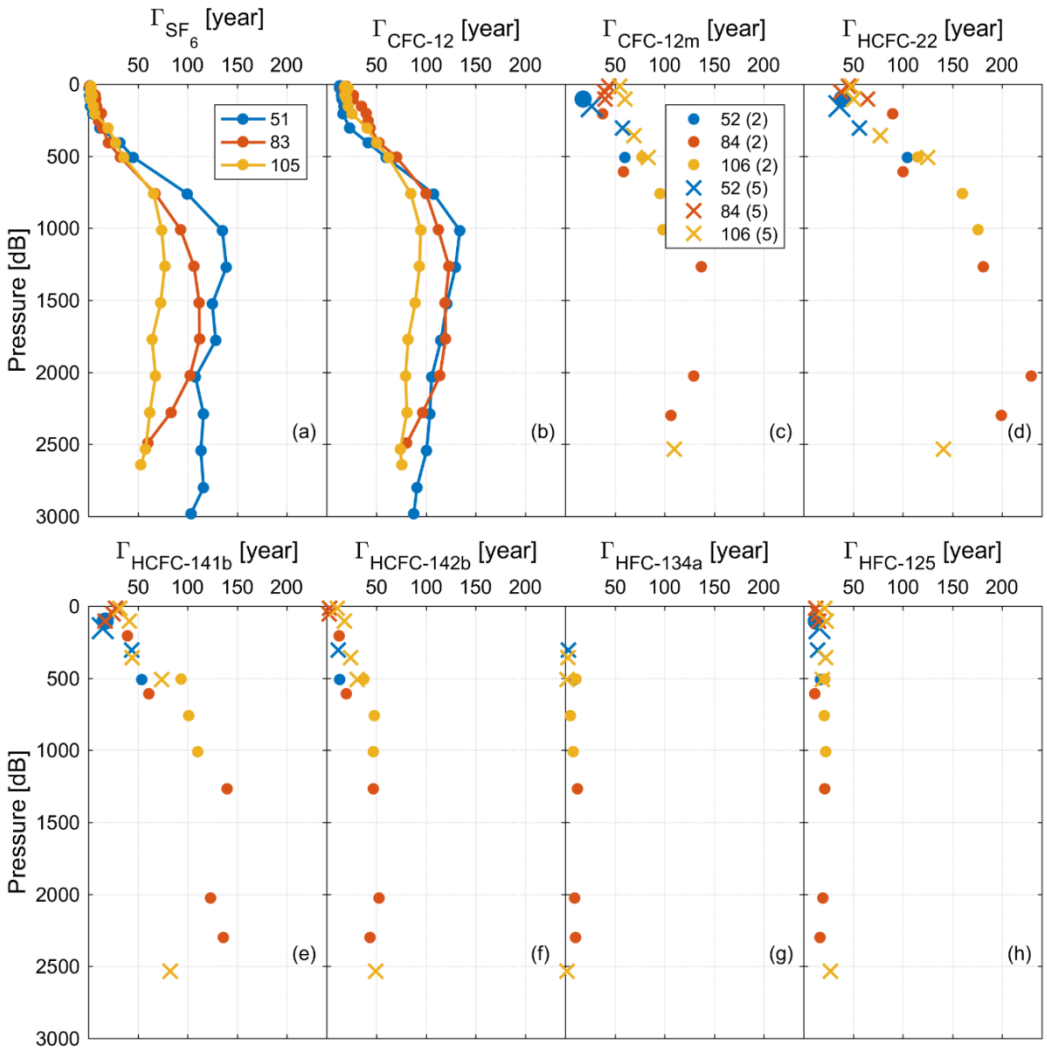


Figure S11. Mean age estimated from (a) SF_6 and (b) CFC-12 in profiles 51, 83 and 105 and (c) CFC-12 (marked as CFC-12m), (d) HCFC-22, (e) HCFC-141b, (f) HCFC-142b, (g) HFC-134a and (h) HFC-125 in profiles 52, 84 and 106 based on Δ/Γ = 1.0 of IG-TTD. The values of the top two points of profile 52 are marked with a bigger size. For the explanation of (2), (5), dots and crosses, refer to Fig. 4.

Table S7. Bottle data of SF_6 and CFC-12 in stations 51, 53, 83, 85, 105 and 107 from cruise MSM72 measured by the PT-GC-ECD and CFC-12, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a and HFC-125 in stations 52, 84 and 106 from cruise MSM72 and profile 30 from cruise AL516 measured by the Medusa-Aqua system (see the Excel file) [a]

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

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

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