

## Lecture 7 – Life in the Ocean – Primary Productivity and Respiration

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**Life determines ocean chemistry and responds to it.** It is not possible to understand the composition of seawater (or marine sediments) without understanding life processes. Organic matter in the ocean is produced by photosynthesis (and chemosynthesis to a lesser extent) and destructed by respiration.

Much of this material is covered in biological oceanography but here we talk about biological oceanography from a chemical oceanography perspective, with an emphasis on chemical tracers and feedbacks.

The topic is important for three key reasons:

1. One cannot understand the chemistry of the oceans without considering biological influences.
2. To understand the limits on biological production in the oceans, we need to understand the underlying chemical constraints (especially the macro (e.g. N and P) and micro (e.g. Fe and Zn) nutrients.
3. The **balance between ocean productivity and respiration is called export production.** Export production is **the flux of biologically produced organic carbon from the surface ocean to the deep ocean and is also referred to as the biological pump.** This biological pump **is a primary control on atmospheric CO<sub>2</sub>.** Changes in the magnitude of the biological pump are one of the main explanations for why atmospheric CO<sub>2</sub> was lower during glacial times than during interglacials. It is important for us to understand **how the biological pump might change in response to increases in anthropogenic CO<sub>2</sub> and global warming.**

### Units

Many different units are used for primary production. The most common are  $\text{mmol C m}^{-2} \text{ d}^{-1}$ ,  $\text{mg C m}^{-2} \text{ d}^{-1}$ ,  $\text{g C m}^{-2} \text{ y}^{-1}$ , and  $\text{Gt C y}^{-1}$ . Chemical Oceanographers always recommend that moles be the preferred unit, i.e.  $\text{mmol C m}^{-2} \text{ d}^{-1}$ . Use of moles makes comparison of stoichiometric ratios between nutrients and carbon easier.

### Global view of primary production:

A map of the distribution of primary production in the global ocean is shown on the following page.

Note the **general patterns:**

Central gyres	-	low
Equatorial zones	-	high, especially toward the eastern boundaries
Coastal regions	-	high
Arabian Sea	-	high
Circumpolar region	-	mostly moderately high

There have been many different estimates of the **total amount of primary production** in the ocean. There is general consensus that the correct value **is about 50 Gt C y<sup>-1</sup>.**

**\*\*Note:** 1 Gt = 1Pg = 10<sup>9</sup> tons = 10<sup>12</sup> kg = 10<sup>15</sup> grams

The total (marine plus terrestrial) global annual net primary production (NPP) has recently been estimated to be 104.9 Gt of C per year (Field et al., 1998), with similar contributions from the terrestrial (56.4 Gt, 53.8%) and oceanic (48.5 Gt, 46.2%) regimes. NPP is defined as the amount of photosynthetically fixed carbon available to the first heterotrophic level in an ecosystem. It can be expressed as the difference between autotrophic photosynthesis and respiration. This estimate was made using satellite data and the co-called CASA-VGPM biosphere model. In general, NPP for both

land and ocean models is determined from the absorbed photosynthetically active (400 to 700 nm) solar radiation (APAR) and an average light utilization efficiency ( $\epsilon$ ).

Even though the total amounts are about equal, the amounts per area are greater on land than in the ocean. Average NPP on non-ice covered land is  $426 \text{ g C m}^{-2} \text{ yr}^{-1}$  while in the ocean it is  $140 \text{ g C m}^{-2} \text{ yr}^{-1}$ . The lower NPP per unit area of the ocean largely results from competition for light between phytoplankton and their strongly absorbing medium, seawater. Only about 7% of the incident radiation as photosynthetically active radiation (PAR) is absorbed by the phytoplankton, with the remainder absorbed by water and dissolved organic matter. In contrast, terrestrial plants absorb about 31% of the PAR incident on land. Even though primary producers in the ocean are responsible for nearly half the total NPP, they represent only 0.2% of the global producer biomass. Thus, the turnover time of plant organic carbon in the ocean (average 2 to 6 days) is about a thousand times faster than on land.

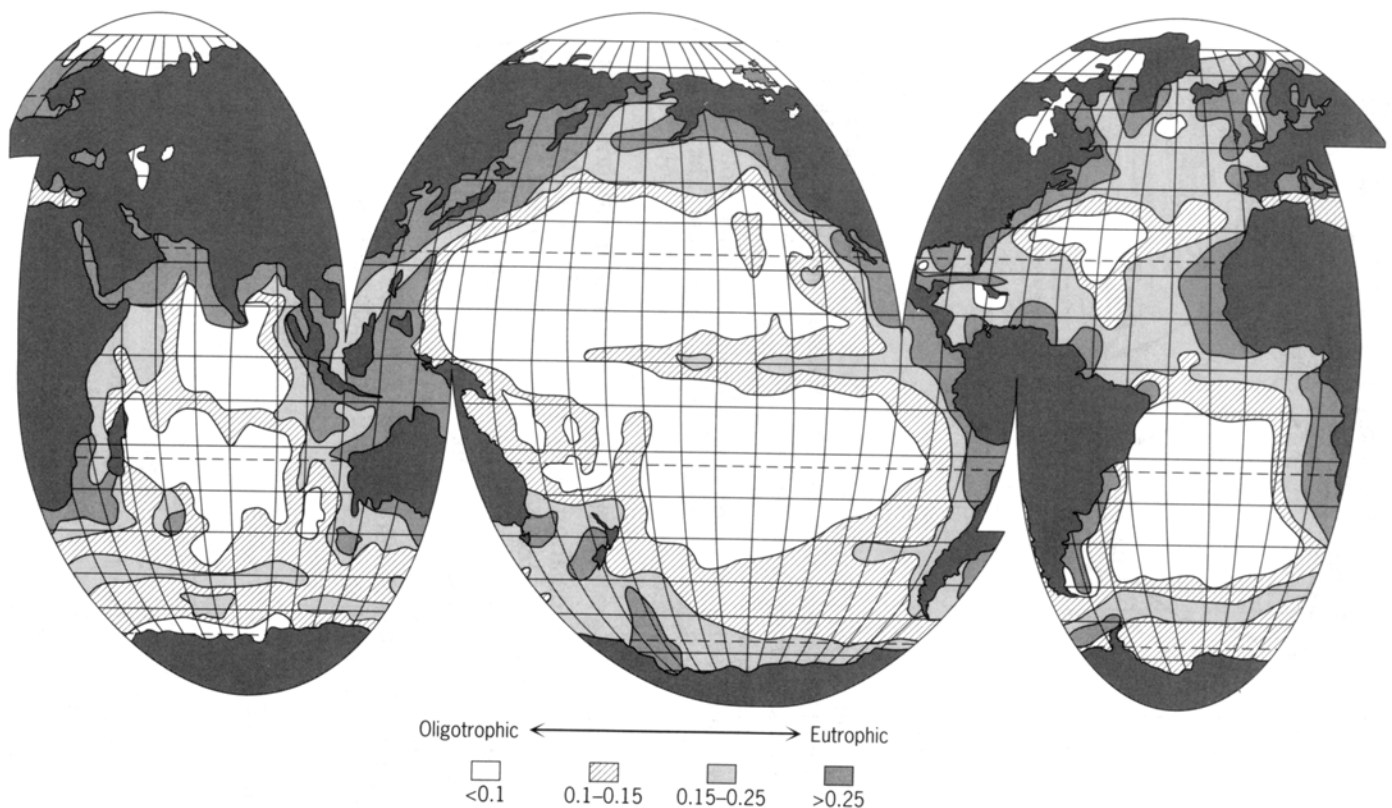


FIGURE 23.17. Distribution of photosynthetic primary productivity ( $\text{g C m}^{-2} \text{ d}^{-1}$ ).  
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### Spatial Variability

The spatial distribution in NPP is non homogenous. There are large regions with low production and smaller areas of high production. Regions of high NPP in the oceans are restricted to estuarine and upwelling systems.

**Methods for Estimating Primary Production** (note that different methods yield different estimates)

Method	Type	Time-scale
$^{14}\text{C}$ assimilation	total	hours - 1 d ( <i>duration of incubation</i> )
$\text{O}_2$ evolution	total	hours - 1 d ( <i>duration of incubation</i> )
$^{15}\text{NO}_3$ assimilation	new	hours - 1 d ( <i>duration of incubation</i> )
$^{15}\text{NH}_4$ assimilation	regenerated	hours - 1 d ( <i>duration of incubation</i> )
Sediment traps below photic zone	new	d - months ( <i>duration of trap deployment</i> )
$\text{NO}_3$ flux to photic zone	new	hours - days
Net $\text{O}_2$ accumulation in photic zone	new	seasonal - annual
$^{238}\text{U}/^{234}\text{Th}$	new	1d - 300d
Remote sensing (coastal zone color scanner)	new, total	days to annual

**Chemical Composition of Biological Particulate Material**

The “average net plankton” >64  $\mu\text{m}$  in size (including phytoplankton and zooplankton) consists of hard parts (shells) and soft parts (organic matter). The average chemical composition of this material is:

**Important minerals of hard parts - shells**

	Mineral	Size ( $\mu\text{m}$ )
Plants		
Coccoliths	$\text{CaCO}_3$ calcite	5
Diatoms	$\text{SiO}_2$ opal	10-150
Silicoflagellates	$\text{SiO}_2$ opal	30
Animals		
Foraminifera	$\text{CaCO}_3$ calcite, aragonite	~100
Radiolaria	$\text{SiO}_2$ opal	~100
Pteropods	$\text{CaCO}_3$ aragonite	~1000
Acantharia	$\text{SrSO}_4$ celestite	~100

**Important major elements in soft parts - protoplasm (except H and O)**

	C	N	P
Zooplankton	103	16.5	1
Phytoplankton	108	15.5	1
Average	106	16	1

The table summarizes the elemental ratios for P:N:C:Ca:Si in different forms of particulate debris settling into the deep sea as caught in deep moored sediment traps, the average ratios for deep and warm surface seawater and the ratios in plankton tows from different ocean areas.

Material		P	N	C	Ca	Si
Particulate debris	Soft tissue	1	16	106	0	0
	Hard parts	0	0	26	26	50
	Composite	1	16	132	26	50
Seawater	Deep	1	15	1000	5000	50
	Warm surface	0	0	868	4974	0
Warm surface	%Removal	100	100	13	0.5	100

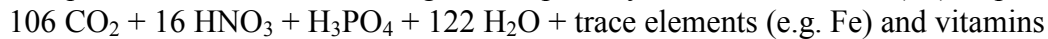
Broecker and Peng (1982)

**The Redfield - Ketchum - Richards or "RKR" Equation**

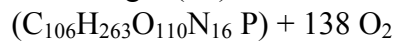
The data for the elemental composition of plankton were assembled to construct an equation to represent average photosynthesis and respiration. The elemental ratio in plankton is called the Redfield Ratio, after Alfred Redfield of Woods Hole. The mean elemental ratio of marine organic particles is thought to be highly conserved (Falkowski et al, 1998) and is given as:

$$\text{P} : \text{N} : \text{C} = 1 : 16 : 106$$

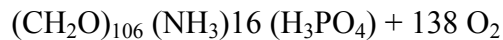
The RKR equation written for the average ocean photosynthesis and aerobic ( $\text{O}_2$ ) respiration is written as:



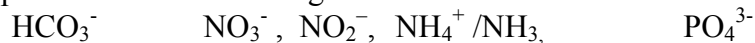
light ( $h\nu$ )  $\downarrow$



or



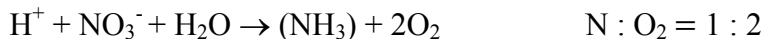
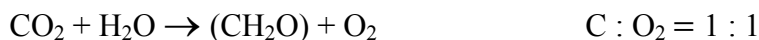
The actual chemical species assimilated during this reaction are:



This is an organic oxidation-reduction reaction – during photosynthesis, C and N are reduced and O is oxidized. During respiration, the reverse occurs. There are no changes in the oxidation state of P.

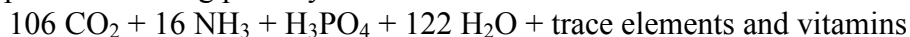
Photosynthesis is endothermic. This means it requires energy from an outside source. In this case the energy source is the sun. Essentially plants convert the photo energy from the sun into high-energy C-C bonds. This is a non-equilibrium reaction whose slow kinetics are enzymatically facilitated. Respiration is exothermic. This means it could occur spontaneously and release energy.

Stoichiometry breakdown of oxygen production (theoretically calculated)

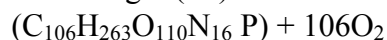


Total oxygen production:  $106\text{C} + 16\text{N} \times 2 = 138\text{O}_2$

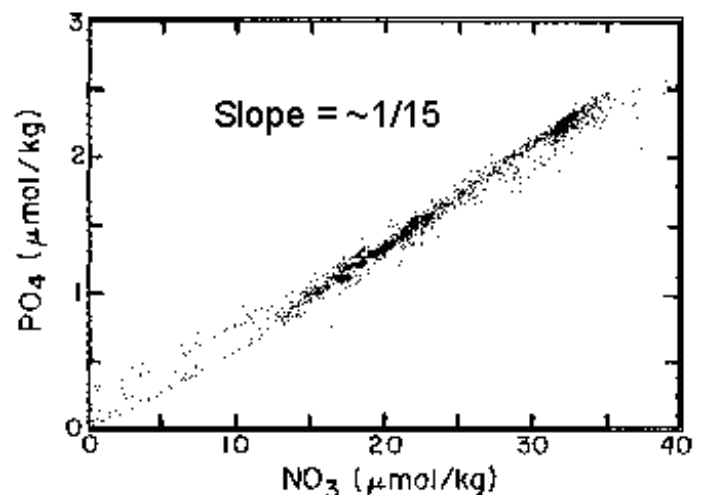
If ammonia is available it is preferentially taken up by phytoplankton. If  $\text{NH}_3$  is used as the N source then less  $\text{O}_2$  is produced during photosynthesis



light ( $h\nu$ )  $\downarrow$



Dissolved seawater N:P ratios are also close to the Redfield ratios. The slope is close to 15 (see figure). Falkowski et al (1998) point out that below the upper 500m, the average N/P ratio for the world's oceans is  $\sim 14.7$ , which corresponds to a small deficit in N. This deficiency corresponds to fixed inorganic nitrogen losses mediated by anaerobic denitrifying bacteria.



**Shortcomings of the RKR paradigm:**

- a. The elemental composition of plankton varies with nutrient availability.
- b. Plankton compositions vary regionally, as indicated by varying respiration ratios.

### Dissolved Element Availability versus Plankton Demand:

1. Both N and P are in short supply (limiting) relative to plankton needs.
2. Inorganic C is present in seawater in ten times excess of that needed for photosynthetic use of all available N and P.
3. O<sub>2</sub>-saturated seawater contains only a slight excess of oxygen versus the amount required to respire all the organic matter that can be photosynthesized from the available N and P.
4. Biogenic tests ("hard body parts") also have global average compositions.
5. Si is limiting for diatom production.

Bioactive Element	mg atom* m <sup>-3</sup>	Availability Ratio (to P)	Use Ratio <sup>⊗</sup>	Availability Use
P	2.3	1	1	1
N	34.5	15	16	0.94
C	2340	1017	106	9.6
O <sub>2</sub> <sup>▲</sup>	367	160	138	1.16

\*for average (deep) seawater, S = 35 ppt and O<sub>2</sub> saturated.

<sup>⊗</sup>RKR plankton values.

<sup>▲</sup>oxygen requirement for total respiration of RKR plankton.

### New Production and Regenerated Production

**New Production** is defined as the primary production that is based on NO<sub>3</sub><sup>-</sup> as N source (from diffusion/upwelling from below and from the atmosphere via nitrogen fixation or nitrification)

**Regenerated Production** is the production based on NH<sub>4</sub><sup>+</sup> and urea as N sources.

The **f-ratio**:

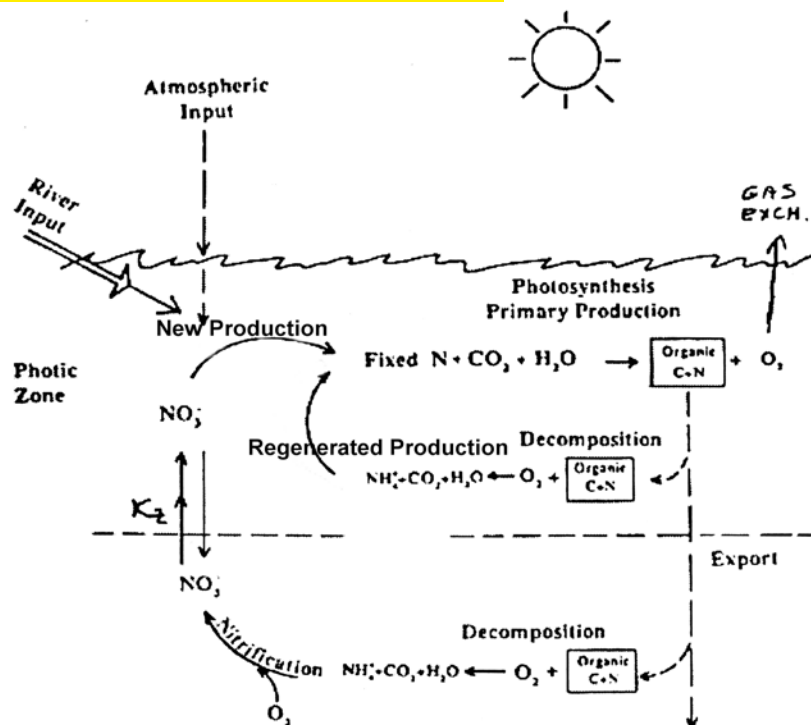
$f = \text{NO}_3 \text{ uptake} / \text{NO}_3 + \text{NH}_4 \text{ uptake}$   
(the original definition by Dugdale and Goering, 1969).

If we write P = gross production and R = respiration then we can also approximate f as:

$f = (P - R)/P$  also called the ratio of **net to gross production**.

At steady state NO<sub>3</sub> uptake should equal particulate and dissolved organic N flux exported out of the euphotic zone and the O<sub>2</sub> flux to the atmosphere (in equivalent units).

This is a schematic diagram of the new and regenerated production cycle (based on N source).



### Magnitude of New Production

A global synthesis of new production was compiled by Chavez and Toggweiler (1995). These estimates were obtained by first estimating the rate of upwelling in the different ocean areas. The units are Sverdrups (10<sup>6</sup> m<sup>3</sup> sec<sup>-1</sup>). The upwelling rate was multiplied by the nitrate concentration upwelled.

Assuming all the  $\text{NO}_3$  is consumed and converted to carbon in the ratio  $\text{C/N} = 106/16 = 6.6$  gives the estimate of new production. The calculation yields a total oceanic new production of  $7.2 \times 10^{15} \text{ g C y}^{-1}$ .

### Predicting New Production

Eppeley and Peterson (1979) wrote a classic paper in which they summarized existing data to suggest that new production should vary regionally in relation to the primary production rate.

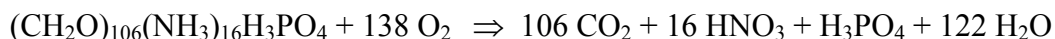
They suggested the relation:  $\text{New/Total} = 0.0025 \text{ Total}$ ; or  $f = 0.0025 \text{ Total Production}$

Other suggested relations include a relation based on sediment traps that indicates that the flux of C to depth for ocean depths bigger than 1000m is:  $J(z) = 0.17 \text{ PP}/z + 0.01 \text{ PP}$ ; where PP is the primary productivity and Z the water column depth. Eppeley gives a comprehensive summary of new production estimates and methods in the book *Productivity of the Ocean: Present and Past* (Wiley and Sons 1989).

Calculations by Falkowski et al (1998) of annual mean export (e.g. new production) using CZCS chlorophyll distributions, the conversion of the chlorophyll data to primary production and the Eppeley and Peterson conversion to new production yielded total global new production of  $16 \text{ Gt C y}^{-1}$ . This is about twice the value of  $7.2 \text{ Gt C y}^{-1}$  estimated by Chavex and Toggweiler. If NPP equals  $50 \text{ Gt C y}^{-1}$  then the corresponding global f-ratios are 0.32 and 0.14, respectively. Most field observations support the lower estimate.

### Respiration

Aerobic respiration corresponds to RKR photosynthesis run backwards:



This means that the dissolved oxygen concentration is a tracer for respiration. In the euphotic zone there is usually excess oxygen above atmospheric saturation because there is net biological production. Production of  $\text{O}_2$  by primary production is greater than consumption of  $\text{O}_2$  by respiration (e.g. net production). Below the euphotic zone there is only consumption by respiration, so the oxygen goes down as respiration proceeds. In some parts of the open ocean with restricted circulation all of the dissolved oxygen is consumed by respiration. Examples of these locations are the oxygen minimum zones in the eastern tropical north and south Pacific and Arabian Sea. At these locations respiration proceeds using nitrate (as oxidizer) to combust the organic matter. In some enclosed basins, like the Black Sea, Cariaco Trench, Saanich Inlet and Framvaren Fjord, respiration also uses up all the nitrate in these cases sulfate is reduced to hydrogen sulfide ( $\text{H}_2\text{S}$ ). The oxidation of the  $\text{NH}_3$  in organic matter to  $\text{NO}_3$  is referred to as nitrification.

Respiration is:

1. An exothermic, enzymatically mediated reaction.
2. Theoretical stoichiometries closely match RKR values
  - a.  $\Delta \text{P} = 1/138 \Delta \text{O}_2 = 1/138 \text{ AOU}$
  - b.  $\Delta \text{N} = 16/138 \Delta \text{O}_2 = 1/8.6 \text{ AOU}$

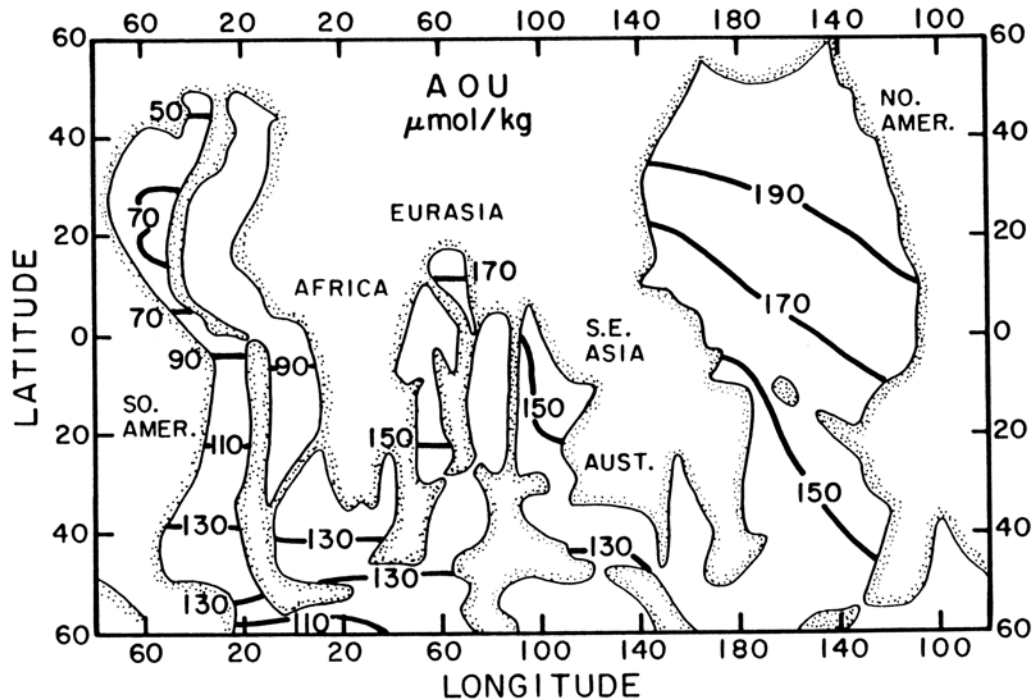
### Apparent Oxygen Utilization (AOU)

We can calculate the extent of respiration by calculating a parameter called the Apparent Oxygen Utilization or AOU. AOU is defined as:  $\text{AOU} = \text{O}_2' - \text{O}_2$

Where:  $\text{O}_2'$  = value of  $\text{O}_2$  the water would have if it was in equilibrium with the atmosphere at the temperature and salinity of the water. This is called saturation. This implies that all waters are in

equilibrium with the atmosphere (100% saturated) when they sink to become the deep ocean water.  $O_2$  in the above equation is the dissolved oxygen actually measured in the same water sample.

The distribution of AOU throughout the ocean at 4000m is shown in the figure below (from Broecker and Peng). The lowest values ( $50 \mu\text{mol kg}^{-1}$ ) are in the North Atlantic. The highest values ( $>190 \mu\text{mol kg}^{-1}$ ) are in the oldest water in the North Pacific.



Distribution of AOU (saturation oxygen content minus measured oxygen content) at a depth of 4000 meters. Based on the results obtained during the GEOSECS program

### Regenerated Nutrients

This term refers to the nutrients released to the water column as a result of respiration, these can be determined from RKR stoichiometries using a calculated AOU. Once you've calculated the AOU in a water sample, you can calculate the  $CO_2$ ,  $HNO_3$  and  $H_3PO_4$  released by respiration.

$$1 \text{ mol } O_2 \text{ consumed} = 106/138 \text{ mol } CO_2 + 16/138 \text{ mol } HNO_3 + 1/138 \text{ mol } H_3PO_4 = \\ = 0.77 \text{ } CO_2 + 0.12 \text{ } HNO_3 + 0.0072 \text{ } H_3PO_4$$

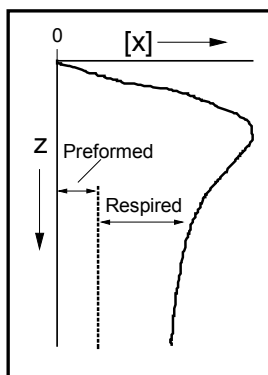
### Preformed Nutrients

Preformed nutrients are those initially present in seawater at the time of down-welling. Hence, preformed nutrient = total nutrient - regenerated nutrient.

The nutrients of oxidative origin are calculated from AOU and subtracted from total nutrients to get the preformed nutrient concentrations. Preformed nutrients are characteristic of waters originating in



different regions and hence can be used as water mass tracers, like conservative elements (Broecker et al, 1985).



Water Type	O <sub>2</sub>	NO <sub>3</sub>	PO <sub>4</sub>
<b>Initial</b>	<b>350*</b>	<b>7.5</b>	<b>0.56</b>
Final Sample	150	30.7	2.01
Regenerated	-200	+23.2	+1.45

\*calculated for saturation at measured T and S

For example :

$$PO_4^{\circ} = PO_4 - \frac{O_{2sat} - O_2}{138} = PO_4 - \frac{AOU}{138}$$

Where,  $PO_4^{\circ}$  = preformed phosphate;  $PO_4$  = measured phosphate.

### Revised Stoichiometric Ratios

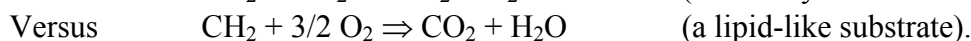
Takahashi et al (1985) first argued that the correct approach for determining stoichiometric regeneration ratios was to utilize data along isopycnal surfaces. They found that the stoichiometric ratios (on  $\sigma_0 = 27.0-27.20$ ) varied for different locations in the Atlantic and Indian oceans (see table). They argued that the widely used RKR values of P:N:C:-O<sub>2</sub> of 1:16:106:138 should be replaced by 1:16:115:172 for the Atlantic and Indian Ocean (this include the C in hard shells).

The following table compares theoretical and actual mean stiochiometries for different oceans (at a  $\sigma_0$  of 27.00-27.20):

Location	# Stations	P	N	CO <sub>2</sub>	(O <sub>2</sub> -2N)*	-O <sub>2</sub>	CaCO <sub>3</sub>
RKR	~	1	16	106	106	138	~
Atlantic	119	1	17.0± 0.4	96 ± 6	138 ± 9	171 ± 8	10 ± 4
Indian	43	1	14.9 ± 0.4	119 ± 5	142 ± 5	172 ± 5	17 ± 4
Atlantic+Indian	162	1	16.3 ± 1.1	103 ± 14	140 ± 8	172 ± 7	12 ± 5

\*oxidation of N is assumed to take 2 O<sub>2</sub>

This approach was improved upon by Anderson and Sarmiento (1994) who calculated the stoichiometric ratios on 20 sites in the South Atlantic, Indian and Pacific Basins between 400 and 4000m. The P:N:C:-O<sub>2</sub> ratios of remineralization below 400m are estimated with uncertainties as 1:16±1:117±14:170±10. These values are very consistent with those of Takahashi et al (1985). In ocean regions where there is denitrification the coefficient for NO<sub>3</sub> is less (12±2). It is clear that more O<sub>2</sub> (~175 moles) is actually required to respire sinking organic matter than was originally calculated from the RKR equation (138 moles). The higher O<sub>2</sub> demand suggests that sinking organic matter has more of a lipid-like nature.



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