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$_5$CF$_3$
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<td>CFC-11, CFC-12, CFC-113, CCl₄, SF₆</td>
<td>Identify most recently formed water; circulation pathways, water mass ages, water mass formation rates, estimation of anthropogenic CO₂ uptake</td>
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<td>³H</td>
<td>Same as trace gases above, but weak signal in S.H.</td>
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GEOchemical Ocean SECTIONS Study (GEOSECS)


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.
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.

Repeat Hydrography Map: On-going and Planned Cruises

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
Assume: conservation of mass, heat, salt

**Definitions:**

$C_i = \text{concentration of some stable conservative property in water mass \text{ “}i\text{” (end-member concentration)}}$

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

$f_i = \text{fraction of the water mixture that is from water mass \text{ “}i\text{”}}$

$f_{mix} = 1.0 = f_1 + f_2 + \ldots + f_i \quad \text{(mass balance equation)}$
Mixing of Two Water Masses

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

\[
1 = f_1 + f_2
\]
\[
C_{\text{mix}} = f_1 C_1 + f_2 C_2
\]

When combined:
\[
f_1 = \frac{C_{\text{mix}} - C_2}{C_1 - C_2}
\]
Mixing of Four Water Masses

We need four equations with four variables. For example:

\[ 1 = f_1 + f_2 + f_3 + f_4 \]

\[ T_{\text{mix}} = f_1 T_1 + f_2 T_2 + f_3 T_3 + f_4 T_4 \]

\[ S_{\text{mix}} = f_1 S_1 + f_2 S_2 + f_3 S_3 + f_4 S_4 \]

\[ \text{NO}_{\text{mix}} = f_1 \text{NO}_1 + f_2 \text{NO}_2 + f_3 \text{NO}_3 + f_4 \text{NO}_4 \]

Thus, we need three stable, conservative tracers:

- \( T_i \) = temperature of water mass “i”
- \( T_{\text{mix}} \) = temperature of a water mixture
- \( S_i \) = salinity of water mass “i”
- \( S_{\text{mix}} \) = salinity of a water mixture
- \( \text{NO}_i \) = NO of water mass “i”
- \( \text{NO}_{\text{mix}} \) = NO of a water mixture
“NO” – A Quasi-Conservative Water Mass Tracer

\[ \begin{align*}
106 \text{ CO}_2 & + 16 \text{ HNO}_3 & + 1 \text{ H}_3\text{PO}_4 & + 122 \text{ H}_2\text{O} & \rightarrow & [(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] & + 138 \text{ O}_2 \\
\text{The elemental changes during respiration:} & & & & & \\
\Delta \text{C} & +106 & \Delta \text{N} & +16 & \Delta \text{P} & +1 & \Delta \text{O} & -276 & \Delta \text{O}_2 & -138
\end{align*} \]

\[ \Delta \text{O}_2 / \Delta \text{N} = -138 / 16 = -8.6 \]

Thus, during the oxidation of organic matter:

For each mole of \( \text{NO}_3^- \) released to a water mass, \( \sim 9 \) moles of \( \text{O}_2 \) is removed

Broecker (1974): "NO" \( \equiv \) 9[\( \text{NO}_3^- \)] + [\( \text{O}_2 \)]

"PO" \( \equiv \) 135[\( \text{PO}_4^- \)] + [\( \text{O}_2 \)]
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.

<table>
<thead>
<tr>
<th>Source</th>
<th>Organic matter</th>
<th>O$_2$</th>
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<tbody>
<tr>
<td></td>
<td>P</td>
<td>N</td>
</tr>
<tr>
<td>Redfield et al., 1963(^a)</td>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>Anderson and Sarmiento, 1994(^b)</td>
<td>1.0</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>Anderson, 1995(^c)</td>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>Kortzinger et al., 2001(^d)</td>
<td>1.0</td>
<td>17.5 ± 2.0</td>
</tr>
<tr>
<td>Hedges et al., 2002(^e)</td>
<td>1.0</td>
<td>17</td>
</tr>
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\(^a\) 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.
PO₄* – Another Quasi-Conservative Water Mass Tracer

Broecker (1985):
\[ \Delta O_2 / \Delta PO_4 = -175 / 1 = -175 \]

Thus, during the oxidation of organic matter:

For each mole of PO₄⁻ released to a water mass, ~175 moles of O₂ is removed

Broecker (1991):

\[
[PO_4^*] \equiv [PO_4^-] + \frac{[O_2]}{175} = 1.95 \, \mu\text{mol/kg}
\]
Separating NADW from AABW

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

$\text{PO}_4^*$ is nearly uniform within the AABW and within the four components of NADW (Broecker et al., 1998):

- AABW: $1.95 \pm 0.07 \ \mu\text{mol kg}^{-1}$
- NADW: $0.73 \pm 0.07 \ \mu\text{mol kg}^{-1}$

Fraction of NADW is:

$$f_{\text{NADW}} = \frac{1.95 - [\text{PO}_4^*]}{1.95 - 0.73}$$

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.
**PO$_4^*$** distribution at 3000 m in the world ocean.

\[
f_{\text{NADW}} = \frac{1.95 - [\text{PO}_4^*]}{1.95 - 0.73} = \frac{1.95 - 1.4}{1.95 - 0.73} = 45\%
\]

*Sarmiento and Gruber, 2006*
Transient Tracers

- Usually anthropogenic compounds with time-varying sources (or sinks)
  - CFCs, CCl₄, SF₆, ¹⁴C, ³H
- They enter the surface waters of the ocean either via gas exchange (e.g., CFCs, CCl₄, SF₆, ¹⁴C) 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 CO₂ inventory in the ocean
N.H. CFCs & SF$_6$ atm. mixing ratios

Year

SF$_6$ x 100, CFC-11 and CFC-12 (ppt)

CFC-12 (ppt)
SF$_6$ x 100 (ppt)
CFC-113 (ppt)
CFC-11 (ppt)
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)
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).
Vertical distributions of CFC-11 (pmol/kg) measured along hydrographic lines in the (a) Atlantic, (b) Indian, and (c) Pacific oceans.
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  
\( \theta \): Potential temperature  
S: Salinity  
t: Time

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<tr>
<td>Upper LSW</td>
<td>4.2</td>
<td>10.5</td>
<td>2.2</td>
<td>3.5</td>
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<tr>
<td>Classical LSW</td>
<td>14.7</td>
<td>23.4</td>
<td>7.4</td>
<td>8.2</td>
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<td>ISOW</td>
<td>5.0</td>
<td>10.4</td>
<td>5.2</td>
<td>5.7</td>
</tr>
<tr>
<td>DSOW</td>
<td>5.9</td>
<td>8.3</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>NADW (total)</td>
<td>29.8</td>
<td>52.6</td>
<td>17.2</td>
<td>19.6</td>
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Estimate Ocean Uptake of Anthropogenic CO₂

\[ TCO_{2}^{\text{ant}} = \Delta C^* - \text{mean of } (TCO_{2}^{m} - \Delta TCO_{2}^{\text{bio}} - TCO_{2}^{\text{eq t}}) \]

- \( TCO_{2}^{\text{ant}} \): Total anthropogenic CO₂
- \( TCO_{2}^{m} \): Total measured CO₂
- \( \Delta TCO_{2}^{\text{bio}} \): Change in total CO₂ due to biological processes
- \( TCO_{2}^{\text{eq t}} \): Total CO₂ in equilibrium with the atmospheric CO₂ 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 CO₂

Objective maps of (left) pCFC-11 (patm) and (right) pCFC-12 (patm) on the (top) 0 m, (middle) 500 m, and (bottom) 1000 m surfaces. Unlabeled contours at an interval of 25 patm for pCFC-11 are included to help discern gradients. For each parameter the color scale is the same for all three subplots to help visualize vertical trends. Individual maps with significantly more detail are available from the website (http://cdiac3.ornl.gov/gb4031).
Deliberate Tracers

- Most commonly used
  - SF$_6$, $^3$He, and now SF$_5$CF$_3$

- 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

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

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 c, J. Balle a, N. Bergman a, G. Budéus f, M. Danielsen d, J.-C. Gascard e, E. Jeansson b,c, S.R. Olafsdottir d, K. Simonsen h,i, T. Tanhua c, K. Van Scoy l, 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/m². 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/m² 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.
Development of SF$_5$CF$_3$ to replace SF$_6$

Use of SF$_5$CF$_3$ for ocean tracer release experiments

David T. Ho, James R. Ledwell, and William M. Smethie Jr.

Figure 2. Maps of the Santa Monica Basin (SMB) and San Pedro Basin (SPB) showing the (a) injection (white lines) and (b) sampling (black lines) sites. The inset in Figure 2a shows the location of the study area with Los Angeles, San Diego, and New York, USA.

Figure 3. Vertical profiles of SF$_5$CF$_3$ (black) and SF$_6$ (gray) for three sampling periods (S1, S2, S3). S1 was conducted 4 weeks after injection, S2 and S3 were conducted 6 and 8 weeks after injection, respectively. The grey curve in Figure 3 represents the model predictions, while the black and gray curves represent the observed data. The model predictions are in good agreement with the observed data, indicating the effectiveness of SF$_5$CF$_3$ as a tracer for ocean studies.