Oceanic Tracers

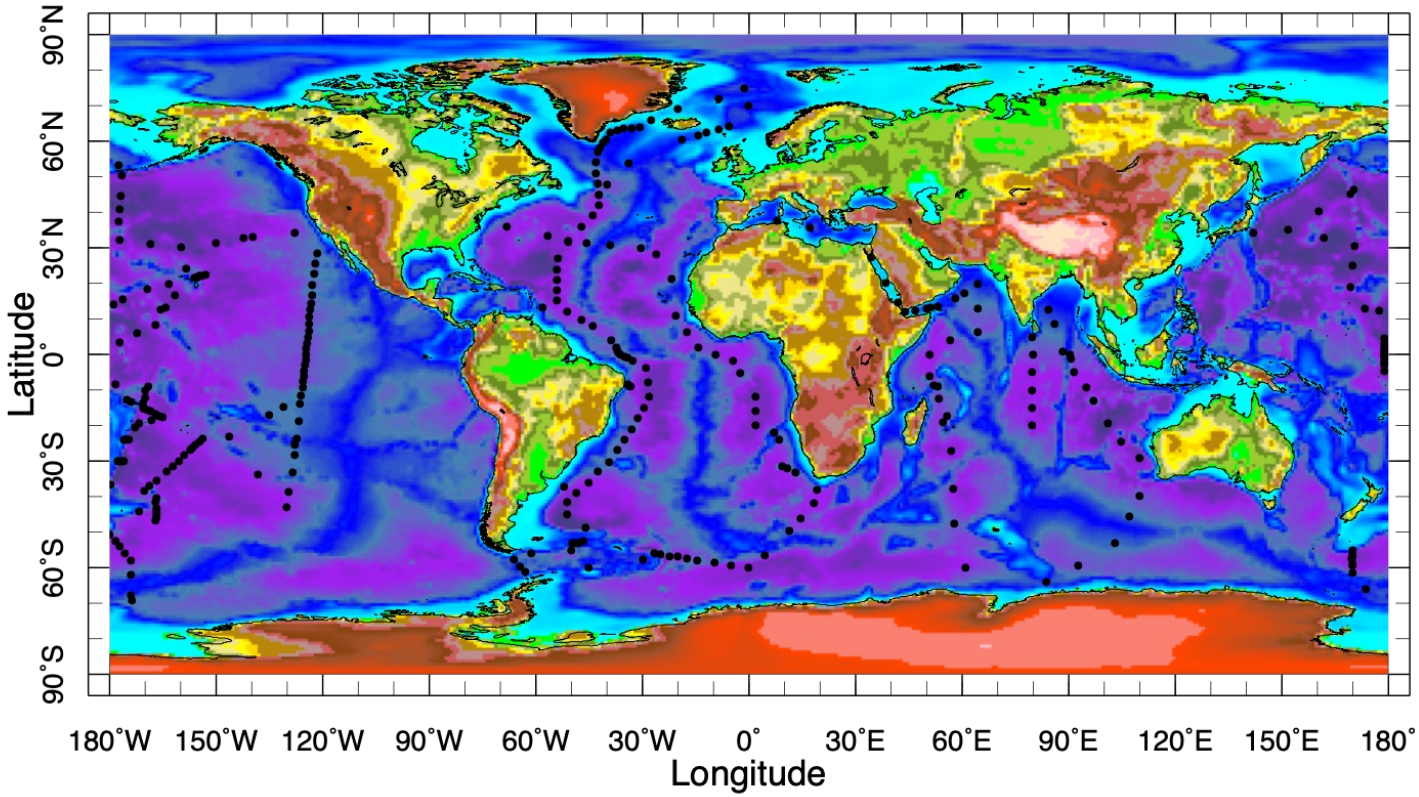
- Classes of oceanic tracers
- Global ocean surveys
- Water-mass mixing calculations
- Quasi-conservative geochemical tracers
- NO, PO, and PO_4*
- Anthropogenic transient and deliberate Tracers
- CFCs, SF_6

Type	Use
Natural - Stable	
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, ^{4}He, Ne	Identify and quantify glacial ice (^{4}He & Ne high, ^{18}O low in glacial ice)
^{3}He	Circulation of CDW onto Antarctic continental shelves (^{3}He 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
^{3}H	Same as trace gases above, but weak signal in S.H.
Bomb ^{14}C	Ocean uptake of anthropogenic CO_2
Anthropogenic - Deliberate	
SF_6, CF_3SF_5	Mixing, circulation, and gas exchange

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GEochemical Ocean SECtions Study (GEOSECS)

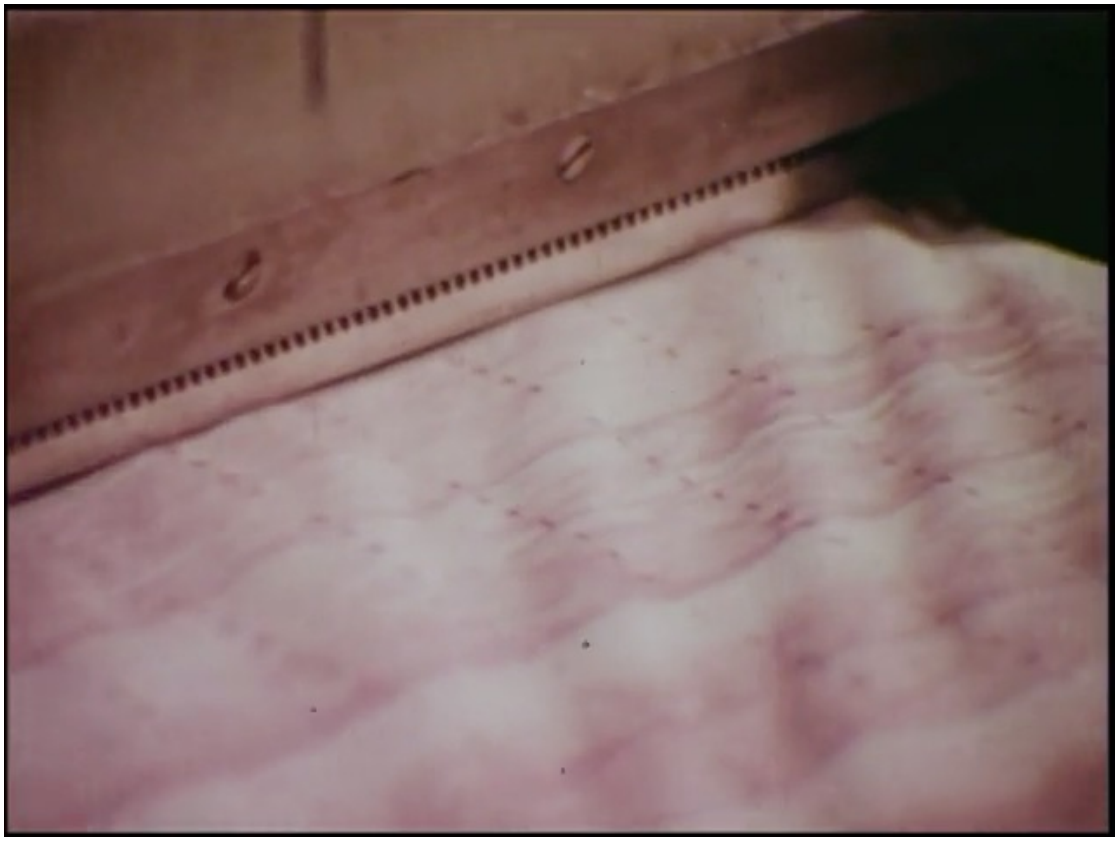
Atlantic from Jul 1972 to May 1973; Pacific from Aug 1973 to Jun 1974; Indian from Dec 1977 to Mar 1978



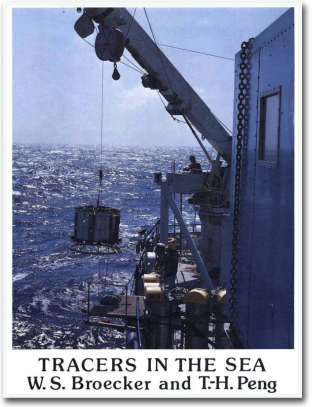
http://iridl.ldeo.columbia.edu/SOURCES/.GEOSECS/

GEOSECS

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



From NSF educational film, "Rivers in the Sea"



"Although GEOSECS made no astounding discoveries, our superb global data set became the basis for a host of subsequent research projects. I benefited greatly; it became the grist for my tome "Tracers in the Sea" which, 30 years later, remains the book on the geochemistry of the oceans."

-Wally Broecker, doi:10.7185/geochempersp

https://www.ldeo.columbia.edu/~broecker/Home_files/TracersInTheSea_searchable.pdf

Transient Tracers in the Oceans (TTO)

1981 & 1983

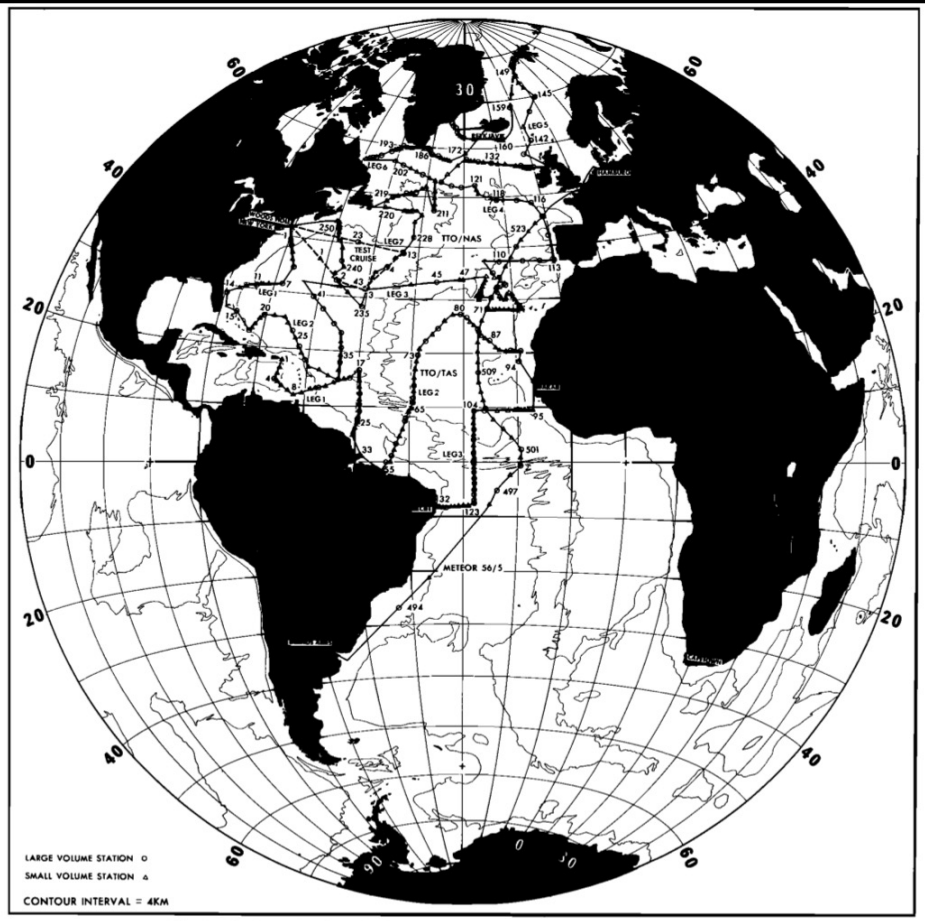
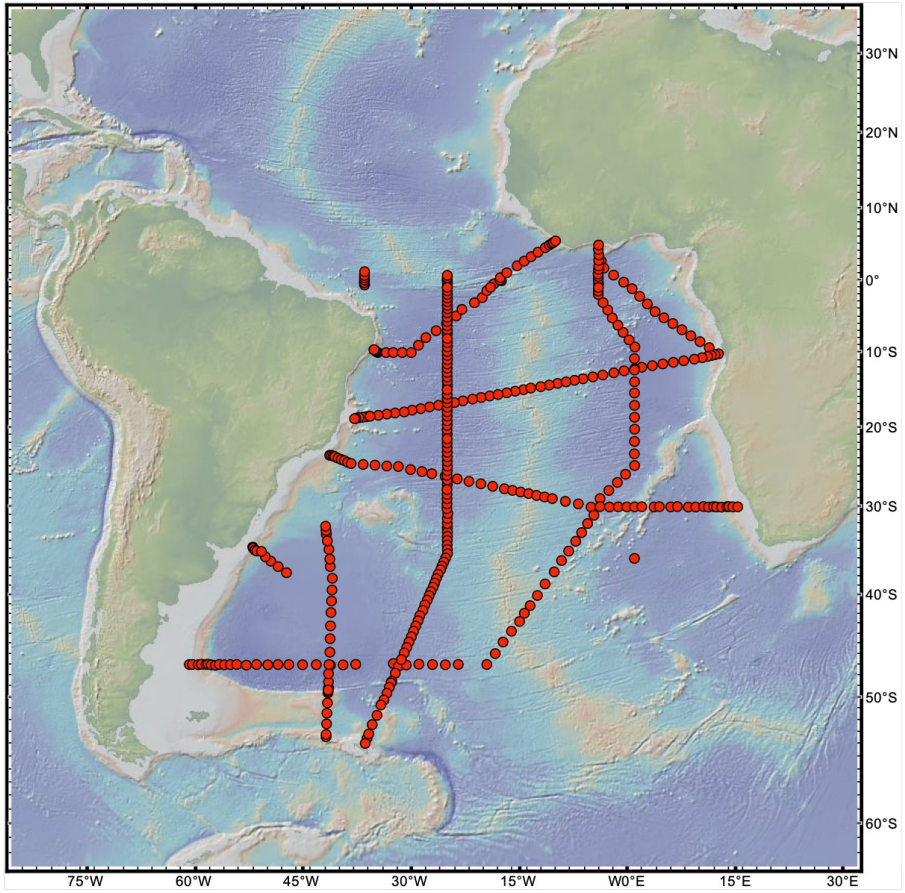


Fig. 1. Cruise track and station locations for the Transient Tracers in the Ocean program.

Brewer et al., 1985

South Atlantic Ventilation Experiment (SAVE)

1987-1989



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World Ocean Circulation Experiment (WOCE)

1990 - 1998

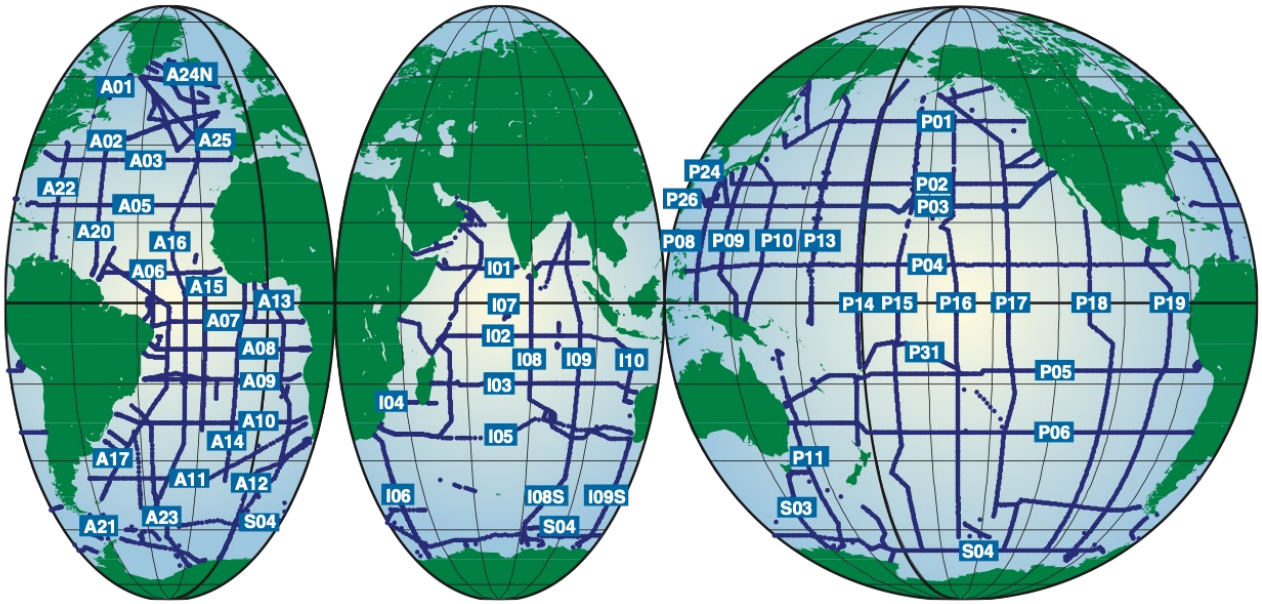
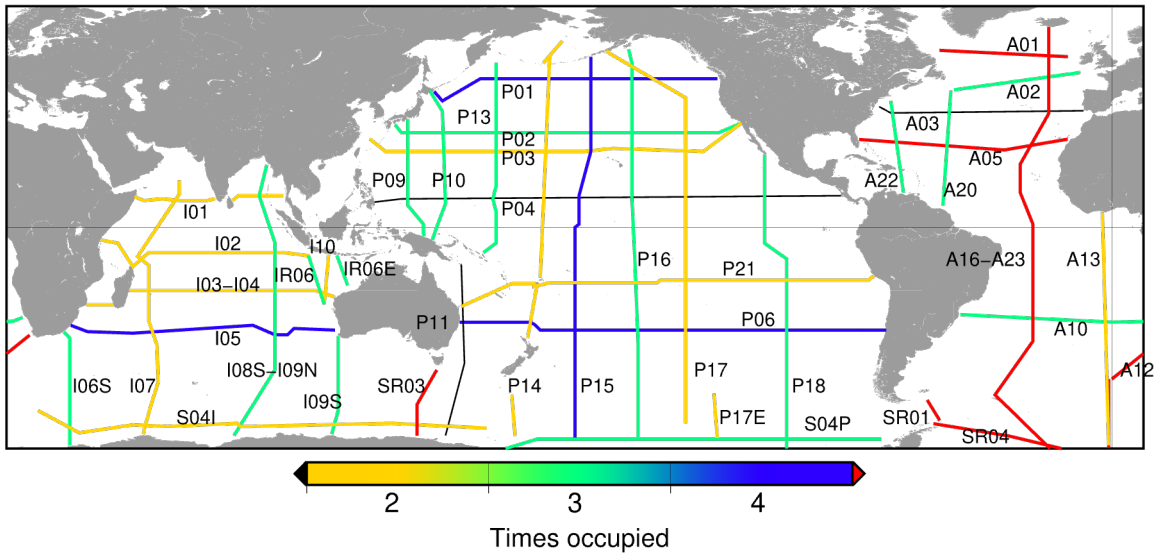


Figure 1. WHP One Time Survey Sections: station positions and line numbers.

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

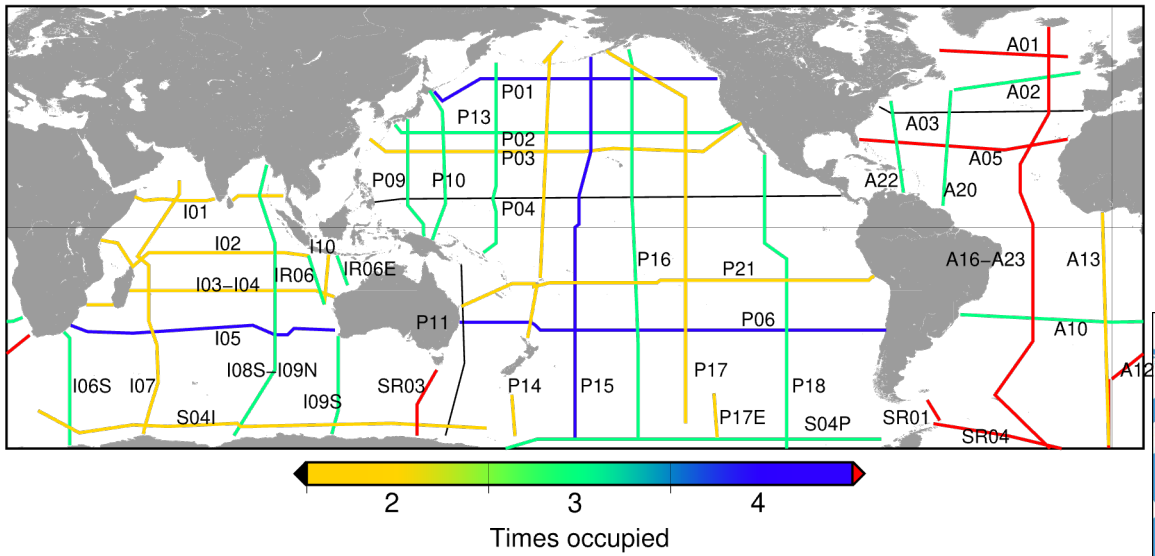
GO-SHIP



https://cchdo.ucsd.edu/products/goship-easyocean

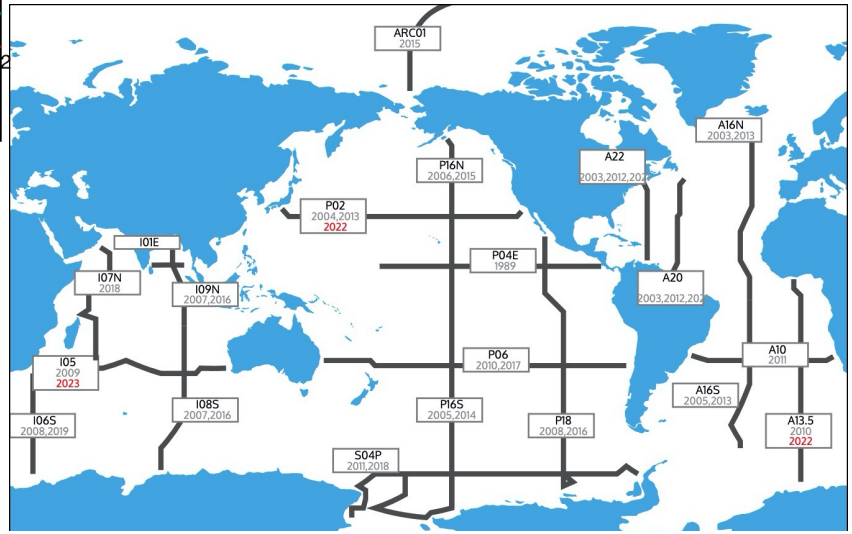
"GO-SHIP brings together scientists with interests in physical oceanography, the carbon cycle, marine biogeochemistry and ecosystems, and other users and collectors of hydrographic data to develop a globally coordinated network of sustained hydrographic sections as part of the global ocean/climate observing system."
- *International GO-SHIP mission statement*

GO-SHIP



https://cchdo.ucsd.edu/products/goship-easyocean

Cruises for the U.S. Global Ocean Carbon and Repeat Hydrography Program, 2003 - 2023
(Red indicates a pending cruise, grey indicates a completed cruise)

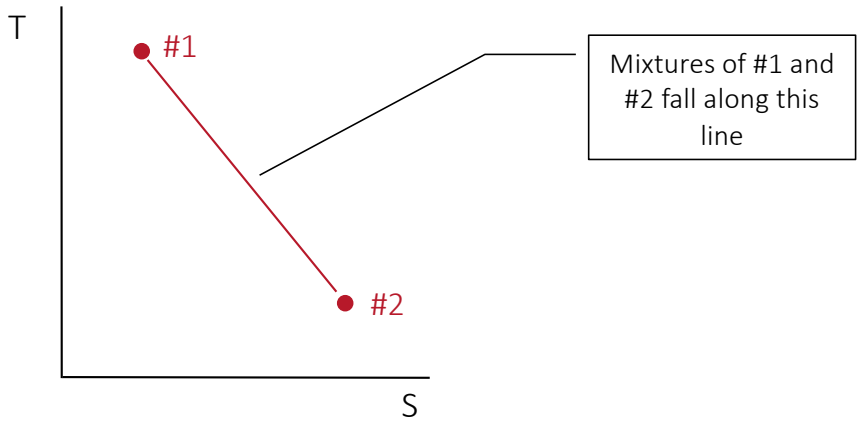


https://usgoship.ucsd.edu/usgoship.ucsd.edu/hydromap/

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Mixing of Two Water Masses

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

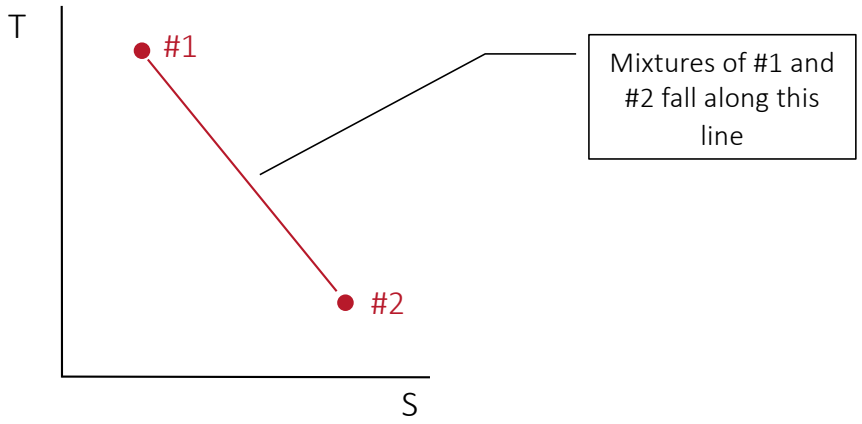


Water mass mixing definitions

- 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)

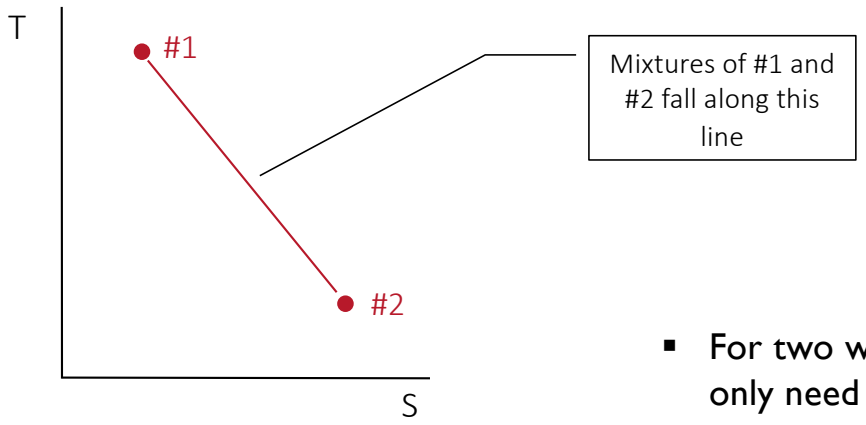
Mixing of Two Water Masses

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Mixing of Two Water Masses

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



$$1 = f_1 + f_2 \qquad (1)$$

$$C_{mix} = f_1 C_1 + f_2 C_2 \qquad (2)$$

Combining:

$$f_1 = \frac{C_{mix} - C_2}{C_1 - C_2}$$

- For two water masses: only need **T** or **S**

Mixing of Four Water Masses

We need four equations with four variables. For example:

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

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

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

$$?_{mix} = f_1?_1 + f_2?_2 + f_3?_3 + f_4?_4$$

Thus, we need three stable, conservative tracers:

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

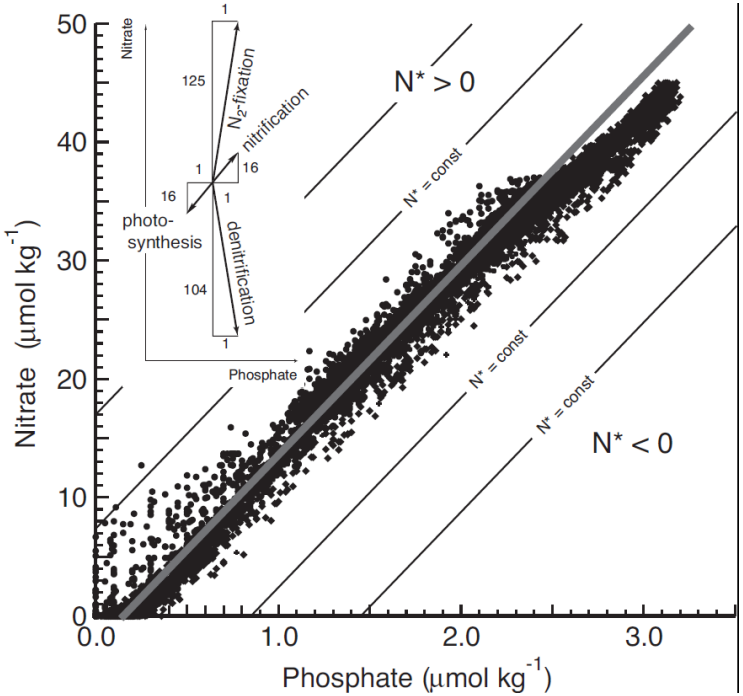
S_i = salinity of water mass "i"
S_{mix} = salinity of a water mixture

$?_i$ = [?] of water mass "i"
$?_{mix}$ = [?] of a water mixture

- What to use for the third conservative tracer?

Quasi-conservative tracers (from Export lecture)

N* is a tracer for denitrification in the ocean



N* is defined as
$N^* = [NO_3] - 16 \times [PO_4] + 2.9$

The solid line shows the linear equation with N:P =16

Values to the right have negative N* (denitrification) to the left have positive N* (nitrogen fixation)

v2024

PO_4 versus Nitrate (WOCE data) from Sarmiento and Gruber (2006)

"NO" – A Quasi-Conservative Water Mass Tracer

106 CO_2 + 16 HNO_3 + H_3PO_4 + 122 H_2O + trace elements (*e.g. Fe, Zn, Mn…*) →

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$$

"NO" – A Quasi-Conservative Water Mass Tracer

$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O +$ trace elements (*e.g. Fe, Zn, Mn…*) →

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$$

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

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" ≡ $135[PO_4^-] + [O_2]$

Earth and Planetary Science Letters, 23 (1974) 100–107
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1

"NO", A CONSERVATIVE WATER-MASS TRACER*

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Received February 20, 1974
Revised version received June 13, 1974

A composite property, $9NO_3 + O_2$, is proposed as a conservative water-mass tracer. The coefficient 9 is chosen so that the increase in "NO" resulting from nitrate introduction during respiration just balances the consumption of dissolved oxygen gas. Because of the pronounced difference in the preformed nitrate content of deep water produced at the northern and southern ends of the Atlantic Ocean "NO" provides an independent means of disentangling the degree of mixing of various water types in the deep sea. Evidence based on data obtained during the Atlantic Geosecs program is presented to demonstrate the sensitivity and reliability of this conservative tracer.

Conservative Behavior of "NO"

AAIW
1150 m

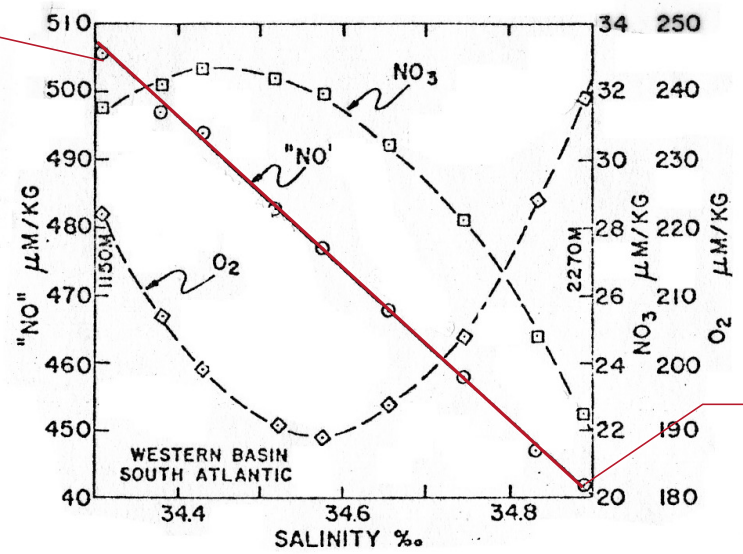


Fig. 5. "NO", NO_3, and O_2 versus salinity at Atlantic Geosecs station 60 in the western basin of the South Atlantic between the core of the AAIW (1150 m) and the top of the NADW (2270 m). The excess NO_3 content is just balanced by the O_2 deficiency yielding a straight line relationship between salinity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

NADW
2270 m

Broecker, 1974

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

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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and William M. Smethie, Jr.

Lamont-Doherty Geological Observatory of
Columbia University, Palisades, New York

Gote Ostlund

Rosenstiel School of Marine and Atmospheric
Sciences, University of Miami, Miami, Florida

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).

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Paper number 90GB02279.
0886-6236/91/90GB-02779$10.00

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

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 et al. (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 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:

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

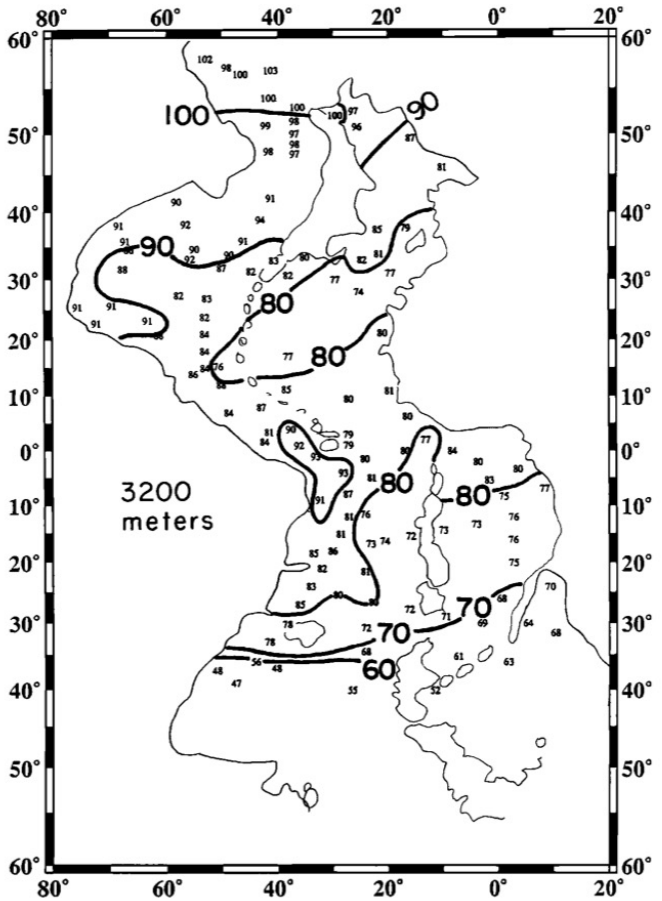
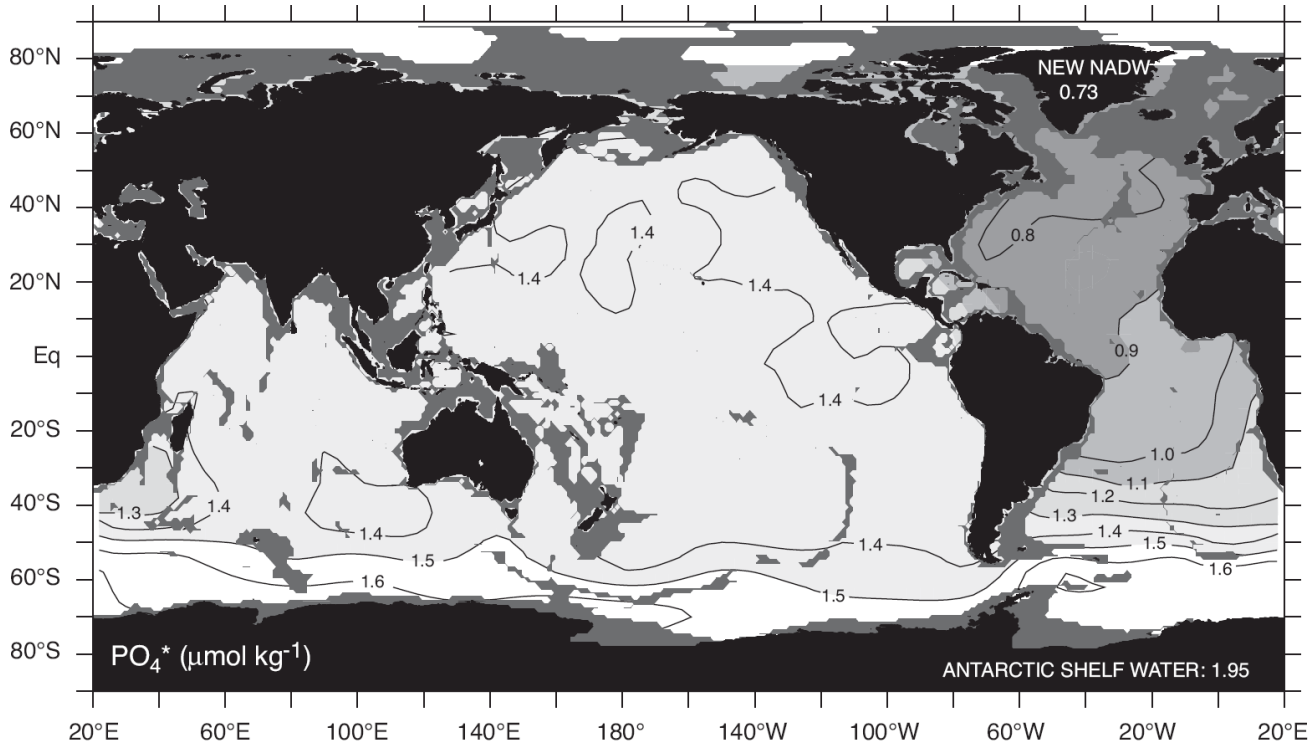


Fig. 4. Map showing percentage of northern component water along the 3200 m depth horizon. The light lines define the geographic boundaries of this horizon.

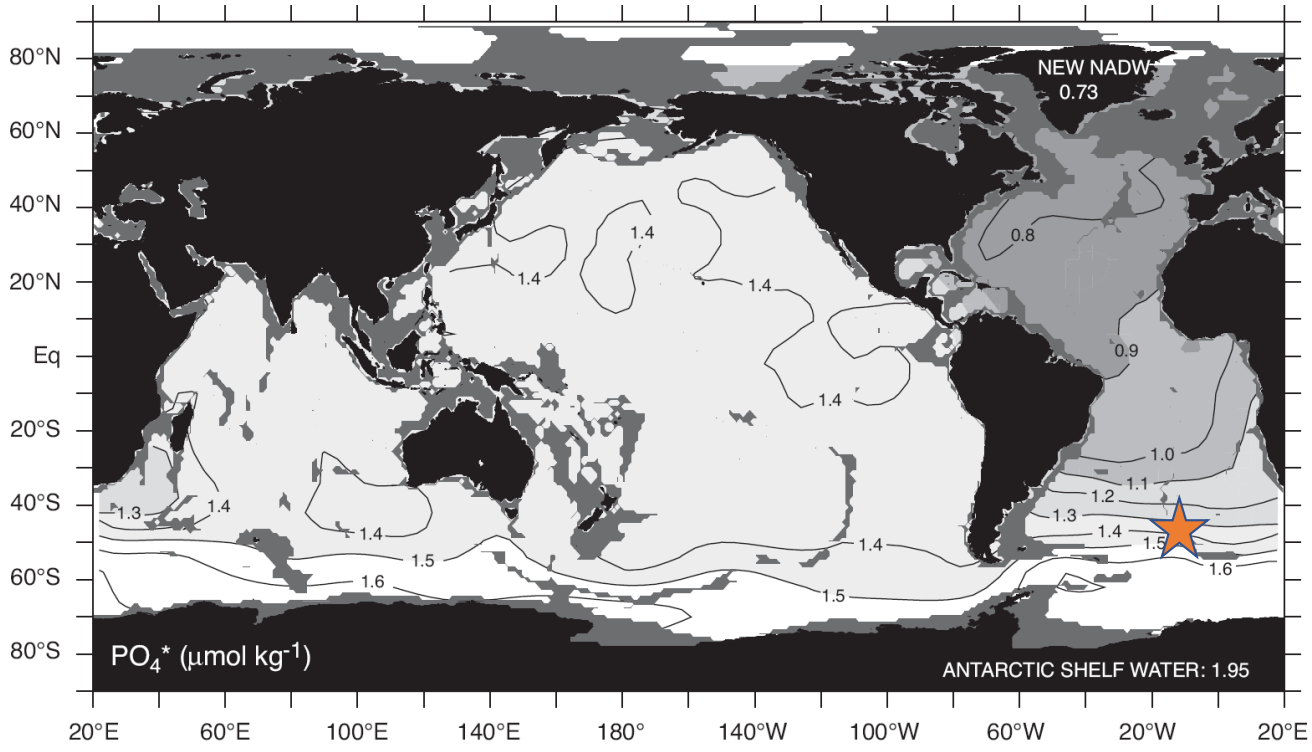
Broecker et al., 1991

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



Sarmiento and Gruber, 2006

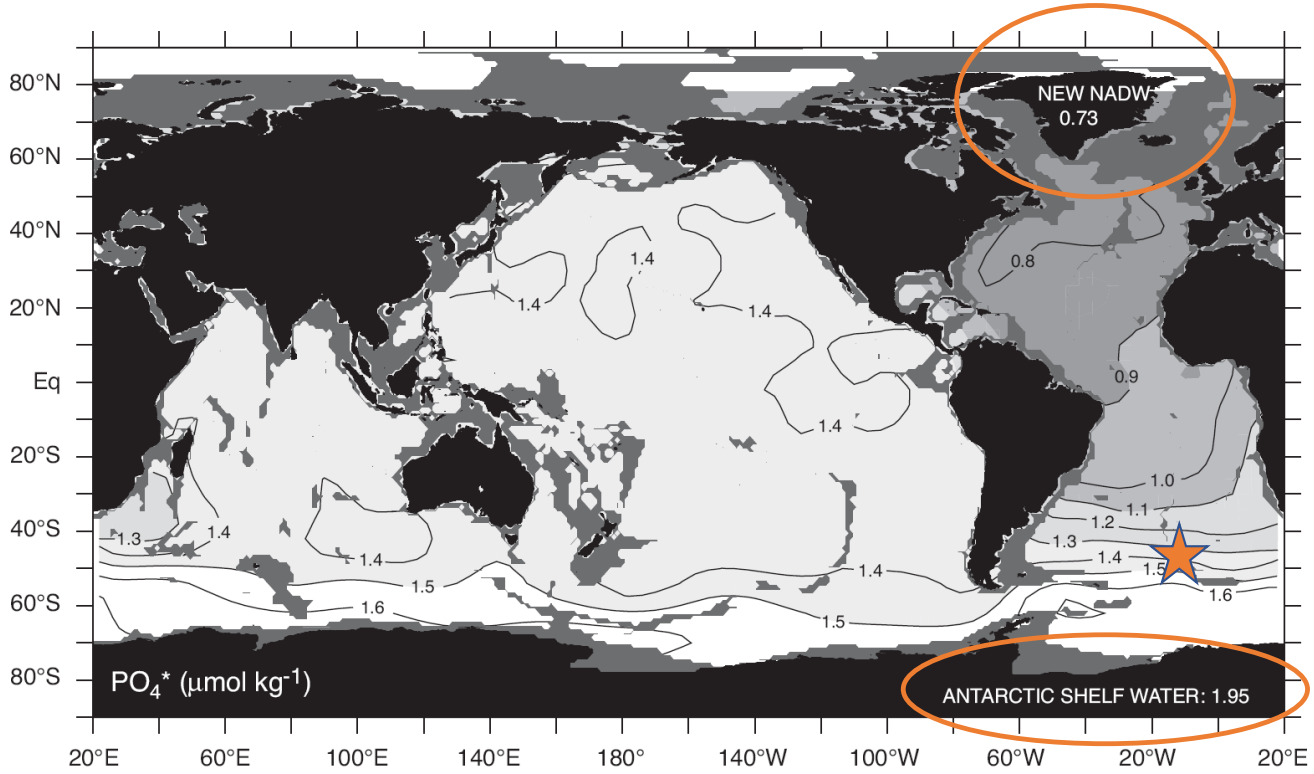
PO_4^* distribution at 3000 m in the world ocean.



PO4* at Orange star = 1.4. What are the relative fractions of NADW and Antarctic Shelf Water?

Sarmiento and Gruber, 2006

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

Quasi-conservative tracers depend on stoichiometry

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.

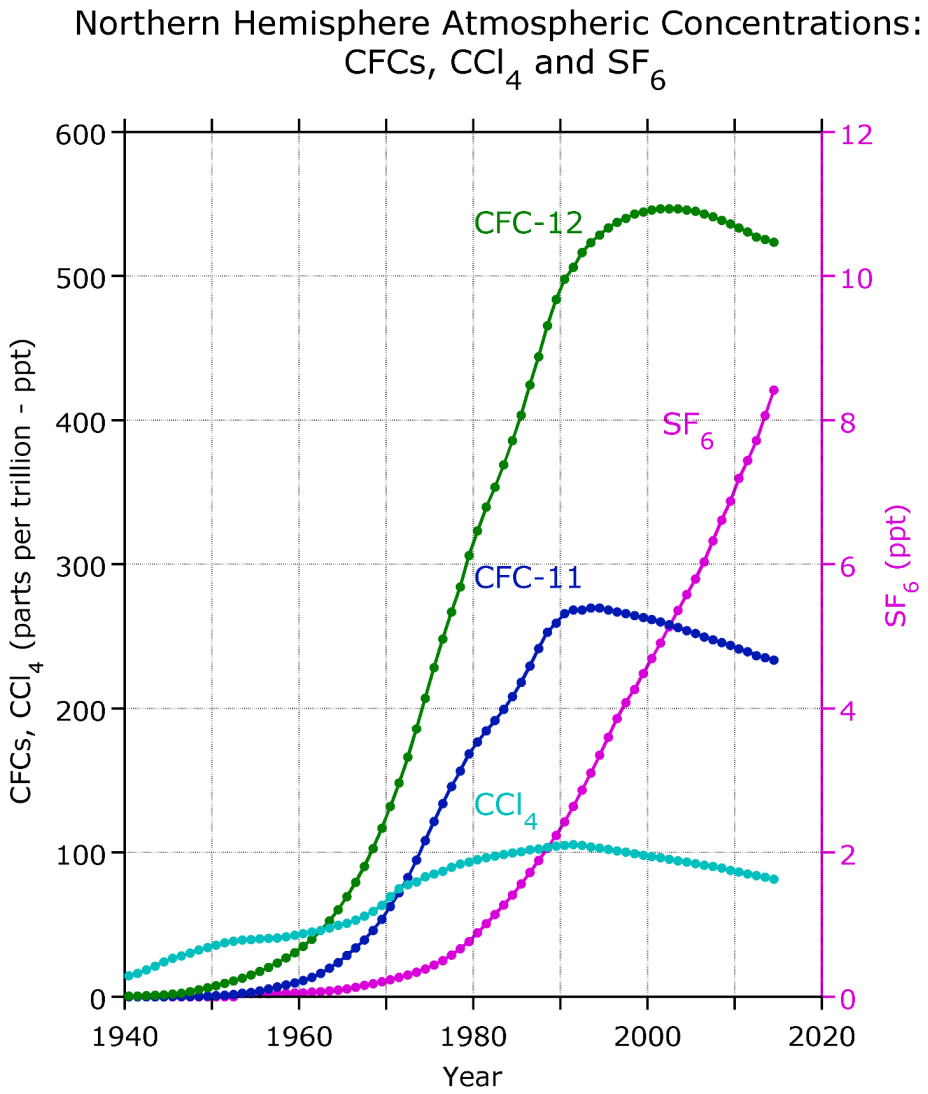
Source	Organic matter			O_2
	P	N	C	
Redfield *et al.*, 1963[a]	1.0	16	106	138
Anderson and Sarmiento, 1994[b]	1.0	16 ± 1	117 ± 14	170 ± 10
Anderson, 1995[c]	1.0	16	106	141–161
Kortzinger *et al.*, 2001[d]	1.0	17.5 ± 2.0	123 ± 10	165 ± 15
Hedges *et al.*, 2002[e]	1.0	17	106	154

$\Delta O_2/\Delta N$	$\Delta O_2/\Delta P$
8.6	138
10.6	170
8.8	141
9.4	165
9.1	154

Emerson and Hedges, 2008

Transient Tracers

- Usually anthropogenic compounds with time-varying sources (or sinks)
  - CFCs, SF_6, ^{14}C, ^{3}H
- They enter the surface waters of the ocean either via gas exchange (e.g., CFCs, SF_6, ^{14}C) or water vapor exchange (^{3}H)
- 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



- CFCs – Cholorfluorocarbons (refrigerant)
- CCl_4 – Carbon Tetracholoride (fumigant)
- SF_6 – Sulphur hexafluoride (semi-conductors)

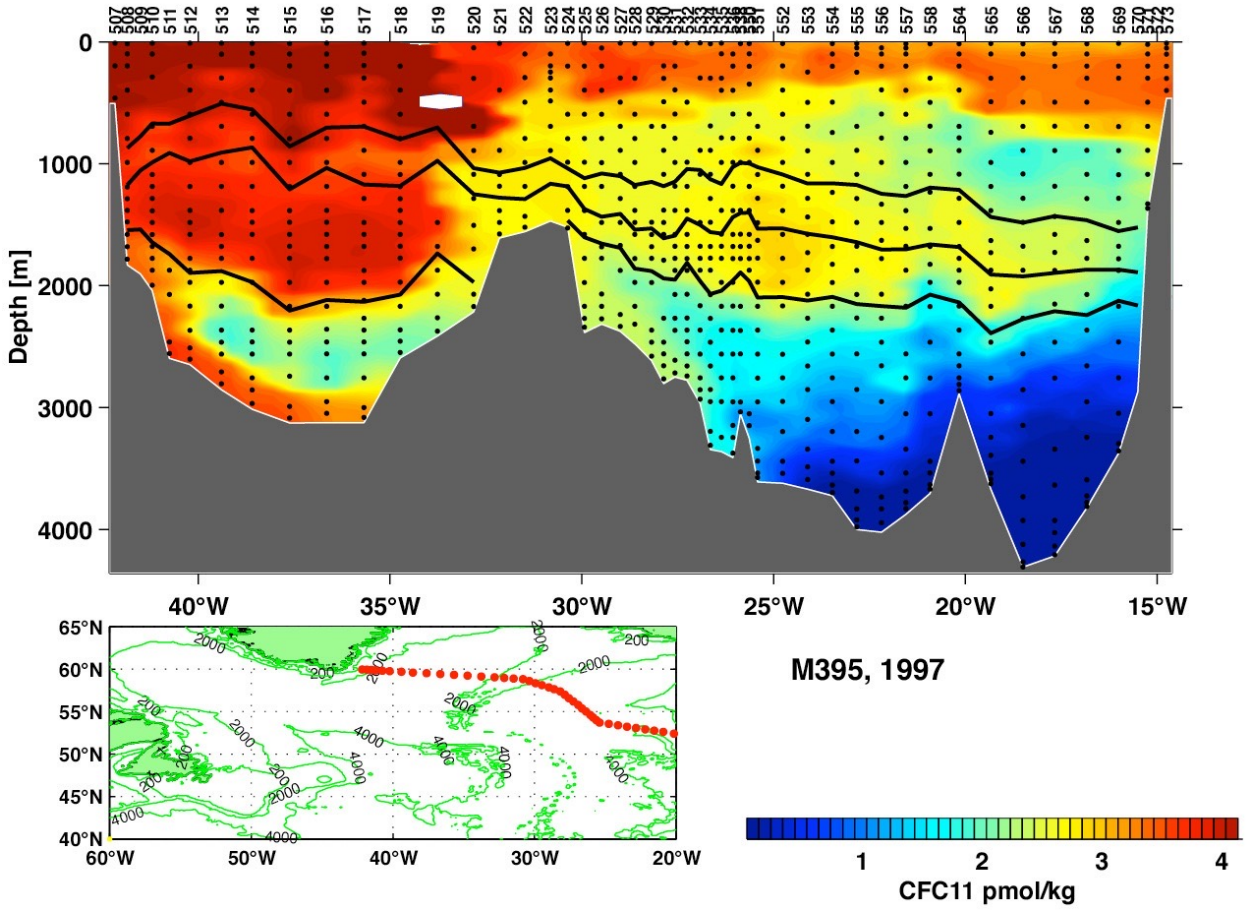
Solubilities of CFCs & SF_6

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

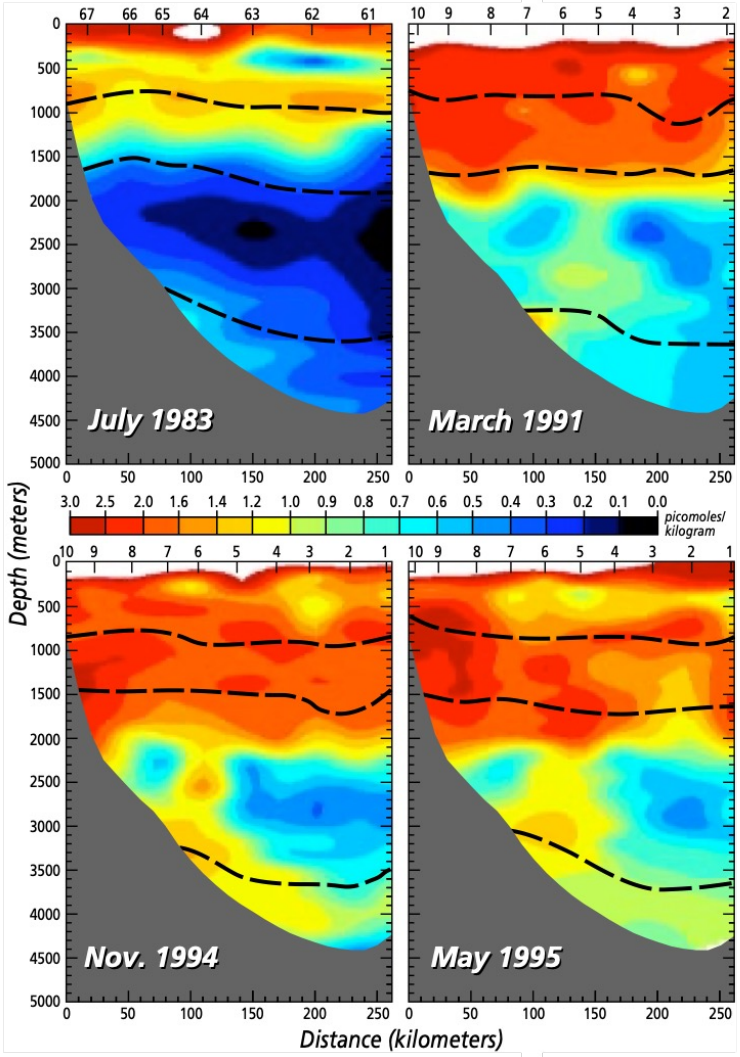
- Weaker function of salinity
- Decreases as salinity increases
- Varies by 50% between salinity of 0 and 35

- 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



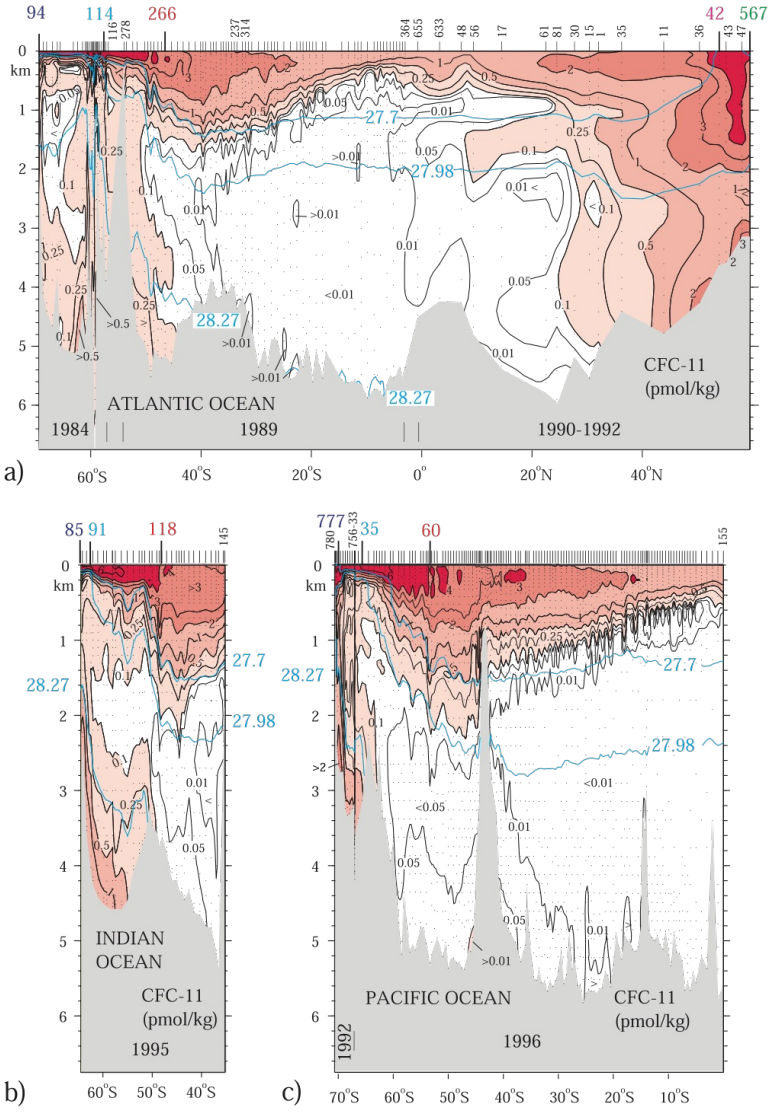
Rhein et al. (2002)



Four chlorofluoro-carbon (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^{-1}) measured along hydrographic lines in the (a) Atlantic, (b) Indian, and (c) Pacific oceans.

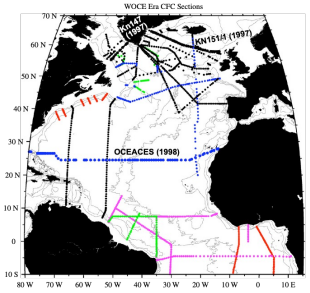


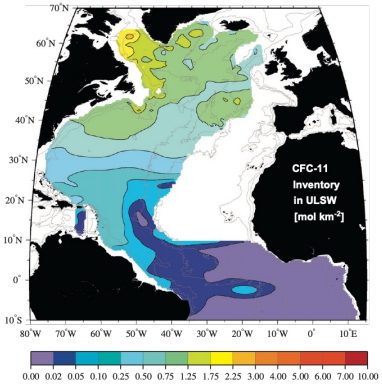
Orsi et al., 2002

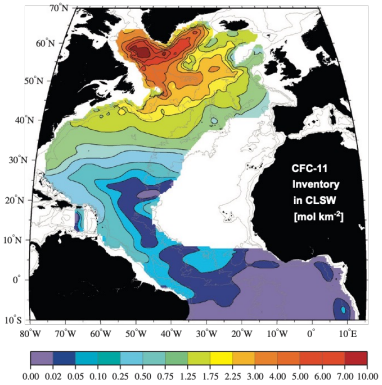
Formation rate of NADW

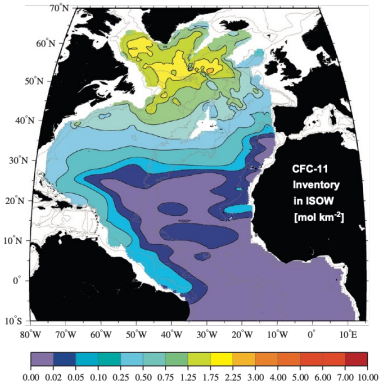
$$I = \int R(t)C(\theta, S, t)dt$$

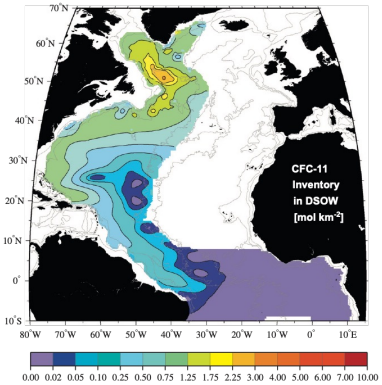
I: Water mass CFC inventory
R: Rate of water mass formation
C: Source water CFC concentration
θ: Potential temperature
S: Salinity
t: Time











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	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

LSW - Labrador Sea Water
ISOW - Iceland Scotland Overflow Water
DSOW - Denmark Strait Overflow Water

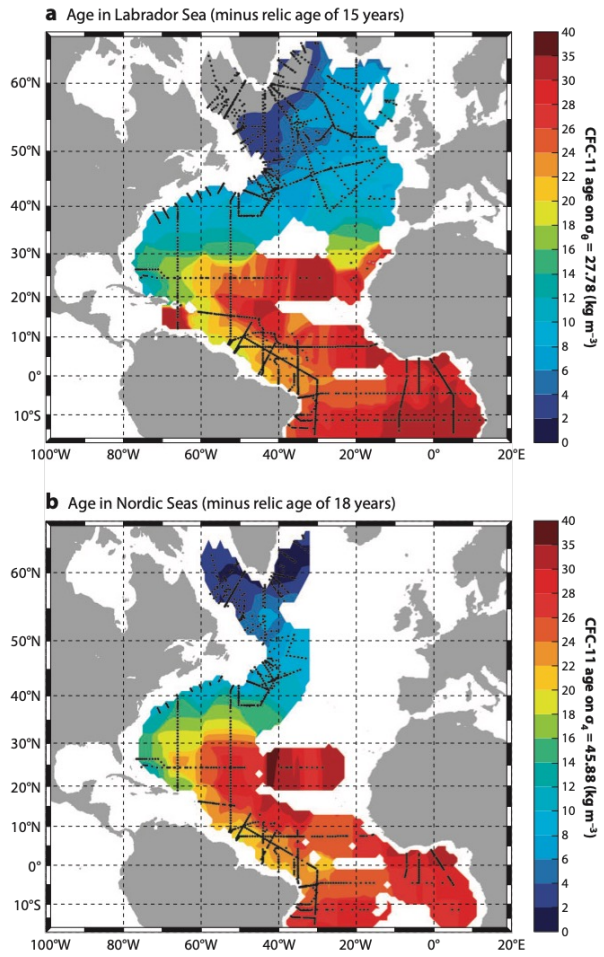


Figure 3

Maps of effective pCFC-11 ages with relic ages subtracted for (*a*) Upper Labrador Sea Water on σ_θ = 27.78 kg m^{-3} and (*b*) Overflow Water on σ_4 = 45.88 kg m^{-3}, except north of 55°N and west of 30°W, where the bottom value is used if σ_θ is greater than 27.88. Data used were collected during the 1990s. Black dots indicate station locations. Unit of contour is 2 years. Figure adapted from Fine et al. (2002).

Fine, 2010

Estimate Ocean Uptake of Anthropogenic CO_2

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

TCO_2^{ant} : Total anthropogenic CO_2

TCO_2^{m} : Total measured CO_2

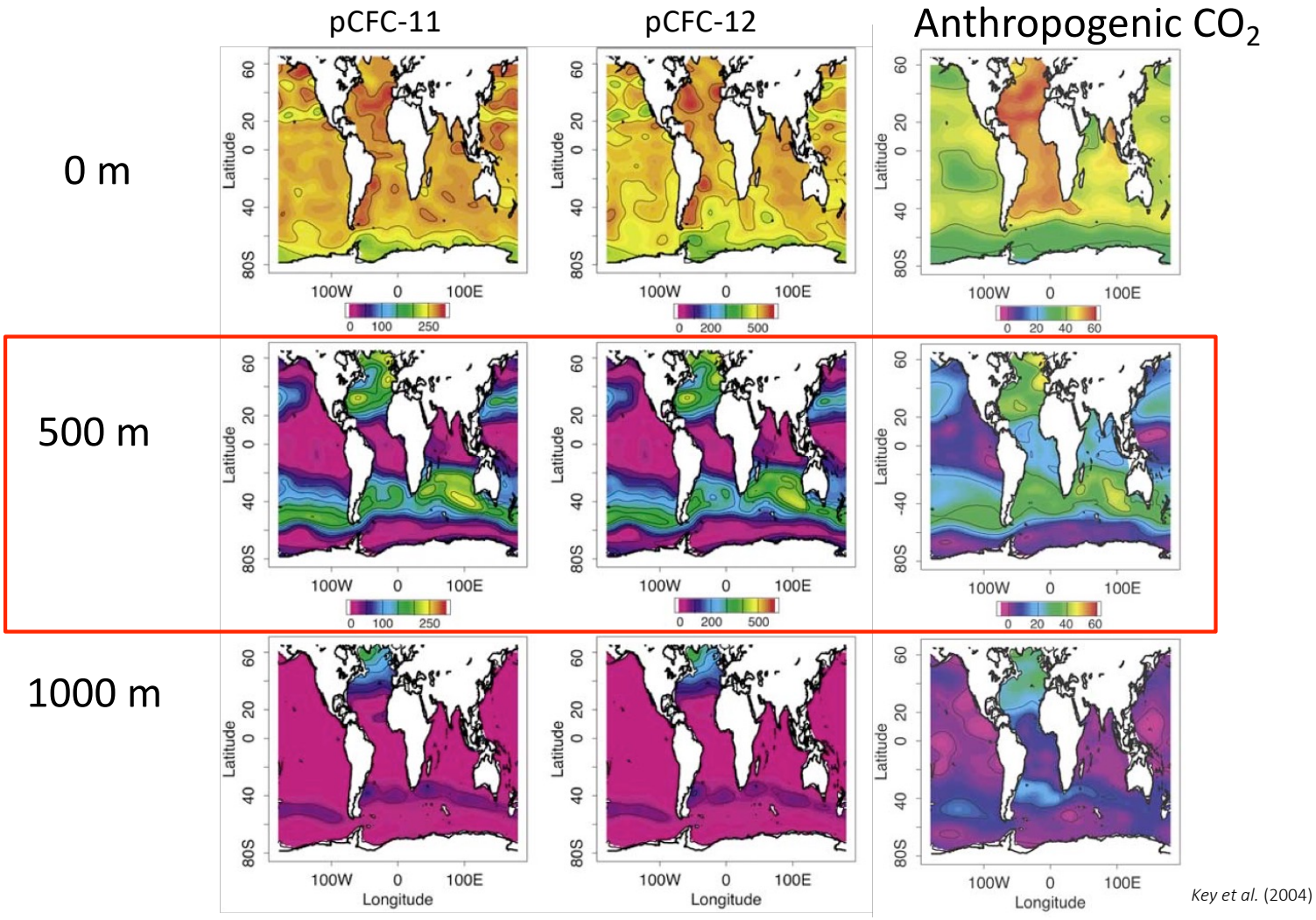
ΔTCO_2^{bio} : Change in total CO_2 due to biological processes

$TCO_2^{eq\ t}$: 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

v2024

see *Gruber et al.*, 1996

Estimate Ocean Uptake of Anthropogenic CO_2



Key et al. (2004)

Deliberate Tracers

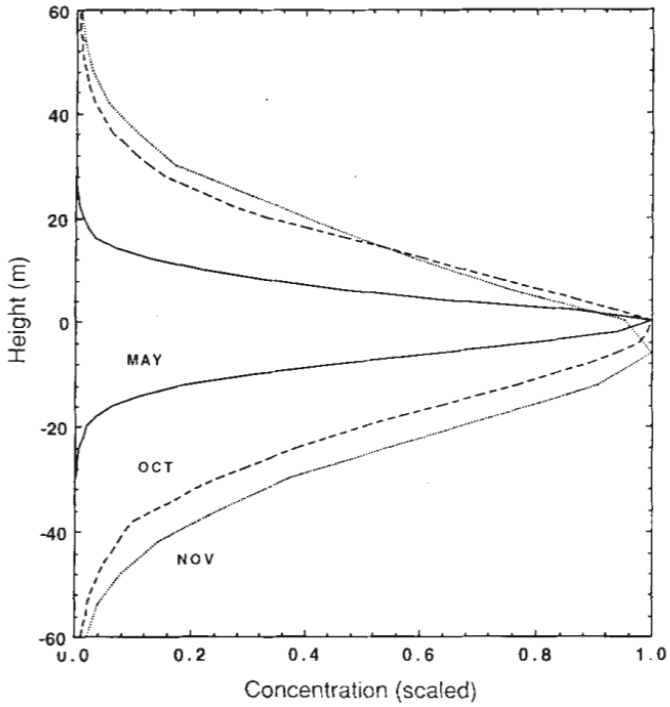
- Most commonly used
  - SF_6, ^3He, and now CF_3SF_5
- Deliberate tracers used to study:
  - Vertical mixing in the ocean
  - Pathways of newly formed deep water
  - Air-sea gas exchange

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



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

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]

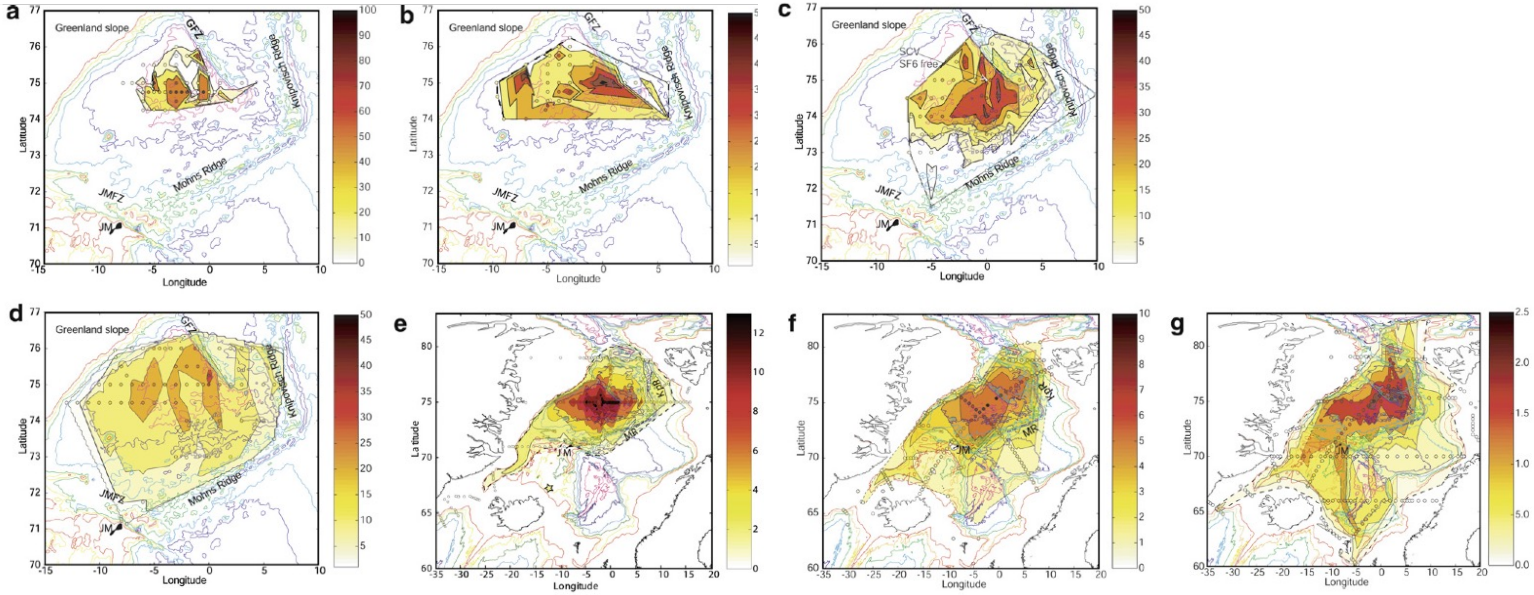


Fig. 10. Evolution of the SF_6 patch during the seven main subsequent cruises following the release. Triangle-based linear interpolation (Delaunay triangulation) contoured map of the Column Integral of SF_6 superimposed on colored bathymetry (black = 0 m, red = 1000 m, yellow = 1500 m, green = 2000 m, 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.

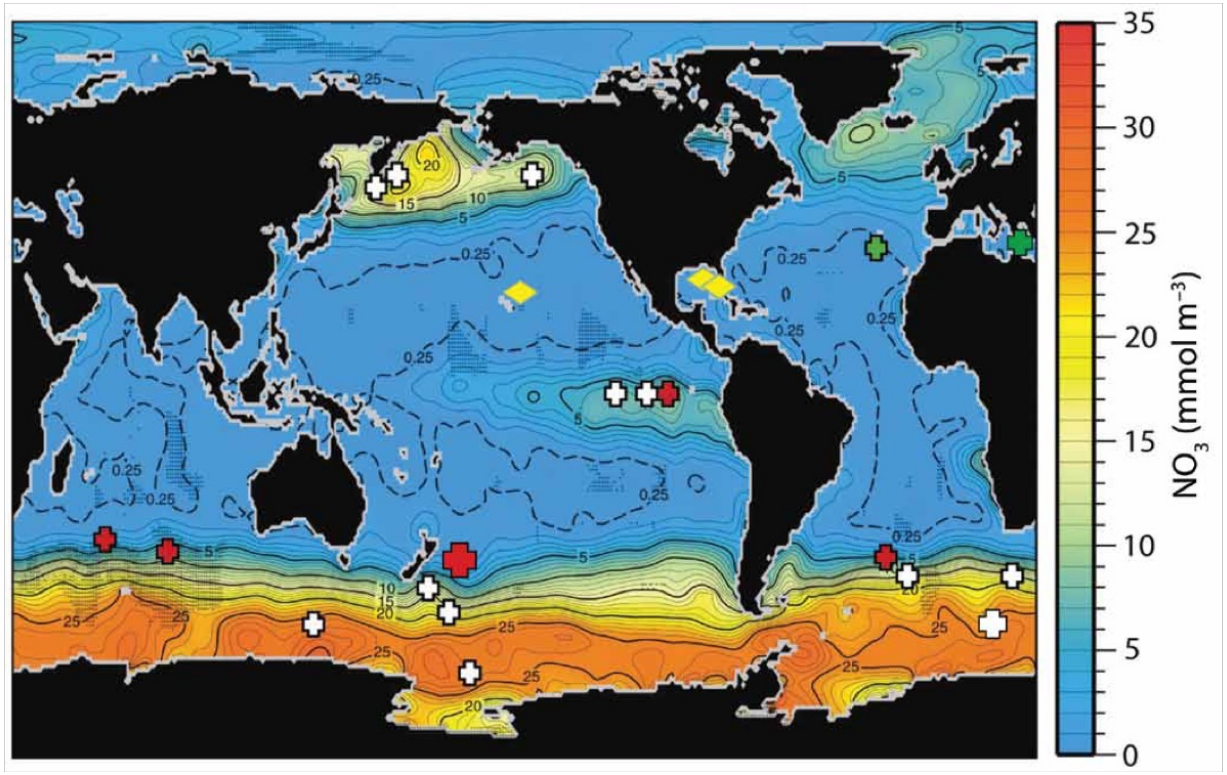


Figure 1. Locations of in situ mesoscale iron enrichment studies (white symbols), iron and/or phosphorous enrichments (green symbols), bloom studies in naturally high iron waters (red symbols), and oceanic geoengineering trials or pilot studies (yellow diamonds), including iron fertilization (Markels and Barber, 2001) and nutrient upwelling using ocean pipes (Lovelock and Rapley, 2007; White et al., 2010). All are overlaid on a map of surface nitrate concentrations for the world ocean. *Nitrate concentrations courtesy of the National Oceanographic Data Centre*

Boyd et al., 2012

T

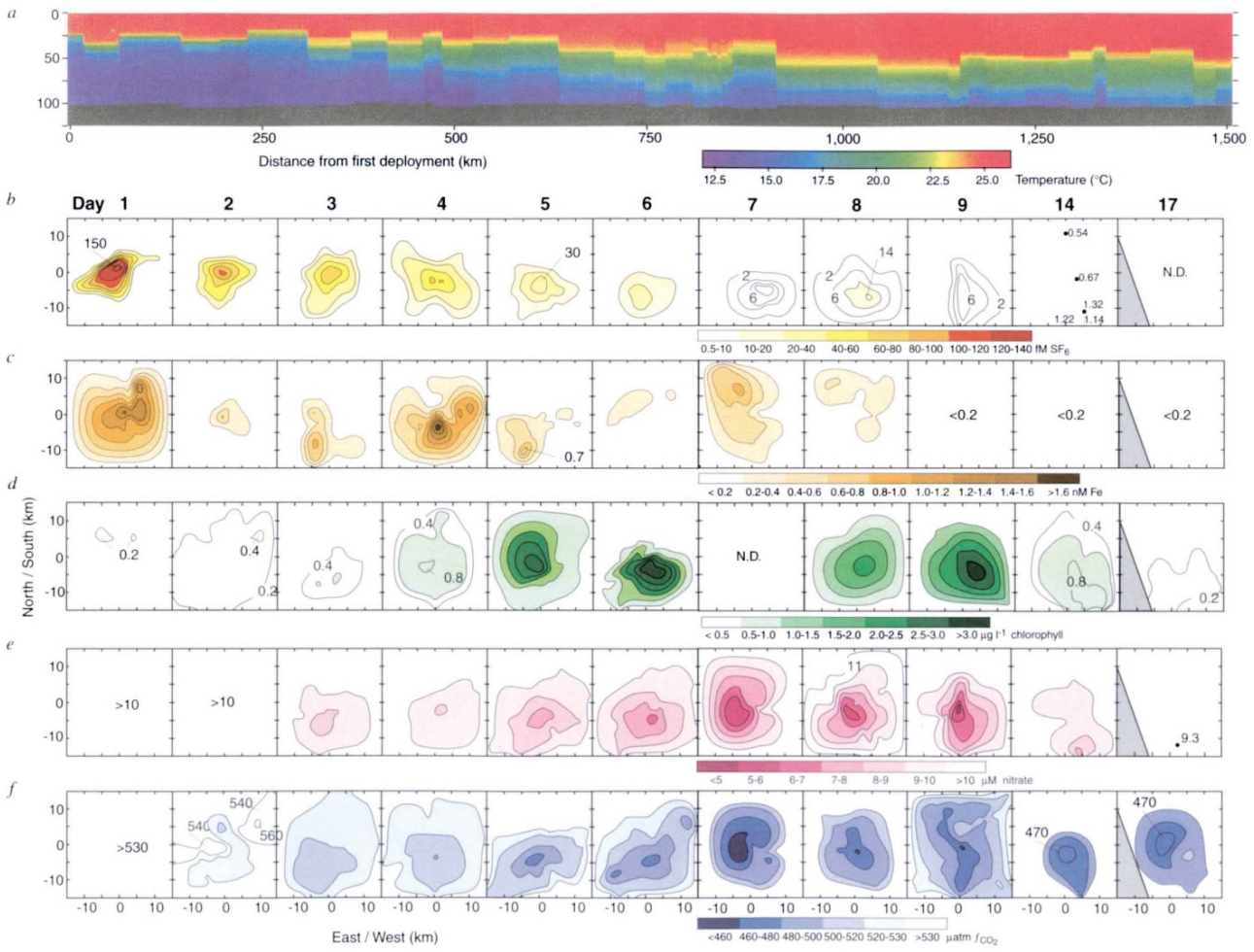
SF_6

Fe

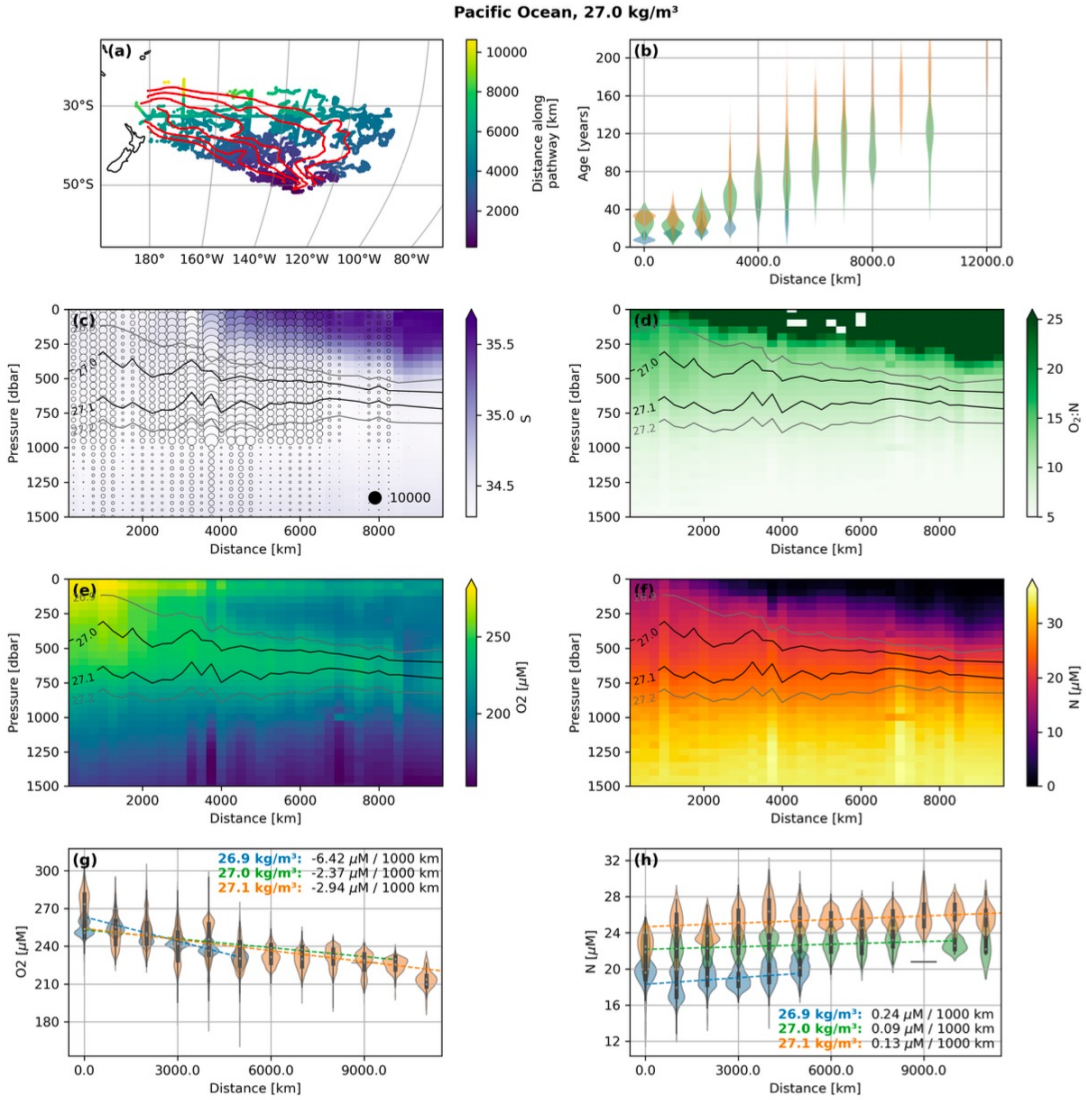
Chl

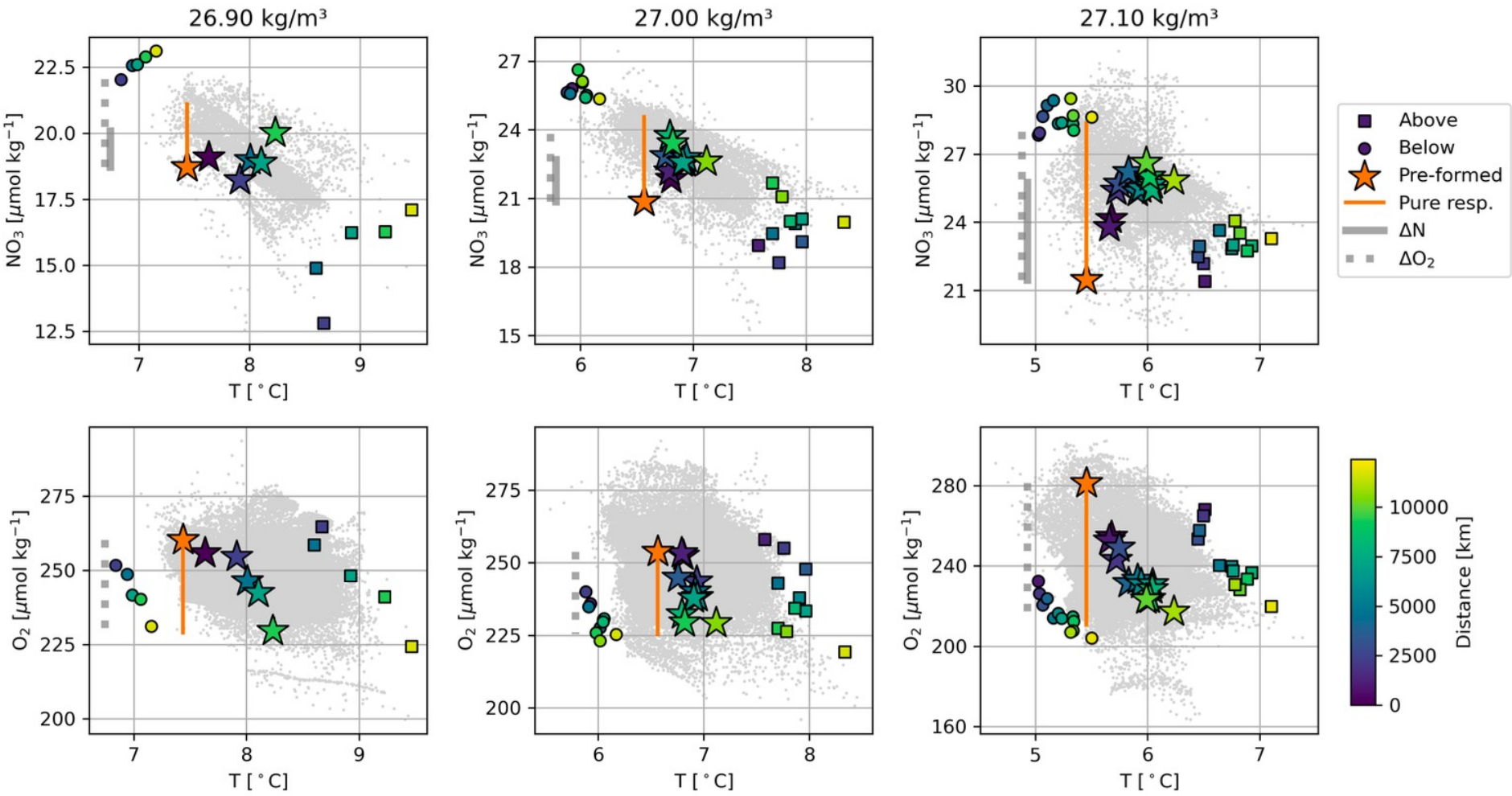
NO_3

CO_2

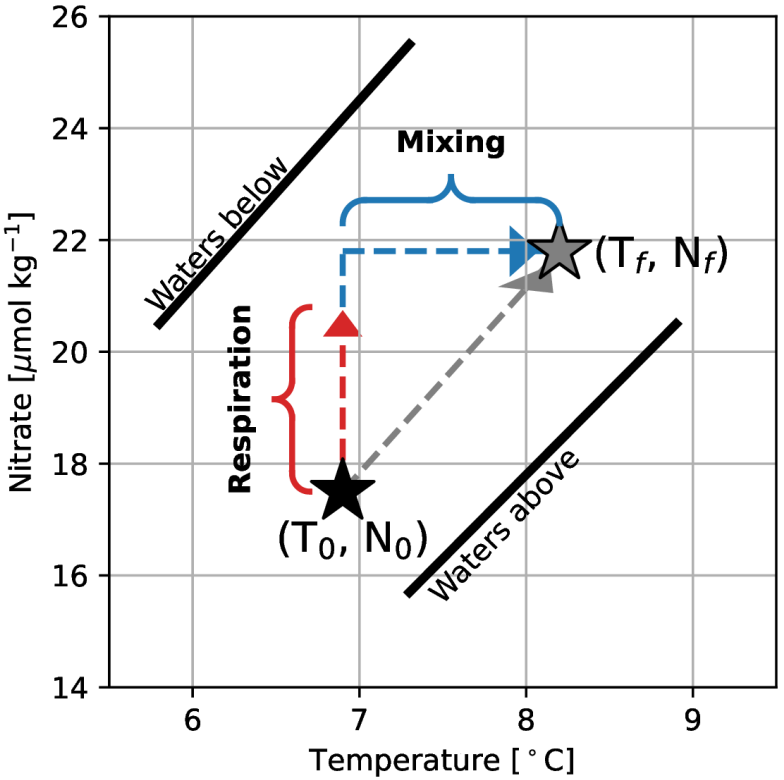


Coale et al., 1996


Pacific Ocean, 27.0 kg/m³
(a)
30°S
50°S
180° 160°W 140°W 120°W 100°W 80°W
Distance along pathway [km]
(b)
Age [years]
Distance [km]
(c)
Pressure [dbar]
10000
S
Distance [km]
(d)
O2:N
(e)
O2 [μM]
(f)
N [μM]
(g)
26.9 kg/m³: -6.42 μM / 1000 km
27.0 kg/m³: -2.37 μM / 1000 km
27.1 kg/m³: -2.94 μM / 1000 km
(h)
26.9 kg/m³: 0.24 μM / 1000 km
27.0 kg/m³: 0.09 μM / 1000 km
27.1 kg/m³: 0.13 μM / 1000 km


26.90 kg/m³
27.00 kg/m³
27.10 kg/m³
NO3 [μmol kg−1]
O2 [μmol kg−1]
T [°C]
Above
Below
Pre-formed
Pure resp.
ΔN
ΔO2
Distance [km]
0
2500
5000
7500
10000

Non-Redfieldian modification of mode water properties along pathways



Vertical mixing will modify oxygen and nitrate according to ratio of properties in layers above and below

Water mass mixing equations:

$$f_{ini}T_{ini} + f_{above}T_{above} + f_{below}T_{below} = T_f$$
$$f_{ini}S_{ini} + f_{above}S_{above} + f_{below}S_{below} = S_f$$
$$f_{ini}O_{2,ini} + f_{above}O_{2,above} + f_{below}O_{2,below} + R = O_{2,f}$$
$$f_{ini}NO_{3,ini} + f_{above}NO_{3,above} + f_{below}NO_{3,below} + r_{(NO_3:O_2)}R = NO_{3,f}$$
$$f_{ini} + f_{above} + f_{below} = 1$$

Four unknowns: f_{ini} f_{above} f_{below} R
Five equations