

## Measures of net oxidant concentration in seawater

GEORGE A. JACKSON\* and PETER M. WILLIAMS\*

(Received 15 October 1986; in revised form 25 June 1987; accepted 24 July 1987)

**Abstract**—Dissolved oxygen deficits in the ocean have been used as a measure of the organic matter oxidized in a volume of water. Such organic matter is usually assumed to be predominantly settled particles. Using dissolved oxygen concentration in this way has two problems: first, it does not differentiate between oxidant consumed by the pool of dissolved organic matter present near the ocean surface and oxidant consumed by organic matter contained by falling particles; second, it does not account for other oxidant sources, such as nitrate, which can be as important to organic matter decay as oxygen in low-oxygen water, such as off Peru or in the Southern California submarine basins.

New parameters provide better measures of the net oxidant concentration in a water parcel. One such, NetOx, is changed only by gaseous exchange with the atmosphere, exchange with the benthos, or the production or consumption of sinking particles. A simplified version of NetOx,

$$\text{NetOx} = [\text{O}_2] + 1.25[\text{NO}_3] - [\text{TOC}],$$

where TOC (total organic carbon), the dissolved organic carbon (DOC) plus the suspended particulate organic carbon (POC), provides an index based on the usually dominant variables.

Calculation of NetOx and a second property, NetOC ( $[\text{O}_2] - [\text{TOC}]$ ), for data from GEOSECS and ourselves in the Atlantic and Pacific oceans using property-property graphs show differences from those from oxygen deficits alone. Comparison of NetOx and NetOC concentrations at high and low latitudes of the Pacific Ocean shows the difference in surface water oxidant concentration is even larger than the difference in oxygen concentration. Vertical particle fluxes off Peru calculated from NetOx gradients are much greater than those calculated from oxygen gradients. The potential value of NetOx and NetOC as parameters to understand particle fluxes implies that determination of TOC should be a routine part of hydrographic measurements.

### INTRODUCTION

CHANGE in oxygen concentration is a widely used indicator of biological activity in the sea. At the ocean's surface, its concentration is near saturation because of photosynthetic production, atmospheric exchange and mixing processes; below the surface, its concentration decreases as organic matter, both that carried from the surface and that which arrives in falling particles, is oxidized. The continuous consumption of oxygen away from the surface had made calculating its disappearance an attractive way to monitor biological activity.

As recently as 15 years ago, the dominant source of subsurface oxygen consumption was perceived to be the dissolved and particulate organic matter carried by a water parcel after it left the surface. Typical concentrations of dissolved organic carbon (DOC) plus suspended particulate organic carbon (POC)—the sum equal to total organic carbon (TOC)—expressed as  $\text{O}_2$  equivalents, are of the order of  $100 \mu\text{mol kg}^{-1}$  near the surface and  $40 \mu\text{mol kg}^{-1}$  in deeper waters (e.g. OGURA, 1970; MENZEL, 1974; WILLIAMS *et al.*, 1980). Typical near-surface  $\text{O}_2$  concentrations range from 200 to  $350 \mu\text{mol kg}^{-1}$ . OGURA

\* Institute of Marine Resources, A-018, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, U.S.A.

(1970) estimated that about a third of the apparent oxygen utilization (AOU) occurred within a few hundred meters of the surface and was caused by oxidation of DOC, while MENZEL and RYTHER (1970) argued from the DOC disappearance that most O<sub>2</sub> consumption occurred in the upper 300 m of the surface. The idea that O<sub>2</sub> consumption is mostly in the upper water column inspired passionate arguments to explain O<sub>2</sub> concentrations in the deep sea (e.g. CRAIG, 1969, 1971a,b; SUSS and GOLDBERG, 1971). Implicit in these arguments was the premise that organic matter moved with water parcels.

The discovery that organic matter falls with vertical fluxes greater than the expected Stokes fall velocities of phytoplankton-sized matter (e.g. McCAVE, 1975; HONJO *et al.*, 1982; DEUSER *et al.*, 1981) has resulted in the frequent assumption that all O<sub>2</sub> consumption results from the oxidation of falling particles (e.g. KAWASE and SARMIENTO, 1986). More recently, JAHNKE and JACKSON (1987) have suggested that significant O<sub>2</sub> utilization occurs from falling particles at the seafloor, especially adjacent to continental margins.

There has even been a revival of the idea that high dissolved organic concentrations dominate oceanic nutrient cycling, with a recent report of very high concentrations of dissolved organic compounds (SUZUKI *et al.*, 1985; SUGIMURA and SUZUKI, 1987). This history emphasizes the need to account for O<sub>2</sub> consumption by entrained organic matter as well as by falling organic particles when describing the fate of O<sub>2</sub> in the ocean.

The increasing interest in sediment traps [e.g. Vertical Transport and Exchange experiment (VERTEX) and Global Ocean Flux Studies (GOFS) programs] and of large-scale programs using their results to interpret the vertical distribution of biological processes and fates of organic matter implies the need for a measure of O<sub>2</sub> consumption that differentiates between oxidation of organic matter formed near the surface and oxidation of matter derived from sinking particulate matter. Such an index should be related to the biological concept of new production (DUGDALE, 1967; EPPLEY and PETERSON, 1979) and be useful for large-scale mass balances.

Within the eastern Pacific there are extensive areas where limited circulation and/or high downward or lateral fluxes of particulate organic matter overwhelm the supply of O<sub>2</sub>. Nitrate and, to some extent, sulfate are reduced in the consumption of organic matter in the resulting anoxic areas. As a result, change in O<sub>2</sub> concentration is not always a complete indicator of organic matter oxidation. Areas where nitrate reduction is extensive include anoxic waters off Peru and the Southern California Basins (e.g. SHOLKOVITZ, 1972; DEUSER, 1975). Similarly, in sediments where organic sedimentation rates are too great to be balanced by O<sub>2</sub> diffusion, nitrate and sulfate drawn from the water column are the dominant oxidants (e.g. BERNER, 1972). TAKAHASKI *et al.* (1985) observed numerous samples with anomalously low nitrate concentrations in analysis of property-property distributions in the Indian Ocean. They ascribed these to denitrification processes. Similar effects can be seen in samples from the Pacific Ocean taken by GEOSECS, with nitrate-phosphate scatter plots showing a curvature at high phosphate concentrations that indicates nitrate reduction despite the lack of samples from the area where nitrate reduction should be the most intense, the upwelling regions on the eastern boundaries (e.g. CRAIG *et al.*, 1981). Such widespread effects argue that nitrate is a significant oxidant source for the degradation of organic matter in the deep ocean.

We propose several new measures of net oxidant concentration which explicitly link the concentrations of the important oxidants and reductants in seawater. The goal is a set of water properties which is unchanged by chemical transformations in a water parcel, such as oxidation of internal DOC, but is changed by the net vertical flux of organic

particles in or out, exchange with the atmosphere, or exchange with the sediments. The net vertical flux could involve the breakup of a falling fecal pellet or other organic aggregates in a volume of water and their subsequent oxidation. A semi-conservative water property, such as NetOx, is a better measure than O<sub>2</sub> utilization alone for comparison with deep ocean particle fluxes.

#### METHODS

We have used data from the GEOSECS program and our own measurements. The GEOSECS program included measurement of TOC at 13 of 116 stations in the Atlantic and 31 of 147 stations in the Pacific. TOC was not measured as part of the Transient Tracers in the Ocean (TTO) program. Although the GEOSECS data set is the most comprehensive available, including hydrographic information as well as TOC (courtesy of Lou Gordon, Oregon State University), it has large spatial gaps (Fig. 1). Methods used for analysis of GEOSECS samples have been described in BAINBRIDGE (1981) and by GORDON (personal communication). GEOSECS data are available from the Physical and Chemical Oceanographic Data Facility at the Scripps Institution of Oceanography. Our methods have been described in WILLIAMS *et al.* (1980) and JACKSON and WILLIAMS (1985).

#### MEASURES

During the oxidation of organic matter, the two O<sub>2</sub> atoms in an O<sub>2</sub> molecule typically gain two electrons each, thereby changing from a valence state of 0 to -2. Oceanic organic matter traditionally has been considered to have carbon in a valence state of 0 (REDFIELD *et al.*, 1963). The transfer of four electrons from carbon to the O<sub>2</sub> molecule changes the carbon valence to +4 and forms CO<sub>2</sub>. The formation of organic matter by photosynthesis is the opposite, reducing carbon from +4 to 0 and each of two O<sub>2</sub> atoms from -2 to 0 (from CO<sub>2</sub> + O<sub>2</sub> to CH<sub>2</sub>O + O<sub>2</sub>). Such organic matter can be either dissolved or particulate. Because the movement of a water parcel from the oceanic surface takes any dissolved or suspended organic matter with it, O<sub>2</sub> is consumed by the TOC in the parcel and, thus, the concentration of O<sub>2</sub> is not an accurate measure of the net capacity of a water parcel to oxidize organic matter.

From a chemical perspective, the important part of these processes is that there are electrons being transferred from donor compounds to recipients. Other compounds can also provide the electrons for the oxidation of organic matter, although O<sub>2</sub> is a preferred compound for energetic reasons. In low O<sub>2</sub> environments, such as the sediments, NO<sub>3</sub><sup>-</sup> can be reduced to NO<sub>2</sub><sup>-</sup>, N<sub>2</sub>O, N<sub>2</sub>, or NH<sub>3</sub> in transfers of 2, 4, 5, and 8 electrons per nitrogen atom. Similar reactions exist and are important for sulfate. An adequate measure of the net oxidation capacity of a water parcel should include a consideration of the redox forms of these two elements as well.

A simple measure of O<sub>2</sub> concentration which compensates for O<sub>2</sub> consumption of organic carbon carried by a water parcel is

$$\text{NetOx}_1 = [\text{O}_2] - [\text{TOC}]. \quad (1)$$

NetOx<sub>1</sub> can be modified further to include oxidation of total organic nitrogen (TON)—composed of both dissolved (DON) and particulate (PON) organic nitrogen—a fraction

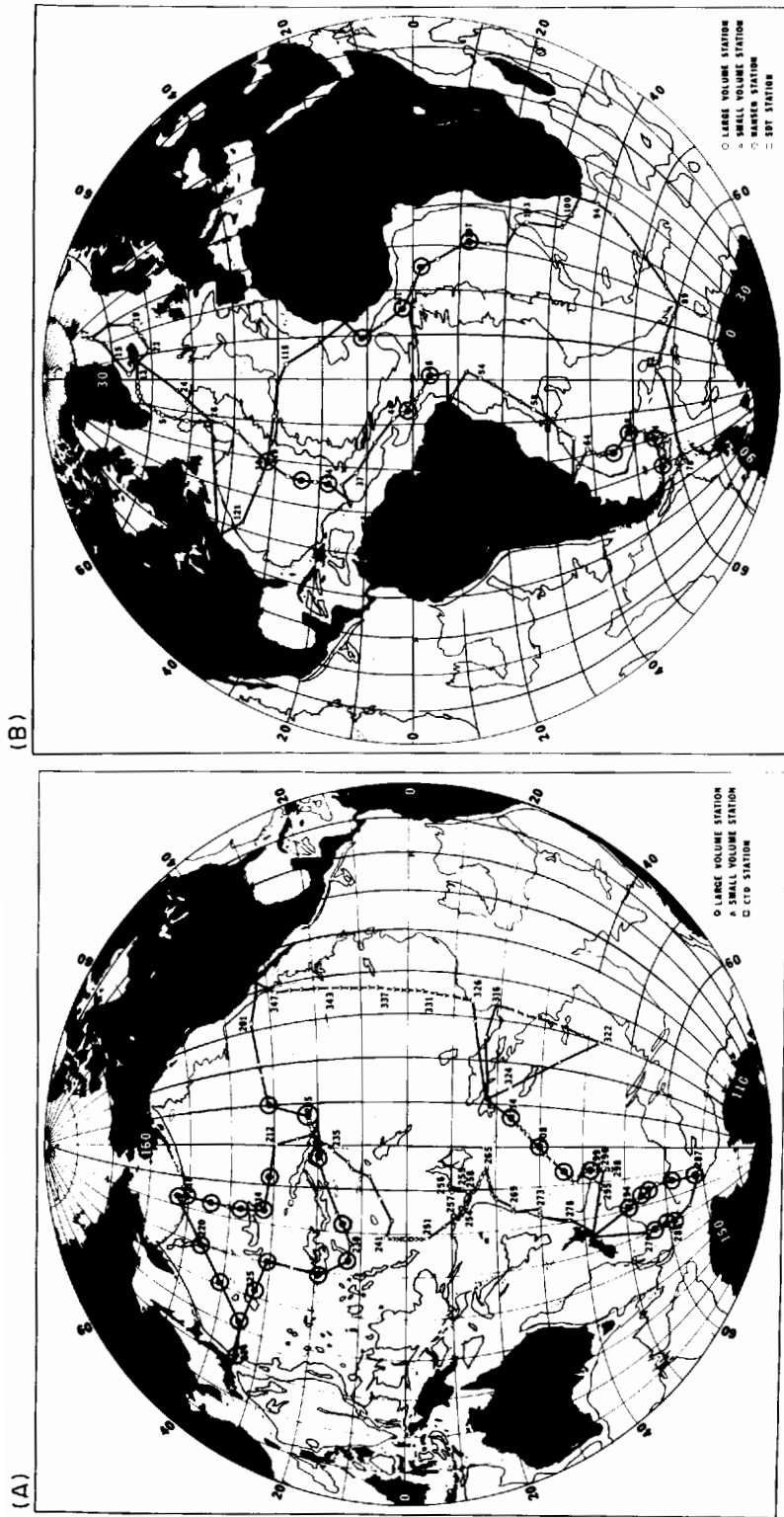


Fig. 1. Location of GEOSECS stations with TOC and hydrographic data. (A) Pacific Ocean. Circled stations = TOC data. TOC was not measured east of 150°W in the Pacific or north of 32°N in the Atlantic or in the Indian Ocean. There are no stations near the anoxic regions of the eastern Pacific.

which is normally 10–20% of TOC. Most TON is present as DON, with DON concentrations ranging from 2–3  $\mu\text{mol kg}^{-1}$  in deep waters to 5–12  $\mu\text{mol kg}^{-1}$  in surface waters (e.g. JACKSON and WILLIAMS, 1985). If the oxidation of N takes it from a valence state of  $-3$  to  $+5$ , equivalent to taking it from  $\text{NH}_3$  to  $\text{NO}_3^-$ , then the relevant measure is

$$\text{NetOx}_2 = [\text{O}_2] - [\text{TOC}] - 2[\text{TON}]. \quad (2)$$

A third measure,  $\text{NetOx}_3$ , responds to consumption of nitrate as well as  $\text{O}_2$  and includes a more complete accounting of nitrogen forms:

$$\begin{aligned} \text{NetOx}_3 = & [\text{O}_2] + 1.25[\text{NO}_3^-] + 0.75[\text{NO}_2^-] + 0.5[\text{N}_2\text{O}] - [\text{TOC}] \\ & - 0.75([\text{TON}] + [\text{NH}_3]). \end{aligned} \quad (3)$$

$\text{NetOx}_3$  is a more rigorous measure of the net oxidant state of a water sample than  $\text{O}_2$ . Note that the nitrogen reference state for  $\text{NetOx}_2$  is  $\text{NO}_3^-$  while that for  $\text{NetOx}_3$  is  $\text{N}_2$ .

Of the six terms used to calculate  $\text{NetOx}_3$ , three terms dominate and  $\text{NetOx}_3$  can be simplified to

$$\text{NetOx} = [\text{O}_2] + 1.25[\text{NO}_3^-] - [\text{TOC}]. \quad (4)$$

Similarly,  $\text{NetOx}_2$  can be simplified to

$$\text{NetOC} = [\text{O}_2] - [\text{TOC}]. \quad (5)$$

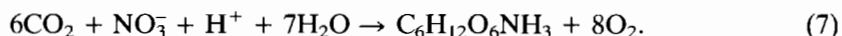
The low concentrations of PON, DON,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ , and  $\text{NH}_3$  relative to DOC and  $\text{NO}_3^-$  in most of the ocean mean that  $\text{NetOx}$  and  $\text{NetOC}$  can be substituted for the more complete measures,  $\text{NetOx}_2$  and  $\text{NetOx}_3$ . We will emphasize  $\text{NetOx}$  and  $\text{NetOC}$  as useful approximations in the data discussion.

Lastly, a complete accounting of the net oxidation state of a water sample should include the redox forms of sulfur:

$$\begin{aligned} \text{NetOx}_4 = & [\text{O}_2] + 1.25[\text{NO}_3^-] + 0.75[\text{NO}_2^-] + 0.5[\text{N}_2\text{O}] + 1.5[\text{SO}_4^{2-}] \\ & - [\text{TOC}] - 0.75([\text{DON}] + [\text{PON}] + [\text{NH}_3]) - 0.5[\text{S}^{2-}] + C_0, \end{aligned} \quad (6)$$

where  $C_0$  is a constant used to offset the high background concentration of  $\text{SO}_4^{2-}$ . In equations (1)–(6), all  $\text{NetOx}$  measures are in  $\text{O}_2$  equivalents and chemical species of nitrogen and sulfur are included. Concentrations of TOC, DOC, and POC are those of C atoms; concentrations of TON, DON, and PON are those of N atoms.

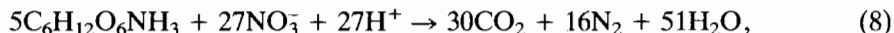
To understand what  $\text{NetOx}_2$  and  $\text{NetOx}_3$  measure, consider some examples. Start with a volume of near-surface water initially containing 250  $\mu\text{mol kg}^{-1}$   $\text{O}_2$ , 4  $\mu\text{mol kg}^{-1}$   $\text{NO}_3^-$ , 80  $\mu\text{mol kg}^{-1}$  DOC, and no DON or particulate matter. Assume that photosynthesis forms organic matter with a stoichiometry given by



Initial  $\text{NetOx}_3$  and  $\text{NetOx}_2$  concentrations are 175 and 170  $\mu\text{mol kg}^{-1}$ , respectively. Production of phytoplankton matter using the 4  $\mu\text{mol kg}^{-1}$   $\text{NO}_3^-$  in the proportions of equation (7) increases  $\text{O}_2$  to 282  $\mu\text{mol kg}^{-1}$ , TOC to 104  $\mu\text{mol kg}^{-1}$ , and TON to 4  $\mu\text{mol kg}^{-1}$ , and decreases  $\text{NO}_3^-$  to 0.  $\text{NetOx}_3$  and  $\text{NetOx}_2$  are unchanged. If this new particulate organic matter sinks from the surface, taking 24  $\mu\text{mol kg}^{-1}$  TOC and 4  $\mu\text{mol kg}^{-1}$  TON from the water parcel,  $\text{O}_2$  concentration remains the same, and  $\text{NetOx}_3$  and  $\text{NetOx}_2$  increase to 202. The net changes in  $\text{O}_2$ ,  $\text{NetOx}_3$ , and  $\text{NetOx}_2$

concentrations from the combined photosynthesis-sinking particle process are 32, 27 and 32, respectively.

The relationship between organic matter consumption and NetOx<sub>3</sub> change varies with the composition of the organic matter but not with the reactions involved. The addition of organic matter and its oxidation by nitrate using the reaction



changes NetOx<sub>3</sub> by 1.13 μmol kg<sup>-1</sup> for every 1 μmol kg<sup>-1</sup> of organic carbon added, the same as if O<sub>2</sub> were the oxidant. If the organic matter had half as much nitrogen, the change in NetOx<sub>3</sub> would be 1.06 μmol kg<sup>-1</sup> and NetOx<sub>2</sub> would not be constant during this process. Oxidation of 1 μmol kg<sup>-1</sup> would, in fact, increase NetOx<sub>2</sub> because of the decrease in carbon uncompensated by a decrease in O<sub>2</sub>.

Different properties of NetOx<sub>2</sub> and NetOx<sub>3</sub> can be seen in this example. The change in NetOx<sub>2</sub> differs from that of NetOx<sub>3</sub> by the nitrate change. If there were significant denitrification, NetOx<sub>2</sub> would be a poor measure of changes in the oxidant concentration caused by degradation of sedimenting organic matter. During the photosynthetic process, prior to particles sinking from the euphotic zone, both NetOx<sub>2</sub> and NetOx<sub>3</sub> are constant. The inclusion of NO<sub>3</sub><sup>-</sup> as an oxidizer makes NetOx<sub>3</sub> a less intuitive quantity.

Particles originating in a water parcel add to the vertical flux when they leave it. This sedimenting organic matter can be considered in terms of its ability to change O<sub>2</sub>, NetOx<sub>2</sub>, and NetOx<sub>3</sub> in a volume of water. Expressed as the amount of O<sub>2</sub> which would be required to convert the reduced carbon and nitrogen to CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, O<sub>2,flux</sub> and NetOx<sub>2,flux</sub> are given by

$$O_{2,flux} = NetOx_{2,flux} = -(POC_{flux} + 2PON_{flux}). \quad (9)$$

The equivalent calculation for NetOx<sub>3,flux</sub> is

$$NetOx_{3,flux} = -(POC_{flux} + 0.75PON_{flux}). \quad (10)$$

The difference between equations (9) and (10) results from the fact that the reference state for NetOx<sub>3</sub> is N<sub>2</sub> rather than NO<sub>3</sub><sup>-</sup>. For material with a C:N ratio of 6:1 (that of living plankton), assuming the oxidation states of organic matter stated earlier, NetOx<sub>3,flux</sub> and O<sub>2flux</sub> will be 12.5 and 33.3% greater than -POC<sub>flux</sub>, respectively, with a ratio of NetOx<sub>3,flux</sub> to O<sub>2flux</sub> of 0.84.

Changes in fluxes through the water column can be related to the rate of disappearance of oxidant-containing material,  $M_{ox}$ . If Ox signifies an oxidant concentration, which could be O<sub>2</sub>, NetOx<sub>3</sub>, or NetOx<sub>2</sub>, then conservation of mass implies that

$$\frac{\partial Ox_{flux}}{\partial z} = M_{ox}. \quad (11)$$

That is, losses of oxidant-consuming organic matter from a water parcel are balanced by increased vertical particle fluxes. Note that appearance and subsequent degradation of a particle in a water parcel is shown by negative  $M_{ox}$ .

NetOx<sub>3</sub> is decreased not by oxidation of particulate or dissolved organic matter present in the water parcel but by input of organic matter into it. Exchange of O<sub>2</sub> with the atmosphere changes both NetOx<sub>3</sub> and O<sub>2</sub> equally, as does O<sub>2</sub> consumption by organic matter in the sediments. The ratio of relative changes of NetOx<sub>3</sub> and O<sub>2</sub> (Fig. 2) illustrates the relative magnitudes of these processes.

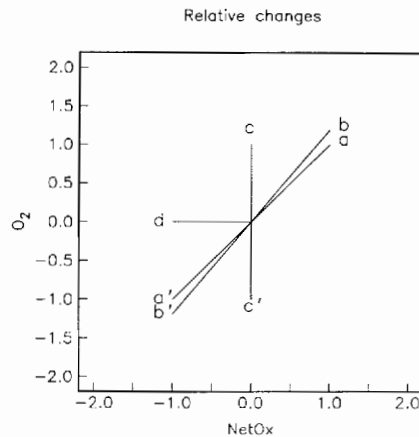


Fig. 2. Relative changes in NetOx<sub>3</sub> and O<sub>2</sub> caused by different processes. Loss (a) or gain (a') of O<sub>2</sub> to atmosphere ( $\Delta O_2/\Delta \text{NetOx}_3 = 1$ ); formation and loss (b) or capture and degradation (b') of organic particle ( $\Delta O_2/\Delta \text{NetOx}_3 = 1.19$ ); production (c) or oxidation (c') of contained organic matter ( $\Delta O_2/\Delta \text{NetOx}_3 = \infty$ ); oxidation (d) of sedimentary organic matter by NO<sub>3</sub> in anoxic environment ( $\Delta O_2/\Delta \text{NetOx}_3 = 0$ ).

Because NetOx<sub>3</sub> is defined to be constant with regard to internal chemical redox transformations, the equation relating its distribution and physical processes is that for a substance with a simple source/sink term,

$$\frac{\partial \text{NetOx}_3}{\partial t} + \mathbf{v} \cdot \nabla \text{NetOx}_3 - \nabla \cdot (K \nabla \text{NetOx}_3) = -M_{\text{NetOx}} \quad (12)$$

$$= -\frac{\partial (\text{NetOx}_3, \text{flux})}{\partial z}, \quad (13)$$

where  $\mathbf{v}$  indicates the water velocity and  $K$  the eddy diffusivity. That is, the only redox changes within a packet of water come from differences in organic matter entering and leaving it.

#### EXAMPLES

A comparison of O<sub>2</sub> and NetOx concentrations reveals the differences between the two (Fig. 3). The greatest differences occur for O<sub>2</sub> concentrations between 200 and 300  $\mu\text{mol kg}^{-1}$ . NetOx concentrations for such samples are frequently 50  $\mu\text{mol kg}^{-1}$  less than those of O<sub>2</sub> because of the high TOC concentrations in this depth interval. In samples with lower but non-negligible O<sub>2</sub> concentrations, the NetOx and O<sub>2</sub> are nearly the same because the contributions from TOC and NO<sub>3</sub><sup>-</sup> almost cancel. At the lowest O<sub>2</sub> concentrations, the O<sub>2</sub> and NetOx again diverge as denitrification causes further decreases in NetOx. The patterns in the Atlantic and the Pacific are similar, although there is no denitrification effect visible in the more oxygenated waters of the Atlantic.

Using NetOx rather than O<sub>2</sub> in property-property plots shows slightly different properties for NetOx in the ocean. The largest difference between a NetOx-potential temperature ( $\theta$ ) graph and one for O<sub>2</sub>- $\theta$  is in the oxidant values in warmer, near-surface waters (for those with  $\theta > 15^\circ$ ; Fig. 4). In the Atlantic, both NetOx and O<sub>2</sub> range from

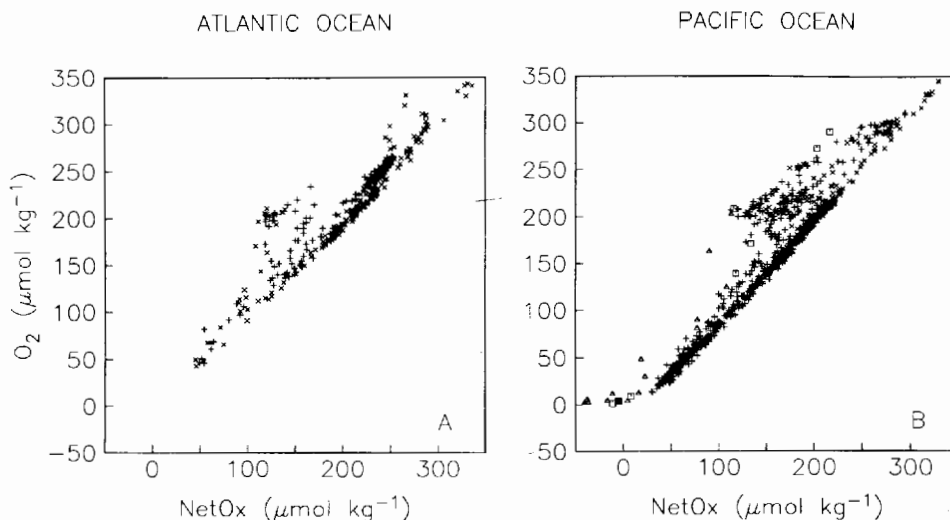


Fig. 3. Relationship between  $O_2$  and NetOx. (A) Atlantic Ocean (GEOSECS). (B) Pacific Ocean: +, north of the equator (GEOSECS); ×, south of the equator (GEOSECS); □, Santa Monica Basin off Southern California; △, off Peru.

about 50 to 350  $\mu\text{mol kg}^{-1}$ ;  $O_2$  at 25° is about 200  $\mu\text{mol kg}^{-1}$  while NetOx is about 120  $\mu\text{mol kg}^{-1}$ . In the Pacific,  $O_2$  ranges from 10 to 350  $\mu\text{mol kg}^{-1}$  while NetOx ranges from 25 to 350  $\mu\text{mol kg}^{-1}$ ; at 25°  $O_2$  is about 200  $\mu\text{mol kg}^{-1}$  while NetOx is about 120  $\mu\text{mol kg}^{-1}$ . Thus, the warm near-surface waters from the low latitudes are seen as deficient in NetOx. The reason for this is the high TOC and low  $\text{NO}_3^-$  concentrations in those waters. The NetOC pattern is almost the same.

A north-south vertical section across the Pacific confirms this (Fig. 5). Lower latitude near-surface waters are low in nitrate and high in TOC relative to those in the higher latitudes. When added to the lower saturation concentrations of  $O_2$  in the warmer water, this results in much lower net oxidant concentrations. Between 65 and 20°S there is a decrease of about 120  $\mu\text{mol kg}^{-1}$   $O_2$ , 16  $\mu\text{mol kg}^{-1}$  NetOC, and 180  $\mu\text{mol kg}^{-1}$  NetOx. Despite the smaller total range of NetOx and NetOC in the Pacific, there is a greater difference in the net oxidant concentrations between lower and higher latitude waters than there is  $O_2$ . Furthermore, the smaller surface values of NetOx and NetOC result in almost no vertical stratification between 20 and 30°S. The high subsurface  $O_2$  maxima at around 100 m depth are much reduced in NetOC and NetOx. North of the equator, all the oxidants show strong vertical stratification. The high NetOx and NetOC of polar surface waters is due to the high  $O_2$  and low TOC content of these cold waters coupled, in the case of NetOx, with high nitrate concentrations. NetOx and NetOC emphasize the differences in net oxidant concentrations between temperate and polar surface waters. For water translated from the higher latitude to the lower, this loss of NetOx and NetOC would occur by escape of  $O_2$  to the atmosphere. The best estimate of this loss is the difference between NetOx concentrations at the two locations. Thus, NetOx differences imply that about 50% more  $O_2$  would be lost to the atmosphere than would comparisons of  $O_2$  concentration differences.

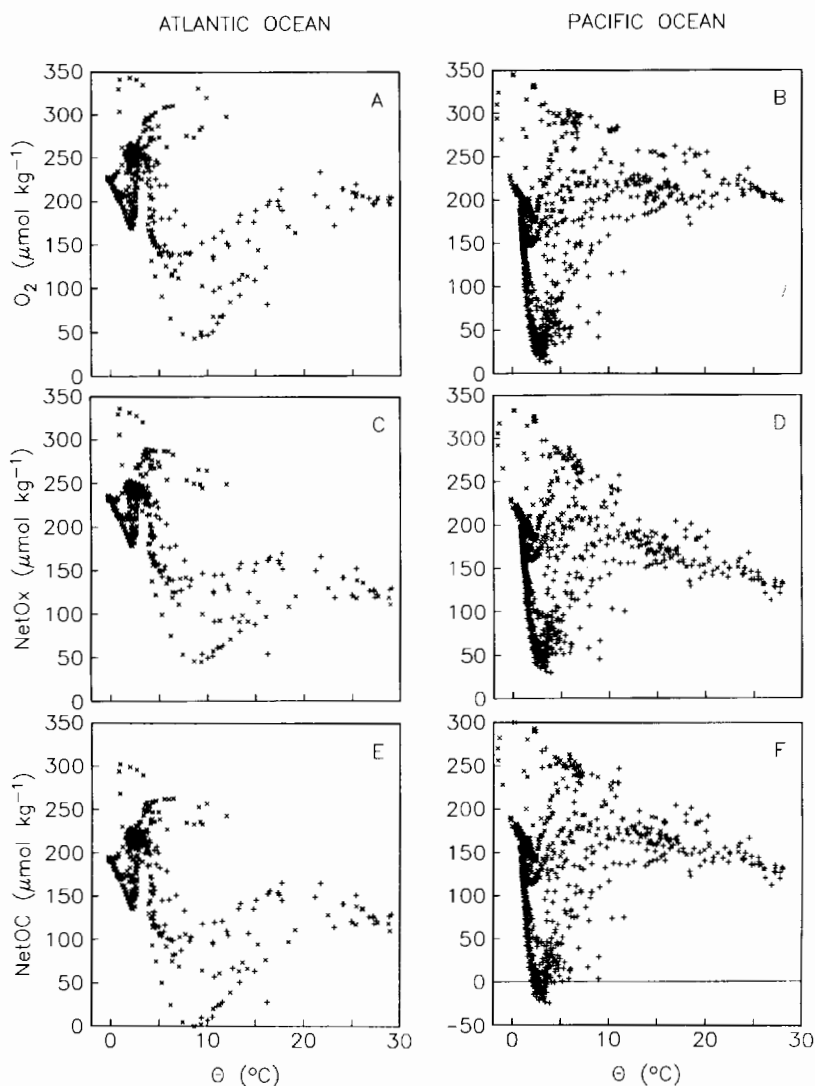


Fig. 4. Relationship between potential temperature ( $\theta$ ) and O<sub>2</sub> (A,B),  $\theta$  and NetOx (C,D), and  $\theta$  and NetOC (E,F) in the Atlantic (A,C,E) and Pacific (B,D,F) oceans. Data from the GEOSECS program.

A vertical profile into the low O<sub>2</sub> environment of the Santa Monica Basin off Southern California shows the expected near-disappearance of O<sub>2</sub> in the deeper part of the water column (Fig. 6). NetOx also shows a decrease through the water column but shows a greater decrease below 600 m because of the additional utilization of NO<sub>3</sub> there. The value of NetOx is virtually identical to NetOx<sub>3</sub> (equation 3). Near the surface, the decrease in DOC with depth partially balances the large decrease in O<sub>2</sub>, resulting in smaller decreases in NetOx than in O<sub>2</sub>. Thus, the total oxidant concentration of a parcel

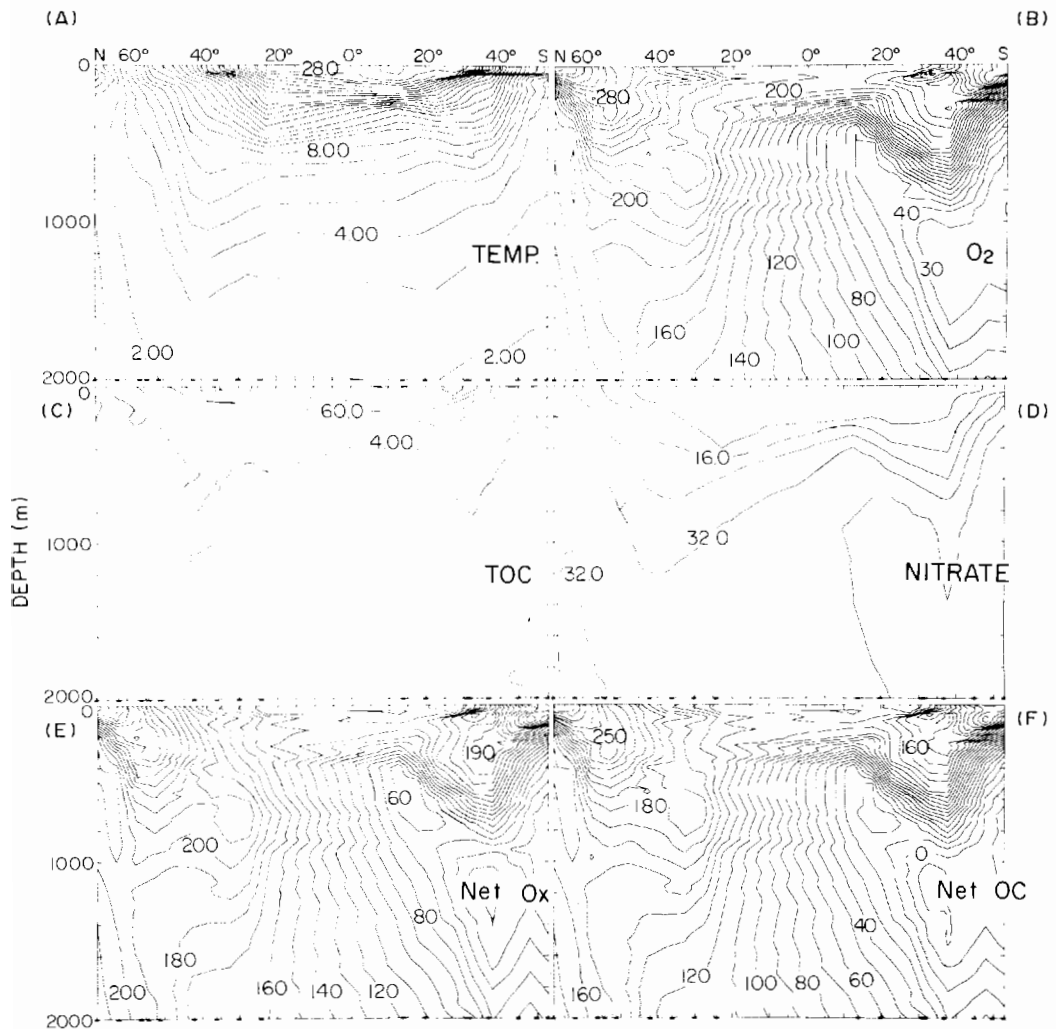


Fig. 5. North-south vertical sections across the Pacific Ocean. (A) T; (B) O<sub>2</sub>; (C) TOC; (D) NO<sub>3</sub>; (E) NetOx; (F) NetOC. Note that the 8  $\mu\text{mol kg}^{-1}$  contour interval of NO<sub>3</sub> is equivalent to the 10  $\mu\text{mol kg}^{-1}$  contour interval of O<sub>2</sub>, TOC, NetOx and NetOC. Data from GEOSECS Stas 213, 214, 215, 217, 218, 219, 231, 234, 288, 289, 291, 292, 294, 301, 305, 308, and 314.

of water shows changes smaller than O<sub>2</sub> near the surface and larger than O<sub>2</sub> in deeper water.

The differences between O<sub>2</sub> and NetOx are even greater off Peru (Fig. 7). Between a depth of 100 and 500 m there is no measurable change in O<sub>2</sub> concentration because it is undetectable. Inclusion of NO<sub>3</sub> in a measure of oxidant concentration shows a slight increase of oxidant concentration with depth below about 125 m, while NetOx reveals a narrow band of very low oxidant concentration between 125 and 300 m caused not only by consumption of NO<sub>3</sub> and O<sub>2</sub> but also by the accumulation of POC and DOC derived from falling particles. This is in the same depth zone where WARD (personal communication) had found extensive denitrification. CODISPOTTI *et al.* (1986) recently observed high

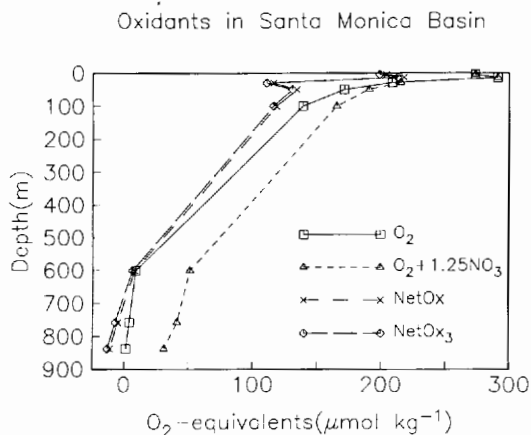


Fig. 6. Concentrations of different oxidant measures in Santa Monica Basin, off Southern California ( $33^{\circ}45'N$   $118^{\circ}47'W$ ), 10 May 1981. Shown are concentrations of  $O_2$  ( $\square$ ),  $O_2 + 1.25NO_3$  ( $\Delta$ ),  $NetOx_3$  ( $\times$ ), and  $NetOx$  ( $\diamond$ ).

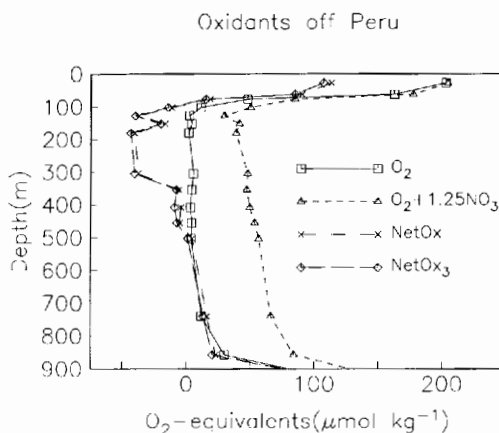


Fig. 7. Concentrations of different oxidant measures off Peru ( $9^{\circ}04'S$ ,  $83^{\circ}37'W$ ), 1966. Shown are concentrations of  $O_2$  ( $\square$ ),  $O_2 + 1.25NO_3$  ( $\Delta$ ),  $NetOx_3$  ( $\times$ ), and  $NetOx$  ( $\diamond$ ).

nitrite concentration up to  $15 \mu M$  in this region. Calculation of  $NetOx$  under such conditions will thus include the contribution of nitrite (equation 3).

A simple model of the Peru situation shows the differences that can result from considering  $NetOx$  rather than  $O_2$ . A simplified form of equation (13), assuming a steady state, 1-dimensional system, yields

$$wOx_z = (KOx_z)_z - M_{Ox}, \quad (14)$$

where the  $z$  subscript indicates a derivative,  $w$  is the vertical velocity, and  $Ox$  is the oxidant of choice. If  $TOC$  and  $NO_3^-$  are unimportant, then the same equation applies for  $O_2$  as for  $NetOx$ . This equation can be solved for  $M_{O_2}$  and  $M_{NetOx}$  given  $w$  and  $K$  and the various derivatives of  $NetOx$  and  $O_2$ . The eddy diffusion,  $K$ , for Peru can be estimated

from data on the density gradient and GARGETT's (1984) relationship;  $w$  can be estimated by assuming that the potential temperature,  $\theta$ , is also at steady state and is determined by vertical advection and eddy diffusion:

$$w\theta_z = (K\theta_z)_z \quad (15)$$

Fitting data for density, potential temperature,  $O_2$ , and NetOx with polynomials and then solving for the values of  $M_{O_2}$  and  $M_{\text{NetOx}}$  yields two different conclusions (Fig. 8). Negative values of  $M_{O_2}$  and  $M_{\text{NetOx}}$  indicate a sink for falling particles. The values of  $-M_{\text{NetOx}}$  are much larger and more localized than those of  $-M_{O_2}$ , where the largest value of  $-M_{\text{NetOx}}$  is  $14 \text{ nmol kg}^{-1} \text{ d}^{-1}$  at 50 m, dropping to half this value by 210 m. The largest value of  $-M_{O_2}$ ,  $9.4 \text{ nmol kg}^{-1} \text{ d}^{-1}$  at 50 m, drops to half this value by 230 m. Thus, using NetOx rather than  $O_2$  leads to an estimate of more localized particle degradation rates that are as much as 49% greater, even though the NetOx consuming value of particulate organic matter is 16% less, assuming Redfield composition.

Although this 1-dimensional analysis of the data indicates the different results possible using NetOx, the situation off Peru is certainly complicated by advective movement of water off the shelf. The very low NetOx water between 100 and 300 m could result from TOC which enters the near-bottom water and which subsequently is advected or mixed offshore. A scatter plot of the NetOx value of this water vs a conservative property such as potential temperature would yield a straight line, whereas a similar scatter plot of TOC with  $O_2$  would reflect  $O_2$  consumed by TOC and would not be linear.

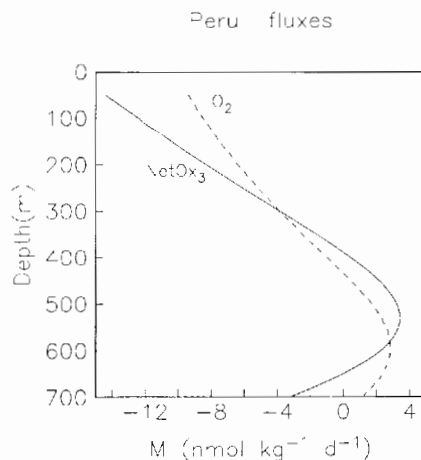


Fig. 8. Vertical distribution of sources and sinks of  $O_2$  and NetOx for the Peru system (Fig. 7). Note that influx of organic matter decreases the NetOx in a water sample, resulting in a negative value of  $M$ . Vertical eddy diffusivity,  $K$ , was calculated using the relationship between density gradient and  $K$  of GARGETT (1984). Vertical velocity  $w$ , was calculated by assuming that  $\theta$  distribution is a 1-dimensional steady state:  $w = K_z + KT_{zz}/T_z$ , where subscripts denote derivatives. Sink strength,  $M$ , was calculated assuming that  $O_2$  and NetOx were in steady state:  $M = -wC_z + K_zC_z + KC_{zz}$ , where  $C$  is the concentration of NetOx or  $O_2$ . For the calculations, the density gradient was fit to an exponential curve, while  $\theta$ , NetOx, and  $O_2$  were fit to power series of 4th, 5th and 5th orders, respectively.

## DISCUSSION

NetOx values represent a series of semi-conservative measures of the net oxidation status of a water parcel. A similar measure has been proposed for atmospheric water droplets (MORGAN, 1982). The definition of these net oxidant measures includes an increasingly greater number of terms necessitated by the reduction of nitrate and then sulfate after available  $O_2$  is reduced despite the decreasing energy yield involved in each succeeding reaction (STUMM and MORGAN, 1981). The equivalence of  $NO_3^-$  and  $O_2$  as reductants in NetOx means that  $O_2$  consumed to produce  $NO_3^-$  does not affect NetOx. Release of dissolved or particulate organic matter by a falling particle with subsequent oxidation will, however, affect NetOx.

The difference between  $O_2$  and NetOx is  $1.25[NO_3^-] - [TOC]$ . Like concentrations of most biologically determined chemical substances, it has its largest change in the upper 1000 m (Fig. 9), ranging from about  $-80$  to  $+20 \mu\text{mol kg}^{-1}$ . In deeper waters its range is  $20 \mu\text{mol kg}^{-1}$ , having an average of about  $0 \mu\text{mol kg}^{-1}$  in the Atlantic and  $10 \mu\text{mol kg}^{-1}$  in the Pacific. Lower values in the deep Atlantic are caused by lower deep-water nitrate concentrations there. There is a near equivalence of  $NO_3^-$  and TOC concentrations in deep waters resulting in almost equal value of  $O_2$  and NetOx there.

TAKAHASHI *et al.* (1985) examined the changes in  $O_2$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , and  $CO_2$  on constant density surfaces in the Atlantic and Indian oceans, correcting total  $CO_2$  concentration changes to separate out changes caused by carbonate dissolution. They concluded that the nutrient distributions could be best explained by oxidation/dissolution of particulate matter having a constant chemical composition (organic P, N and C) different than that of the Redfield ratio. Their suggested ratio for P:N:C: $-O_2$  of organic debris is 1:16:103:172. If the  $O_2$  consumption of the organic nitrogen in this debris is subtracted, assuming two  $O_2$  atoms per N atom, then the C: $-O_2$  ratio is 103:140. This implies that it takes 1.36  $O_2$  to convert 1 C atom from its organic form to  $CO_2$ . However, TAKAHASHI *et al.*

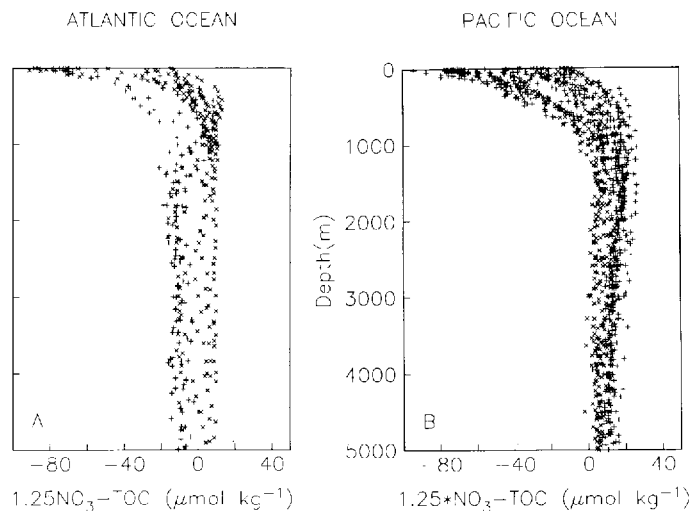


Fig. 9. Difference between NetOx and  $O_2$  ( $1.25[NO_3^-] - [TOC]$ ) as a function of depth for the Atlantic (A) and Pacific (B) oceans. Data from the GEOSECS program.

(1985) were unable to prove that the new C:  $-O_2$  ratio was not the result of  $\Sigma CO_2$  variation in the ocean caused by increases in atmospheric  $CO_2$  during the last century. They noted that the  $CO_2:O_2$  ratio could be decreased by 30% this way, resulting in a need for only 1  $O_2$  to oxidize each C. They suggested that the best estimate for the composition of organic matter is one which requires 1.36  $O_2$  molecules to fully oxidize each C atom. For this composition the average C oxidation state would not be 0 as assumed earlier but would be  $-1.44$ . Comparison of net oxidant concentration calculated for C having the traditional redox state with one having this state,

$$\text{NetOx}' = [O_2] - 1.36[\text{TOC}] + 1.25[\text{NO}_3], \quad (16)$$

shows that the differences between NetOx and NetOx' are small and that the two values are easily interconverted (Fig. 10). Thus, if the redox state of organic carbon implied by the relationships of TAKAHASHI *et al.* (1985) is accurate, the effect on the NetOx relationships discussed here will be small and easily convertible to the new ratios.

SUZUKI *et al.* (1985) have recently reported results (not validated as yet) from a new technique for the measurement of total dissolved nitrogen with results significantly higher than those determined by the traditional methods of WILLIAMS *et al.* (1980) and others. Suzuki *et al.* reported that the sum of  $NO_3^-$  and DON was almost constant in the water column, having a value of 32–50  $\mu\text{mol kg}^{-1}$ . This was predominantly in the form of DON near the surface and nitrate in deep waters. If the oxidation of DON to nitrate involves two  $O_2$  molecules, the production of nitrate in the deep ocean involves a consumption of 70–100  $\mu\text{mol kg}^{-1}$   $O_2$  more than just for the 30–80  $\mu\text{mol kg}^{-1}$  TOC calculated here. The role of  $O_2$  consumption by reduced organic matter advected from the surface could be still greater if TOC analyses are correspondingly low (SUGIMURA and SUZUKI, 1987). Such a large  $O_2$  consumption potential would result in vastly higher net oxidant budgets for the world's oceans.

The use of NetOx<sub>4</sub> (equation 6) for oceanic modeling rather than NetOx is limited by the reference states for sulfur. There is, unfortunately, no convenient reference state for

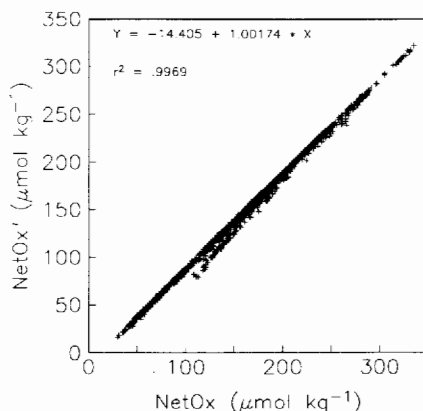


Fig. 10. Effect of change in carbon redox state on NetOx. NetOx is the value calculated using Redfield ratio; NetOx' is the value assuming a carbon oxidation state of  $-1.44$ . A linear regression gives the relationship between the two as  $\text{NetOx}' = a\text{NetOx} + b$ , where  $a = 1.0017$  and  $b = -14.405$ . The value of  $r^2 = 0.9969$ .

the sulfur system such as  $\text{CO}_2$  provides for the carbon system and  $\text{N}_2$  for the nitrogen. Measurable concentrations of reduced sulfur compounds are found in small enclosed basins (DEUSER, 1975). Sulfur reduction in the sediments generates, among other compounds,  $\text{S}^{2-}$ , most of which precipitates from solution as the mineral  $\text{FeS(s)}$ . Because  $\text{S}^{2-}$  is precipitated, there is no way to quantify the process without monitoring the disappearance of soluble sulfate. WILSON (1975) has noted that the sulfate to chlorinity ratio is essentially constant in all oceanic waters. The measured range in this ratio is less than 0.4%, although sulfate depletion in isolated areas such as the Black Sea can be as great as 4% (WILSON, 1975). In such areas,  $\text{NetOx}_4$  is the important measure of the net oxidant status of the water. In most of the ocean, the constancy of the sulfate to chlorinity ratio and the inertness of chloride imply that sulfate depletion is relatively small. If sulfate reduction is equal in importance to nitrate reduction, there could be decreases in sulfate concentration comparable to that of nitrate, namely, on the order of  $10 \mu\text{mol kg}^{-1}$ . Given that the background concentration of sulfate in seawater is  $28 \text{ mmol}$  (e.g. GOLDHABER and KAPLAN, 1974), this would cause a change in sulfate concentration of about 0.04%. To measure these changes, a precision of  $\pm 0.01\%$  might be necessary. Classical gravimetric techniques have precisions of about  $\pm 0.16\%$  (RILEY, 1975). Thus, the inclusion of  $\text{SO}_4^{2-}$  concentration in calculation of the net oxidant concentration of a sample would present severe analytical problems.

However, simple calculations suggest that decreases in sulfate concentrations caused by sulfate reduction in the sediments are generally small relative to nitrate reduction. BERNER (1972) has noted that iron pyrite,  $\text{FeS}$ , is the dominant form in which reduced sulfide is lost to the sediments. He estimated that  $7 \times 10^{12} \text{ g}$  of sulfur are formed into pyrite annually and lost to the oceanic system. The reduction of each sulfide from  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$  involves 8 electrons and is equivalent to the reduction of two  $\text{O}_2$  molecules. The oceanic sulfur reduction rate is thus  $3.3 \times 10^{11} \text{ mol O}_2\text{-equiv. y}^{-1}$ . In comparison, about  $40 \times 10^{12} \text{ g}$  of nitrogen are reduced to  $\text{N}_2$  annually in the ocean (DELWICHE, 1970). This is  $3.6 \times 10^{12} \text{ mol O}_2\text{-equiv. y}^{-1}$ . To the extent that nitrate and sulfate reduction take place in the same anoxic sediments, changes in  $\text{NetOxS}$  from sulfate reduction will be much smaller than those caused by nitrate reduction.

The complicated sulfur cycle in the hydrothermal circulation systems at mid-oceanic ridges is another potential sink for  $\text{NetOx}_4$ . Low sulfate and high sulfide concentrations in hydrothermal vent waters are expressions of a sulfur cycle that includes transport of oceanic sulfate into the mid-oceanic ridges, dissolution of sulfate present in the rocks, precipitation of anhydrite ( $\text{CaSO}_4\text{(s)}$ ), oxidation of ferrous to ferric iron by reduction of sulfate to sulfide, precipitation of iron pyrite, and ejection back into the water column of water low in sulfate and high in sulfides (EDMOND *et al.*, 1979; McDUFF and EDMOND, 1982; VON DAMM *et al.*, 1985). Sulfate fluxes into the oceanic ridges have been estimated at  $3.8\text{--}4.0 \times 10^{12} \text{ mol y}^{-1}$ ; sulfide fluxes out have been estimated at  $9.4\text{--}12 \times 10^{12} \text{ mol y}^{-1}$  (EDMOND *et al.*, 1979; VON DAMM *et al.*, 1985). Oxidation of the sulfide to sulfate in the water column consumes  $\sim 2 \times 10^{12} \text{ mol y}^{-1}$  of oxygen.  $\text{NetOx}_4$  flux associated with sulfate removal is  $\sim -6 \times 10^{12} \text{ mol y}^{-1}$ ; that associated with sulfide addition is  $\sim -0.6 \times 10^{12} \text{ mol y}^{-1}$ . The total  $\text{NetOx}_4$  flux would then be  $-6.6 \times 10^{12} \text{ mol y}^{-1}$ .  $\text{NetOx}$  and  $\text{NetOx}_4$  are not directly affected by this sulfur flux but they are reduced by the re-oxidation of sulfide to sulfate,  $2.4 \times 10^{12} \text{ mol y}^{-1}$ . These changes in the different  $\text{NetOx}$  quantities are the result of inorganic precipitation and oxidation processes and are the benthic equivalent of  $\text{O}_2$  exchange with the atmosphere

occurring at the ocean's surface. In size, they are comparable to NetOx changes caused by nitrate reduction.

#### CONCLUSION

New measures of the net oxidant concentration in seawater promise to be useful new water properties which reflect vertical fluxes of organic matter in the ocean and estimate the oxidation–reduction (redox) processes of various basins having different origins and histories. To exploit this potential and calculate NetOx over the world's oceans, the determination of TOC and TON will have to become standard hydrographic measurements.

*Acknowledgements*—We would like to thank Betsy Stewart for help with data manipulation and analysis, Sarilee Anderson for computational help, Joe Reid and Rick Jahnke for extensive discussions, Ken Robertson for collection and laboratory analysis of our samples, and Lou Gordon for providing the TOC data from GEOSECS. This research was supported by DOE grants DE-FG05-85-ER60341 (GAJ) and DE-FG05-85-ER60339 (PMW).

#### REFERENCES

- BAINBRIDGE A. E. (1981) *GEOSECS Atlantic expedition: Vol. 1, Hydrographic data, 1972–1973*, National Science Foundation, Washington, D.C., 121 pp.
- BERNER R. A. (1972) Sulfate reduction, pyrite formation, and the oceanic sulfur budget. In: *Changing chemistry of the oceans*, D. DRYSEN and D. JAGNER, editors, Wiley-Interscience, New York, pp. 347–361.
- CODISPOTTI L. A., G. E. FRIEDERICH, T. T. PACKARD, H. E. GLOVER, P. J. KELLY, R. W. SPINRAD, R. T. BARBER, J. W. ELKINS, B. B. WARD, F. LIPSCHULTZ and N. LOSTAUNAU (1986) High nitrite levels off northern Peru: a signal of instability in the marine denitrification rate. *Science*, **233**, 1200–1202.
- CRAIG H. (1969) Abyssal carbon and radiocarbon in the Pacific. *Journal of Geophysical Research*, **74**, 5491–5506.
- CRAIG H. (1971a) The deep metabolism: oxygen consumption in abyssal ocean water. *Journal of Geophysical Research*, **76**, 5078–5086.
- CRAIG H. (1971b) Son of abyssal carbon. *Journal of Geophysical Research*, **76**, 5133–5139.
- CRAIG H., W. S. BROECKER and D. SPENCER (1981) *GEOSECS Pacific expedition: Vol. 4, Sections and profiles*. National Science Foundation, Washington, D.C., 251 pp.
- DELWICHE C. C. (1970) The nitrogen cycle. *Scientific American*, **233**, 137–146.
- DEUSER W. (1975) Reducing environments. In: *Chemical oceanography*, Vol. 3, 2nd edn., J. P. RILEY and G. SKIRROW, editors, Academic Press, London, pp. 1–37.
- DEUSER W. G., E. H. ROSS and R. F. ANDERSON (1981) Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transfer of matter to the deep ocean. *Deep-Sea Research*, **28**, 495–505.
- DUGDALE R. C. (1967) Nutrient limitation in the sea: dynamics, identification, and significance. *Limnology and Oceanography*, **12**, 685–695.
- EDMOND J. M., C. MEASURES, R. E. McDUFF, L. H. CHAN, R. COLLIER, B. GRANT, L. I. GORDON and J. B. CORLISS (1979) Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: the Galapagos data. *Earth and Planetary Science Letters*, **46**, 1–18.
- EPPLEY R. W. and B. J. PETERSON (1979) Particulate organic matter flux and planktonic new production in the deep ocean. *Nature*, **282**, 677–680.
- GARGETT A. E. (1984) Vertical eddy diffusivity in the ocean interior. *Journal of Marine Research*, **42**, 359–393.
- GOLDHABER M. B. and I. R. KAPLAN (1974) The sulfur cycle, In: *The sea*, Vol. 2, E. D. GOLDBERG, editor, Wiley-Interscience, New York, pp. 569–655.
- HONJO S., S. J. MANGANINI and J. COLE (1982) Sedimentation of biogenic matter in the deep ocean. *Deep-Sea Research*, **29**, 609–625.
- JAHNKE R. A. and G. A. JACKSON (1987) The role of the seafloor in maintaining deep ocean chemistry. *Nature*, **329**, 621–623.
- JACKSON G. A. and P. M. WILLIAMS (1985) Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. *Deep-Sea Research*, **32**, 223–235.

- KAWASE M. and J. L. SARMIENTO (1986) Circulation and nutrients in middepth Atlantic waters. *Journal of Geophysical Research*, **91**, 9749–9770.
- MCCAVE I. N. (1975) Vertical flux of particles in the ocean. *Deep-Sea Research*, **22**, 491–502.
- MCDUFF R. E. and J. M. EDMOND (1982) On the fate of sulfate during hydrothermal circulation at mid-oceanic ridges. *Earth and Planetary Science Letters*, **57**, 117–132.
- MENZEL D. W. (1974) Primary productivity, dissolved and particulate organic matter, and the sites of oxidation of organic matter. In: *The sea*, Vol. 5, E. D. GOLDBERG, editor, Wiley-Interscience, New York, pp. 659–678.
- MENZEL D. W. and J. H. RYTHER (1970) Distribution and cycling of organic matter in the oceans. In: *Organic matter in natural waters*, D. W. HOOD, editor, University of Alaska, pp. 31–54.
- MORGAN J. J. (1982) Factors governing the pH, availability of H<sup>+</sup>, and oxidation capacity of rain, In: *Atmospheric chemistry*, E. D. GOLDBERG, editor, Springer-Verlag, New York, pp. 17–40.
- OGURA N. (1970) The relation between dissolved organic carbon and apparent oxygen utilization in the Western North Pacific. *Deep-Sea Research*, **17**, 221–231.
- REDFIELD A. C., B. H. KETCHUM and F. A. RICHARD (1963) The influence of organisms on the composition of sea water. In: *The sea*, Vol. 2, M. N. HILL, editor, Interscience, New York, pp. 26–77.
- RILEY J. P. (1975) Analytical chemistry of sea water. In: *Chemical oceanography*, Vol. 3, 2nd edn., J. P. RILEY and G. SKIRROW, editors, Academic Press, London, pp. 193–514.
- SHOLKOVITZ E. R. (1972) The chemistry and physical oceanography and the interstitial water chemistry of the Santa Barbara Basin. Ph.D thesis, University of California, San Diego, 183 pp.
- STUMM W. and J. J. MORGAN (1981) *Aquatic chemistry*, 2nd edn., Wiley-Interscience, New York, 780 pp.
- SUESS H. E. and E. GOLDBERG (1971) Comments on paper by H. Craig, 'Abyssal carbon and radiocarbon in the Pacific'. *Journal of Geophysical Research*, **76**, 5131–5132.
- SUGIMURA Y. and Y. SUZUKI (1987) A high temperature catalytic oxidation method of non-volatile dissolved organic carbon in seawater by direct injection of liquid samples. *Marine Chemistry*, in press.
- SUZUKI Y., Y. SUGIMURA and T. ITOH (1985) A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. *Marine Chemistry*, **16**, 83–97.
- TAKAHASHI T., W. S. BROECKER and S. LANGER (1985) Redfield ratio based on chemical data from isopycnal surfaces. *Journal of Geophysical Research*, **90**, 6907–6924.
- VON DAMM K. L., J. M. EDMOND, B. GRANT, C. I. MEASURES, B. WALDEN and R. F. WEISS (1985) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochimica et Cosmochimica Acta*, **49**, 2197–2220.
- WILLIAMS P. M., A. F. CARLUCCI and R. OLSON (1980) A deep profile of some biologically important properties in the central North Pacific gyre. *Oceanologica Acta*, **3**, 471–476.
- WILSON T. R. S. (1975) Salinity and the major elements of sea water. In: *Chemical oceanography*, Vol. 1, 2nd edn., J. P. RILEY and G. SKIRROW, editors, Academic Press, London, pp. 365–413.