Oceanic Tracers

OCN 623 – Chemical Oceanography
16 March 2017

Reading: Libes, Chapter 10 - pp. 237-249 and 256-257
Chapter 24 - pp. 661-667 and 680-692

Student Learning Outcomes (SLOs)

At the completion of this module, students should be able to:

1. Identify the *four classes of oceanic tracers,* explain their general uses, and provide examples of each

2. Calculate the relative contributions of *multiple water masses* to a single mixed water mass

3. Calculate and use *quasi-conservative geochemical tracers*

4. Explain the use of anthropogenic *transient* and *deliberate tracers*

Outline

1. Classes of oceanic tracers

2. Water-mass mixing calculations

3. Quasi-conservative geochemical tracers
   - NO and PO_4*

4. Anthropogenic transient and deliberate tracers
   - CFCs, SF_6, CF_3SF_5

1. Classes of Oceanic Tracers

1. *Stable Conservative (SC)*

Potential temperature	J = consumption rate – prod rate = 0
Salinity	λ = radioactive decay rate constant = 0
Freons	
SF_6	
^3He	
"NO"	

2. *Stable, Non-conservative (SNC)*

0_2	$J \neq 0$
NO_3^-	λ = 0
PO_4^-	
ΣCO_2	
CH_4	

3. *Radioactive, Conservative (RC)*

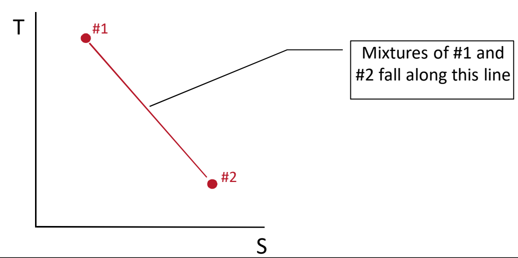
^{222}Rn	$\lambda \neq 0$	$\{X\}_t = e^{-\lambda t}\{X\}_0$
^{3}H (or T)	J = 0	$\lambda = \frac{0.693}{t_{1/2}}$

4. *Radioactive, Non-conservative (RNC)*

^{226}Ra	$J \neq 0$
^{230}Th	$\lambda \neq 0$
^{234}U	
$\Sigma^{14}CO_2$	

2. 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

Definitions:

C_1 = concentration of some stable conservative property in water mass "1" (end-member concentration)

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

f_1 = fraction of the water mixture that is from water mass "1"

$f_1 + f_2 = 1$ (mass balance equation)

Mixing of Two Water Masses

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

$$1 = f_1 + f_2$$

$$C_{mix} = f_1 C_1 + f_2 C_2$$

When combined:

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

Thus, we need one stable conservative tracer

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

Group Task

Using the data below, what fraction of the Ala Wai Harbor water comes from the Ala Wai Canal, and what fraction comes from the ocean?

	Salinity, g/kg
Ala Wai Canal	2
Ala Wai Harbor	31
Ocean Water	35

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	Salinity, g/kg
Ala Wai Canal	2
Ala Wai Harbor	31
Ocean Water	35

12% Ala Wai Canal water

88% ocean water

3. "NO" – A Quasi-Conservative Water-Mass Tracer

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

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" ≡ $9[NO_3^-] + [O_2]$

Negative Linear Relationship – Dissolved Oxygen *vs.* Nitrate

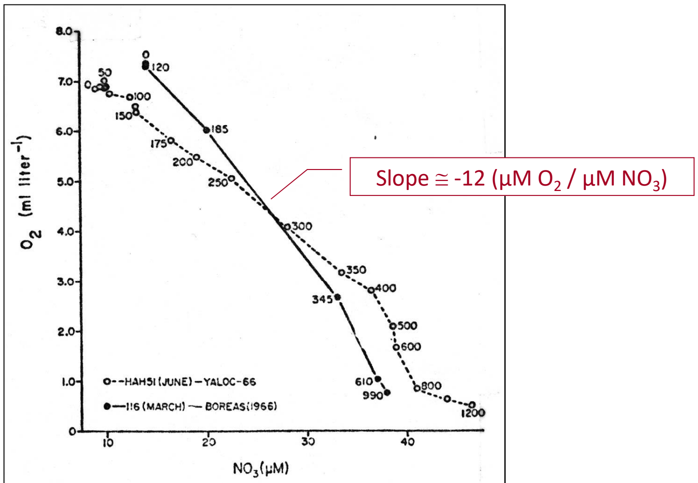

Fig. 5. Oxygen-nitrate diagram. Data presented as in Fig. 4.

Conservative Behavior of "NO"

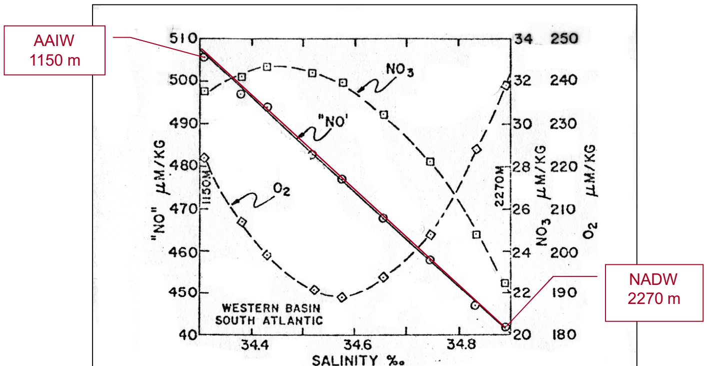

Fig. 5. "NO", NO_3, and O_2 versus salinity at Atlantic Geosecs station 60 in the western basin of the South Atlantic between the core of the AAIW (1150 m) and the top of the NADW (2270 m). The excess NO_3 content is just balanced by the O_2 deficiency yielding a straight line relationship between salinity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

Broecker, 1974

Group Task

Define a quasi-conservative water-mass tracer using <u>phosphate and O_2</u> instead of nitrate and O_2

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

The elemental changes during respiration:

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

$\Delta O_2 / \Delta P = -138 / 1 = -138$

Thus, during the oxidation of organic matter:

For each mole of PO_4^- released to a water mass, ~138 moles of O_2 is removed

Broecker (1991): $PO_4^* \equiv [O_2] + 138[PO_4^-]$

C-N-P Ratios Observed in the Ocean

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.

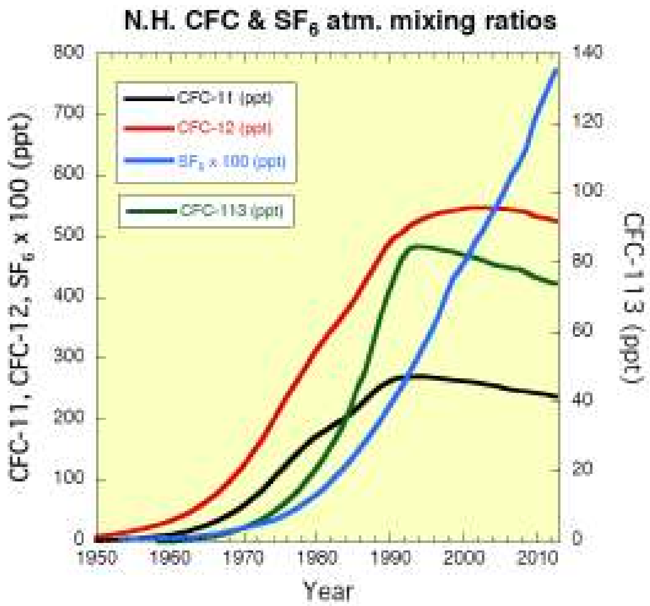
Source	Organic matter			O_2
	P	N	C	
Redfield *et al.*, 1963[a]	1.0	16	106	138
Anderson and Sarmiento, 1994[b]	1.0	16 ± 1	117 ± 14	170 ± 10
Anderson, 1995[c]	1.0	16	106	141–161
Kortzinger *et al.*, 2001[d]	1.0	17.5 ± 2.0	123 ± 10	165 ± 15
Hedges *et al.*, 2002[e]	1.0	17	106	154

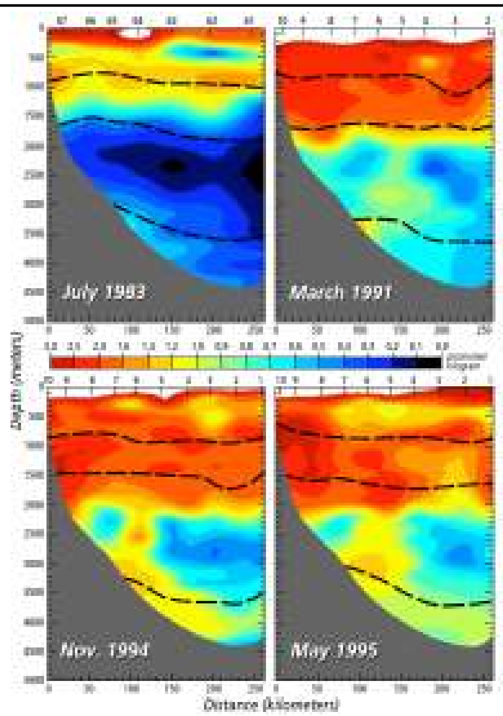
[a] The first and original stoichiometry was determined from observations of the $NO_3^-:PO_4^{3-}$ ratios in ocean deep waters and then assuming a stoichiometry for organic matter.
[b] This value used the same approach as [a] and included DIC and O_2 on dineutral surfaces below 400 m.
[c] These values 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

4. Transient Tracers

- Usually anthropogenic compounds with time-varying sources (or sinks)
  - CFCs, SF_6, ^{14}C, ^3H
- Enter the surface ocean either via gas exchange (e.g., CFCs, SF_6, ^{14}C) or water vapor exchange (^3H)
- Used to examine...
  - Downward penetration of surface perturbations
  - Newly formed subsurface water after leaving the surface
  - Water-mass formation rates
  - Ocean circulation and mixing (validation/calibration of GCMs)
  - Anthropogenic CO_2 inventories in the ocean





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

Deliberate Tracers

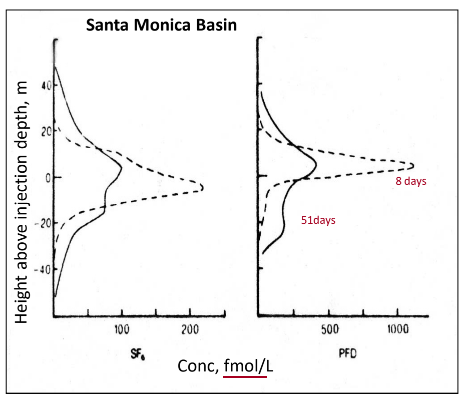
Used to study short time/space-scale processes...

- Vertical mixing
- Pathways of newly formed deep water
- Air-sea gas exchange

In situ Measurement of Vertical Eddy Diffusion

Example - use injected SC tracer to measure rate of vertical eddy diffusion (diapychnal mixing):

- Sulfurhexafluoride (SF_6), very soluble gas
- Perflurodecalin (PFD), emulsified insoluble liquid
- Trifluoromethyl sulfur pentaflouride (SF_5CF_3), soluble gas



- Add tracer at point in water col
- Measure tracer diffusion over time
- Use gas chromatograph with electron-capture detector
- Detection limit = 10^8 molecules!

Iron Enrichment Experiments

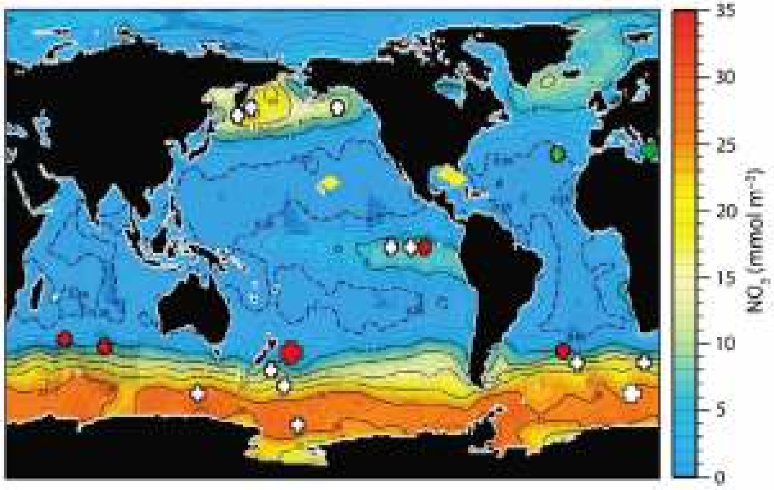
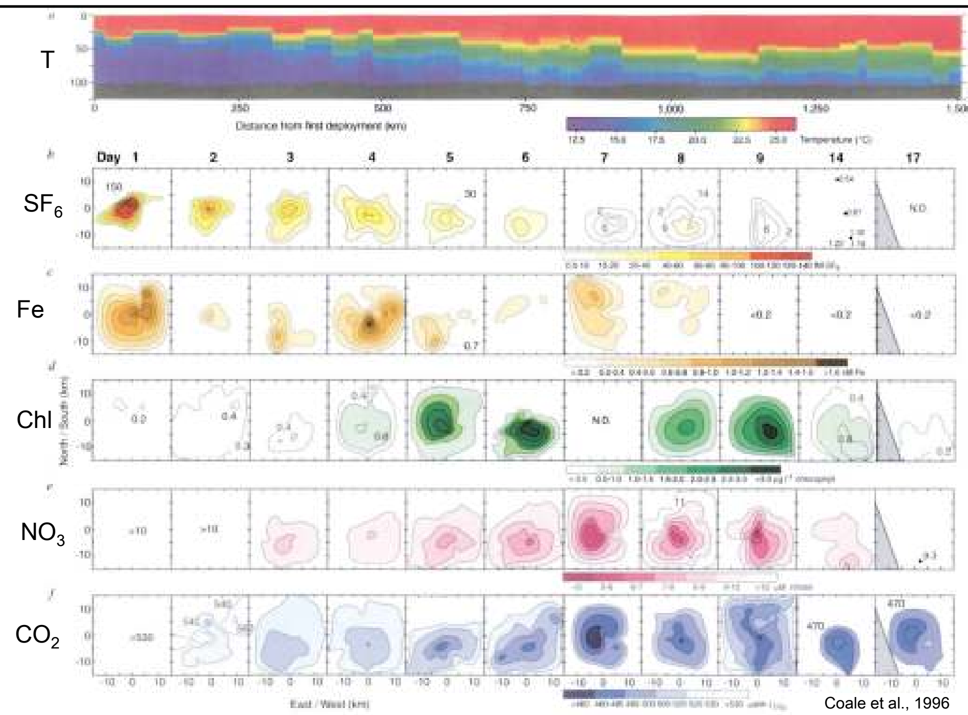


Figure 1. Locations of in situ mesoscale iron enrichment studies (white symbols), iron and/or phosphorous enrichments (green symbols), bloom studies in naturally high iron waters (red symbols), and oceanic geoengineering trials or pilot studies (yellow diamonds), including iron fertilization (Markels 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*

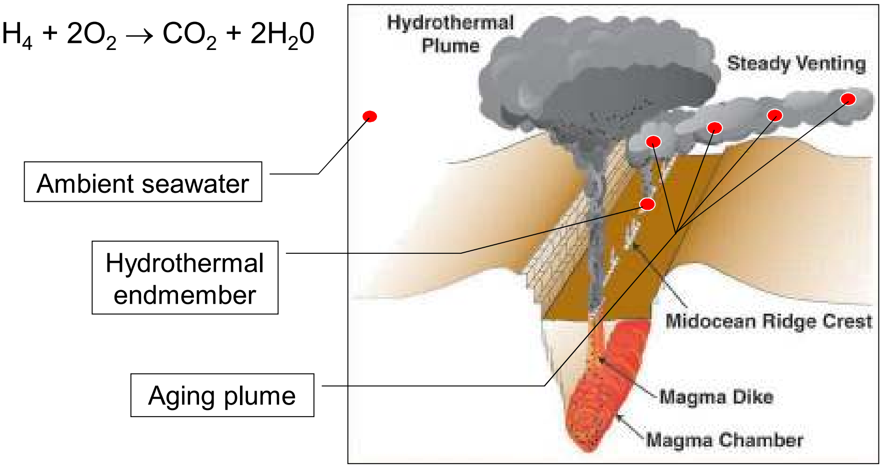
Boyd et al., 2012



Coale et al., 1996

Example: Calculate the rate of CH_4 oxidation in a hydrothermal plume

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_20$



http://oceanexplorer.noaa.gov/explorations

1. Assume steady state (Question: What is in steady state?)
2. Collect water samples from:
   - The "endmember" vent fluid
   - Ambient seawater
   - The plume at increasing distances from the vent
3. Measure the following chemical species in the samples:
   - ^{3}He (SC) - Decrease in conc with increasing distance is due solely to mixing of the plume with ambient seawater
   - ^{222}Rn (RC) - Decrease in conc is due to mixing + radioactive decay of ^{222}Rn
   - CH_4 (SNC) - Decrease in conc is due to mixing + CH_4 oxidation
4. Use the concentrations and the ^{222}Rn "time stamp" to compute the CH_4 oxidation rate