Deep-Sea Research I 72 (2013) 61–71

Contents lists available at SciVerse ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsri

Transit time distributions and oxygen utilization rates in the Northeast Pacific Ocean from chlorofluorocarbons and sulfur hexafluoride

Rolf E. Sonnerup [a,*], Sabine Mecking [b], John L. Bullister [c]

[a] Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle, USA
[b] Applied Physics Laboratory, University of Washington, Seattle, USA
[c] Pacific Marine Environmental Laboratory, National Ocean and Atmosphere Administration, Seattle, USA

ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form
23 October 2012
Accepted 31 October 2012
Available online 13 November 2012

Keywords:
Ocean tracers
Biological production
Oxygen utilization rates
Ventilation timescales
North pacific subtropical thermocline
Transit time distributions
Chlorofluorocarbons
Sulfur hexafluoride

ABSTRACT

Depth profiles of dissolved chlorofluorocarbon-11 (CFC-11) and sulfur hexafluoride (SF_6) were measured during a September 2008 cruise in the Northeast Pacific Ocean. For each water sample, the two tracers were used in concert to estimate likely mean ages and widths of parameterized 1-D transit time distributions (TTDs). In shallow waters (<250 m), the TTDs' mean ages were relatively loosely constrained due to the slow decrease of atmospheric CFC-11 since 1994. In the main thermocline (25.0–26.6 σ_θ, ~300–550 m), the CFC-11/SF_6 tracer pair constrained TTDs' mean ages to within $\pm 10\%$. Deeper than 26.8 σ_θ (~600 m), SF_6 levels in 2008 were too low for the CFC-11/SF_6 tracer pair to constrain the TTDs' mean ages. Within the main thermocline of the subtropical North Pacific Ocean (20°–37°N along 152°W), the TTDs' mean ages were used to estimate Oxygen Utilization Rates (OURs) of ~11 μmol kg^{-1} yr^{-1} on 25.0–25.5 σ_θ (~160 m), attenuating to very low rates (0.12 μmol kg^{-1} yr^{-1}) by 26.8–27.0 σ_θ (~600 m). Depth integration of the in-situ OURs implied an average carbon remineralization rate of 1.7 ± 0.3 mol C m^{-2} yr^{-1} in this region and depth range, somewhat lower than other independent estimates. Along the 152°W section, depth integrating the apparent OURs implied carbon remineralization rates of 2.5–3.5 mol C m^{-2} yr^{-1} from 20°N to 30°N, 3.5–4.0 mol C m^{-2} yr^{-1} from 30°N to 40°N, and 2–2.7 mol C m^{-2} yr^{-1} north of 45°N.

1. Introduction

The fact that mixing in the ocean interior can bias chlorofluorocarbon (CFC) and other tracer-derived ages away from mean (ideal) transit timescales has long been recognized (Jenkins, 1987; Thiele and Sarmiento, 1990; Doney and Bullister, 1992; Doney et al., 1997). Over the past decade, the idea that combinations of transient tracer ages could be used to estimate the impacts of mixing on CFC ages (Sonnerup, 2001; Hall et al., 2002; Waugh et al., 2002), and constrain the distribution of transit times in the ocean interior (Waugh et al., 2002, 2003, 2004) has been explored in some detail. The latter approach is attractive because full knowledge of the transit time distribution (or TTD) at a location in the ocean interior would afford more accurate means of quantifying mean ventilation ages (Waugh et al., 2002, 2003), anthropogenic CO_2 uptake (Hall et al., 2002; Waugh et al., 2006), and temporal changes in ocean transport (Waugh et al., 2003; Sonnerup et al., 2008), over the often biased estimates which result from using CFC ages alone.

Recently, the US CLIVAR CFC measurement groups have modified their analytical systems to include measurements of dissolved sulfur hexafluoride (SF_6) on the same samples (Bullister and Wisegarver, 2008). The widespread availability of two tracer ages from water samples affords the opportunity to constrain the 1-D TTD at sample locations in the ocean interior, provided the two tracer timescales are independent and some assumptions are in place (Waugh et al., 2002, 2003). Although they are not entirely independent, the CFC and SF_6 tracers have, in pilot studies, together shown promise in constraining TTDs and mean transit timescales (Waugh et al., 2002), anthropogenic CO_2 levels (Hall et al., 2002; Bullister et al., 2006), and decadal changes in ocean transport from tracer age changes (Sonnerup et al., 2008).

We deployed a combined CFC/SF_6 analytical system during a 2008 University of Washington student cruise in the Northeast Pacific Ocean. Here we used the concurrent CFC and SF_6 observations from the thermocline to evaluate the constraint that this tracer pair, in 2008, places on a 1-D TTD form, focusing on how well the TTD's mean transit timescale can be constrained. A central focus of the cruise overall was to measure and compare biological carbon fluxes from a variety of approaches, and between the subarctic and subtropical North Pacific Ocean. In this light, we exploited the mean transit timescales from the

* Corresponding author.
E-mail address: rolf.sonnerup@noaa.gov (R.E. Sonnerup).

0967-0637/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dsr.2012.10.013

two-tracer tuned TTDs, in conjunction with dissolved oxygen measurements, to estimate oxygen utilization rates in the thermocline. Our effort refines prior efforts where pCFC ages alone were used to estimate thermocline oxygen utilization rates, and thus overlying biological carbon export rates, yet were hindered by uncertainties about the impacts of mixing on the CFC ages (Doney and Bullister, 1992; Warner et al., 1996; Sonnerup et al., 1999; Feely et al., 2004; Mecking et al., 2006). The meridional trend in carbon export rates from the sea surface was estimated by depth integrating (from the base of the mixed layer to the bottom of the thermocline) the apparent oxygen utilization rates. In subsequent manuscripts we will highlight the added utility of the twin-tracer constrained TTDs in quantifying decadal changes in ventilation and anthropogenic CO_2.

2. Tracer measurements and ages in the Northeast Pacific during 2008

Dissolved CFC-11 and SF_6 were measured using analytical techniques outlined in (Bullister and Wisegarver, 2008) during the September 2008 University of Washington Student Cruise (STUD2008), initially along 145°W in the subarctic Pacific, and then reoccupying a portion of the P16N line from 47°N to 20°N along 152°W (Fig. 1). Detection limits for CFC-11 and SF_6 were approximately 0.002 pmol kg^{-1} and 0.02 fmol kg^{-1}, respectively. Based on replicate samples and standards, and on the saturation levels measured in sea surface samples during STUD2008, we estimate the precision of the CFC-11 measurements as 0.004 pmol kg^{-1} or 2% of the CFC-11 concentration, whichever is larger. The corresponding precision for SF_6 was 0.04 fmol kg^{-1}, or 4% of the SF_6 concentration, whichever is larger. These error estimates are approximately double the optimum attainable with this type of analytical equipment (Bullister and Wisegarver, 2008), a difference which may be due in part to the fact that this was the first use of this set of equipment in the field.

Partial pressure ages for SF_6 (pSF_6 ages) and CFC-11 (pCFC-11 ages) were determined by (1) calculating each subsurface sample's partial pressure from its dissolved tracer concentration using the solubility functions determined by Bullister et al. (2002) and Warner and Weiss (1985), respectively, (2) comparing the partial pressure with the tracer's atmospheric history (Fig. 2 and 3) assigning a date that the sample was last at the surface by assuming it was at or near saturation (Table 1) with respect to the atmosphere at that time (Doney and Bullister, 1992). Uncertainties in the tracer ages vary with outcrop date because the percentage annual changes in the atmosphere vary with time. Based on uncertainties of ±4% for the SF_6 measurement and ±4% for the sea-surface saturation state, relative uncertainties in the pSF_6 ages determined in 2008 were on the order of ±1.0–1.5 years for pSF_6 ages < 12 years and, due to the early rapid growth of atmospheric SF_6, only ±0.5 years for pSF_6 ages from about 12 to 30 years, and ±3 years for pSF_6 ages > 30 years. Prior to 1995, there are larger uncertainties in the atmospheric history for SF_6, which is based on estimates of SF_6 release, and not on measurements (See Bullister et al. (2006) and cdiac.ornl.gov/oceans/new_atmCFC.html for discussion). For pCFC-11 ages determined in 2008, the corresponding uncertainties based on measurement uncertainties of ±2% and saturation uncertainties of ±2%, were ±0.5 years or less for pCFC-11 ages > 30 years, and about ±1 year for pCFC-11 ages from 18 to 30 years. Because the decrease in atmospheric CFC-11 levels since about 1994 (Fig. 2), about 0.5% yr^{-1}, has been slow relative to measurement and saturation level uncertainties, pCFC-11 ages < 18 years could not be determined to better than ±50% with this dataset. For these younger pCFC-11 ages, the concurrent pSF_6 measurement was used to distinguish pre- and post-1994 vintages.

Dissolved CFC-11 was detectable (≥ 0.002 pmol kg^{-1}) to depths greater than 1000 m along the entire 152°W section (Fig. 3). In 2008, CFC-11 penetrated to potential density anomalies (σ_θ) of 27.2 σ_θ in the subtropics, and 27.4 σ_θ north of 37°N. In the subtropics (south of 37°N), the pronounced subsurface CFC-11

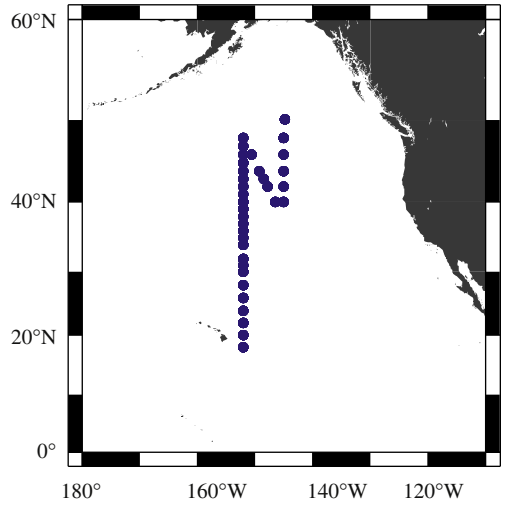

Fig. 1. Station locations where CFC-11 and SF_6 depth profiles were measured during the September 2008 University of Washington student cruise in the North Pacific Ocean.

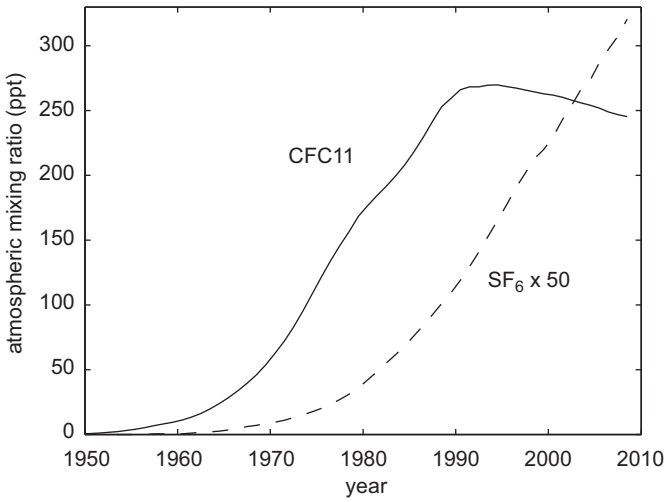

Fig. 2. Trends in atmospheric concentrations of CFC-11 (in parts-per-trillion, ppt), and SF_6 (dashed line, x 50 (ppt)) for the northern hemisphere troposphere. See Bullister et al. (2006) for discussion, and cdiac.ornl.gov/oceans/new_atmCFC.html for data and updates.

Table 1
Sea surface saturation levels employed when calculating pSF_6 and pCFC-11 ages from the dissolved tracer concentrations, and when calculating the TTDs' tracer burdens. In a diagnostic model using climatological isopycnal transport fields to simulate CFC uptake into the North Pacific thermocline, these saturation levels were most consistent with the WOCE-era isopycnal CFC inventories (Mecking et al., 2004).

Density Horizon	Saturation level (%)
$\sigma_\theta < 25.4$	100
$25.4 \le \sigma_\theta < 26.0$	95
$26.0 \le \sigma_\theta < 26.4$	90
$26.4 \le \sigma_\theta < 26.6$	85
$26.6 \le \sigma_\theta$	80