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Comparison of Time-Dependent Tracer Ages in the Western North Pacific: Oceanic Background Levels of SF_6, CFC-11, CFC-12 and CFC-113

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To verify the actual usefulness of time-dependent tracer dating techniques in the ocean, we simultaneously obtained two cross sections of sulfur hexafluoride (SF_6) and chlrofluoromethanes (CFC-11, trichlorofluoromethane; CFC-12, dichlorodifluromethane; CFC-113, trichlorotrifluoroethane) in the western North Pacific in 1998. The vertical distribution patterns of SF_6 and CFC-113 were similar in shape to those of CFC-11 and CFC-12. Maximum penetration depths of SF_6 and CFC-113 remained around 800 m in the subpolar region and 400 m in the tropical region, while the maximum penetration depths of CFC-11 and CFC-12 were still found below 1000 m depth. We also found all maximum contents of these tracers around 26.6–26.8σ_θ with a gradual decrease southward. This suggested that a new subsurface water mass in the subpolar region spread out over the entire North Pacific, which agrees closely with previous studies based on the salinity minimum. Moreover, we compared the tracer ages (the elapsed period of a water mass from when the water mass left from the ocean surface) using ten time-dependent tracer dating techniques, CFC-11, CFC-12, CFC-113, SF_6, CFC-11/CFC-12, CFC-113/CFC-11, CFC-113/CFC-12, SF_6/CFC-11, SF_6/CFC-12 and SF_6/CFC-113. This quantitative evaluation of multiple tracer dating techniques in the ocean was the first confirmation of its usefulness based on the observational data on the ocean basin-wide scale. We conclude that SF_6/CFC-11, SF_6/CFC-12, SF_6/CFC-113 and SF_6 dating techniques would be the most promising tools for determining the age of water mass not only just for the past several decades but for the future, too.

Keywords:
· Sulfur hexafluoride,
· trichloro-trifluoroethane,
· tracer dating techniques,
· western North Pacific.

1. Introduction

The chlorofluromethanes (CFC), CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are important tools to clarify the behavior of water masses, and they have been used in extensive field surveys to study water movements such as the World Ocean Circulation Experiment (WOCE, 1999). Using the observed oceanic CFC-11/CFC-12 with its atmospheric time history and solubilities, we can evaluate the apparent formation year and tracer ages (apparent ages) of water mass from when the water mass left the surface during the past several decades (Smethie *et al.*, 1988). In addition, we can also use CFC partial pressure dating techniques to estimate tracer ages, with their atmospheric time history and solubilities (Doney and Bullister, 1992). Many recent studies have been carried out, estimating tracer ages from the above dating techniques, to elucidate the behavior of water masses and the amount of oceanic anthropogenic carbon, and to validate model calculations (e.g., Watanabe *et al.*, 1994, 2000; Gruber *et al.*, 1996; Warner *et al.*, 1996; Doney *et al.*, 1997). These dating techniques have greatly contributed to the advance of oceanography.

Unfortunately, using the ratio and/or the partial pressure dating techniques is associated with two problems, not only just for the past two decades but also the future. (1) The increasing rate of CFC-11/CFC-12 in the atmosphere already appears to be constant and/or decreasing after the end of 1970s (Walker *et al.*, 2000). It is thus difficult to apply the CFC-11/CFC-12 dating technique to any water mass produced after the end of 1970s.

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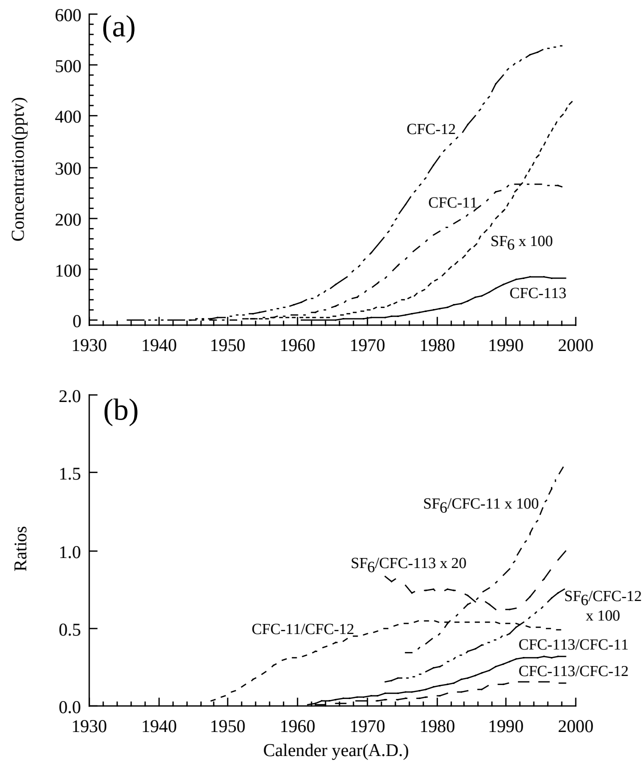


Fig. 1. Atmospheric time history of SF_6 and CFC. (a) Concentrations of SF_6, CFC-11, CFC-12 and CFC-113 (pptv). (b) Ratios of CFC-11/CFC-12, CFC-113/CFC-11, CFC-113/CFC-12, SF_6/CFC-11, SF_6/CFC-12 and SF_6/CFC-113. These figures are based on Walker *et al*. (2000), Maiss and Brenninkmeijer (1998), and Bullister *et al*. (2002).

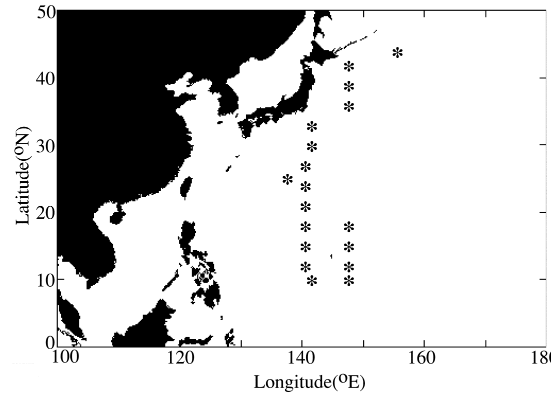


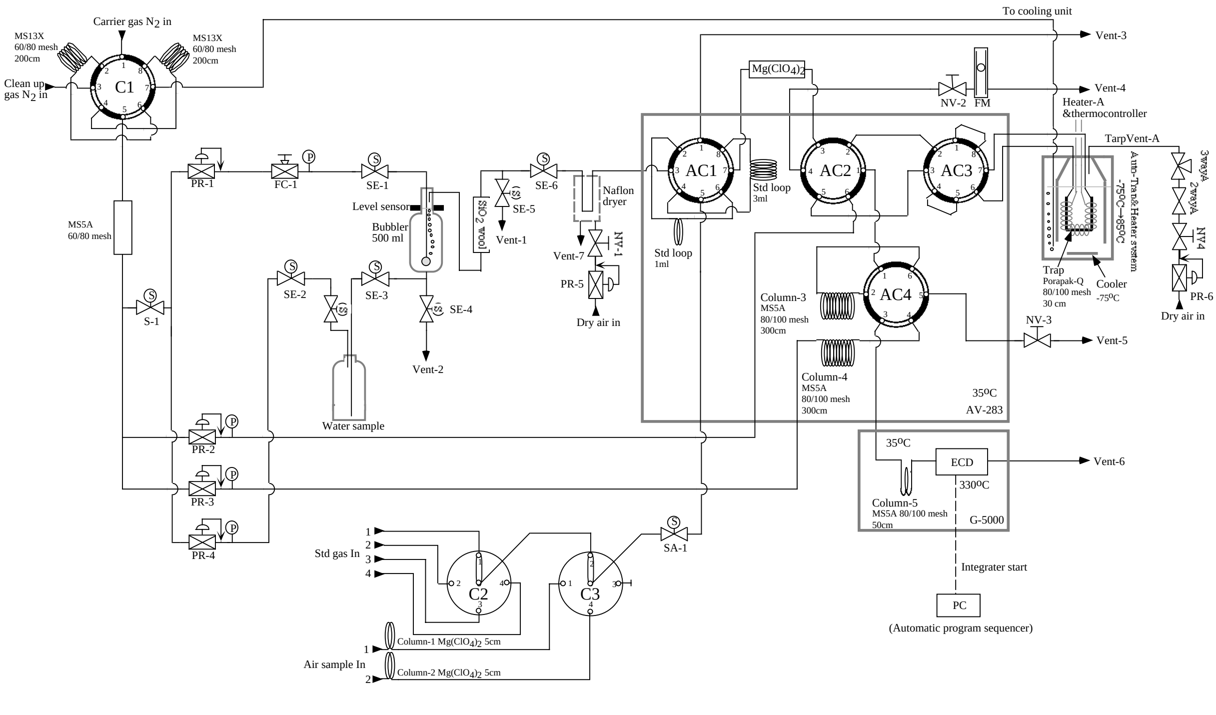
Fig. 2. Sampling locations for SF_6 and CFC in the western North Pacific.

(2) Moreover, due to the world-wide ban on the production of CFC in industrial countries, the atmospheric increasing rate of CFC after the mid-1990s almost would have been almost constant and/or gradually decrease. Thus it is almost impossible to use only CFC partial pressure dating techniques to get tracer ages in the future (Walker *et al*., 2000).

To solve the first problem, it is useful to apply CFC-113/CFC-11 and/or CFC-113/CFC-12 dating techniques (Fig. 1) (Wisegarver and Gammon, 1988). CFC-113 ($C_2Cl_3F_3$) is an artificial product used as a solvent in the electronics industry. The atmospheric residence time of CFC-113 is about 90 years and its concentration has increased with time after 1970 and decreased since the mid-1990s (Walker *et al*., 2000). It enters the ocean by gas exchange and is not affected by chemical and biological activities since it is an inert gas. Thus CFC-113 is available as a third CFC tracer in addition to CFC-11 and CFC-12. Unfortunately it is difficult to determine the oceanic content of CFC-113 due to its lower concentration than CFC-11 and CFC-12. Thus only a few studies have been done to elucidate water movement using CFC-113 (Wisegarver and Gammon, 1988). Despite the recent atmospheric decrease of CFC-113 due to a ban on its production, it is still important in obtaining the tracer age of water masses during the past two decades.

To overcome the first and/or second problems, it is essential to use SF_6 as a potential time-dependent ocean tracer (Law *et al*., 1994). The atmospheric residence time is 3200 years, which is longer than those of CFC (Ravishankara *et al*., 1993), and its concentration has been rapidly increasing with time after 1970s (Fig. 1(a)) (Bullister *et al*., 2002). It is also an inert gas and is not affected by oceanic chemical and biological activities. Despite a recent slowdown in the rate of increase of SF_6 in the atmosphere, SF_6/CFC has continued to increase (Fig. 1(b)). Thus SF_6 also would be a useful time-dependent tracer. While many experiments have used an artificial release of SF_6 to determine the oceanic horizontal-vertical diffusivities, and/or the piston velocity in the ocean or a lake (Wanninkhof *et al*., 1985; Upstill-Goddard *et al*., 1990; Ledwell and Watson, 1991; Watson *et al*., 1991), there have been a few studies to estimate water movement by using the background level of SF_6 because it was difficult to determine SF_6 due to its lower concentration than CFC of the order of a few thousand-fold (Watson and Liddicoat, 1985; Law *et al*., 1994).

To verify the usefulness of the above dating techniques, it is necessary simultaneously to determine SF_6 and CFC-113 with CFC-11 and CFC-12 in the ocean, and to compare the tracer ages with each other. The only previous study reported the results of multiple tracer ages in the Persian Gulf, but it addressed only local conditions and did not show the SF_6 partial pressure dating technique (Law and Watson, 2001). Unfortunately, there are no examples of the simultaneous and extensive observation of SF_6, CFC-113, CFC-11 and CFC-12. We here have simultaneously tried to measure these time-dependent (a)SF_6



(b) CFCs (CFC-11, CFC-12, CFC-113)

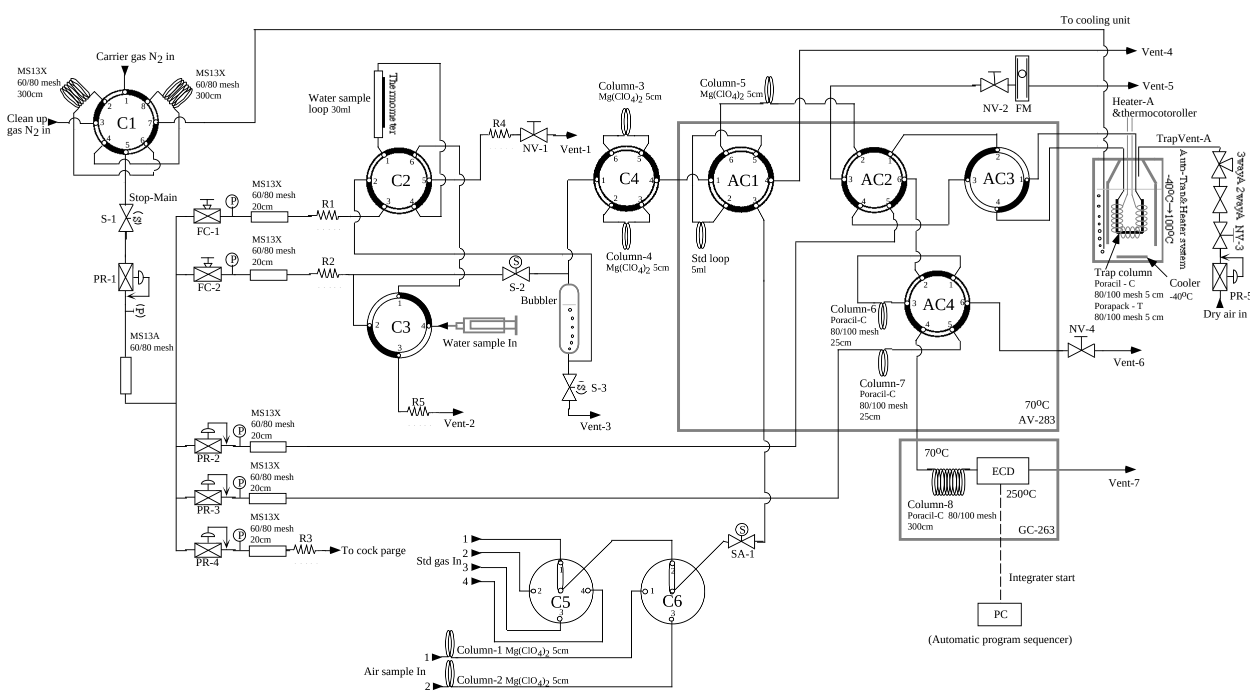


Fig. 3. Diagrams of the analytical systems for SF_6 and CFC. (a) The analytical system for SF_6; (b) The analytical system for CFC-11, CFC-12 and CFC-113. “C”, “AC”, “PR”, “FC”, “R”, “S”, “SA”, “SE”, “NV” and “FM” represent the manual cock, the automatic air actuated cock, the pressure controller, the flow controller, the resistance, the manual stop valve, the automatic air actuated stop valve, the automatic electromagnetic actuated stop valve, the needle valve and the flow meter, respectively. Personal computers were used as automatic program sequencers to control the automatic air actuated cocks, stopcocks, valves, and the trapping-heating systems.

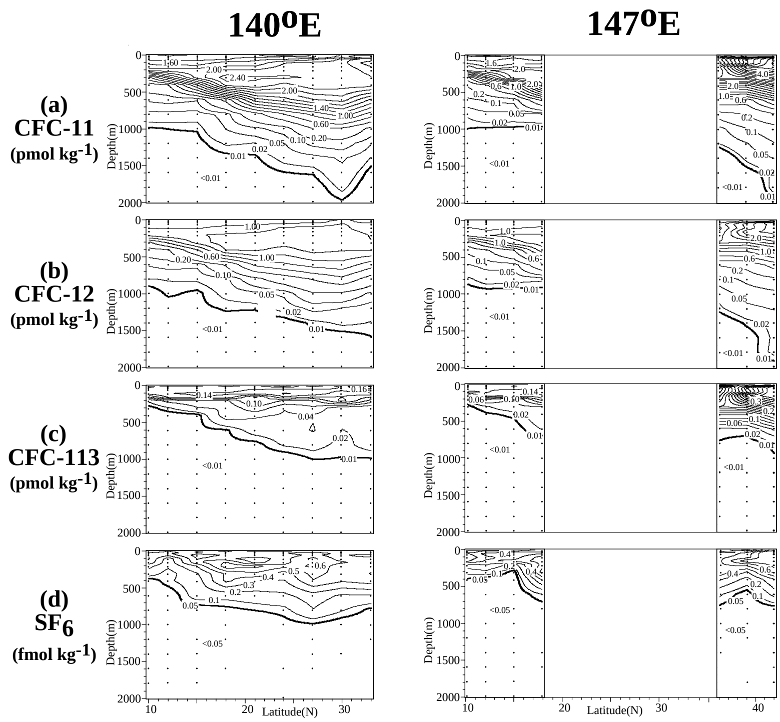


Fig. 4. Distributions of SF_6 (fmol kg^{-1}) and CFC (pmol kg^{-1}) along 140°E and 147°E. (a) CFC-11; (b) CFC-12; (c) CFC-113; (d) SF_6.

tracers in the western North Pacific, and compare ten tracer ages using the combined dating techniques: CFC-11 partial pressure, CFC-12 partial pressure, CFC-113 partial pressure, SF_6 partial pressure, CFC-11/CFC-12 ratio, CFC-113/CFC-11 ratio, CFC-113/CFC-12 ratio, SF_6/CFC-11 ratio, SF_6/CFC-12 ratio and SF_6/CFC-113 ratio.

2. Sampling and Methods

We obtained the samples of SF_6 and CFC at 18 stations from 44°N to 10°N along sections of 140°E and 147°E, on the NH98 cruise of the R/V No. 2 Hakurei Maru between August and October 1998 (Fig. 2). Using 12-liter X-Niskin bottles equipped with a CTD from 25 depths at each station, we drew sea water samples into a 1200 ml glass bottle for SF_6 and a 120 ml glass syringe for CFC. Both SF_6 and CFC were measured using shipboard electron capture detectors (Hitachi 5000A and Hitachi 263-30E). Air samples were also measured. In order to avoid contamination and to obtain high precision data, we determined the contents of SF_6 and CFC using automated analytical systems for water samples of 500 ml for SF_6 and 30 ml for CFC based on the reports of Law *et al.* (1994), Bullister and Weiss (1988) and Wisegarver and Gammon (1988). We used a personal computer as an automatic program sequencer to control air-actuated cocks, stopcocks, valves, and trapping-heating systems (Fig. 3). In both analytical systems, a set of 25 water samples from a hydrocast, together with replicate water samples, blank and standard runs, could be processed in less than 12 hours. The precision of analysis for replicate water samples was usually less than 0.05 fmol kg^{-1} (fmol = 10^{-15} mole) for SF_6 and less than 0.01 pmol kg^{-1} (pmol = 10^{-12} mole) for CFC. We also used the gravimetric standard gas of SF_6 in a 1 μm mesh ground aluminum cylinder with N_2. All CFC were reported on the SIO 1993 calibration scale.

3. Results and Discussion

3.1 Penetration depths of SF_6 and CFC in the western North Pacific

Along 140°E and 147°E, CFC-11 and CFC-12 generally decreased southward from high latitude and with depth, finding that agrees with previous CFC data (Fig. 4) (Watanabe *et al.*, 1994, 1997; Warner *et al.*, 1996; Tokieda *et al.*, 1996). The spatial distributions of SF_6 and CFC-113 were also similar in shape to those of CFC-11 and CFC-12. Maximum penetration depths of SF_6 and CFC-113 remained around 800 m in the subpolar region and 400 m in the tropical region, while other CFC were still found near 2000 m in the subpolar region. These

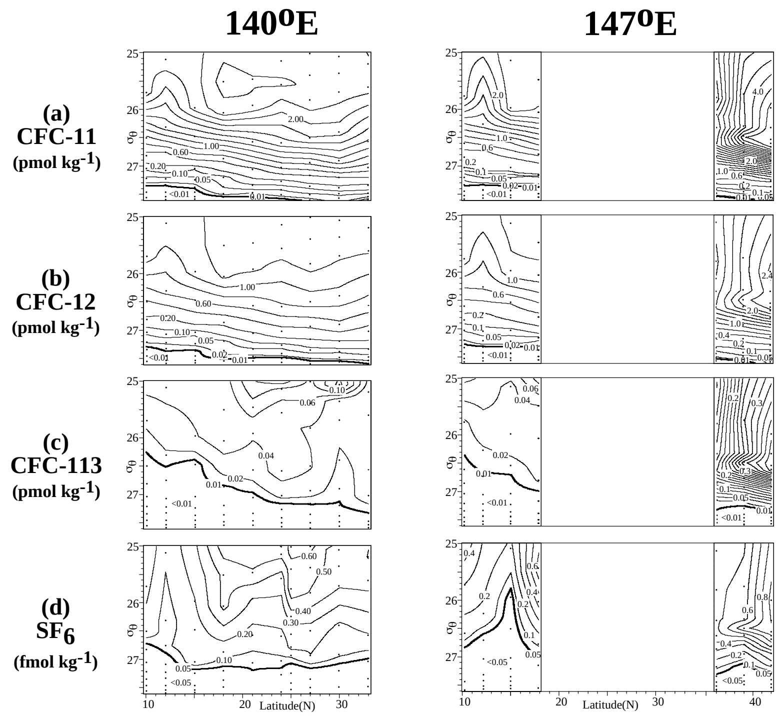


Fig. 5. Distributions of SF_6 (fmol kg^{-1}) and CFC (pmol kg^{-1}) on isopycnal surfaces along 140°E and 147°E. (a) CFC-11; (b) CFC-12; (c) CFC-113; (d) SF_6.

maximum penetration depths generally shallow in the order of CFC-11, CFC-12, CFC-113 and SF_6 in the entire western North Pacific. The difference in the penetration depths is due to differences in the starting time of anthropogenic emissions (Fig. 1).

On the isopycnal surfaces, we found that all the maximum concentrations of SF_6 and CFC were around 26.6–26.8σ_θ in the subpolar region (Fig. 5), and they gradually became less clear southward. A minimum of salinity was also found around 26.6–26.8σ_θ (Fig. 6). These facts suggest that the new water mass around 26.6–26.8σ_θ spread out over the whole of the North Pacific, which agrees with previous studies about the North Pacific Intermediate Water (Reid, 1965; Fine *et al*., 1981; VanScoy *et al*., 1991; Watanabe *et al*., 1994; Warner *et al*., 1996; Tokieda *et al*., 1996). CFC-11, CFC-12, CFC-113, SF_6 would still be available for clarification of the intermediate water in the North Pacific.

3.2 Distributions of tracer ages in the western North Pacific

3.2.1 Ten time-dependent tracer dating techniques

To elucidate the quantitative usefulness of SF_6 and CFC dating techniques in the ocean, it is essential to compare the formation year of water mass (t) and/or the tracer age of water mass (τ) from each dating technique. We here used the ten following dating techniques; CFC-11 partial pressure, CFC-12 partial pressure, CFC-113 partial pressure, SF_6 partial pressure, CFC-11/CFC-12 ratio, CFC-113/CFC-11 ratio, CFC-113/CFC-12 ratio, SF_6/CFC-11 ratio, SF_6/CFC-12 ratio and SF_6/CFC-113 ratio dating techniques. Each τ was calculated by using the following equations and comparing the atmospheric time history of SF_6 and CFC (Fig. 1).

For each partial pressure dating technique of SF_6 and CFC (Doney and Bullister, 1992),

$$pC_{(t)} = C_{\mathrm{obs}}/\alpha(S, T) \tag{1}$$

and

$$\tau = t_0 - t \tag{2}$$

where $pC_{(t)}$ is the oceanic partial pressure of SF_6 or CFC in the formation year of the water mass (t) under the equilibrated condition between the air and sea. "C_{obs}", "α", "S", "T" and "t_0" are the observed oceanic concentrations of SF_6 or CFC, their solubility, salinity, water potential temperature, and the date of observation, respectively.

For each ratio dating technique, CFC-11/CFC-12, CFC-113/CFC-11, CFC-113/CFC-12, SF_6/CFC-11, SF_6/CFC-12 and SF_6/CFC-113,

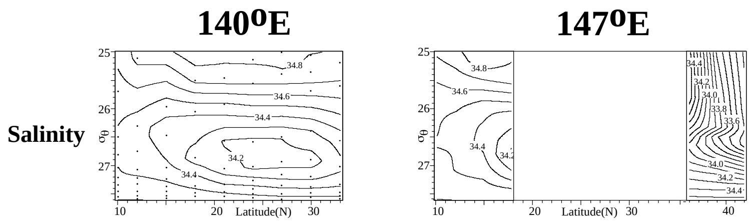


Fig. 6. Distributions of salinity on isopycnal along 140°E and 147°E.

Table 1. Constraint conditions for ten tracer dating techniques. The conditions were determined based on the atmospheric time histories of SF_6 and CFC in Fig. 1 (Maiss and Brenninkmeijer, 1998; Walker *et al.*, 2000; Bullister *et al.*, 2002).

Dating technique	Lower limited age (A.D.)	Upper limited age (A.D.)	Other constraint conditions
CFC-11	1947.5	1991.5	
CFC-12	1939.5	1998.5	Sampling date: 1998.5
CFC-113	1960.5	1993.5	
SF_6	1952.5	1998.5	Sampling date: 1998.5
CFC-11/CFC-12	1947.5	1978.5	CFC-11 age ≥ 1947.5 and CFC-12 age ≥ 1947.5
CFC-113/CFC-11	1960.5	1993.5	CFC-11 age ≥ 1960.5 and CFC-113 age ≥ 1960.5
CFC-113/CFC-12	1960.5	1992.5	CFC-12 age ≥ 1960.5 and CFC-113 age ≥ 1960.5
SF_6/CFC-11	1975.5	1998.5	pSF_6/pCFC-11 ≥ 0.0034 and CFC-11 age ≥ 1975.5
SF_6/CFC-12	1972.5	1998.5	pSF_6/pCFC-12 ≥ 0.0016 and CFC-12 age ≥ 1972.5
SF_6/CFC-113	1990.5	1998.5	pSF_6/pCFC-113 ≥ 0.0310 and CFC-113 age ≥ 1990.5

$$[pC_a/pC_b]_{(t)} = [C_{a,\mathrm{obs}}/\alpha_a(S, T)]/[C_{b,\mathrm{obs}}/\alpha_b(S, T)] \quad (3)$$

where "*a*" and "*b*" refer to one tracer within CFC-11, CFC-12, CFC-113 and SF_6.

We here assume that SF_6 and CFC was in the equilibrium between the atmosphere and sea. Moreover, under some constrained conditions based on the atmospheric time histories (Table 1), we calculated τ using Eqs. (1)–(3) with the atmospheric time histories of SF_6 and CFC (Maiss and Brenninkmeijer, 1998; Walker *et al.*, 2000; Bullister *et al.*, 2002) and their solubilities (Warner and Weiss, 1985; Bu and Warner, 1995; Bullister *et al.*, 2002).

3.2.2 Distributions of formation year and tracer age

In both observational lines, all values for the formation year of water mass (t) by SF_6 and CFC partial pressure dating techniques generally became old southward from high latitude and with depth (Fig. 7). All isolines of t for 1970 remained around 600 m in the subpolar region, and 300 m in the tropical region. These spatial distributions of t were broadly similar in shape to each other, while they were somewhat different in detail. Typical vertical profiles of ten tracer ages (τ) are also shown in Fig. 8. Considering the constrained conditions and the standard deviations (Tables 1 and 2), all tracer ages around $27.0\sigma_\theta$ almost agree with each other in both regions. With shoaling, these tracer ages (except CFC-11/CFC-12) gradually became young and almost agreed with the sampling date or the upper limit age.

These tracer ages are scattered and it is difficult to discuss their quantitative usefulness. Thus we have tried to estimate the absolute difference in τ between any two tracer ages ($\Delta\tau$) (Table 2). If we use these multiple dating techniques and find that only some of $\Delta\tau$ agree with each other, we cannot know whether these tracer ages actually reveal the true age of the water mass. However, if all $\Delta\tau$ completely agree with each other, within some deviation, despite the different source functions, there is a high probability that these tracer ages are almost close to the true age, at least within that deviation. If all $\Delta\tau$ are within five years, these tracer ages would be useful enough to discuss the behavior of water masses on a decadal time scale (Watanabe *et al.*, 2001) or to estimate the amount of oceanic anthropogenic carbon on a decadal time scale (e.g., Watanabe *et al.*, 2000; Ono *et al.*, 2001).

3.3 *Comparison of the tracer ages in the past three decades*

3.3.1 Average tracer ages in the entire water column

In all our data, all $\Delta\tau$ except CFC-11/CFC-12 almost agreed with each other within 1–9 years (average: 5 ± 2 years) (Table 2). The large $\Delta\tau$ of the CFC-11/CFC-12-related ages (12–22 years, average: 15 ± 3 years) were

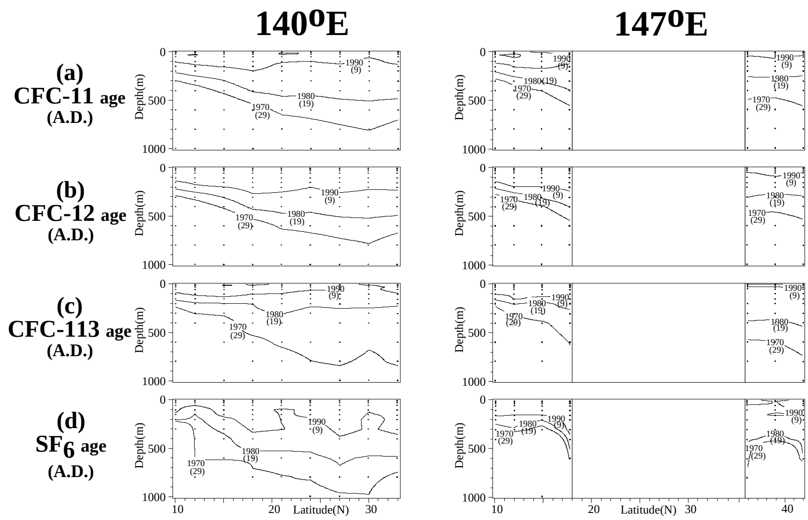


Fig. 7. Distributions of formation year of water mass (t) and tracer age (τ) estimated by SF_6 and CFC partial pressure techniques along 140°E and 147°E. (a) CFC-11 partial pressure dating technique; (b) CFC-12 partial pressure dating technique; (c) CFC-113 partial pressure dating technique; (d) SF_6 partial pressure dating technique. The numbers in parentheses are tracer ages (yr).

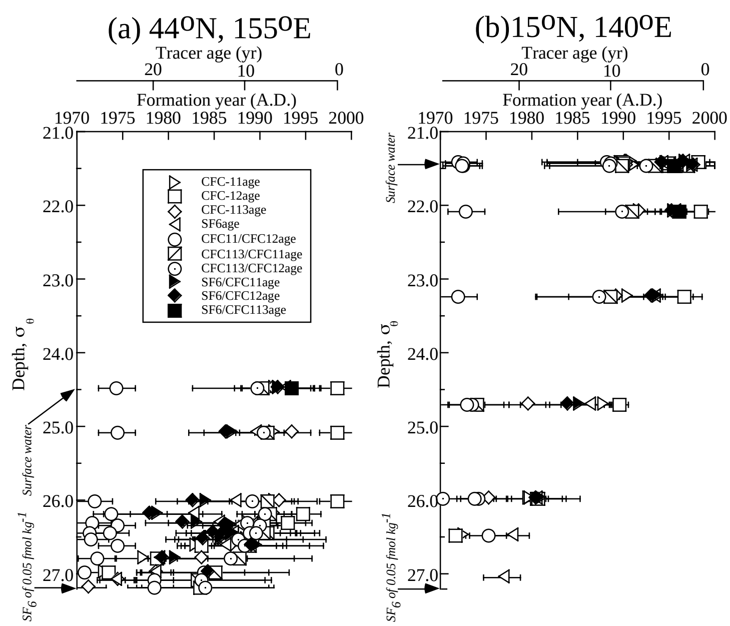


Fig. 8. Typical vertical profiles of formation year of water mass (t) and tracer age (τ) estimated by ten tracer dating techniques. (a) 44°N, 155°E; (b) 15°N, 140°E. The standard deviations in Table 2 were used as a measure of error.

mainly caused by the atmospheric CFC-11/CFC-12 ratio being constant after the end of the 1970s and by the ventilation time of the water mass above 1000 m being within 30 years in the North Pacific (Watanabe *et al*., 1994; Warner *et al*., 1996; Yamanaka *et al*., 1998).

Furthermore, some of these tracers in the atmosphere already have been constant or decreasing after the end of 1970s or the mid-1990s (Fig. 1). The average values of $\Delta\tau$ in the entire water column would be insufficient to clarify the usefulness of tracer dating techniques. It is thus necessary to compare $\Delta\tau$ in detail during any given period. To verify the quantitative usefulness of tracer ages

Table 2. Comparison of differences in tracer age between ten tracer dating techniques ($\Delta\tau$, years). The estimations were calculated under the constrained conditions in Table 1. Three time periods, 1970s, 1980s and 1990s were determined based on CFC-12 age. The error and the number in parentheses were the standard deviation and the number of data used in the calculation, respectively.

		CFC-11	CFC-12	CFC-113	SF_6	CFC-11/CFC-12	CFC-113/CFC-11	CFC-113/CFC-12	SF_6/CFC-11	SF_6/CFC-12	SF_6/CFC-113
CFC-11	All data		4 ± 3 (289)	5 ± 5 (267)	5 ± 4 (210)	14 ± 5 (250)	6 ± 6 (201)	6 ± 5 (194)	4 ± 3 (148)	5 ± 4 (157)	4 ± 2 (38)
	1970s		1 ± 0 (21)	4 ± 2 (20)	5 ± 2 (18)	2 ± 2 (21)	8 ± 3 (20)	7 ± 4 (20)	8 ± 5 (5)	12 ± 5 (13)	—
	1980s		1 ± 1 (47)	6 ± 4 (39)	4 ± 3 (41)	11 ± 3 (47)	11 ± 7 (39)	10 ± 7 (39)	6 ± 4 (38)	6 ± 4 (38)	—
	1990s		5 ± 2 (113)	2 ± 2 (112)	3 ± 2 (106)	17 ± 2 (113)	3 ± 2 (112)	3 ± 3 (112)	4 ± 3 (105)	4 ± 3 (105)	4 ± 2 (38)
CFC-12	All data			9 ± 7 (261)	6 ± 7 (208)	17 ± 7 (250)	9 ± 6 (201)	9 ± 5 (196)	4 ± 4 (148)	5 ± 4 (159)	2 ± 2 (39)
	1970s			4 ± 2 (20)	5 ± 2 (18)	3 ± 2 (21)	8 ± 3 (20)	7 ± 4 (20)	7 ± 5 (5)	11 ± 5 (13)	—
	1980s			7 ± 5 (39)	4 ± 3 (41)	12 ± 4 (47)	11 ± 8 (39)	11 ± 7 (39)	5 ± 3 (38)	5 ± 4 (39)	—
	1990s			6 ± 2 (114)	4 ± 3 (108)	22 ± 3 (113)	7 ± 3 (112)	8 ± 3 (114)	4 ± 4 (105)	4 ± 4 (107)	2 ± 2 (39)
CFC-113	All data				5 ± 4 (199)	12 ± 6 (229)	3 ± 3 (201)	3 ± 3 (196)	6 ± 5 (140)	6 ± 5 (151)	4 ± 2 (39)
	1970s				5 ± 3 (17)	6 ± 4 (20)	4 ± 2 (20)	3 ± 2 (20)	7 ± 6 (4)	10 ± 5 (12)	—
	1980s				7 ± 5 (35)	7 ± 5 (39)	5 ± 3 (39)	4 ± 3 (39)	9 ± 6 (32)	9 ± 6 (33)	—
	1990s				4 ± 3 (107)	16 ± 3 (112)	1 ± 1 (112)	2 ± 1 (114)	5 ± 3 (104)	5 ± 3 (106)	4 ± 2 (39)
SF_6	All data					15 ± 7 (196)	6 ± 6 (174)	7 ± 5 (175)	1 ± 2 (148)	2 ± 2 (159)	1 ± 1 (39)
	1970s					6 ± 4 (18)	7 ± 4 (17)	6 ± 4 (17)	4 ± 2 (5)	6 ± 3 (13)	—
	1980s					14 ± 4 (41)	11 ± 9 (35)	11 ± 8 (35)	2 ± 2 (38)	2 ± 2 (39)	—
	1990s					20 ± 4 (106)	5 ± 4 (105)	5 ± 4 (107)	1 ± 1 (105)	1 ± 1 (107)	1 ± 1 (39)
CFC-11/CFC-12	All data						12 ± 6 (201)	12 ± 5 (194)	19 ± 5 (148)	18 ± 5 (157)	22 ± 3 (38)
	1970s						9 ± 5 (20)	8 ± 5 (20)	12 ± 7 (5)	13 ± 5 (13)	—
	1980s						9 ± 5 (39)	8 ± 5 (39)	17 ± 4 (38)	16 ± 5 (39)	—
	1990s						16 ± 4 (112)	15 ± 4 (112)	20 ± 5 (105)	19 ± 5 (105)	22 ± 3 (38)
CFC-113/CFC-11	All data							1 ± 0 (194)	7 ± 6 (140)	7 ± 6 (149)	4 ± 2 (38)
	1970s							1 ± 1 (20)	8 ± 5 (4)	10 ± 6 (12)	—
	1980s							1 ± 0 (39)	13 ± 9 (32)	12 ± 9 (33)	—
	1990s							1 ± 1 (112)	5 ± 4 (104)	5 ± 4 (104)	4 ± 2 (38)
CFC-113/CFC-12	All data								7 ± 6 (140)	7 ± 6 (151)	5 ± 2 (39)
	1970s								8 ± 5 (4)	9 ± 6 (12)	—
	1980s								13 ± 9 (32)	12 ± 9 (33)	—
	1990s								6 ± 4 (104)	6 ± 4 (106)	5 ± 2 (39)
SF_6/CFC-11	All data									1 ± 0 (148)	1 ± 1 (38)
	1970s									1 ± 1 (5)	—
	1980s									1 ± 0 (38)	—
	1990s									1 ± 1 (105)	1 ± 1 (38)
SF_6/CFC-12	All data										1 ± 1 (39)
	1970s										—
	1980s										—
	1990s										1 ± 1 (39)
SF_6/CFC-113	All data										
	1970s										
	1980s										
	1990s										

Table 3. Grading the usefulness of ten time-dependent tracer dating techniques in the North Pacific in the 1970s, 1980s and 1990s. Considering the standard deviation in Table 2, we define "Excellent" as the complete agreement of all $\Delta\tau$ within five years, "Good" as the agreement of all $\Delta\tau$ except for one dating technique, "Fair" as that except for two dating techniques, and "Failure" as that except for more than three techniques. We did not address the CFC-11/CFC-12 ratio ages after the 1980s. Numbers in parenthesis are the numbers of the dating technique that $\Delta\tau$ did not agree with each other. The remarks are based on the constraint conditions in Table 1.

Dating technique	1970s	Remark	1980s	Remark	1990s	Remark
CFC-11	Good (1)		Excellent (0)		Excellent (0)	before 1991.5
CFC-12	Good (1)		Excellent (0)		Excellent (0)	
CFC-113	Excellent (0)		Excellent (0)		Excellent (0)	before 1993.5
SF_6	Excellent (0)		Excellent (0)		Excellent (0)	
CFC-11/CFC-12	Good (1)	before 1978.5	Failure (5)		Failure (9)	
CFC-113/CFC-11	Excellent (0)		Excellent (0)		Excellent (0)	before 1993.5
CFC-113/CFC-12	Excellent (0)		Excellent (0)		Excellent (0)	before 1992.5
SF_6/CFC-11	Excellent (0)	after 1975.5	Excellent (0)		Excellent (0)	
SF_6/CFC-12	Fair (2)	after 1972.5	Excellent (0)		Excellent (0)	
SF_6/CFC-113	—		—		Excellent (0)	

on a decadal time scale, we have divided all our estimates into $\Delta\tau$ in 1970s, 1980s and 1990s based on CFC-12 partial pressure age (Table 1).

3.3.2 Tracer ages in 1970s, 1980s and 1990s

Considering the standard deviations, we found that all $\Delta\tau$ in the 1970s were almost consistent within five years, as expected in the field study on a decadal time scale (Table 2). All $\Delta\tau$ of the CFC-11/CFC-12-related ages were small enough to study the behavior of the water mass (average: 7 ± 4 years). SF_6 and CFC partial pressure ages, and CFC ratio ages are also in good agreement, despite the possibility of water mixing in the subsurface water, suggesting that these tracer ages are adequate to determine the age of the water mass in the 1970s.

In the 1980s, all the $\Delta\tau$ results except CFC-11/CFC-12 have good consistency, which is enough to discuss the behavior of the water mass in the 1980s. All $\Delta\tau$ of the CFC-11/CFC-12-related ages in the 1980s were 7–17 years (average: 12 ± 4 years), which almost agreed with the difference of 10 years expected from the end of 1970s when CFC-11/CFC-12 had been constant.

In the 1990s, $\Delta\tau$ of the CFC-11/CFC-12-related ages was 15–22 years (average: 18 ± 3 years), which also agreed with the difference of 20 years as an expected value. The results of $\Delta\tau$ except the CFC-11/CFC-12 completely agreed with each other within five years, and these values of $\Delta\tau$ were also smaller than those in the 1970s and 1980s. However, some of the CFC-related dating techniques were already constrained due to the decrease of atmospheric CFC concentration (Table 1). Thus SF_6, CFC-12 and SF_6/CFC dating techniques are the most useful tools for determining the age of water mass produced in the 1990s since there are no constraints on their use. This evaluation of tracer dating techniques is the first confirmation of their usefulness based on observational data on an ocean basin-wide scale, although this has been predicted theoretically based on Fig. 1 (Maiss and Brenninkmeijer, 1998; Walker *et al.*, 2000; Bullister *et al.*, 2002).

3.3.3 Usefulness of tracer dating techniques

Yamanaka *et al.* (1998) demonstrated ages using model calculations, that the vertical diffusion and the isopycnal horizontal mixing of water masses usually age τ old by only with 1–4 years in the North Pacific. On the other hand, recent studies in the North Pacific reported the change of oceanic uptake rate of anthropogenic carbon and the change of water ventilation based on tracer, dissolved inorganic carbon and dissolved oxygen data set on a decadal time scale (Emerson *et al.*, 2001; Ono *et al.*, 2001; Watanabe *et al.*, 2001). When we discuss the change of water movement and/or of the change of oceanic anthropogenic carbon uptake on a decadal time scale, differences of $\Delta\tau$ within five years would be permissible.

We here grade ten tracer dating techniques on the decadal time scale based on $\Delta\tau$ within five years. Considering the standard deviation of $\Delta\tau$ in Table 2, we defined "Excellent" as the complete agreement of all $\Delta\tau$ within five years, "Good" as the agreement of all $\Delta\tau$ except for one dating technique, "Fair" as that except for two dating techniques, and "Failure" as that except for more than three dating techniques (Table 3). We do not here address the use of CFC-11/CFC-12 ratio age after the 1980s as the dating technique was already unused by then.

We found that all the tracer ages except SF_6/CFC-12 could be graded as Excellent or Good in the 1970s, and all tracer ages except CFC-11/CFC-12 graded Excellent in the 1980s in 1990s under some constrained conditions.

In particular, the CFC-12 and SF_6 partial pressure dating techniques are sufficiently powerful tools to obtain the age of water mass in the past thirty years, without constraint. Since the 1980s, the SF_6/CFC dating techniques are also available. It is certain that the atmospheric content of CFC-12 will decrease in the near future due to a world-wide ban on CFC-12 in the industrial countries, although the present concentration still increasing. Thus SF_6 and SF_6/CFC tracer ages will be the most important tools if the atmospheric content of SF_6 keeps increasing in future.

Our result is the first confirmation of the actual usefulness of ten time-dependent tracers to obtain the ages of water mass using the extensive observational data set on the ocean basin-wide scale. In the North Pacific, the recent anthropogenic carbon uptake estimated by the tracer age method almost agrees with that found by a different method based on DIC data on the decadal time scale (Watanabe *et al*., 2000; Ono *et al*., 2000). There is also a high probability that these tracer ages were close to the true age of water mass in the past several decades, at least in the North Pacific. However, the number of samples in our study may nevertheless be insufficient to get a representative spatial distribution of the ages. In future, there is a need to observe many samples of SF_6 with CFC-11, CFC-12 and CFC-113 simultaneously, and to compare their differences in tracer ages over the basin-wide scale.

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References

Bu, X. and M. J. Warner (1995): Solubility of chlorofluorocarbon 113 in water and seawater. *Deep-Sea Res.*, **42**, 1151–1161.

Bullister, J. L. and R. F. Weiss (1988): Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep-Sea Res.*, **35**, 839–853.

Bullister, J. L., D. P. Wisegarver and F. A. Menzia (2002): The solubility of sulfur hexafluoride in water and seawater. *Deep-Sea Res.*, **49**, 175–187.

Doney, S. C. and J. L. Bullister (1992): A chlorofluorocarbon section in the eastern North Atlantic. *Deep-Sea Res.*, **39**, 1857–1883.

Doney, S. C., W. J. Jenkins and J. L. Bullister (1997): A comparison of ocean tracer dating techniques on a meridional section in the eastern North Atlantic. *Deep-Sea Res.*, **44**, 603–626.

Emerson, S., S. Mecking and J. Abell (2001): The biological pump in the subtropical North Pacific: nutrient sources, Redfield ratios, and recent changes. *Global Biogeochem. Cycles*, **15**, 535–554.

Fine, R. A., J. L. Reid and H. G. Ostlund (1981): Circulation of tritium in the Pacific Ocean. *J. Phys. Oceanogr*., **11**, 3–14.

Gruber, N., J. L. Sarmiento and T. F. Stocker (1996): An improved method for detecting anthropogenic CO_2 in the oceans. *Global Biogeochem. Cycles*, **10**, 809–837.

Law, C. S. and A. J. Watson (2001): Determination of Persian Gulf Water transport and oxygen utilization rates using SF_6 as a novel transient tracer. *Geophys. Res. Lett*., **28**, 815–818.

Law, C. S., A. J. Watson and M. I. Liddicoat (1994): Automated vacuum analysis of sulfur hexafluoride in seawater: derivation of the atmospheric trend (1970–1993) and potential as transient tracer. *Mar. Chem*., **48**, 57–69.

Ledwell, J. R. and A. J. Watson (1991): The Santa Monica Basin tracer experiment: a study of diapycnal and isopycnal mixing. *J. Geophys. Res*., **96**, 8695–8718.

Maiss, M. and C. A. M. Brenninkmeijer (1998): Atmospheric SF_6: trends, sources, and prospects. *Environ. Sci. Tech*., **32**, 3077–3086.

Ono, T., Y. W. Watanabe and S. Watanabe (2000): Recent increase of DIC in the western North Pacific. *Mar. Chem*., **72**, 317–328.

Ono, T., T. Midorikawa, Y. W. Watanabe, K. Tadokoro and T. Saino (2001): Temporal increase of phosphate and apparent oxygen utilization in the subsurface waters of western subarctic Pacific from 1968 and 1998. *Geophys. Res. Lett*., **28**, 3285–3288.

Ravishankara, A., S. Solomon and A. A. Turnipseed (1993): Atmospheric lifetimes of long-lived halogenated species. *Nature*, **259**, 194–199.

Reid, J. L. (1965): Intermediate waters of the Pacific Ocean. Dr. Sci. Thesis, Johns Hopkins University.

Smethie, W. M. J., D. W. Chipman and K. P. Koltermann (1988): Chlorofluoromethanes in the Arctic Mediterranean seas: evidence for formation of bottom water in the Eurasian Basin and deep-water exchange through Fram Strait. *Deep-Sea Res*., **35**, 347–369.

Tokieda, T., S. Watanabe and S. Tsunogai (1996): Chlorofluorocarbons in the western North Pacific in 1993 and formation of North Pacific Intermediate Water. *J. Oceanogr*., **52**, 478–490.

Upstill-Goddard, R. C., A. J. Watson, P. S. Liss and M. I. Liddicoat (1990): Gas transfer velocities in lakes measured with SF_6. *Tellus*, **42B**, 364–377.

VanScoy, K. M., D. B. Olson and R. A. Fine (1991): Ventilation of North Pacific Intermediate Water: the role of the Alaskan Gyre. *J. Geophys. Res*., **96**, 16801–16810.

Walker, S. J., R. F. Weiss and P. K. Salameh (2000): Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC11, CFC12, CFC113 and carbon tetrachloride. *J. Geophys. Res*., **105**, 14285–14296.

Wanninkhof, R., J. R. Ledwell and W. S. Broecker (1985): Gas

exchange-wind speed relation measured with sulfur hexafluoride on lake. *Science*, **227**, 1224–1226.
Warner, M. J. and R. F. Weiss (1985): Solubility of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res*., **32**, 1485–1497.
Warner, M. J., J. L. Bullister, D. P. Wisegarver, R. H. Gammon and R. F. Weiss (1996): Basin-wide distribution of chlorofluorocarbons CFC-11 and CFC-12 in the North Pacific: 1985–1989. *J. Geophys. Res*., **101**, 20525–20542.
Watanabe, Y. W., K. Harada and K. Ishikawa (1994): Chrolofluorocarbons in the central North Pacific and southward spreading time of North Pacific Intermediate Water. *J. Geophys. Res*., **99**, 25195–25213.
Watanabe, Y. W., A. Ishida, M. Tamaki, K. Okuda and M. Fukasawa (1997): Water column inventories of CFCs and production rate of intermediate water in the North Pacific. *Deep-Sea Res*., **44**, 1091–1104.
Watanabe, Y. W., T. Ono and A. Shimamoto (2000): Increase in the uptake rate of oceanic anthropogenic carbon in the North Pacific determined by CFC age. *Mar. Chem*., **72**, 295–315.
Watanabe, Y. W., T. Ono, A. Shimamoto, T. Sugimoto, M. Wakita and S. Watanabe (2001): Possibility of a reduction in the formation rate of the subsurface water in the North Pacific. *Geophys. Res. Lett*., **28**, 3285–3288.
Watson, A. J. and M. I. Liddicoat (1985): Recent history of atmospheric tracer gas concentrations deduced from measurements in the deep sea: application to sulfur hexafluoride and carbon tetrachloride. *Atmos. Environ*., **19**, 1477–1484.
Watson, A. J., R. C. Upstill-Goddard and P. S. Liss (1991): Air-sea gas exchange in rough and stormy seas measured by a dual-tracer technique. *Nature*, **349**, 145–147.
Wisegarver, D. P. and R. H. Gammon (1988): A new transient tracer: measured vertical distribution of F-113 in the North Pacific subarctic gyre. *Geophys. Res. Lett*., **15**, 188–191.
WOCE (1999): WOCE Hydrographic Program Office. http://whpo.ucsd.edu/index.htm
Yamanaka, G., Y. Kitamura and M. Endo (1998): Formation of North Pacific Intermediate Water in Meteorological Research Institute ocean general circulation model 2: transient tracer experiments. *J. Geophys. Res*., **103**, 30905–30921.