Oceanic Water Mass Tracers

Reading: Libes, Chapters 10 and 24

Outline

1. Classes of oceanic tracers
2. Global ocean surveys
3. Water-mass mixing calculations
4. Quasi-conservative geochemical tracers
    - NO, PO, and PO_4^*
5. Anthropogenic transient and deliberate Tracers
    - CFCs, SF_6, SF_5CF_3

Natural - Stable	**Use**
O_2	Water mass analysis, non-conservative
PO_4, NO_3, SiO_2	Nutrients high in Pacific water, low in Atlantic Water
NO, PO, PO_4^*	Water mass analysis, quasi-conservative
^{18}O, ^4He, Ne	Identify and quantify glacial ice (^4He & Ne high, ^{18}O low in glacial ice)
^3He	Circulation of CDW onto Antarctic continental shelves (^3He high in CDW); gas exchange
Natural - Radioactive	
^{14}C	Large scale deep water circulation and mixing; ocean CO_2 uptake on century to millennial time scales
Anthropogenic - Transient	
CFC-11, CFC-12, CFC-113, CCl_4, SF_6	Identify most recently formed water; circulation pathways, water mass ages, water mass formation rates, estimation of anthropogenic CO_2 uptake
^3H	Same as trace gases above, but weak signal in S.H.
Bomb ^{14}C	Ocean uptake of anthropogenic CO_2
Anthropogenic - Deliberate	
SF_6, SF_5CF_3	Mixing, circulation, and gas exchange

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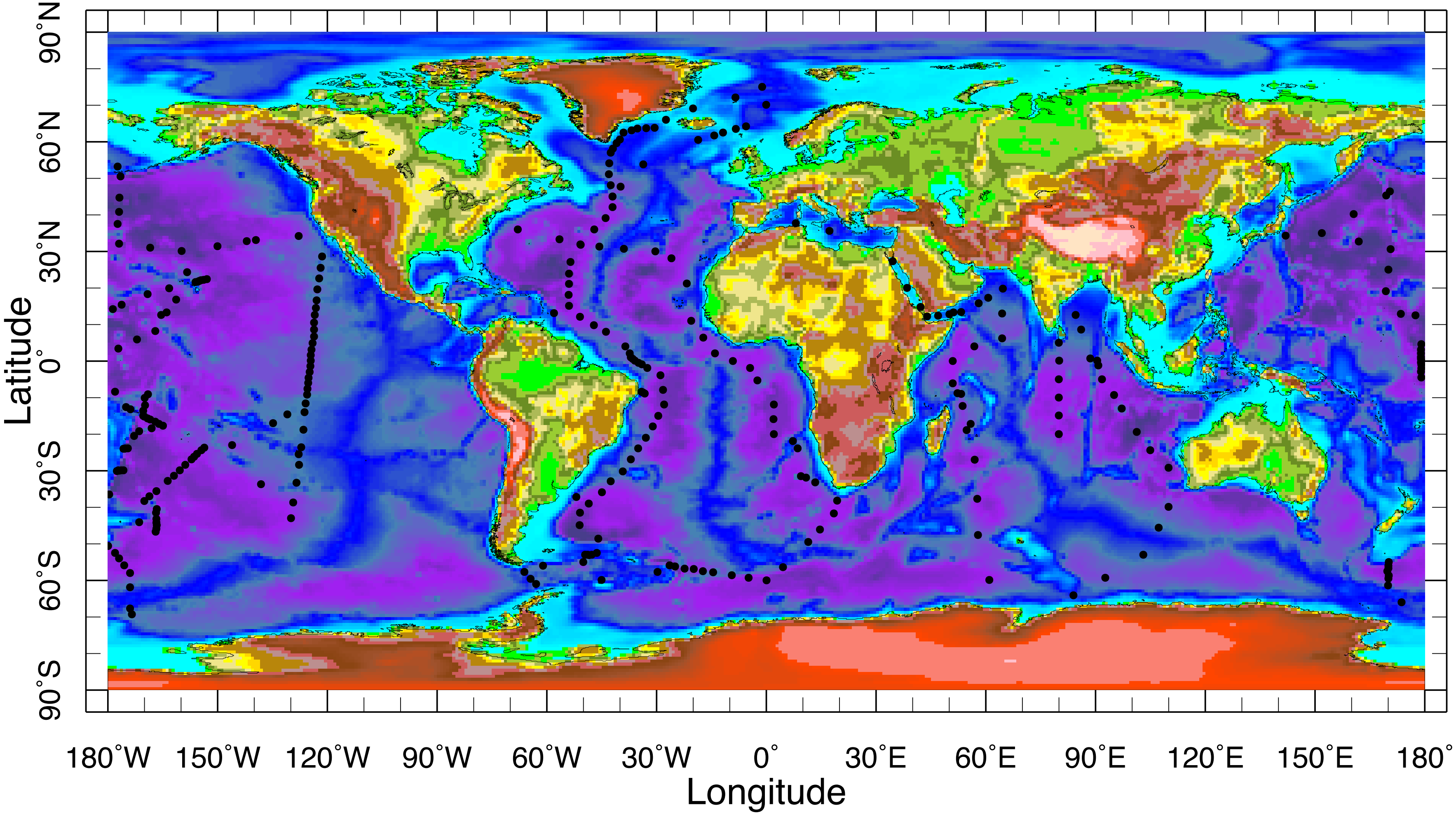
GEochemical Ocean SECtions Study (GEOSECS)

Atlantic from Jul 1972 to May 1973; Pacific from Aug 1973 to Jun 1974; Indian from Dec 1977 to Mar 1978



http://iridl.ldeo.columbia.edu/SOURCES/.GEOSECS/

Transient Tracers in the Oceans (TTO)

1981 & 1983

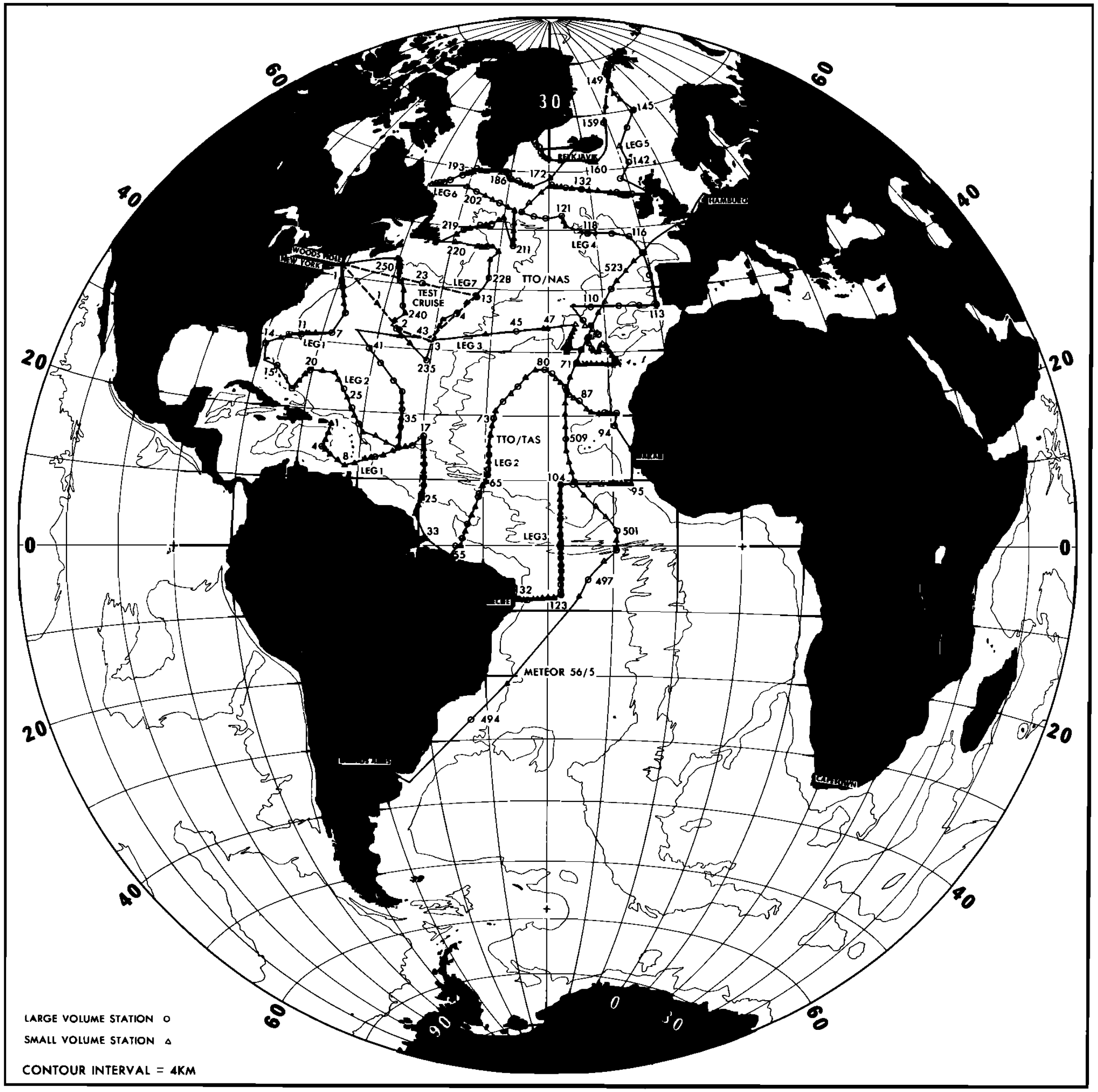
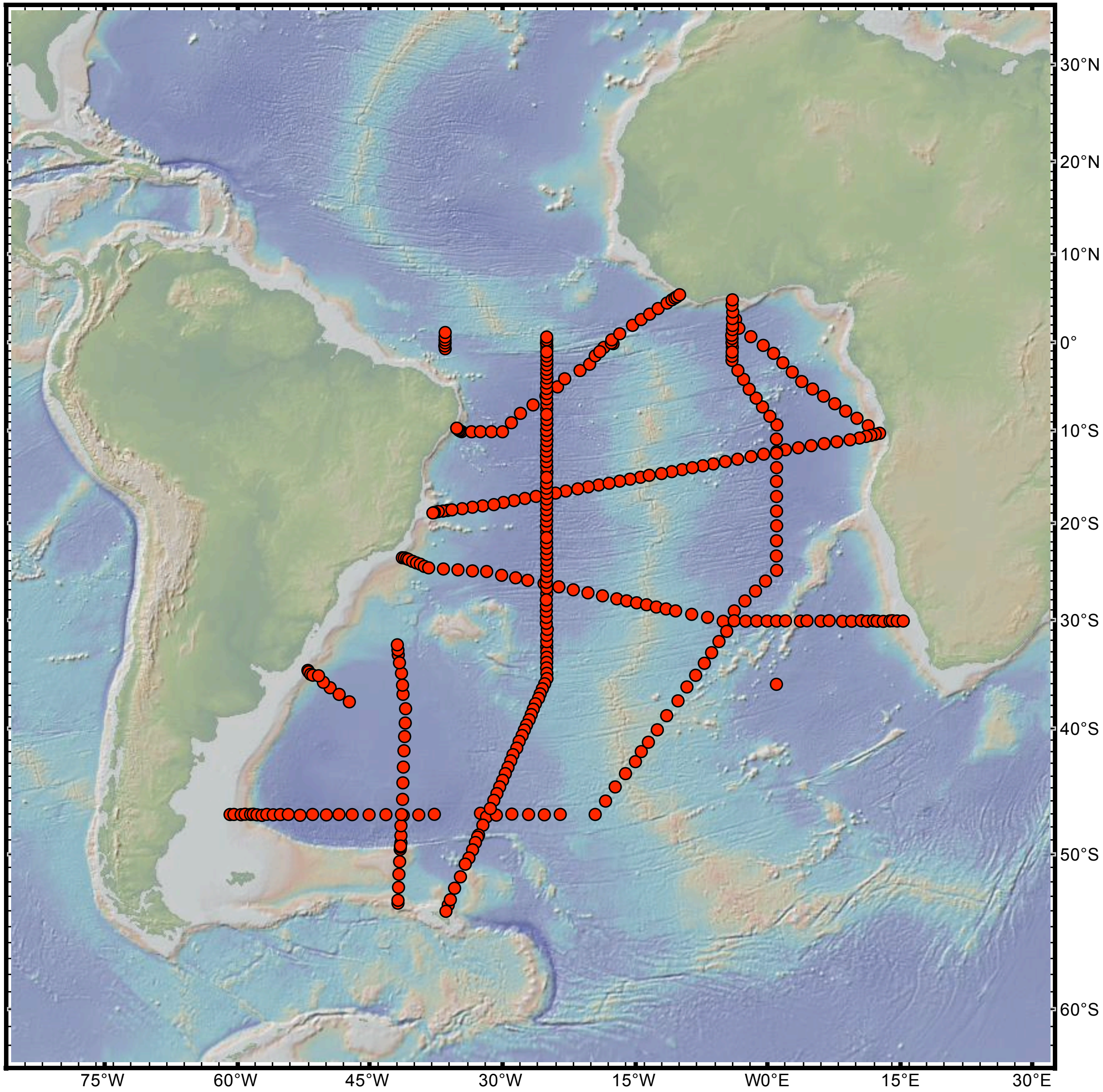


Fig. 1. Cruise track and station locations for the Transient Tracers in the Ocean program.

Brewer et al., 1985

South Atlantic Ventilation Experiment (SAVE)

1987-1989



World Ocean Circulation Experiment (WOCE)

1990 - 1998

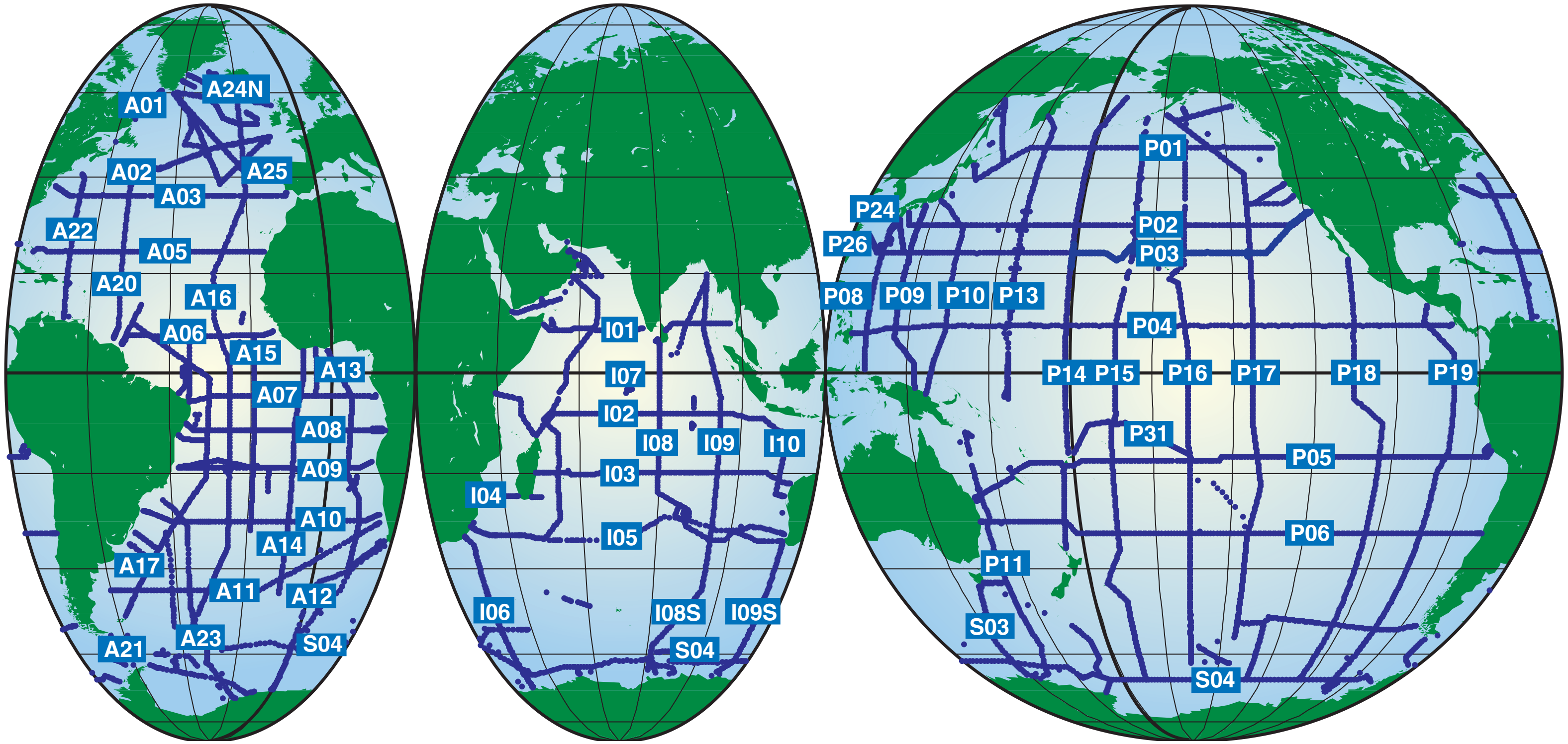
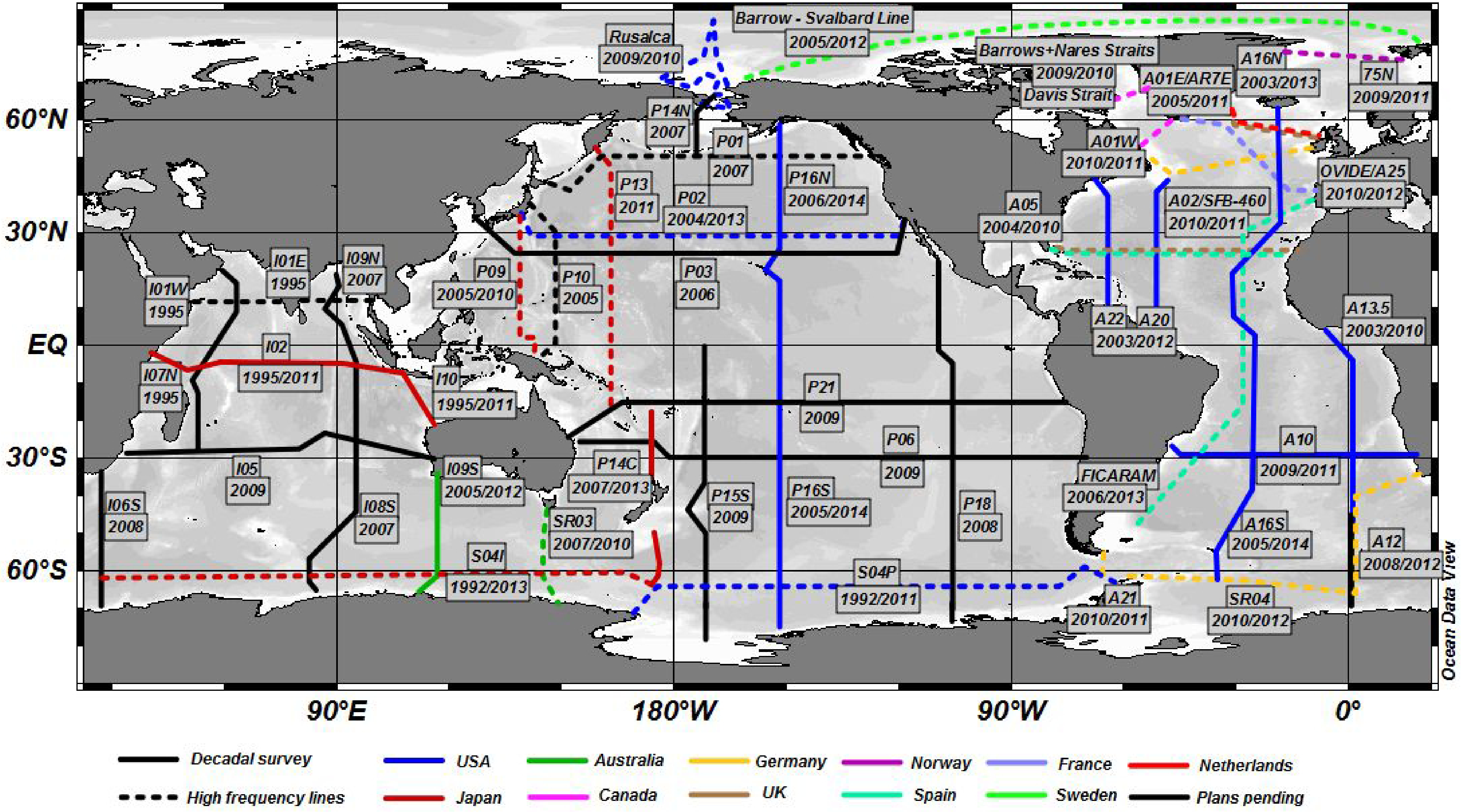


Figure 1. WHP One Time Survey Sections: station positions and line numbers.

http://woce.nodc.noaa.gov/wdiu/updates/Data_Resource.pdf

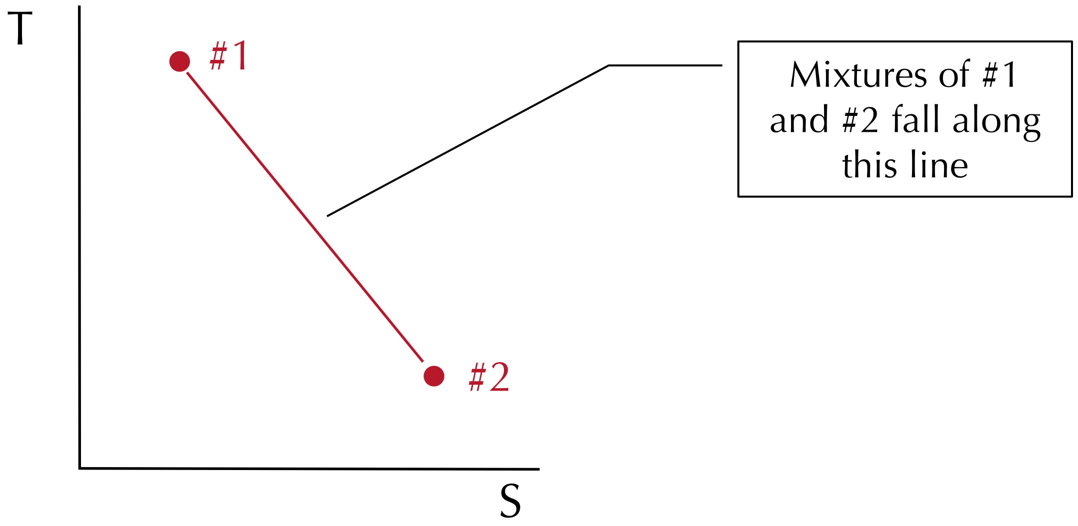
Repeat Hydrography Map: On-going and Planned Cruises



http://www.go-ship.org/RefSecs/GO-SHIPMap_May2010b.pdf

Mixing of Two Water Masses

1. Plot two stable conservative tracers for each water mass on an X-Y plot (*e.g.*, T, S)
2. Link points with a linear “mixing line”
3. Water samples with compositions falling along the mixing line are composed of mixtures of the two water masses



Water Mass Mixing Definitions

Assume: conservation of mass, heat, salt

Definitions:

C_i = concentration of some stable conservative property in water mass "i" (end-member concentration)

C_{mix} = concentration of some stable conservative property in a water mixture

f_i = fraction of the water mixture that is from water mass "i"

$f_{mix} = 1.0 = f_1 + f_2 + \ldots + f_i$ (mass balance equation)

Mixing of Two Water Masses

For two water masses, we need two equations with two variables:

$$1 = f_1 + f_2$$

$$C_{mix} = f_1C_1 + f_2C_2$$

When combined: $f_1 = \dfrac{C_{mix} - C_2}{C_1 - C_2}$

Mixing of Four Water Masses

We need four equations with four variables. For example:

$$1 = f_1 + f_2 + f_3 + f_4$$

$$T_{mix} = f_1T_1 + f_2T_2 + f_3T_3 + f_4T_4$$

$$S_{mix} = f_1S_1 + f_2S_2 + f_3S_3 + f_4S_4$$

$$NO_{mix} = f_1NO_1 + f_2NO_2 + f_3NO_3 + f_4NO_4$$

Thus, we need three stable, conservative tracers:

T_i = temperature of water mass "i"
T_{mix} = temperature of a water mixture

S_i = salinity of water mass "i"
S_{mix} = salinity of a water mixture

NO_i = NO of water mass "i"
NO_{mix} = NO of a water mixture

"NO" – A Quasi-Conservative Water Mass Tracer

$$106\,CO_2 + 16\,HNO_3 + 1\,H_3PO_4 + 122\,H_2O \Longleftrightarrow [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 138\,O_2$$

The elemental changes during respiration:

ΔC	ΔN	ΔP	ΔO	ΔO_2
+106	+16	+1	-276	-138

$$\Delta O_2 / \Delta N = -138 / 16 = -8.6$$

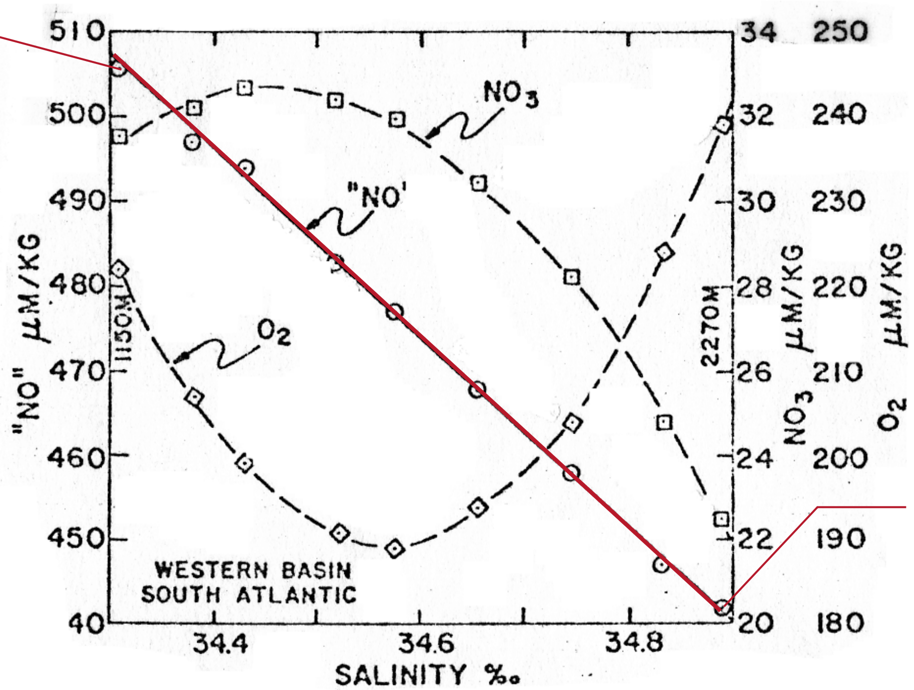
Thus, during the oxidation of organic matter:

For each mole of NO_3^- released to a water mass, ~9 moles of O_2 is removed

Broecker (1974): "NO" ≡ $9[NO_3^-] + [O_2]$

"PO" ≡ $135[PO_4^-] + [O_2]$

Conservative Behavior of “NO”



AAIW
1150 m

NADW
2270 m

Fig. 5. “NO”, NO_3, and O_2 versus salinity at Atlantic Geosecs station 60 in the western basin of the South Atlantic between the core of the AAIW (1150 m) and the top of the NADW (2270 m). The excess NO_3 content is just balanced by the O_2 deficiency yielding a straight line relationship between salinity and “NO”.

Broecker, 1974

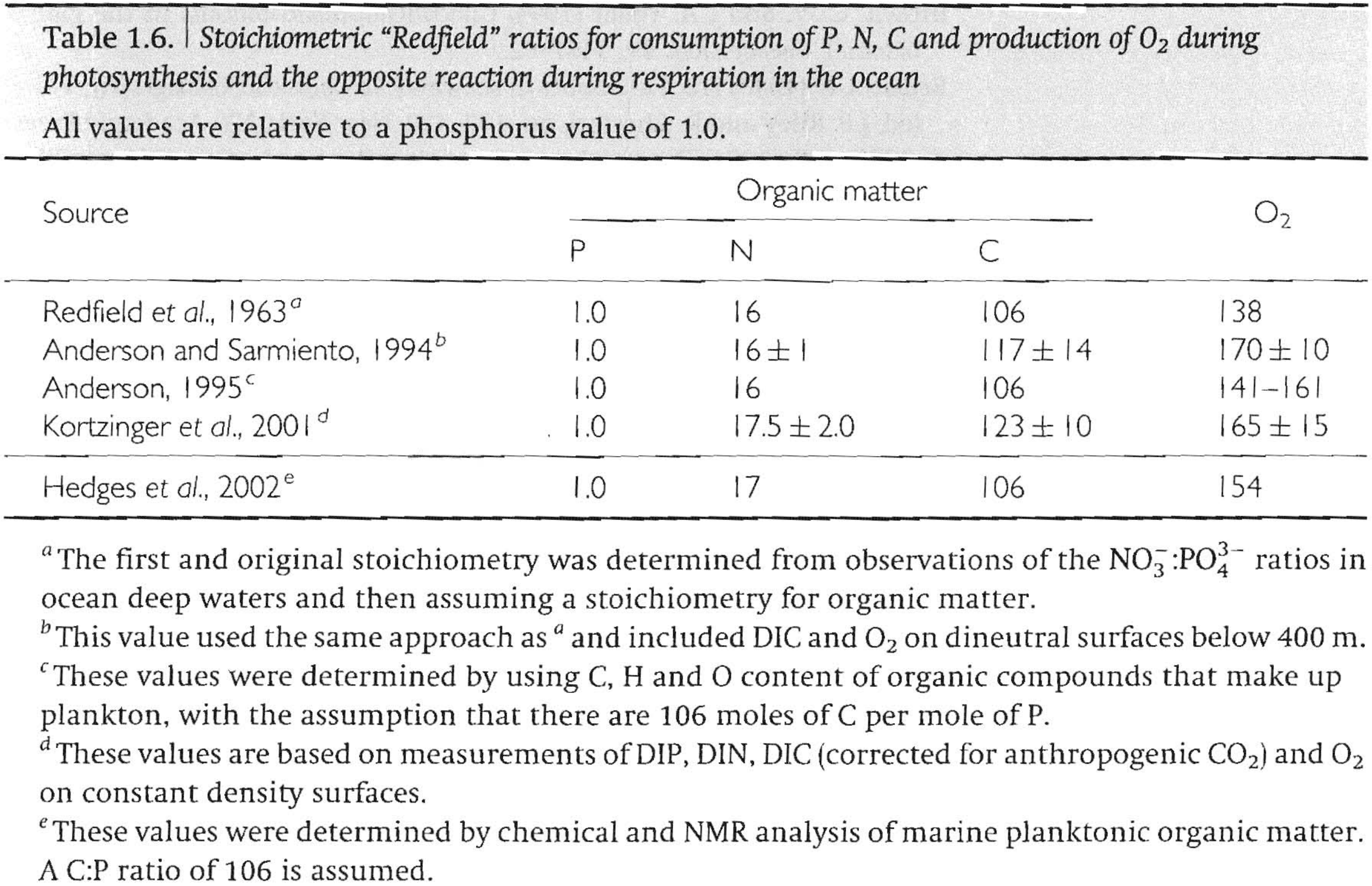


Table 1.6. *Stoichiometric "Redfield" ratios for consumption of P, N, C and production of O_2 during photosynthesis and the opposite reaction during respiration in the ocean*

All values are relative to a phosphorus value of 1.0.

Source	Organic matter			O_2
	P	N	C	
Redfield *et al.*, 1963[a]	1.0	16	106	138
Anderson and Sarmiento, 1994[b]	1.0	16 ± 1	117 ± 14	170 ± 10
Anderson, 1995[c]	1.0	16	106	141–161
Kortzinger *et al.*, 2001[d]	1.0	17.5 ± 2.0	123 ± 10	165 ± 15
Hedges *et al.*, 2002[e]	1.0	17	106	154

[a] The first and original stoichiometry was determined from observations of the $NO_3^-:PO_4^{3-}$ ratios in ocean deep waters and then assuming a stoichiometry for organic matter.

[b] This value used the same approach as [a] and included DIC and O_2 on dineutral surfaces below 400 m.

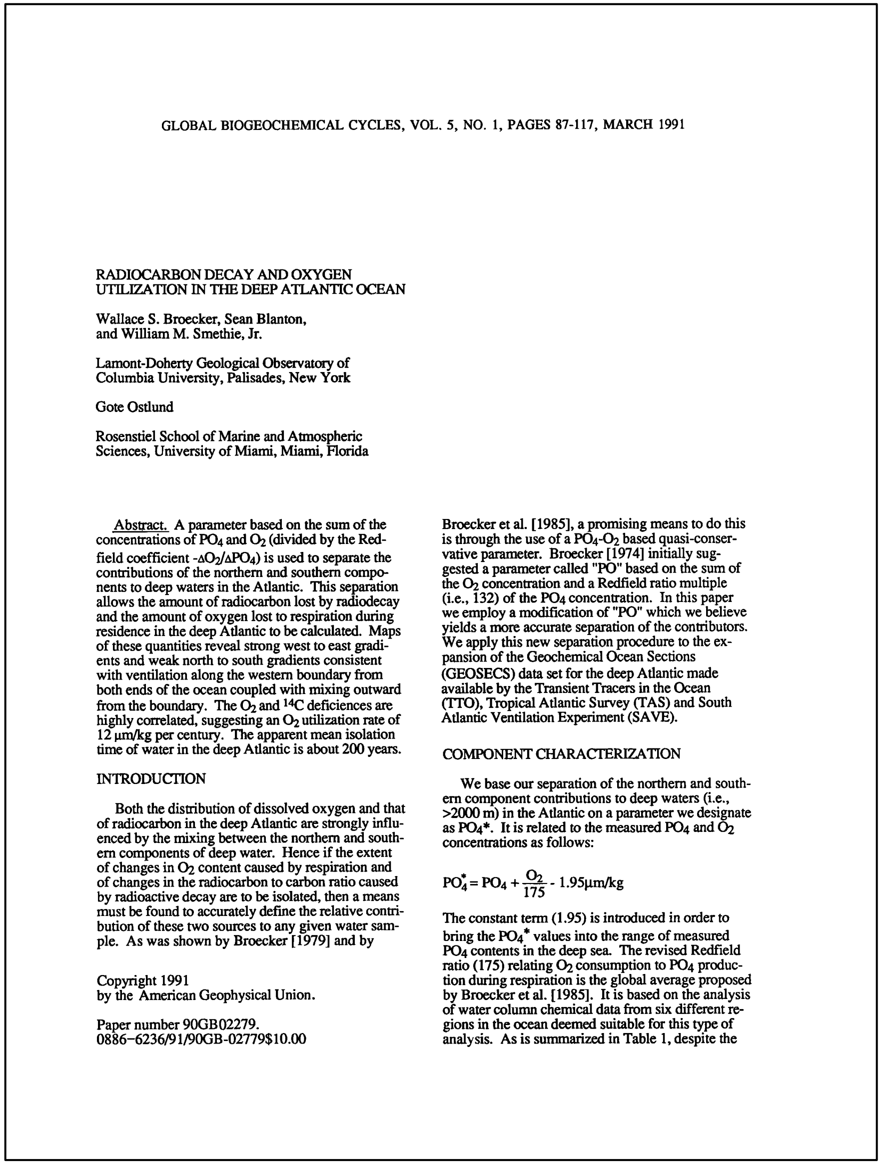
[c] These values were determined by using C, H and O content of organic compounds that make up plankton, with the assumption that there are 106 moles of C per mole of P.

[d] These values are based on measurements of DIP, DIN, DIC (corrected for anthropogenic CO_2) and O_2 on constant density surfaces.

[e] These values were determined by chemical and NMR analysis of marine planktonic organic matter. A C:P ratio of 106 is assumed.

Emerson and Hedges, 2008

PO_4* – Another Quasi-Conservative Water Mass Tracer



GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 5, NO. 1, PAGES 87-117, MARCH 1991

RADIOCARBON DECAY AND OXYGEN UTILIZATION IN THE DEEP ATLANTIC OCEAN

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Abstract. A parameter based on the sum of the concentrations of PO_4 and O_2 (divided by the Redfield coefficient $-\Delta O_2/\Delta PO_4$) is used to separate the contributions of the northern and southern components to deep waters in the Atlantic. This separation allows the amount of radiocarbon lost by radiodecay and the amount of oxygen lost to respiration during residence in the deep Atlantic to be calculated. Maps of these quantities reveal strong west to east gradients and weak north to south gradients consistent with ventilation along the western boundary from both ends of the ocean coupled with mixing outward from the boundary. The O_2 and ^{14}C deficiences are highly correlated, suggesting an O_2 utilization rate of 12 µm/kg per century. The apparent mean isolation time of water in the deep Atlantic is about 200 years.

INTRODUCTION

Both the distribution of dissolved oxygen and that of radiocarbon in the deep Atlantic are strongly influenced by the mixing between the northern and southern components of deep water. Hence if the extent of changes in O_2 content caused by respiration and of changes in the radiocarbon to carbon ratio caused by radioactive decay are to be isolated, then a means must be found to accurately define the relative contribution of these two sources to any given water sample. As was shown by Broecker [1979] and by Broecker et al. [1985], a promising means to do this is through the use of a PO_4-O_2 based quasi-conservative parameter. Broecker [1974] initially suggested a parameter called "PO" based on the sum of the O_2 concentration and a Redfield ratio multiple (i.e., 132) of the PO_4 concentration. In this paper we employ a modification of "PO" which we believe yields a more accurate separation of the contributors. We apply this new separation procedure to the expansion of the Geochemical Ocean Sections (GEOSECS) data set for the deep Atlantic made available by the Transient Tracers in the Ocean (TTO), Tropical Atlantic Survey (TAS) and South Atlantic Ventilation Experiment (SAVE).

COMPONENT CHARACTERIZATION

We base our separation of the northern and southern component contributions to deep waters (i.e., >2000 m) in the Atlantic on a parameter we designate as PO_4*. It is related to the measured PO_4 and O_2 concentrations as follows:

$$PO_4^* = PO_4 + \frac{O_2}{175} - 1.95 \mu m/kg$$

The constant term (1.95) is introduced in order to bring the PO_4^* values into the range of measured PO_4 contents in the deep sea. The revised Redfield ratio (175) relating O_2 consumption to PO_4 production during respiration is the global average proposed by Broecker et al. [1985]. It is based on the analysis of water column chemical data from six different regions in the ocean deemed suitable for this type of analysis. As is summarized in Table 1, despite the

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0886–6236/91/90GB-02779$10.00

Broecker (1985):

$$\Delta O_2 / \Delta PO_4 = -175 / 1 = -175$$

Thus, during the oxidation of organic matter:

For each mole of PO_4^- released to a water mass, ~175 moles of O_2 is removed

Broecker (1991):

$$[PO_4^*] \equiv [PO_4^-] + \frac{[O_2]}{175} - 1.95\ \mu mol/kg$$

Separating NADW from AABW

Salinity (S) is conservative, but 4 water masses that combine to form NADW have different S.

PO_4^* is nearly uniform within the AABW and within the four components of NADW (*Broecker et al.*, 1998):

AABW: 1.95 ± 0.07 µmol kg^{-1}
NADW: 0.73 ± 0.07 µmol kg^{-1}

Fraction of NADW is:

$$f_{NADW} = \frac{1.95 - [PO_4^*]}{1.95 - 0.73}$$

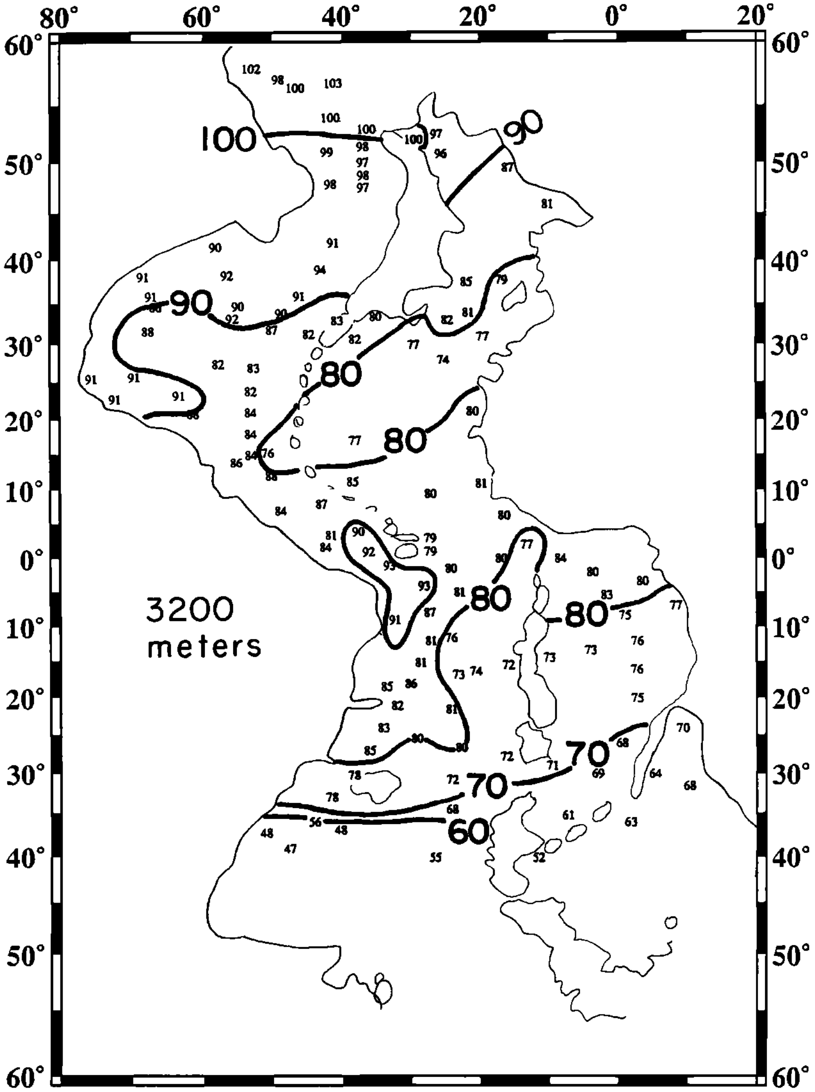
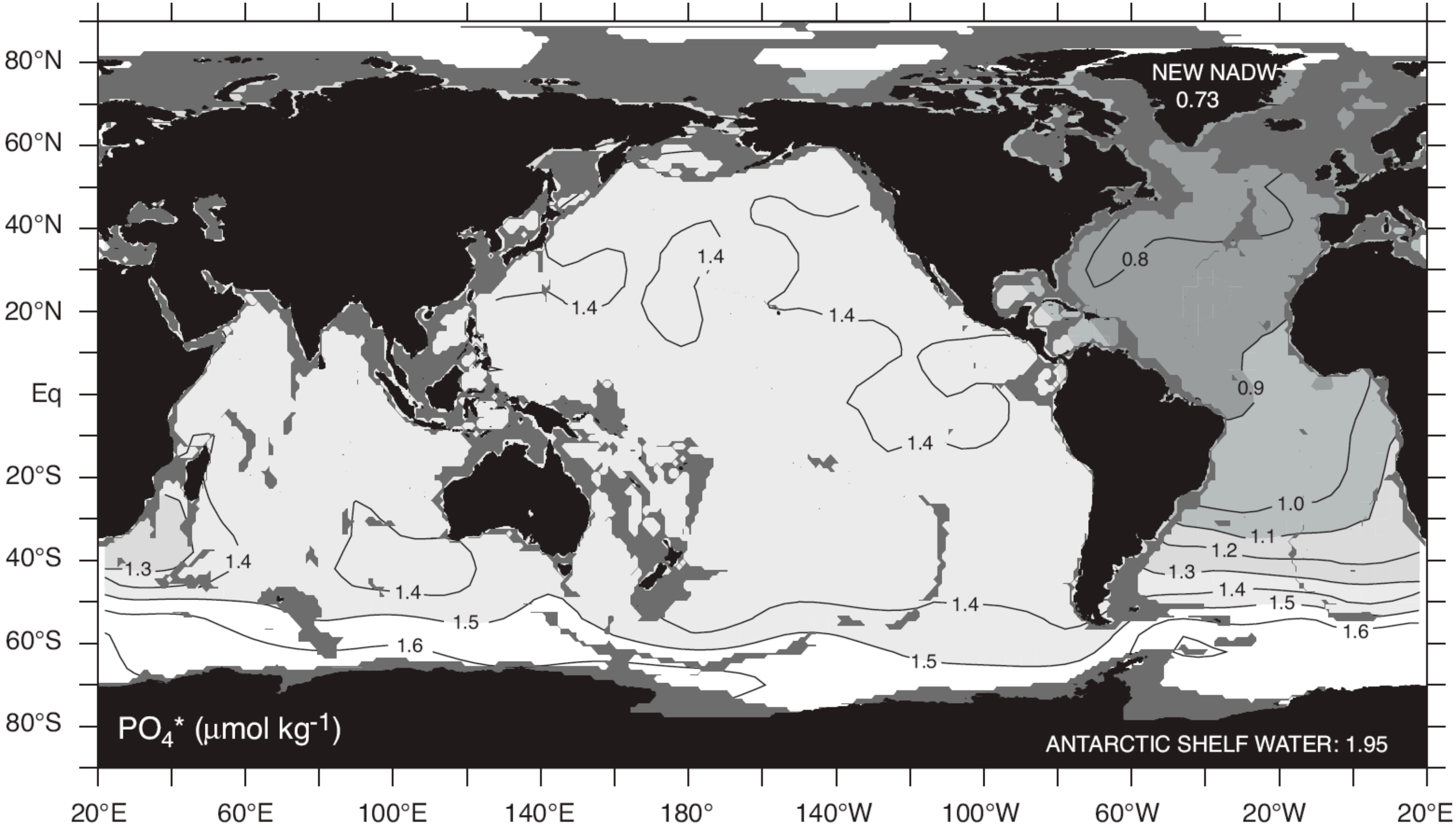


Fig. 4. Map showing percentage of northern component water along the 3200 m depth horizon. The light lines define the geographic boundaries of this horizon.

Broecker et al., 1991

PO_4^* distribution at 3000 m in the world ocean.



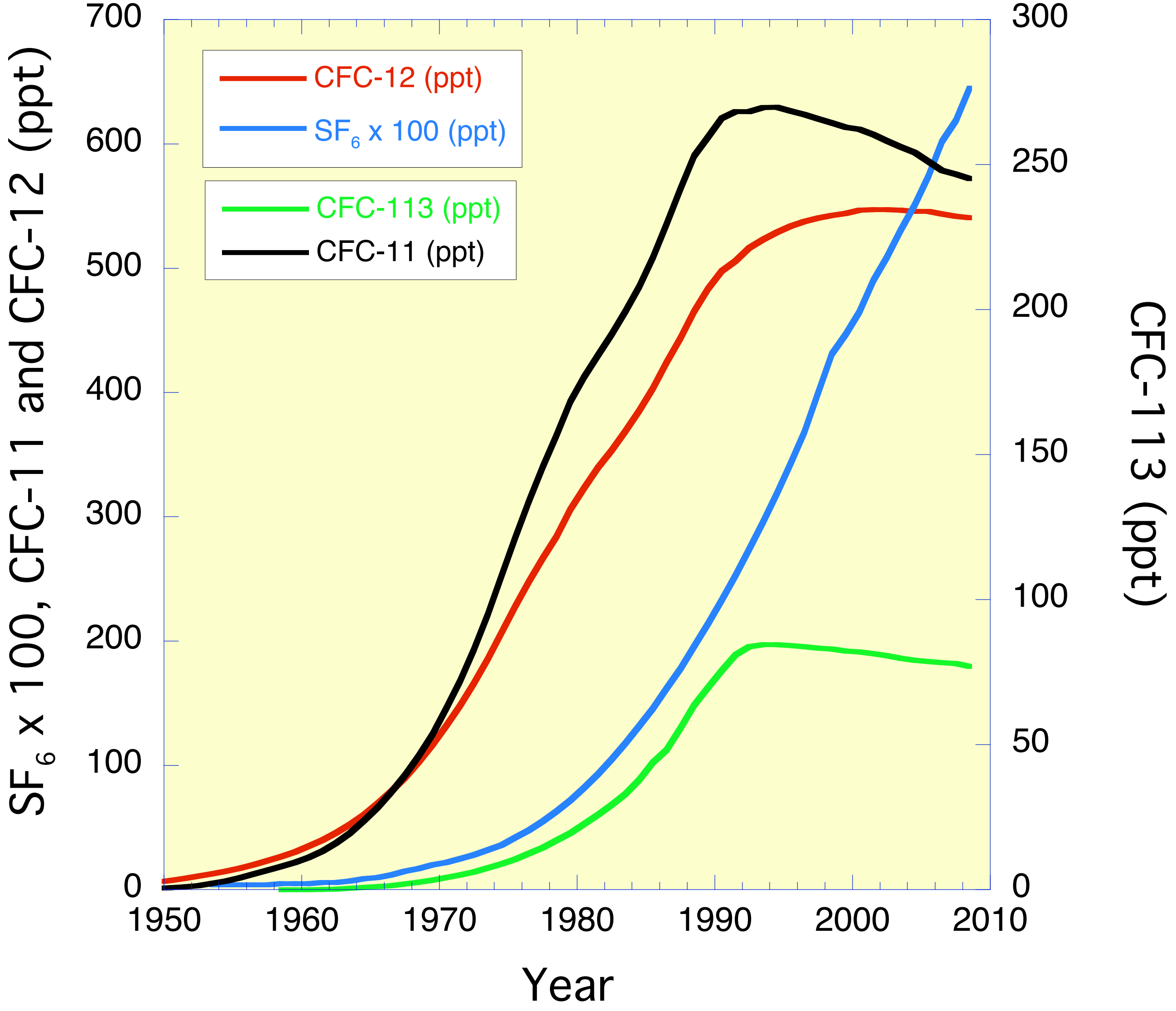
$$f_{NADW} = \frac{1.95 - [PO_4^*]}{1.95 - 0.73} = \frac{1.95 - 1.4}{1.95 - 0.73} = 45\%$$

Sarmiento and Gruber, 2006

Transient Tracers

- Usually anthropogenic compounds with time-varying sources (or sinks)
  - $CFCs$, CCl_4, SF_6, ^{14}C, ^3H
- They enter the surface waters of the ocean either via gas exchange (e.g., CFCs, CCl_4, SF_6, ^{14}C) or water vapor exchange (^3H)
- Transient tracers allow:
  - Penetration of surface perturbations into the interior of the oceans to be visualized.
  - Delineation of pathways that newly formed subsurface water follows after leaving the surface.
  - Investigation of ocean circulation and mixing, and validation/ calibration of GCMs.
  - Determination of water mass formation rates
  - Estimation of anthropogenic CO_2 inventory in the ocean

N.H. CFCs & SF_6 atm. mixing ratios



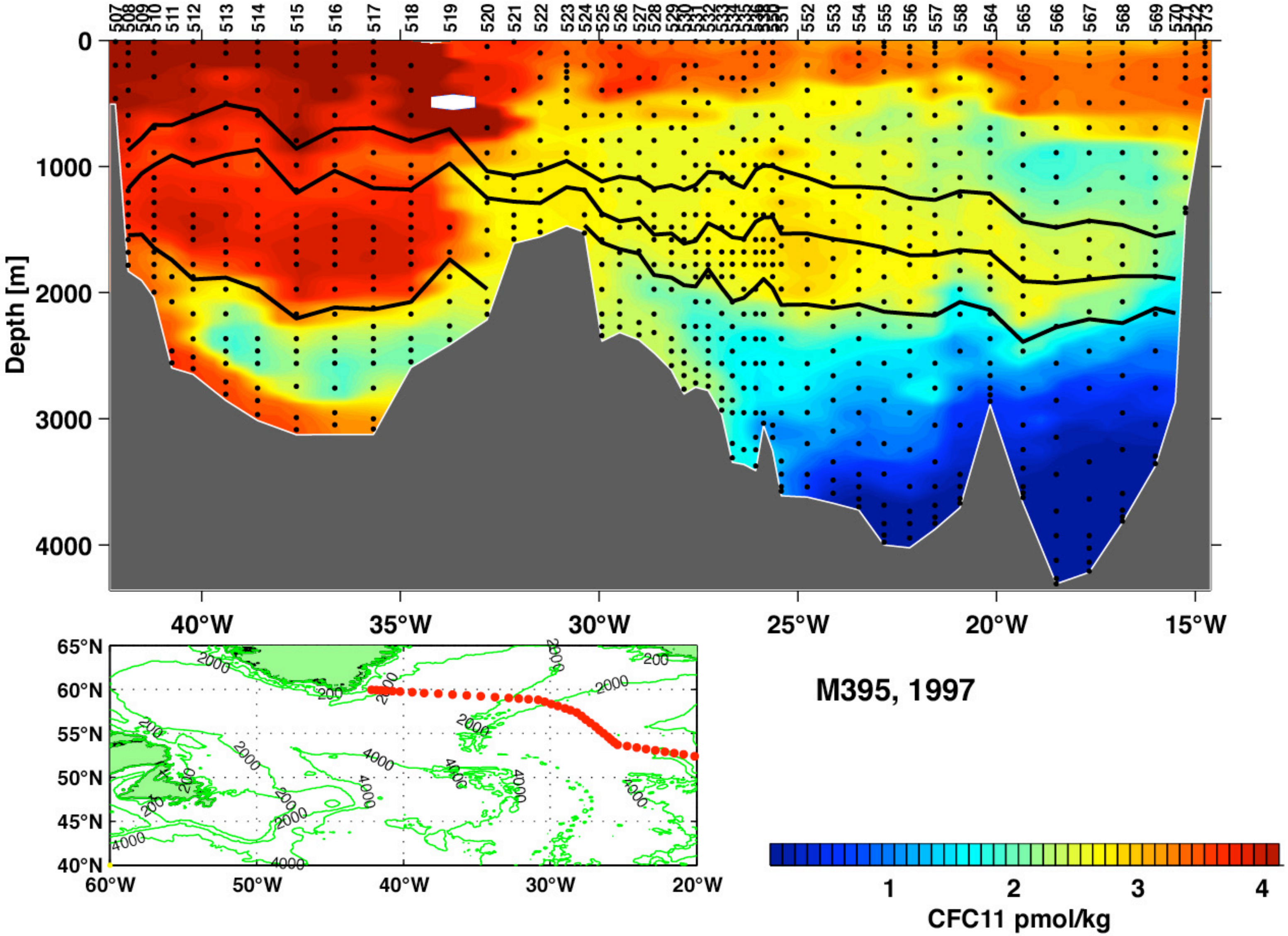
Solubilities of CFCs & SF_6

- Strong function of temperature
- Increases as temperature decreases
- Ranges by a factor of about 3.5 between 0 and 25°C

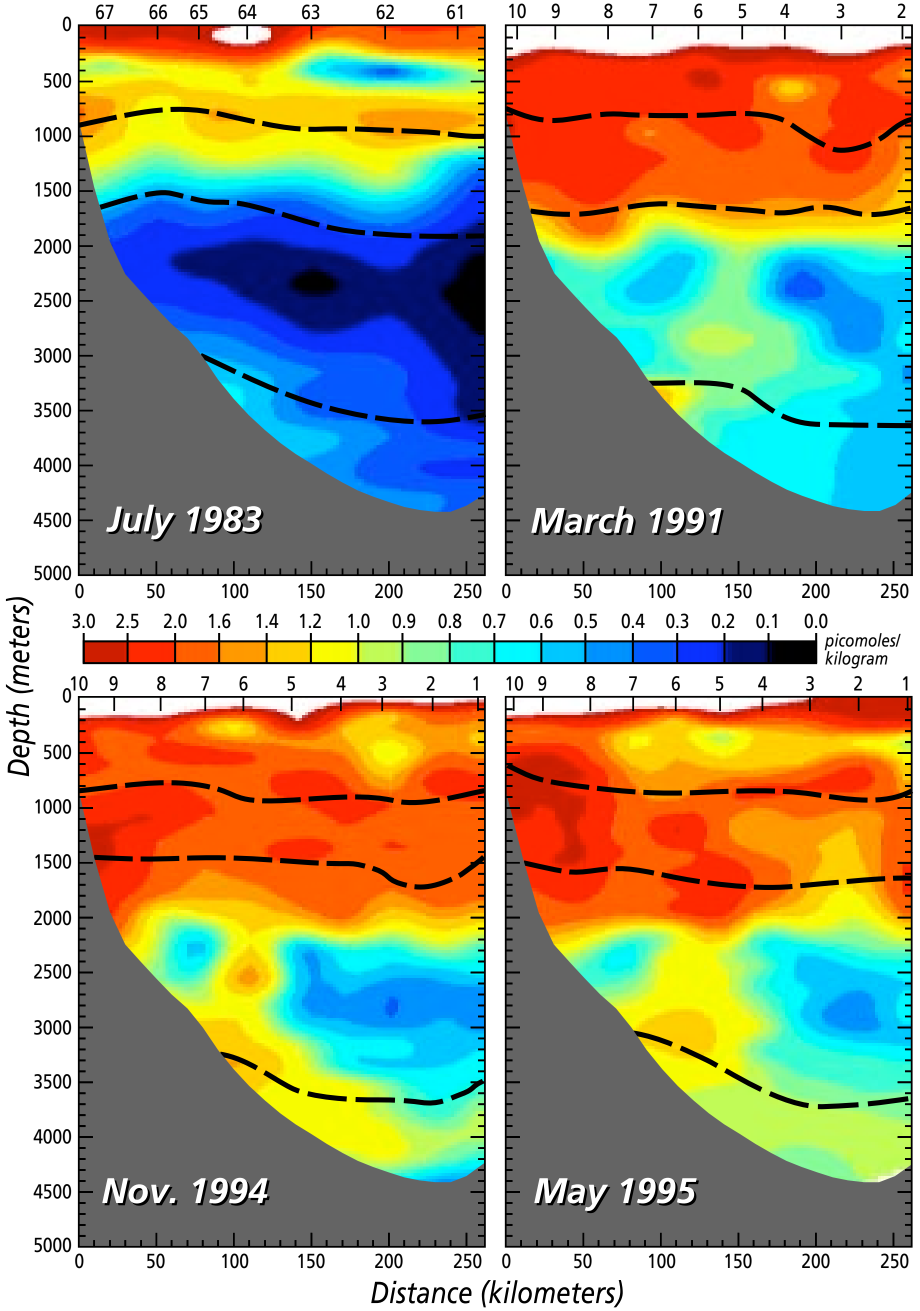
- Weaker function of salinity
- Decreases as salinity increases
- Varies by 50% between salinity of 0 and 35

- Solubilities are well known (± 1% or better)
    - CFC-11 & CFC-12: Warner and Weiss, *Deep Sea Res. I*, 32:1485-1497, 1985
    - CFC-113: Bu and Warner, *Deep Sea Res. I*, 42:1151-1161, 1995
    - SF_6: Bullister, Wisegarver and Menzia, *Deep Sea Res. I*, 49:175-187, 2002

Pathway of Labrador Sea Water



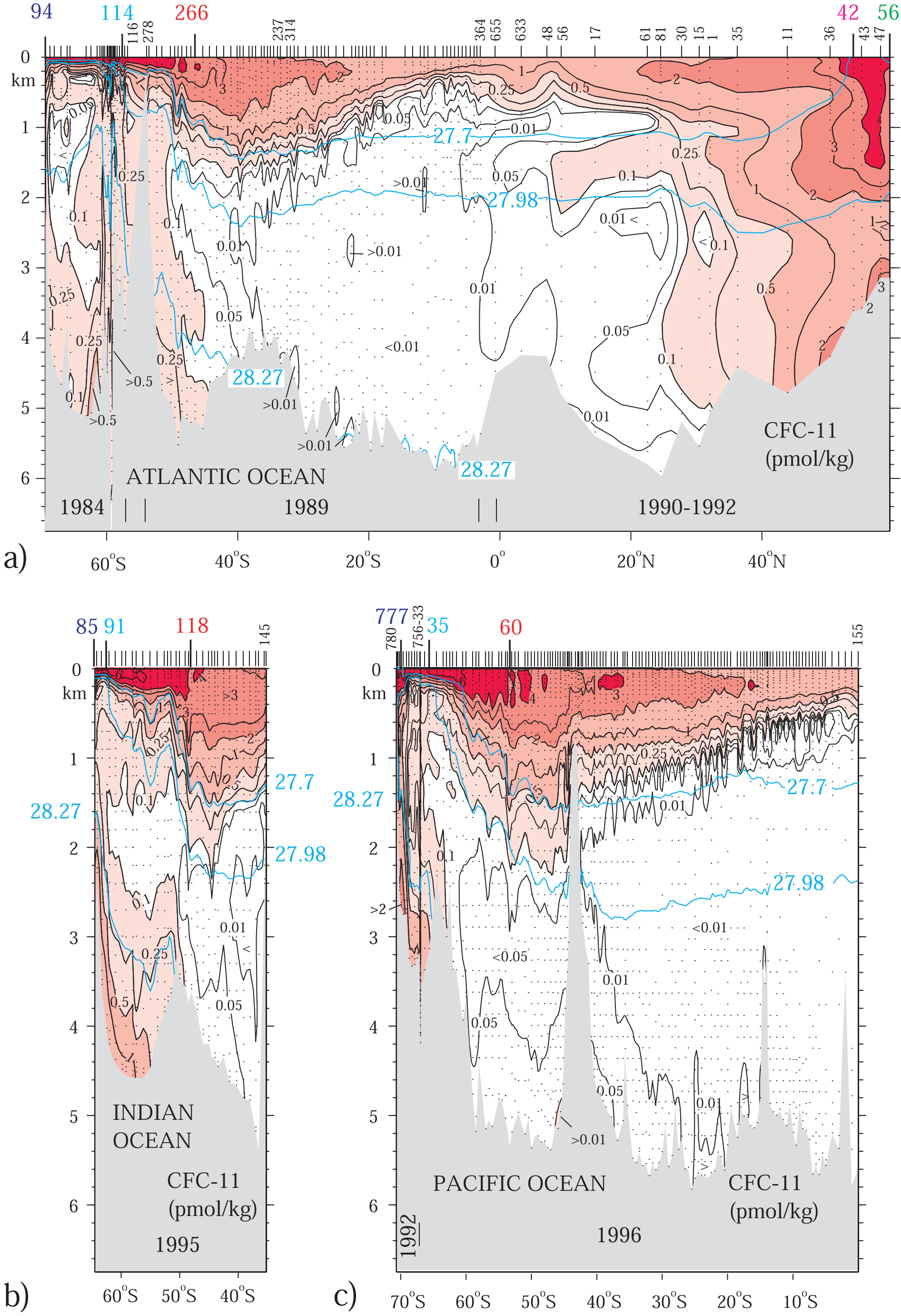
Rhein et al. (2002)



Four chlorofluorocarbon (CFC) sections taken at various times along 55°W south of the Grand Banks. Note the absence of any significant CFC signal at the depth of the Labrador Sea Water (about 1,500 meters depth) in 1983, but the sudden flooding of these depths with CFCs in the later sections, as newly formed Labrador Sea Water flows around the Grand Banks and into the Sargasso Sea. These changes correspond to the tritium increases seen in the Bermuda time series (see figure opposite).

Jenkins and Smethie, Oceanus, 1996

Vertical distributions of CFC-11 (pmol/kg) measured along hydrographic lines in the (a) Atlantic, (b) Indian, and (c) Pacific oceans.

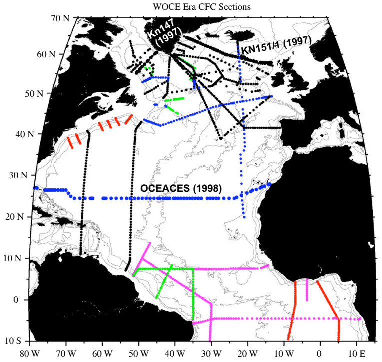


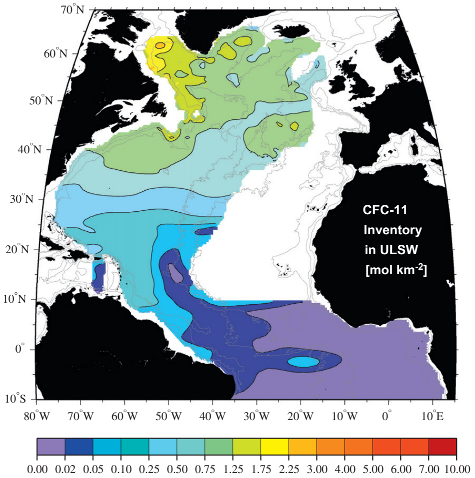
Orsi et al., 2002

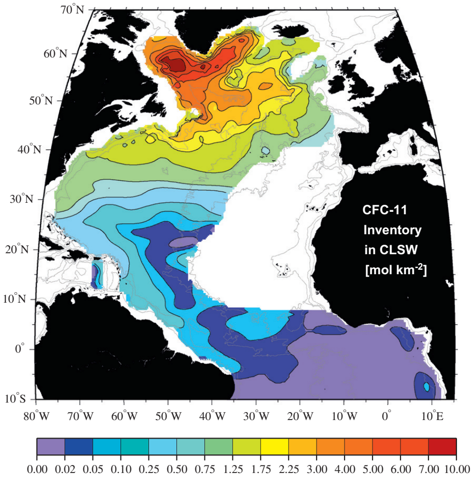
Formation rate of NADW

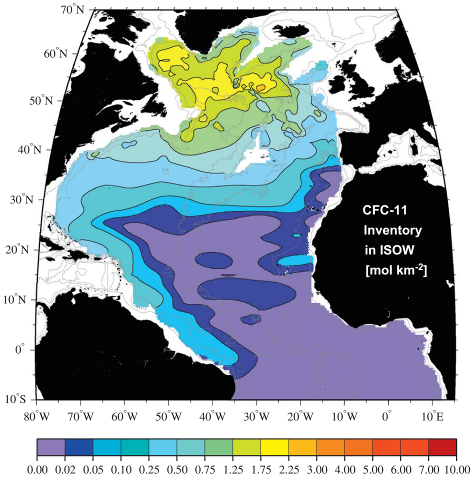
$$I = \int R(t)C(\theta, S, t)dt$$

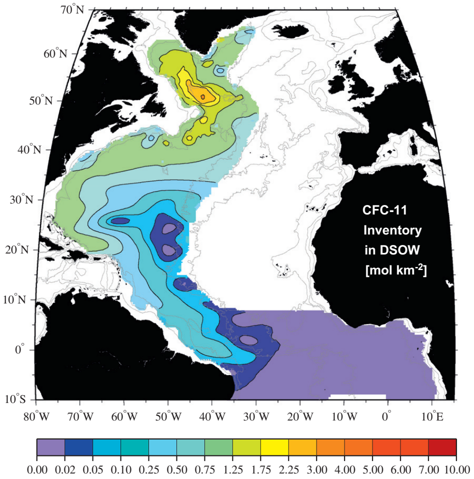
I: Water mass CFC inventory
R: Rate of water mass formation
C: Source water CFC concentration
θ: Potential temperature
S: Salinity
t: Time











LeBel et al., 2008

Water Mass	**CFC-11 Inventory (million mol) 1970-1990** (Smethie and Fine, 2001)	**CFC-11 Inventory (million mol) 1970-1997** (LeBel et al., 2008)	**Formation Rate 1970-1990 (Sv)** (Smethie and Fine, 2001)	**Formation Rate 1970-1997 (Sv)** (LeBel et al., 2008)
Upper LSW	4.2	10.5	2.2	3.5
Classical LSW	14.7	23.4	7.4	8.2
ISOW	5.0	10.4	5.2	5.7
DSOW	5.9	8.3	2.4	2.2
NADW (total)	29.8	52.6	17.2	19.6

Estimate Ocean Uptake of Anthropogenic CO_2

$$TCO_2^{ant} = \Delta C^* - \text{mean of } (TCO_2^{m} - \Delta TCO_2^{bio} - \boxed{TCO_2^{eq\ t})}$$

TCO_2^{ant} : Total anthropogenic CO_2

TCO_2^{m} : Total measured CO_2

ΔTCO_2^{bio} : Change in total CO_2 due to biological processes

$TCO_2^{eq\ t}$: Total CO_2 in equilibrium with the atmospheric CO_2 present at the time when the water parcel was last at the surface, which is determined from the pCFC age

see *Gruber et al.*, 1996

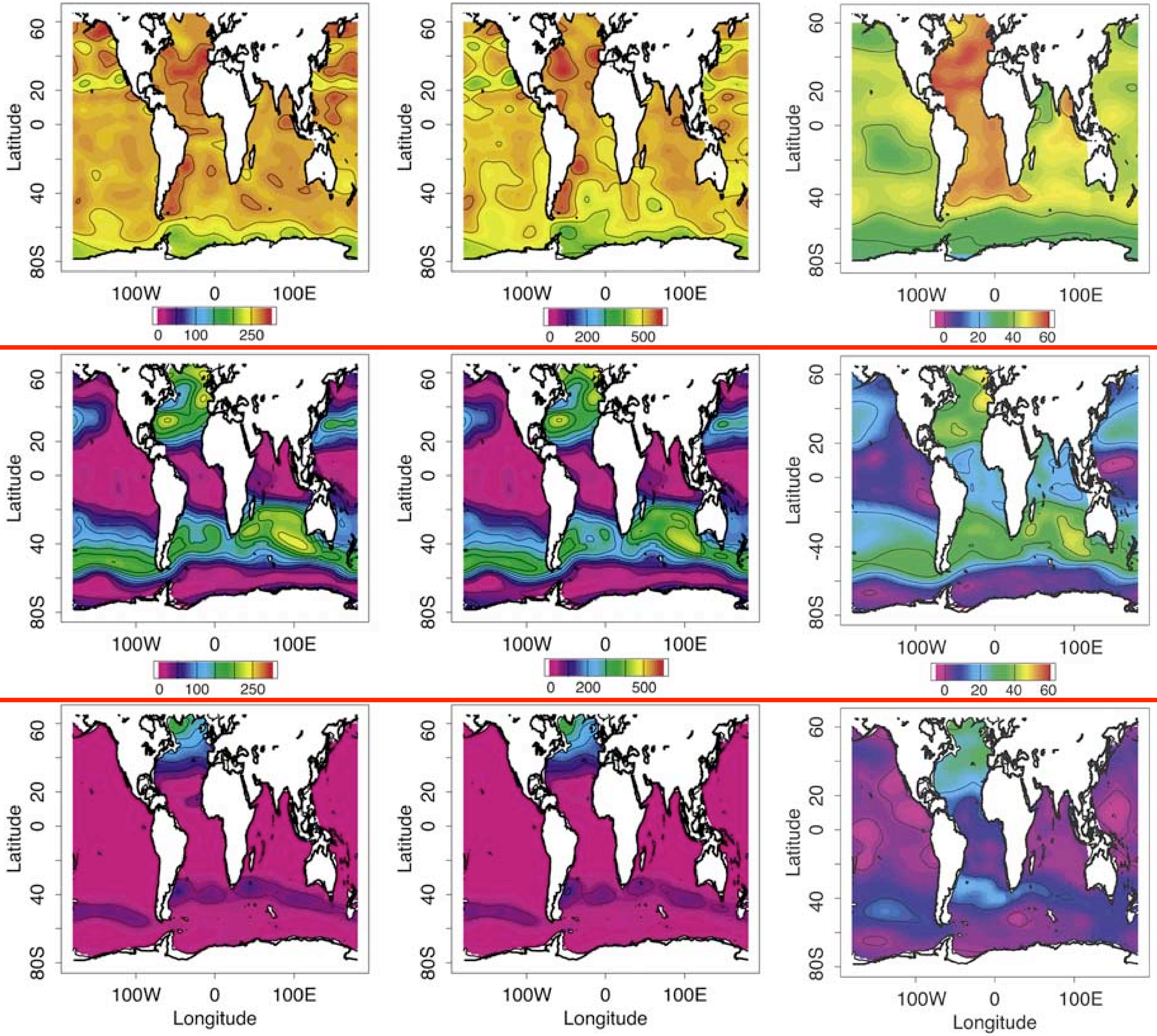
Estimate Ocean Uptake of Anthropogenic CO_2

pCFC-11 | pCFC-12 | Anthropogenic CO_2

0 m

500 m

1000 m

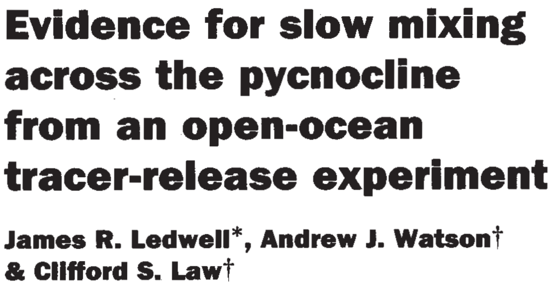


Key et al. (2004)

Deliberate Tracers

- Most commonly used
  - SF_6, ^3He, and now SF_5CF_3
- Deliberate tracers used to study:
  - Vertical mixing in the ocean
  - Pathways of newly formed deep water
  - Air-sea gas exchange

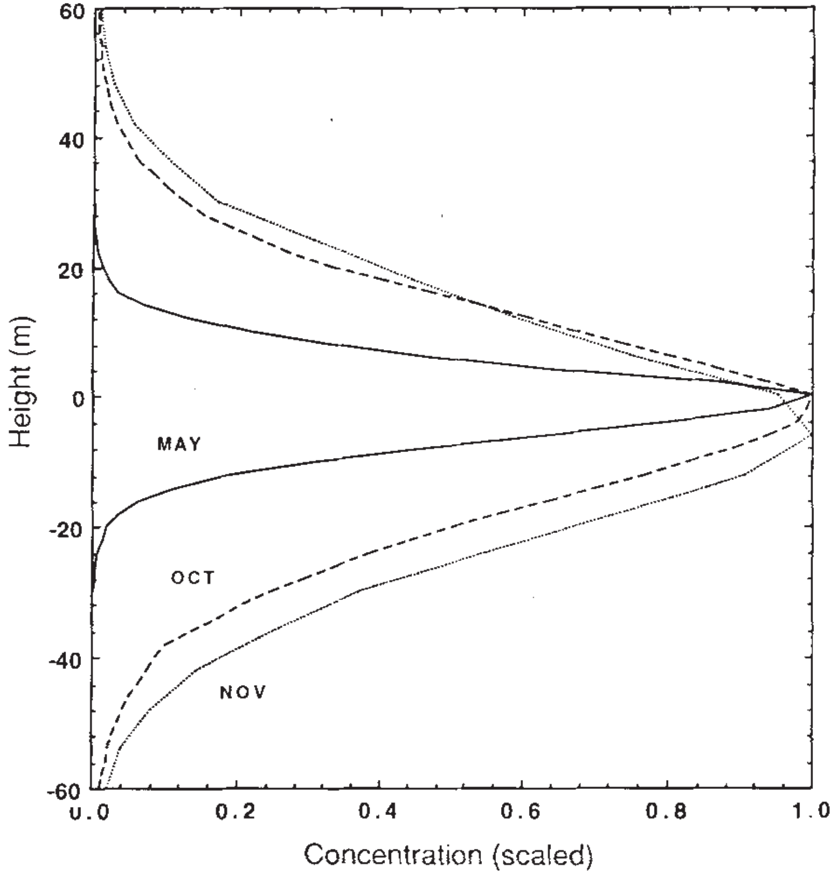
Measurement of Vertical Eddy Diffusivity



Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment

James R. Ledwell*, Andrew J. Watson† & Clifford S. Law†

- North Atlantic Ocean
- SF_6 injected at 310 m
- Measured tracer diffusion over time



$$K_z = \frac{1}{2}\frac{d\sigma_z^2}{dt} = 0.11\ \mathrm{cm^2\ s^{-1}}$$

Ledwell et al., 1993

The Greenland Sea tracer experiment 1996–2002: Horizontal mixing and transport of Greenland Sea Intermediate Water

M.-J. Messias [a,*], A.J. Watson [a], T. Johannessen [b], K.I.C. Oliver [a], K.A. Olsson [b,c], E. Fogelqvist [c], J. Olafsson [d], S. Bacon [e], J. Balle [a], N. Bergman [a], G. Budéus [f], M. Danielsen [d], J.-C. Gascard [g], E. Jeansson [b,c], S.R. Olafsdottir [d], K. Simonsen [h,1], T. Tanhua [c], K. Van Scoy [i], J.R. Ledwell [j]

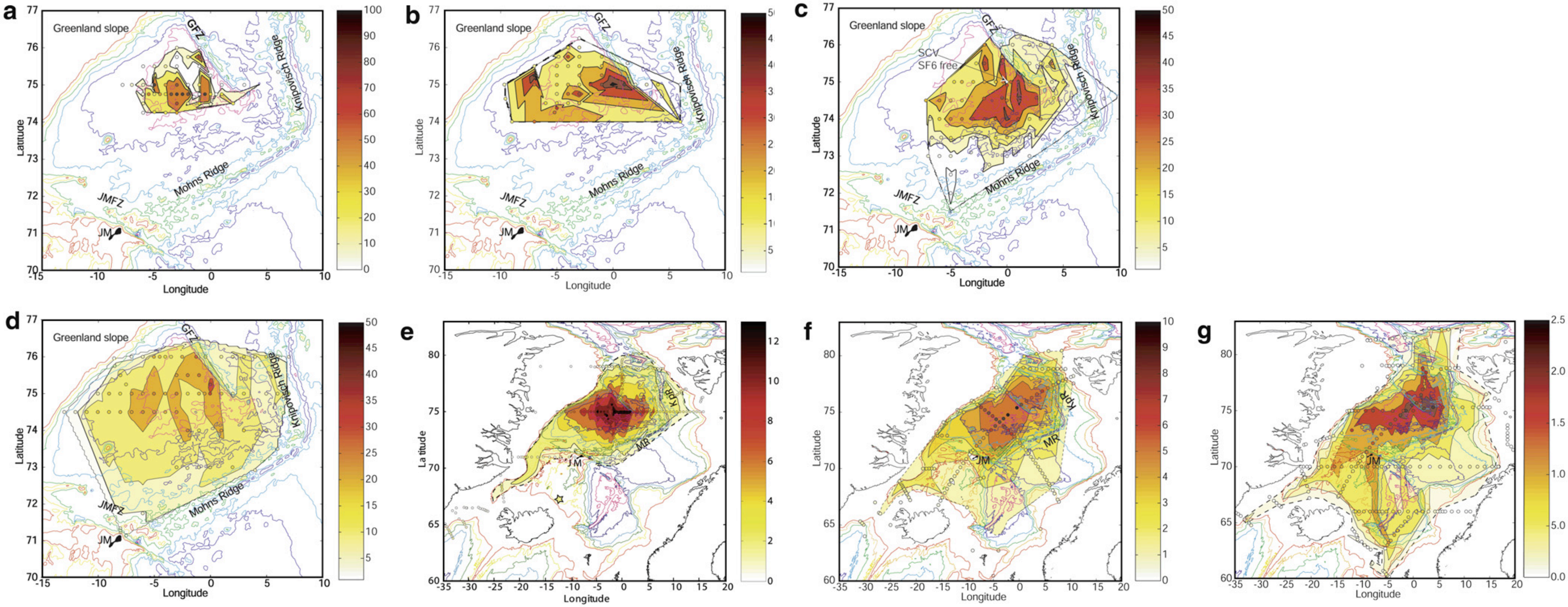


Fig. 10. Evolution of the SF_6 patch during the seven main subsequent cruises following the release. Triangle-based linear interpolation (Delaunay triangulation) contoured map of the Column Integral of SF_6 superimposed on colored bathymetry (black = 0 m, red = 1000 m, yellow = 1500 m, green = 2000 m, cyan = 2500 m, dark blue = 3000 m, magenta = 3500 m) from November/December 1996 (a), February/March 1997 (b), May 1997 (c), March 1998 (d), September 1998 where the star indicates the position of the profile shown in Fig. 11 (e), July 1999 (f) and June 2002 (g). Contours have been chosen to give a rough sketch of the distribution of the tracer. The dot at the station positions are colored according to the scale concentration for more details. Where there are dashed lines, the full extent of the tracer patch cannot be properly delineated from the survey coverage. The column integral for each station is given in units of nmol/m^2. The column integral includes the background concentration as well as the tracer from the release and therefore the tracer patch is defined as SF_6 concentrations >1 nmol/m^2 for all the cruises except June 2002. By June 2002 the SF_6 patch was well diluted and in order to obtain the true distribution of the SF_6 from the release, CFCs concentrations were used here to subtract the background SF_6. For the maps e–f–g, drawing of these contours has been guided so it does not interpolate over land.

Messias et al., 2008

T

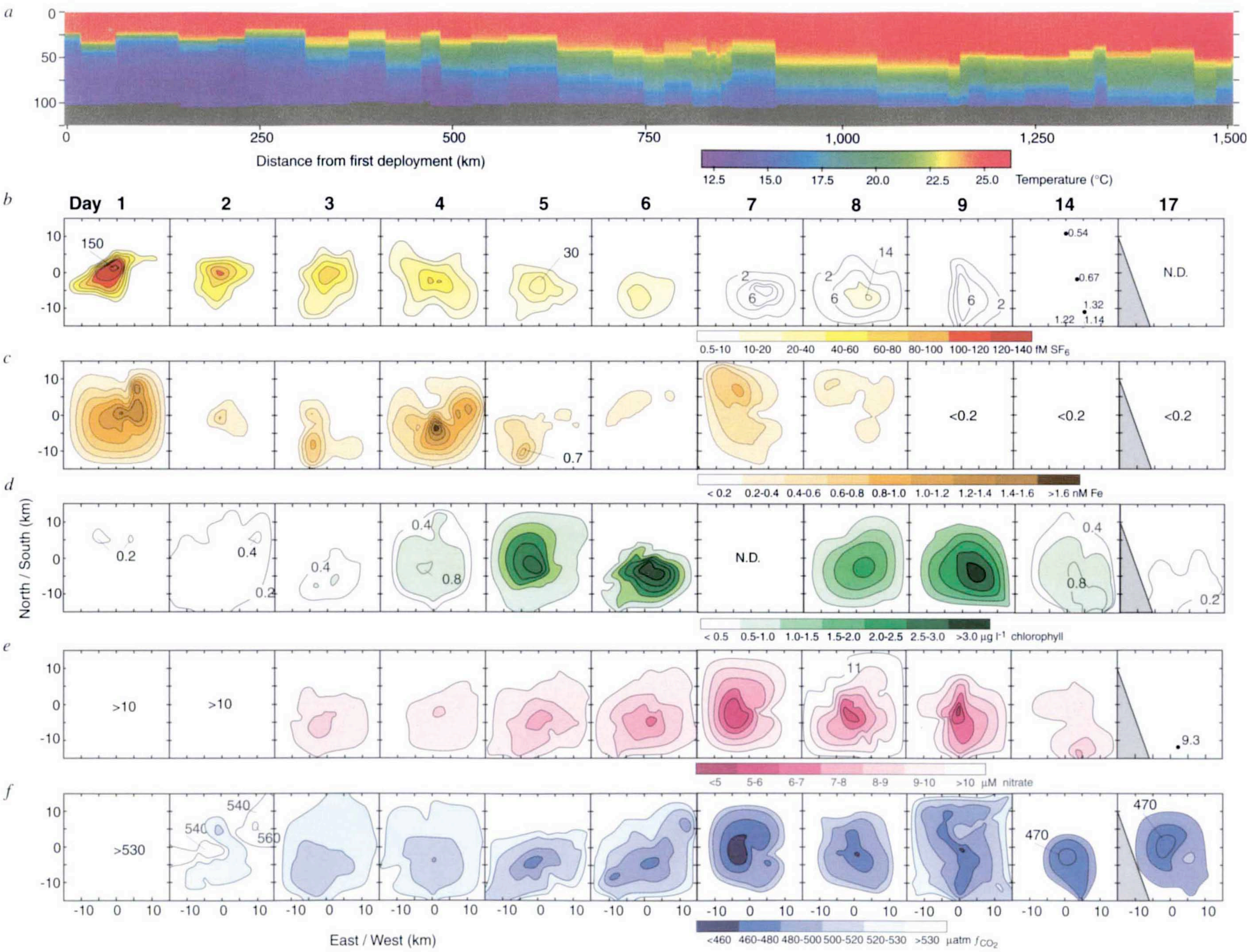
SF_6

Fe

Chl

NO_3

CO_2

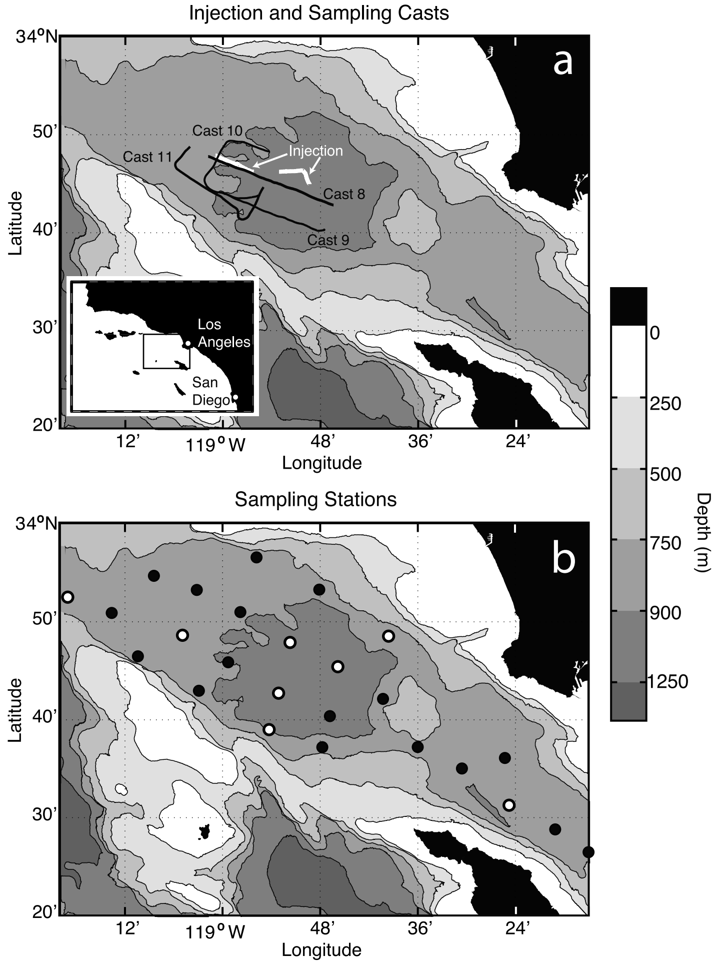


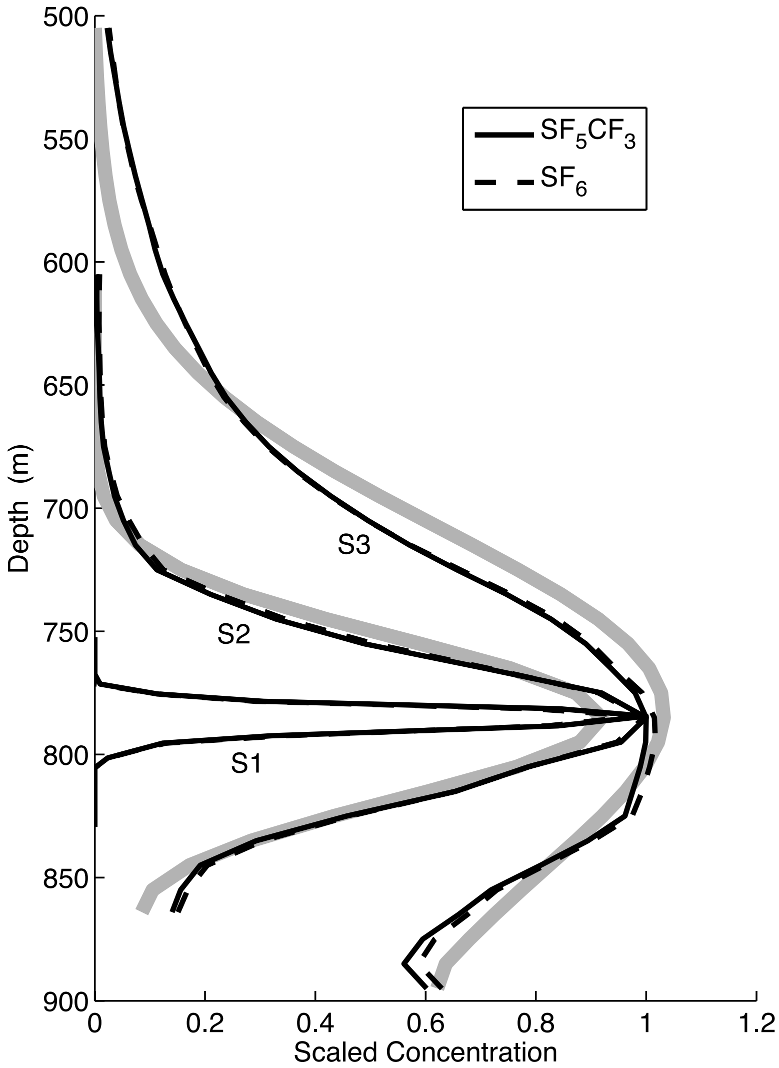
Coale et al., 1996

Development of SF_5CF_3 to replace SF_6

Use of SF_5CF_3 for ocean tracer release experiments

David T. Ho,[1] James R. Ledwell,[2] and William M. Smethie Jr.[1]





Ho et al., 2008