Respiration corresponds to the RKR reaction 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 O₂ by primary production is greater than consumption of O₂ by respiration. 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 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 and sulfate is reduced to hydrogen sulfide (H₂S).

**Aerobic respiration**
Oxygen is consumed and nutrients are released.

\[
(CH₂O)_{106}(NH₃)_{16}(H₃PO₄) + 138 \text{O}_2 \\
\text{Algal Protoplasm} \\
\downarrow \text{bacteria} \\
106 \text{CO}_2 + 16 \text{HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} + \text{trace elements}
\]

The oxidation of the NH₃ in organic matter to NO₃ is referred to as nitrification.

**Apparent Oxygen Utilization**
We can calculate the extent of respiration by calculating a parameter called the Apparent Oxygen Utilization or AOU. AOU is defined as:

\[
\text{AOU} = O'_2 - O_2
\]

where: \(O'_2\) = value of O₂ 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. O₂ is the dissolved oxygen actually measured in the same water sample.

The distribution of AOU throughout the ocean at 4000m is shown in the attached Figure 9-1 (from Broecker and Peng). The lowest values (50 µmol kg⁻¹) are in the North Atlantic. The highest values (>190 µmol kg⁻¹) are in the oldest water in the North Pacific.

North-south sections of AOU in the western Atlantic and western Pacific Oceans are shown in Figures 9-2a,b. Some key intermediate and deep density surfaces (\(\sigma_o = 27.0, 27.5\) and \(\sigma_4 = 45.2\)) are indicated.
Fig 9-1 Distribution of AOU at 4000m in the world's oceans. Lowest values are in the Atlantic and the largest (>190 µmol kg⁻¹) are in the Pacific. (from Broecker and Peng, 1982).

Fig 9-2 a,b Sections of AOU through the Atlantic and Pacific
Regenerated Nutrients

Once you've calculated the AOU in a water sample you can calculate the CO₂, HNO₃ and H₃PO₄ released by respiration.

\[
1 \text{ mol O}_2 \text{ consumed} = \frac{106}{138} \text{ mol CO}_2 + \frac{16}{138} \text{ mol HNO}_3 + \frac{1}{138} \text{ mol H}_3\text{PO}_4
\]

\[
= 0.77 \text{ CO}_2 + 0.12 \text{ HNO}_3 + 0.0072 \text{ H}_3\text{PO}_4
\]

Preformed Nutrients

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

An example from Park (1967) of the relationships between AOU:PO₄:NO₃:Si is shown in Fig. 9-3. The location of these profiles is at 44°N; 127°W (off the coast of Oregon). The nutrients of oxidative origin (P₀ₐ) were 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 (e.g. Broecker, 1974; Broecker et al, 1985). Broecker (1974) originally proposed that O₂ and NO₃ and O₂ and PO₄ data can be combined in such a way that the alteration by respiration is cancelled. From the original RKR respiration equation given above, roughly 1/9 mole of N is released as NO₃ and 1/135 mole of P is released as PO₄ for each mole of O₂ consumed. Thus the sum of 9NO₃ + O₂ was defined as "NO" and 135PO₄ + O₂ as "PO". Both NO and PO should be nearly conservative tracers. An example of NO₃, O₂ and "NO" versus salinity for a single station in the western basin of the South Atlantic is shown in Fig. 9-4. You can see that O₂ and NO₃ show curvature with salinity but "NO" varies linearly, or conservatively, between two end members that represent the core of the AAIW (at 1150m) and the top of the NADW (at 2270m).

Revised Stoichiometric Ratios

Isopycnal surfaces are surfaces of constant density. Potential temperature and salinity are perfectly correlated on isopycnal surfaces. In the ocean most mixing and transport occur on isopycnal surfaces. The winter surface outcrops of various isopycnal surfaces in the North Atlantic Ocean are shown in Fig. 9-5. The densest waters that outcrop at the surface have a density of σ₀ = 27.6. The north-south distribution of density surfaces in the 0 - 1500m depth range of the western side of the Atlantic, Indian and Pacific Oceans are shown in Fig. 9-6. The density surfaces shoal and outcrop at high latitude, then sink to maximum depths at mid-latitudes. They tend to shoal again near the equator where there is upwelling. To a first approximation the distributions of tritium (³H), which is a tracer for water, which has an atmospheric source, follow these density surfaces.

Takahashi et al (1985) first argued that the correct approach for determining stoichiometric regeneration ratios was to utilize data along isopycnal surfaces. The change in NO₃ and PO₄ concentrations along isopycnal surfaces away from the surface outcrop can be estimated from:
Fig. 10-3
(From Park 1967)

Fig. 10-4
(From Broecker 1974)

Fig. 5. "NO₃", NO₂, and O₃ versus salinity at Atlantic Ocean station 60 in the western basin of the South Atlantic between the core of the SSW (150 m) and the top of the NADW (2270 m). The excess NO₃ content is just balanced by the O₃ deficiency yielding a straight line relationship between salinity and "NO₃".
Figure 10-5. Map showing the winter outcrops of isopycnal surfaces in the North Atlantic Ocean. This map was constructed from the NOAA Geophysical Fluid Dynamics Group's oceanographic data files (689) by Jorge Sarmiento of Princeton University who kindly supplied this diagram for use in the book.
Figure 1. Sections along the western side of the world's three major oceans showing how the depth of various isopycnal horizons changes with latitude. The heavy dashed line shows the depth at which the tritium concentration of the water (at the time of the GEOSECS surveys) was one quarter that of the overlying surface water. Based on data obtained as part of the GEOSECS program (424,425,426).
\[ \Delta P = [PO_4] - [PO_4]^0 = R_{PO4/O2} \times AOU \]
\[ \Delta N = [NO3] - [NO3]^0 = R_{NO3/O2} \times AOU \]

They found that the stoichiometric ratios (on \( \sigma_o = 27.0-27.20 \)) varied for different locations in the Atlantic and Indian oceans (Table 9-1). They argued that the widely used RKR values of P:N:C:-O_2 of 1:16:106:138 should be replaced by 1:16:122+22:172 for the Atlantic and Indian Ocean.

This approach was improved upon by Anderson and Sarmiento (1994) who calculated the stoichiometric ratios on 20 neutral surfaces in the South Atlantic, Indian and Pacific Basins between 400 to 4000m. Neutral surfaces are almost the same as isopycnal surfaces but are considered to be a more precise estimate of the horizons upon which water masses preferentially move and mix (McDougall, 1987). The -O_2/P, C_{org}/P and N/P utilization ratios are shown in Fig. 9-7a,b,c. The P:N:C:-O_2 ratios of remineralization below 400m are estimated with uncertainties as 1:16\pm1:117\pm14:170\pm10. These values are very consistent with those of Takahashi et al (1985). In ocean regions where there is denitrification the coefficient for NO_3 is less (12\pm2).

It is clear that more O_2 (~170 moles) is actually required to respire sinking organic matter than was originally calculated from the RKR equation (138 moles). The RKR type organic matter has an oxidation state as for carbohydrate. The higher O_2 demand suggests that sinking organic matter has more of a lipid-like nature.

\[
\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}
\]

versus

\[
\text{CH}_2 + \frac{3}{2} \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}
\]

Broecker et al (1985) used these improved stoichiometric ratios to analyze the origin and flow patterns of deep waters in the ocean. The compositions characteristic of the main end-member waters, bottom waters, outflow waters and circumpolar common water are shown in Table 9-2. The flow patterns are indicated in Fig 9-8. All three oceans are fed by bottom and intermediate waters originating in the Atlantic to form mid-depth water. These three mid-depth waters flow back to the Antarctic. Here they merge and mix with Weddell Sea bottom water to form common water. The relationships between the various oceans and the three end-member waters are shown in Fig. 9-9 using temperature and PO_4^0 as master variables. Common (Circumpolar) water turns out to consist of about 50% southern component water (e.g. Weddell Sea) and 25% each of northern and intermediate component water.

**Calculation of Rates of O_2 utilization**

If waters on isopycnal (or neutral) surfaces can be dated then the rate of O_2 consumption can be determined. This has been done in the Atlantic by Jenkins (1982).

Tritium was used to calculate water ages. Tritium (\(^3\text{H}\)) has an atmospheric source. The natural source of \(^3\text{H}\) is very small but it was greatly enhanced by atmospheric nuclear bomb testing in the early 1960's. The source of the \(^3\text{H}\) is neutrons escaping from the bomb test. The \(^3\text{H}\) (and \(^{90}\text{Sr}\)) content of rain in Ireland is shown in Fig. 9-10. Note the large \(^3\text{H}\) input around 1963-1964. Tritium is a tracer for water as HTO and has a half life of 12.5 years. When tritium beta decays it turns into a helium isotope (\(^3\text{He}\)). North-south sections of \(^3\text{H}\) for the Atlantic, Indian and Pacific Oceans are shown in Fig. 9-11. Note the similarity of the \(^3\text{H}\) and density (Fig 9-6) distributions.
Figure 2. The O/P utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.2.

Figure 6. The C/P utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.3.

Figure 7. The N/P utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.4.

Fig 10-7
(From Anderson and Smayda 1994)
### Table 9-1 (from Takahashi et al. 1985)

**Molecular Ratio of O, N, C, O₂, and CaCO₃ Changes in the Atlantic and Indian Oceans**

<table>
<thead>
<tr>
<th>Number of Stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>e₂</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Redfield ratio*</td>
</tr>
<tr>
<td>North Atlantic</td>
</tr>
<tr>
<td>South Atlantic</td>
</tr>
<tr>
<td>Atlantic mean</td>
</tr>
<tr>
<td>South Indian</td>
</tr>
<tr>
<td>Indian mean</td>
</tr>
<tr>
<td>Atlantic and Indian mean</td>
</tr>
</tbody>
</table>

For the oxidation of nitrogen a reaction NH₃ + 2O₂ = NO₃⁻ + H₂O + H⁺ (i.e., N : O₂ = 1 : 2) is assumed.

*Utilization by plankton after Redfield et al. [1963].

### Table 9-2 (from Broecker et al., 1985)

**Potential Temperature, Salinity, Potential Density, Initial Phosphate, Dissolved Oxygen, Silicate, D/H, Excess Helium-3, and ¹³C to C Ratio for Key Water Types**

<table>
<thead>
<tr>
<th>Water Type</th>
<th>°C</th>
<th>%o</th>
<th>σ₀</th>
<th>µm/kg</th>
<th>µm/kg</th>
<th>µm/kg</th>
<th>µm/kg</th>
<th>%</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom waters*</td>
<td>2.5</td>
<td>34.94</td>
<td>45.88</td>
<td>280</td>
<td>12</td>
<td>1.0</td>
<td>0</td>
<td>-70</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>Intermediate component, Indian</td>
<td>4.6</td>
<td>34.8</td>
<td>47.6</td>
<td>112</td>
<td>-3</td>
<td>3</td>
<td>-153</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate component, Pacific</td>
<td>4.6</td>
<td>34.5</td>
<td>47.4</td>
<td>112</td>
<td>-3</td>
<td>3</td>
<td>-153</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outflow waters</td>
<td>2.4</td>
<td>34.91</td>
<td>45.87</td>
<td>225</td>
<td>126</td>
<td>-20</td>
<td>-6</td>
<td>-158</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>Western Atlantic</td>
<td>2.3</td>
<td>34.86</td>
<td>45.86</td>
<td>235</td>
<td>124</td>
<td>-25</td>
<td>-8</td>
<td>-163</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>Eastern Atlantic</td>
<td>1.7</td>
<td>34.72</td>
<td>45.86</td>
<td>172</td>
<td>118</td>
<td>-1.3</td>
<td>-180</td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indian</td>
<td>1.5</td>
<td>34.67</td>
<td>45.80</td>
<td>156</td>
<td>130</td>
<td>-1.3</td>
<td>20</td>
<td>-210</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>Common water</td>
<td>1.6</td>
<td>34.74</td>
<td>45.87</td>
<td>195</td>
<td>95</td>
<td>-10</td>
<td>0</td>
<td>-154</td>
<td>1.33</td>
<td></td>
</tr>
</tbody>
</table>

*Waters that enter the three major oceans from the Antarctic. The density values are based on the equation of state for seawater by Cox et al. [1970] and Ekman [1908] and the adiabatic temperature gradient formulated by Helland-Hansen [1912].

*σ₀* rather than *σ₄*. 
Fig 9-8 (from Broecker et al, 1985)

Fig 9-9 (from Broecker et al, 1985)
Figure. Plot of the mean $^3$H content of rain at Valencia, Ireland from 1952 to 1974 (solid circles). Also given is the total annual northern hemisphere $^{90}$Sr deposition (open circles). From this comparison it is clear that the time history of the input of these two isotopes is quite similar. The differences are related to the ratio of escaping neutrons (producing $^3$H) to uranium fissions (producing $^{90}$Sr) for the various bombs tested. This diagram was published by Dreisigacker and Roether (61).
Figure 9-11. Sections showing the vertical distribution of tritium (in T.U.) along traverses in the western part of the three major oceans. The heavy dashed line denotes the depth at which the tritium concentration reaches one-quarter that in overlying surface water. These results were obtained by Göte Oslund of the University of Miami as part of the GEOSecs program (51,52,54,56).
Jenkins (1982) used the tritium-helium method to data water on different isopycnal surfaces in the North Atlantic around Bermuda. He then plotted AOU versus age on individual density surfaces (e.g. $\sigma_0 = 26.80$ which is at about 400m in Fig. 9-12). The slope gives the oxygen utilization rate (OUR) on a given isopycnal surface. He then plotted the OUR versus depth (Fig. 9-13). OUR decreases exponentially with depth below the euphotic zone ($Z$ in m) according to:

$$\ln \text{OUR} = -(0.68 \pm 0.17) - (0.00295 \pm 0.00027) \ Z$$

The earlier estimates by Riley (1951) using a simpler model for three different density surfaces were in remarkably good agreement.

When Jenkins integrated the OUR from 100m to the bottom he obtained the total deep water O$_2$ consumption of:

$$\int \text{OUR} = 5.7 \ \text{mol O}_2 \ \text{m}^{-2} \ \text{yr}^{-1}$$

Using the RKR ratios this is equivalent to an organic carbon consumption of 4.5 mol C m$^{-2}$ yr$^{-1}$. The paradox was that this organic carbon consumption rate was about double the accepted primary production for this region. The expected new production would be about 10% of this. Jenkins suggested that the historical primary production rates were low because they were based on small bottle, long incubation time technique.

Shulenberger and Reid (1981) reached a similar conclusion with a slightly different study in the mid-latitude Pacific. They measured a subsurface oxygen maximum with saturation ratios reaching 120% or more. The oxygen maximum was produced by net primary production but the O$_2$ was prevented from escaping to the atmosphere because of stratification of the surface layer due to summer heating. The primary production estimated from this oxygen accumulation was much greater than primary production measured by the $^{14}$C method (Table 9-3).

Table 9-3

<table>
<thead>
<tr>
<th>Region</th>
<th>Max excess oxygen (mg C m$^{-2}$)</th>
<th>$^{14}$C primary productivity (mg C m$^{-2}$ d$^{-1}$)</th>
<th>Implied O$_2$ production from $^{14}$C rate (mol O$_2$ m$^{-2}$ yr$^{-1}$)</th>
<th>Excess O$_2$ consumption (mol O$_2$ m$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Central North Pacific</td>
<td>0.77</td>
<td>0.26</td>
<td>2.92</td>
<td>6.42</td>
</tr>
<tr>
<td>Sta. A-1*</td>
<td>0.53</td>
<td>0.08</td>
<td>1.23</td>
<td>4.42</td>
</tr>
<tr>
<td>Sta. A-3*</td>
<td>0.56</td>
<td>0.11</td>
<td>0.67</td>
<td>4.92</td>
</tr>
<tr>
<td>(B) Sargasso Sea (H.B.S., 1960)</td>
<td>0.46</td>
<td>0.12</td>
<td>2.09</td>
<td>7.60</td>
</tr>
<tr>
<td>(C) NE North Pacific (ANDERSON, 1969)</td>
<td>1.23</td>
<td>1.2</td>
<td>1.93</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Note that excess O$_2$ may accumulate in fewer than 120 days, but this is unlikely to take >120 days. Hence rates of O$_2$ production as measured from excess O$_2$ may be much too low, but are unlikely to be too high. All possible losses of O$_2$ are ignored.

* Simulated in situ productivity data near 26°N, 155°W in August. Primary productivity station numbers from S.I.O. (1975): Oxygen data from the hydrocast closest to the productivity data (A-1 and A-2 and hydrocast A2-04; A-3 and hydrocast A2-16; A-4 and hydrocast A3-04).† Daily productivity measured equal to 6 times the hourly rate (see also text on p. 914). † Average over May to September.
Fig 9-12 and 9-13
References:


