

MEDITERRANEAN NUTRIENT BALANCE AND  
EPISODES OF ANOXIA

Jorge L. Sarmiento and Timothy Herbert

Atmospheric and Oceanic Sciences Program,  
Princeton University,  
Princeton, New Jersey

J.R. Toggweiler

Geophysical Fluid Dynamics Laboratory  
National Oceanic and Atmospheric Adminis-  
tration, Princeton University,  
Princeton, New Jersey

Abstract. We examine the causes of anoxia in regions such as the Eastern Mediterranean, which have exchange over sills with adjacent basins. Box models show that the concentration of the limiting nutrient is the major determinant of deep oxygen levels. The most effective way of increasing nutrient concentrations to the point where anoxia occurs is to change the flow pattern across the sills ventilating the basins. With a sill exchange pattern such as that in the present Strait of Sicily, it is difficult to obtain anoxia in the Eastern Mediterranean without also driving the Western Mediterranean to low oxygen and high nutrient levels. Episodes of anoxia in the Eastern Mediterranean are associated with a freshening of surface waters. A reversal in flow directions, presumably resulting from the observed freshening, will inevitably lead to anoxia associated with increased sediment burial rates of the limiting nutrient and will leave the Western Mediterranean largely unaffected, in keeping with the observational evidence.

Copyright 1988  
by the American Geophysical Union.

Paper number 88GB03434.  
0886-6236/88/88GB-03434\$10.00

## 1 INTRODUCTION

The purpose of this paper is to present a set of simple nutrient and oxygen balance models from which one can obtain quantitative estimates of the conditions that are necessary for the development of anoxia in "open" basins which have exchange over a sill with waters outside the basin. The primary example we consider is the coupled system of the Western and Eastern Mediterranean basins, which exchange with each other over a sill in the Strait of Sicily and which have external exchange over sills in the Strait of Gibraltar and the Bosphorus. The Miocene to Recent sediment record of these two basins shows evidence of numerous anoxic episodes in the Eastern Mediterranean, none of which appear to have been accompanied by anoxic episodes in the Western Mediterranean.

In Sarmiento et al. [1988] we explored the causes of anoxia in the global ocean, which is in effect a "closed" basin. We investigated there the hypothesis that global episodes of anoxia are related to increased surface productivity and/or stagnation, showing that neither mechanism is a likely cause for the majority of the ocean. The key to understanding the oxygen balance is the nutrient budget in

high-latitude deep water formation regions. The world ocean has an average  $\text{PO}_4$  content of  $2.2 \mu\text{mol L}^{-1}$ , with nitrate in approximate Redfield ratio to this. These nutrient levels are high enough to cause global anoxia, so long as essentially all of the nutrient that outcrops anywhere in the surface ocean is utilized by organisms and sent into the abyss in reduced form along with carbon in its appropriate Redfield ratio. The present conditions of high deep ocean oxygen levels exist because, in the high-latitude deep water formation regions, organisms do not utilize all the nutrients; thus these regions export high oxygen levels to the abyss without an accompanying large oxygen demand from reduced nutrients and carbon.

Consideration of the Mediterranean nutrient budget shows, as in the world ocean, that the link between anoxia and stagnation and productivity, the two favored hypotheses for anoxic episodes, is different from what has usually been thought. The key to anoxia is not the rate of supply of oxygen by deep water formation, or the rate of its utilization by remineralization of reduced organic matter produced in the surface, but rather the proportion of reduced nutrients relative to oxygen sent to the deep ocean by deep water formation processes and surface biological production. The Mediterranean differs from the world ocean, in that nutrient levels at present are almost an order of magnitude lower, so that even though essentially all of the nutrient in deep water formation regions is presently sent down to the abyss in reduced form, the deep oxygen demand is only a small fraction of the oxygen input by deep water formation. Present deep  $\text{PO}_4$  levels in the Mediterranean are of the order of  $0.40 \mu\text{mol L}^{-1}$  in the Western Mediterranean and  $0.21 \mu\text{mol L}^{-1}$  in the Eastern Mediterranean. At a very minimum, the  $\text{PO}_4$  levels would have to increase to  $1.37 \mu\text{mol L}^{-1}$ , with appropriate amounts of nitrate, in order to obtain anoxia. Our problem is to explain how this might have happened, and why it has happened only in the Eastern Mediterranean, which presently has the lowest nutrient content, while the Western Mediterranean apparently remained much as it is at present.

An increase in the Mediterranean nutrient level can be accomplished only by changing the external source and sink

terms, including exchange across the sills and river inputs. We show that the behavior of a basin is very different depending on whether the surface and deep waters are flowing in or out at the sills. We suggest that a change in the direction of the surface and deep water flow in the Strait of Sicily between the Western and Eastern Mediterranean is the most likely cause of changes in the oxygen content of the Eastern Mediterranean deep waters.

In the following section, we discuss the present Mediterranean circulation pattern, and inferences from the sedimentary record of how the circulation may have changed. We then proceed to develop a model for the present Mediterranean circulation pattern which demonstrates, as explained above, that the key to developing anoxia in the Eastern Mediterranean is to increase its nutrient content. The next two sections develop a nutrient budget for the present Mediterranean, which is needed as a baseline to consider an anoxia scenario in more detail. In order to develop the nutrient budget, we need first to consider the water and salinity budgets. This turns out to be a difficult undertaking due to the large range of estimates for the various transports that exist in the literature. The final nutrient budget obtained is then used to develop a quantitative scenario for how anoxia may have occurred.

## 2. BACKGROUND

Although the eastern Mediterranean, which is linked to the western basin by the Strait of Sicily (sill depth 330 m; Hopkins, [1978]), is presently well oxygenated [Miller et al., 1970], black, organic carbon-enriched laminated bands, termed sapropels, punctuate its Miocene to Recent deep sea record [Olausson, 1961; Ryan, 1972; Stanley, 1978; Cita et al., 1977; Kidd et al., 1978; Van der Zwaan and Gudjonsson, 1986]. The most recent of these episodes, which occurred only 11,000-8,000 years ago (see summary of  $^{14}\text{C}$  dates in Vergneaud-Grazzini et al. [1986, table VII]), is recorded by sapropels at locations deeper than about 600 m. The characteristic duration of these anoxic events lies in the range of 1,000-10,000 years [Kidd et al., 1978]. Since the early work of Olausson [1961], it has been clear that the formation of late Pleisto-

cene sapropels is related to global climate cycles.

The present Mediterranean circulation configuration is determined by strong evaporative loss [Lacombe and Tchernia, 1972; Bethoux, 1979]. This leads to a pattern of inflow of fresher waters at the surface in both the Strait of Gibraltar and the Strait of Sicily, and outflow of more saline waters at depth, for the Mediterranean as a whole as well as the eastern basin. In the past, however, Eastern Mediterranean waters have reacted extremely sensitively to climate shifts. Oxygen isotope curves [Vergneaud-Grazzini et al., 1977; Williams and Thunell, 1979; Vergneaud-Grazzini et al., 1986] show changes of 1.5-1.7‰ in excess of global glacial to interglacial fluctuations [cf. Shackleton and Opdyke, 1973]. In most, but not all cases sapropels coincide with glacial retreat, and show a marked lightening of  $\delta^{18}\text{O}$  relative to the global isotopic trend [Cita et al., 1977; Williams and Thunell, 1979; Rossignol-Strick et al., 1982]. Sapropel foraminiferal faunas often indicate a freshening of eastern basin surface waters [Ryan, 1972; Vergneaud-Grazzini et al., 1977; Williams and Thunell, 1979]. These indications of reduced surface salinity have led to a near unanimous agreement that increased salinity stratification and low rates of vertical mixing ("stagnation") are essential to sapropel formation.

For Olausson and others, glacial meltwater at ice age terminations provides a salinity cap which reduces vertical mixing and promotes anoxia. Other authors invoke periodic pulses of freshwater from the Black Sea, controlled by glacial-eustatic sea level rises, as a means of stratifying the eastern basin water column [Ryan, 1972; Vergneaud-Grazzini et al., 1977; Williams and Thunell, 1979]. More recently, Rossignol-Strick and coworkers [Rossignol-Strick et al., 1982; Rossignol-Strick, 1985] have suggested that heavy Nile river discharge triggers anoxia. They show that the timing of sapropel events coincides more closely to periods of heavy monsoonal precipitation over Africa than to glacial melting in Eurasia. Rossignol-Strick [1985] presents a correlation of "monsoonal index" for the past 425 kyr, derived from variations in orbital parameters, and sapropel formation. The match is too close to be fortu-

itous, and indicates that orbital cycles, principally the precessional cycle, drive local climate change that leads periodically to anoxia. Because the response of oxygen depletion to orbital forcing is almost immediate, the mechanism which triggers anoxia must act within a few kiloyears at most.

By contrast, the Western Mediterranean appears to have remained well oxygenated during the same time span, and recent studies of outflow of Mediterranean water through the Strait of Gibraltar indicate that the outflow has continued unabated with properties similar to those which exist at present [e.g., Oppo and Fairbanks, 1987; Zahn et al., 1987] despite earlier arguments to the contrary (e.g., Huang et al. [1972]; see Diester-Haas [1973] for a contrasting point of view, however). Coring by the Deep Sea Drilling Project on leg 42 [Whitmarsh et al., 1974] shows that the western basin has typically remained oxygenated during other episodes of eastern basin anoxia.

To date there has been no attempt to model the dynamics of Eastern Mediterranean anoxia in terms of circulation velocities and nutrient cycling. The model we present below allows us to test the usual assumption that stagnation causes anoxia, and to discuss the range of parameters, such as river inflow and exchange over sills, that will lead to anoxia in similar silled basins.

### 3. THE MODEL

Figure 1 schematically illustrates the two types of patterns that are involved in the Mediterranean circulation. The upper panel shows a pattern which is representative of both the present Mediterranean as a whole as well as the eastern basin. Such a circulation pattern is very efficient at getting rid of inflowing nutrients and thus tends to become a nutrient desert. The reason is that the exchange at the sill brings in nutrient poor upper ocean waters and exports deep basin waters enriched in nutrients. The deep enrichment is a result of the regeneration of organic matter which removes nutrients from the surface. Equilibrium between inflowing nutrients (from rivers, atmospheric deposition, and flow over the sill) and outflowing nutrients over the sill is reached only when the deep waters

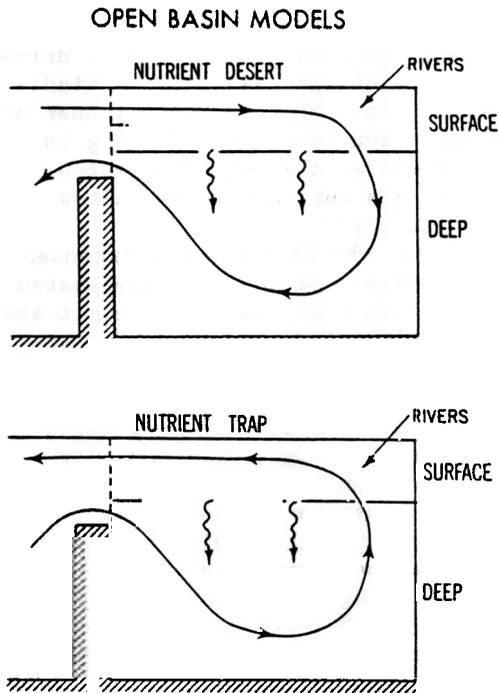


Fig. 1. Schematics of open basin type models. The solid lines indicate the pattern of circulation and the wavy lines indicate sinking of organic matter from the surface. The upper panel illustrates a reverse estuary nutrient desert type circulation such as exists in the Mediterranean at the present time. This circulation will tend to import low nutrient waters and export high nutrient waters, thus becoming depleted. The lower panel illustrates an estuary nutrient trap circulation pattern which tends to import nutrient rich water from outside the basin and export nutrient poor water, thus becoming enriched in nutrients.

of the desert basin have very low nutrient content.

The lower panel of Figure 1 illustrates a circulation pattern that is very inefficient at getting rid of inflowing nutrients and thus tends to become a nutrient trap. In a nutrient trap it is common for a high fraction of inflowing nutrients to be lost to the sediments. The nutrient trap circulation pattern is analogous to the present Black Sea and to many fjords, where surface waters are too fresh to convect down into the salty water flowing over the sill from outside the basin. It is also analogous to the Gulf of Califor-

nia, where heating of surface waters prevents convection from occurring despite high evaporation rates [Bray, 1988], and to the Western Mediterranean with respect to exchange with the Eastern Mediterranean over the Strait of Sicily. In these basins, exchange over the sill exports nutrient depleted surface waters and replaces them with nutrient rich deep waters brought in from outside the basin. Nutrients will accumulate in the basin until a steady balance is achieved where the rate of loss to the sediments is equal to the input from rivers, the atmosphere, and net input from outside the basin. The two circulation types illustrated in Figure 1 have been termed lagoonal and estuarine, respectively, by Berger [1970], who has discussed their implications for the oxygen as well as silica and calcium carbonate budgets for the major ocean basins.

Figure 2 shows a schematic for the circulation of the Mediterranean as a whole, and includes the symbols that will be used for the model. R is river runoff, T is water transport and C is concentration, with subscripts s and d symbolizing surface and deep; superscripts G, S, and B, symbolizing the Straits of Gibraltar and Sicily and the Bosphorus; and superscripts W and E symbolizing the Western and Eastern Mediterranean.  $F_p$  is particulate organic phosphorus flux, which is assumed to have negligible sediment loss ( $\gamma=0$ ) except in the nutrient trap scenario to be discussed later. K is vertical mixing.

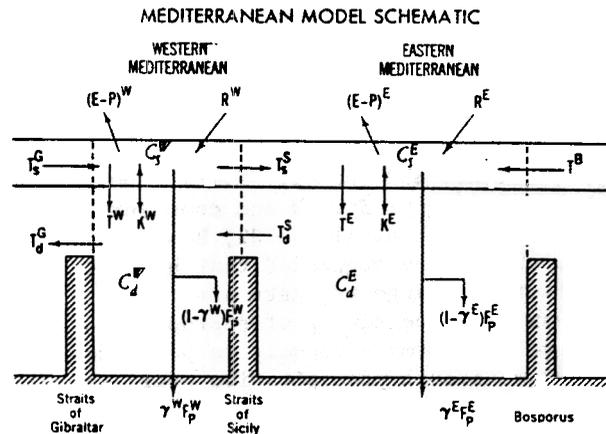


Fig. 2. Detailed schematic of Mediterranean model with circulation analogous to the present Mediterranean. See text for discussion of symbols.

The direction of the arrows indicates the present direction of water transport.

In developing the model, we focus on the the present circulation, discussing first the Eastern Mediterranean, and then covering the Western Mediterranean at the end of the section.

The problem of finding a solution for the oxygen distribution in the present Mediterranean simplifies considerably if we obtain the solution in terms of a limiting nutrient. As geochemists we prefer using  $PO_4$  rather than nitrate because the ability of organisms to produce as well as consume nitrate adds additional unknowns to the problem. The steady state equation for conservation of  $PO_4$  in the deep box of the Eastern Mediterranean is

$$(1 - \gamma^f)F_r^f = (T^f + K^f)(PO_{4,d}^f - PO_{4,s}^f) \quad (1)$$

where we have used the relationship  $T^f = T_d^f$ . This gives a solution for  $(1 - \gamma^f)F_r^f$  which is substituted into the deep box oxygen equation

$$O_{2,d}^f = O_{2,s}^f - \frac{r(1 - \gamma^f)F_r^f}{T^f + K^f} \quad (2)$$

to obtain

$$O_{2,d}^f = O_{2,s}^f - r(PO_{4,d}^f - PO_{4,s}^f) \quad (3)$$

where  $r$  is the Redfield ratio of oxygen consumption to  $PO_4$  remineralization during the degradation of organic matter.

It is important to point out that, although (3) is expressed in terms of concentrations that one would, in a typical box modeling approach, take to represent the average within the box referred to, the appropriate concentrations to use for  $PO_4^f$  and  $O_2^f$  are those representative of the properties of water that sinks to form the deep water of the Eastern Mediterranean in the wintertime. This distinction was dealt with explicitly in Sarmiento et al. [1988] by including a separate surface box to represent deep water formation regions. In the case of the Mediterranean the addition of such a box would confuse the already complex model of Figure 2 without adding insight, since this region does not play the important role in the Mediterranean that it does for the world ocean, as will be discussed below.

As a test of the balance in (3) we make use of approximate values for the present Eastern Mediterranean taken from GEOSECS station 404 in the Ionian Basin at  $35^\circ 35' N$ ,  $17^\circ 15' E$ , which is just east of the end of the Strait of Sicily [Weiss et al., 1983]. Bryden and Stommel [1984] argue, from a consideration of the hydraulics at the sill of the Strait of Sicily and a consideration of the buoyancy relationships within the eastern basin, that the water flowing out over the sill would have to be within a few hundred meters of the 330 m sill depth, and that it could not come from below 1000 m. We thus choose the data at 664 m to represent the properties of the water flowing out of the sill. The properties at this depth do not differ greatly from the average for the entire deep basin. At this depth we find  $O_{2,d}^f = 197 \mu\text{mol kg}^{-1}$ , and  $PO_{4,d}^f = 0.20 \mu\text{mol kg}^{-1}$ . We assume initially that  $O_{2,s}^f$  is equal to the saturation value of  $O_2$  at the temperature and salinity at 664 m, which is  $248 \mu\text{mol kg}^{-1}$ . We take  $r = 169$  from Takahashi et al. [1985] and assume that  $PO_{4,s}^f$  in the sinking water is 0. With these values we are unable to obtain a balance:

$$O_{2,d}^f = 248 - 169(0.2 - 0.0) = 214 \mu\text{mol kg}^{-1}$$

compared to the observed  $197 \mu\text{mol kg}^{-1}$ . Increasing  $PO_{4,s}^f$  above 0 gives an even higher  $O_{2,d}^f$ . The most likely explanation is that  $O_{2,s}^f$  is in fact undersaturated by approximately  $17 \mu\text{mol kg}^{-1}$  when it leaves the surface, giving a value of  $248 - 17 = 231 \mu\text{mol kg}^{-1}$ . Undersaturations of this order would not be viewed as unusual in rapidly convecting regions where deep water is forming. Another possible explanation is that the Redfield ratio is underestimated; however, in order to redress the above imbalance,  $r$  would have to take on a value of 255, which seems unlikely.

As an illustration of how we develop the anoxia scenarios, we focus our attention on (3). We show later that the basic form of this equation is preserved no matter what the direction of exchange is across the Strait of Sicily. In the world ocean study we carried out previously [Sarmiento et al., 1988], we arrived at an equation identical in form to (3). We concluded in that study that the  $PO_4$  content of the

surface water in deep water formation regions, analogous to  $PO_4^f$ , in (3), was the critical factor in controlling the oxygen content. This is not the case for basins in low-latitude regions such as the Mediterranean, where  $PO_4^f$ , the concentration of  $PO_4$  in the surface waters, is generally close to zero due to efficient uptake of nutrients by organisms. This is not likely to change significantly through time because it is typical for such regions to be always nutrient limited. It may not always be the case that  $PO_4^f$  is 0 in deep convecting regions, where the supply of nutrients can often exceed the ability of organisms to take it up; however, if  $PO_4^f$  is greater than 0, anoxia becomes even harder to achieve and we wish in the following argument to find a lower limit for conditions that must be met in order for the present Eastern Mediterranean to go anoxic. We thus assume that  $PO_4^f$  remains 0 at all times.

$O_2^f$  in (3) will only change if the temperature changes; and then not enough, in most circumstances, to lead to anoxia. We have no way of estimating how the Redfield ratio,  $r$ , may have changed through time nor any measurements that may help us determine this. We therefore assume that it has remained constant with time, particularly over the short time scales we are interested in considering here.

The key to understanding the oxygen budget in (3) is therefore the deep box  $PO_4$ ,  $PO_4^d$ . In the world ocean case, this term is not important because  $PO_4$  has a residence time of 20,000 to 100,000 years (see discussion in section 7), which gives it too long a response time to explain the rapid response of the oxygen to the orbital forcing that is observed [Rossignol-Strick, 1985]. This is not the case in the Mediterranean, as shall be discussed below, where the  $PO_4$  residence time is much shorter.

By setting  $O_2^d = 0$  in (3), and keeping  $PO_4^f$  at 0 and  $O_2^f$  at its present value of  $231 \mu\text{mol kg}^{-1}$ , we can find that the condition for anoxia is that  $PO_4^d$  must increase from its present value of  $0.2 \mu\text{mol kg}^{-1}$  to a value of

$$PO_4^d = 231/169 = 1.37 \mu\text{mol kg}^{-1}$$

This concentration is a lower limit for anoxia. The most likely scenario, judging

from the Black Sea at present, where  $PO_4$  concentrations go above  $7 \mu\text{mol L}^{-1}$  [Fonselius, 1974], is that the  $PO_4$  would go well above  $1.37 \mu\text{mol L}^{-1}$ .

The  $PO_4^d$  budget is determined by external sources and sinks. If we balance all the external sources and sinks to the entire eastern basin, we can solve for  $PO_4^d$  and obtain

$$PO_4^d = \frac{R^f PO_4^f + T_d^s PO_4^s + T^d PO_4^d - \gamma^f F_f^f}{T_d^s} \quad (4)$$

where  $PO_4^f$  is river concentration and all other terms are as explained above. This is the balance that will give us the conditions that must be met in order for anoxia to occur with the present circulation, and which will be considered further below.

An important point regarding (3) is that, if the appropriate concentrations are used, it should hold for any water parcel in the ocean, as long as the Redfield ratio is constant, and as long as any mixing that takes place occurs with water that has the same starting value of  $PO_4$  and  $O_2$  when it leaves the surface. We now derive the relationship (3) for the Western Mediterranean, assuming that these conditions apply, i.e.,  $PO_4^v \approx 0$  and  $O_2^v \approx O_2^f$ . The steady state equation for  $PO_4$  conservation in the deep box is

$$(1 - \gamma^v) F_v^v = -(T^v + K^v) PO_4^v - T_d^s PO_4^d + (T_d^c + K^v) PO_4^d$$

This gives a solution for  $(1 - \gamma^v) F_v^v$  which is substituted into the deep box oxygen equation

$$0 = (T^v + K^v) O_2^v + T_d^s O_2^d - (T_d^c + K^v) O_2^d - r(1 - \gamma^v) F_v^v$$

to obtain

$$0 = (T^v + K^v) (O_2^v + r PO_4^v) + T_d^s (O_2^d + r PO_4^d) - (T_d^c + K^v) (O_2^d + r PO_4^d)$$

We now substitute

$(O_{2,d}^I + rPO_{4,d}^I) - (O_{2,d}^E + rPO_{4,d}^E)$ , obtained from (3), into (7) and make use of the relationships  $PO_{4,d}^V \approx PO_{4,d}^I \approx 0$  and  $O_{2,d}^V \approx O_{2,d}^I$ , and  $T_d^C = T_d^V + T_d^S$  (see Figure 2) to obtain from (7)

$$O_{2,d}^V - O_{2,d}^E - rPO_{4,d}^V \quad (8)$$

The anoxia scenario we develop will require that we keep  $PO_{4,d}^V$  low enough in the Western Mediterranean that the oxygen remains high. Equation (9), obtained from balancing the external  $PO_4$  sources and sinks for the Western Mediterranean, gives the relevant balance

$$PO_{4,d}^V = (R^V PO_{4,r}^V + T_d^C PO_{4,s}^C - T_d^S PO_{4,s}^S + T_d^S PO_{4,d}^S - \gamma^V F_r^V) / T_d^C \quad (9)$$

From this it is evident that the high inflow of  $PO_4$  from an anoxic deep Eastern Mediterranean ( $T_d^S PO_{4,s}^S$ ) will drive the Western Mediterranean  $PO_4$  up, unless other terms change to compensate for this tendency.

In order to use the above approach to develop a quantitative anoxia scenario, we need first to examine the balances in (4) and (9) with observations from the present Eastern Mediterranean prior to the beginning of anthropogenic fertilization. This is the subject of the following two sections.

#### 4. WATER AND SALT BALANCE IN THE PRESENT MEDITERRANEAN

There have been a large number of studies of the Mediterranean water and salt balance (e.g., see the synthesis of Hopkins [1978]) with considerable disagreement still continuing to appear in the literature. The only water balance study which contains in it each of the terms that we need to know for our model (see Figure 2) is that of Bethoux [1979]. However, all of the terms in his water balance are at the high end of other published estimates, including a series of recent studies that we find particularly compelling. We therefore develop a new water and salt balance for the Mediterranean, making use of these recent measurements and a synthesis of older work.

One of the major points that needs to be kept in mind in looking at the water transports is that the transport through a sill of a pure end member water type, which is what we wish to obtain, is always smaller than the actual current flow in the sill area. Within a sill region, mixing dilutes the pure water types, such that the actual flow needed to transport a given amount of the pure end-member increases.

Previous estimates of Mediterranean water outflow in the Strait of Gibraltar range between 690 and 1680  $ML\ s^{-1}$  ( $1\ MLs^{-1} = 1 \times 10^6\ Ls^{-1}$ ) [McGill, 1969; Knauss, 1978; Bethoux, 1979; Tchernia, 1980; Lacombe et al., 1981; Bryden and Stommel, 1984]. Bryden and Pillsbury [1988] have recently completed current meter and salinity measurements in the Strait of Gibraltar which give an outflow salinity flux of 1460  $\text{‰}MLs^{-1}$  based on an Atlantic water salinity of 36.2 $\text{‰}$ . The transport of the Mediterranean end-member flowing out through the sill can be found by dividing their measurement by the difference in salinity between the Mediterranean end member and the inflowing Atlantic surface end-member. We use the recent estimates of salinities of inflowing and outflowing waters of Van Geen et al [1988], which are 36.20 $\text{‰}$  and 38.45 $\text{‰}$ , respectively, to find a salinity difference between outflow and inflow of 2.25 $\text{‰}$ . This salinity difference, which is comparable to those given by or obtained from Wust [1961], McGill [1969], Lacombe and Tchernia [1972], Tchernia [1980], and Bryden and Pillsbury [1988], gives a Mediterranean outflow transport of 650  $ML\ s^{-1}$  (Figure 3a), comparable to the transport estimates of McGill [1969] and Bryden and Pillsbury [1988], for Western Mediterranean deep water. One can then use conservation of salt transport across the Strait of Gibraltar to find for the transport of Atlantic water to the Mediterranean the value 690  $ML\ s^{-1}$  (Figure 3a).

The net inflow of freshwater into the Eastern Mediterranean from the Black Sea through the Bosphorus has been estimated as 5.7 to 6.5  $ML\ s^{-1}$  [Merz, 1928; Emelianov and Shimkus, 1986]. We use a value of 6  $ML\ s^{-1}$  (Figure 3a).

Bethoux [1979] gives river runoff (R) fluxes of 7  $ML\ s^{-1}$  and 9  $ML\ s^{-1}$  for the Western and Eastern Mediterranean, respectively, with a total of 16  $ML\ s^{-1}$  for the

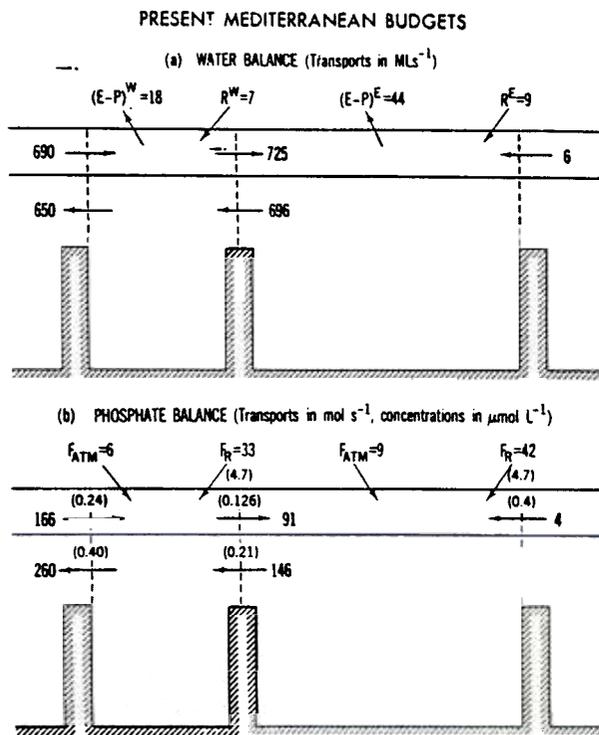


Fig. 3. Water and  $\text{PO}_4$  balance for present Mediterranean.  $\text{PO}_4$  concentrations are given in parantheses in part b.

whole Mediterranean. These numbers of his are taken from Tixeront [1970], and are in reasonable agreement with estimates by McGill [1969], United Nations Environmental Programme (UNEP) [1977], Valiron [1980] and Emelyanov and Shimkus [1986], all of which range between 13 and 16  $\text{ML s}^{-1}$ , though they are significantly larger than the estimate of 11  $\text{ML s}^{-1}$  by Tchernia [1980]. The values of Bethoux [1979] are therefore used in our model (Figure 3a).

The evaporation (E) and precipitation (P) numbers given by Bethoux [1979] can be used to obtain estimates for E-P (which does not include river runoff) of 29  $\text{ML s}^{-1}$  and 69  $\text{ML s}^{-1}$  for the Western and Eastern Mediterranean respectively, for a total of 98  $\text{ML s}^{-1}$ . This total number is greater than any of the other estimates which can be obtained from McGill [1969], Tixeront [1970], and Emelyanov and Shimkus [1986], all of which range between 59 and 84  $\text{ML s}^{-1}$ . Given the Black Sea inflow of 6  $\text{ML s}^{-1}$ , the net inflow of 40  $\text{ML s}^{-1}$  through the Strait of Gibraltar, and the total Mediterranean river runoff of 16  $\text{ML}$

$\text{s}^{-1}$ , all estimated as discussed above, we conclude that the total net Mediterranean E-P flux must be 62  $\text{ML s}^{-1}$ . We therefore use this number for the present Mediterranean, which is in the low range of previously published results, and apportion it out to the Eastern and Western Mediterranean according to Bethoux's [1979] breakdown, giving us a net E-P of 18  $\text{ML s}^{-1}$  for the Western Mediterranean, and 44  $\text{ML s}^{-1}$  for the Eastern (see Figure 3a).

We obtain the flow through the Strait of Sicily by considering the water and salt balance for the Eastern Mediterranean. The water balance gives us a net inflow across the Strait of Sicily, using the above numbers, of 29  $\text{ML s}^{-1}$ . In order to balance the salt flux we need to know the salinity of the inflowing and outflowing waters. The values we choose, 37.2‰ for the surface inflow and 38.75‰ for the deep outflow, are taken from Wust [1961] and are in good agreement with estimates by Lacombe and Tchernia [1972], Bethoux [1980a], and Manzela et al. [1988]. The salt balance and water balance constraints enable us to find an inflow of 725  $\text{ML s}^{-1}$  and an outflow of 696  $\text{ML s}^{-1}$ , as shown in Figure 3a. These numbers are at the low end of the estimates summarized by Manzela et al. [1988], but it is likely that the higher transport estimates are not applicable to the pure end members.

#### 5. PHOSPHORUS BALANCE IN THE PRESENT MEDITERRANEAN

For purposes of our study we wish to obtain a baseline  $\text{PO}_4$  budget for the Recent Mediterranean prior to anthropogenic perturbations. The most important  $\text{PO}_4$  source, and the most difficult to determine due to large anthropogenic effects, is the rivers. There are two previous studies of the full Mediterranean  $\text{PO}_4$  balance that we are aware of. McGill [1969] found that the net outflow of  $\text{PO}_4$  through the Strait of Gibraltar was 61  $\text{mol s}^{-1}$ , the vast majority of which was provided by a river input of 58.3  $\text{mol s}^{-1}$  obtained from a river flow of 14  $\text{ML s}^{-1}$  with an average phosphorus content of 4.2  $\mu\text{mol L}^{-1}$ . The remaining input is from the Black Sea. However, the river concentration estimates are not satisfactory for our purposes, since they were actually

obtained from measurements of nitrate, by assuming a ratio of 1 mol of  $\text{PO}_4$  for each 16 mol of nitrate.

A subsequent study by Bethoux [1980b] made use of the UNEP [1977] phosphorus input estimates of  $365 \text{ mol s}^{-1}$  for the Mediterranean as a whole, to estimate a net outflow at the Strait of Gibraltar of  $365 \text{ mol s}^{-1}$ . This ignores the minor Black Sea input of 1.2 to  $4.4 \text{ mol s}^{-1}$  [McGill, 1969; Fonselius, 1974]. However, the UNEP [1977] phosphorus input to the Mediterranean is due to agricultural and other anthropogenic sources. It seems unlikely that the exchange through the Strait of Gibraltar has been modified significantly, as yet, in response to these recent anthropogenic sources. The UNEP [1977] phosphorus flux estimate includes an estimated non-riverine component of 16%, which brings the river flux to  $307 \text{ mol s}^{-1}$ , with an average river concentration of  $23 \mu\text{mol L}^{-1}$ , 5.5 times greater than the McGill [1969] estimate. UNEP et al. [1984] breaks down the river input into a background flux of  $41 \text{ mol s}^{-1}$ , and a pollution source of  $266 \text{ mol s}^{-1}$ , giving a pre-anthropogenic average river concentration of  $3.1 \mu\text{mol L}^{-1}$ , a number in good agreement with McGill [1969]. We cannot assess the accuracy of the UNEP et al. [1984] background river flux, however, since the original sources are not given.

Given the difficulty of obtaining reliable pre-anthropogenic river concentrations of phosphate, we have decided to proceed by fixing the  $\text{PO}_4$  transports through the sills and from the atmosphere as much as possible from independent information. This allows us to find the river flux from differences between the other numbers.

In the following treatment we assume, as did McGill [1969] and Bethoux [1980b], that loss of phosphorus to the sediments within the Mediterranean is negligible. Such an approach is not unreasonable for nutrient desert circulation patterns such as dominate the Mediterranean as a whole at the present time, but cannot be ignored in the case of nutrient traps such as the Black Sea [e.g., Fonselius, 1974].

The flows given in Figure 3a can be combined with  $\text{PO}_4$  concentrations to calculate phosphorus transports. For the Strait of Gibraltar we use estimates of  $0.24 \mu\text{mol L}^{-1}$  for the Atlantic inflow and  $0.40 \mu\text{mol L}^{-1}$  for the outflow, both obtained by A. Van Geen (personal communi-

cation 1988), using the technique described in Van Geen et al. [1988]. Both concentrations are higher than previous estimates by Coste [1969], McGill [1969], Bethoux [1980b], and Emelyanov and Shimkus [1986], which fall in the range of 0.02 to  $0.20 \mu\text{mol L}^{-1}$  for the inflow, and 0.28 to  $0.35 \mu\text{mol L}^{-1}$  for the outflow. We choose the Van Geen estimates since they are based on recent measurements and are consistent with the salinities given in the previous section. The  $\text{PO}_4$  transports obtained with these concentrations and the water transports in Figure 3 are  $166 \text{ mol s}^{-1}$  flowing in with Atlantic water, and  $260 \text{ mol s}^{-1}$  flowing out, with a net outward transport of  $94 \text{ mol s}^{-1}$  that must be accounted for by sources within the Mediterranean (see Figure 3b).

We assume that  $\text{PO}_4$  removal from the Atlantic inflowing waters is negligible. Any  $\text{PO}_4$  that is removed by organisms would likely be regenerated at depth, much of it presumably within the inflowing water, but perhaps also within the outflowing water, thus increasing the net outward flux of  $\text{PO}_4$  from the Mediterranean. Our assumption of no net removal of  $\text{PO}_4$  from the inflowing water thus in effect minimizes the outward  $\text{PO}_4$  transport from the Mediterranean at the Strait of Gibraltar.

The net inflow of phosphorus to the Eastern Mediterranean from the Black Sea is taken from the work of Fonselius [1974] as approximately  $4 \text{ mol s}^{-1}$  (Figure 3b), which is only a minor contribution to the  $94 \text{ mol s}^{-1}$  needed to balance the budget. This number, divided by the net water inflow shown in Figure 3a gives an effective  $\text{PO}_4$  concentration in the net inflow of  $0.4 \mu\text{mol L}^{-1}$ . Fonselius gives a range of  $\text{PO}_4$  inflows and outflows which result in a net transport of between 2.4 and  $4.4 \text{ mol s}^{-1}$ . All of these exceed the estimate of  $1.2 \text{ mol s}^{-1}$  given by McGill [1969]. We have chosen an upper limit for the Black Sea inflow, as this makes it easier to achieve anoxia in the scenarios discussed below.

Bergametti [1987] summarizes recent atmospheric phosphorus fallout measurements in Corsica which give an annual average of  $33 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ . Assuming that this number applies to the whole Mediterranean, one can multiply it by the Western and Eastern Mediterranean areas of  $0.854 \times 10^{12} \text{ m}^2$  and  $1.647 \times 10^{12} \text{ m}^2$ , respectively [Emelyanov and Shimkus,

1986], to obtain the remarkably large phosphorus inputs of  $28 \text{ mol s}^{-1}$  for the Western Mediterranean and  $54 \text{ mol s}^{-1}$  for the Eastern Mediterranean, for a total of  $82 \text{ mol s}^{-1}$ ; almost enough to balance the entire  $\text{PO}_4$  loss of  $94 \text{ mol s}^{-1}$  through the Strait of Gibraltar. It is therefore of considerable importance to assess how much of this atmospheric phosphorus input is nonanthropogenic, since the phosphorus budget we are trying to construct is for the unperturbed Mediterranean prior to anthropogenic effects, and to estimate how much of the nonanthropogenic phosphorus dissolves in seawater.

P. Buat-Menard (personal communication 1988) has suggested to us that a reasonable order of magnitude estimate for how much of the fallout phosphorus at Corsica is from uncontaminated Saharan dust is about 50%. Combining this with Duce's [1986] order of magnitude estimate of 1/3 for the fraction of the phosphorus that eventually dissolves in seawater, gives us  $6 \text{ mol s}^{-1}$  and  $9 \text{ mol s}^{-1}$  of atmospheric input for the Western and Eastern Mediterranean, respectively (see Figure 3b), for a total of  $15 \text{ mol s}^{-1}$ , which is 16% of the net outflow at the Strait of Gibraltar, i.e., of the total input to the Mediterranean. This percentage is comparable to the estimate by Graham and Duce [1979] that the atmospheric contribution of phosphorus to the world ocean is 10% of the river contribution. The difficulty in obtaining a reliable number for the atmospheric input is one of the two weakest points in our phosphorus budget estimate, the other being the amount of phosphorus in rivers that eventually becomes dissolved in the Mediterranean.

Given the  $\text{PO}_4$  loss through the Strait of Gibraltar of  $94 \text{ mol s}^{-1}$ , the net Black Sea input of  $4 \text{ mol s}^{-1}$ , and the total atmospheric input of  $15 \text{ mol s}^{-1}$ , one can calculate, from the differences, a required total Mediterranean river phosphorus input of  $75 \text{ mol s}^{-1}$ . Dividing this by the total river water input of  $16 \text{ ML s}^{-1}$  gives a mean river concentration of  $4.7 \text{ } \mu\text{mol L}^{-1}$ . This mean river concentration can be used to estimate a river phosphorus input of 33 and  $42 \text{ mol s}^{-1}$  for the Western and Eastern Mediterranean, respectively.

How does the mean river concentration of  $4.7 \text{ } \mu\text{mol L}^{-1}$  compare with previous studies? Meybeck [1982] has made a compilation of river phosphorus measurements,

obtaining a global average, based on the relatively small number of measurements for non-polluted rivers that were available, of  $0.32 \text{ } \mu\text{mol L}^{-1}$  for dissolved inorganic  $\text{PO}_4$ ,  $0.81 \text{ } \mu\text{mol L}^{-1}$  for dissolved organic phosphorus,  $10.32 \text{ } \mu\text{mol L}^{-1}$  for particulate inorganic phosphorus, and  $6.77 \text{ } \mu\text{mol L}^{-1}$  for particulate organic phosphorus. The total,  $17.90 \text{ } \mu\text{mol L}^{-1}$ , is almost twice the global average estimate of  $10 \text{ } \mu\text{mol L}^{-1}$  which Froelich et al [1982] obtain by a consideration of the pre-agricultural crustal erosion rate.

What fraction of the total phosphorus carried by rivers is actually "reactive"? Froelich et al. [1982] and Broecker and Peng [1982] use a global average river concentration for "reactive" phosphorus delivery to the ocean of 1 to  $1.3 \text{ } \mu\text{mol L}^{-1}$ . This, in effect, amounts to using only the dissolved component, which in the case of the Meybeck compilation is  $1.13 \text{ } \mu\text{mol L}^{-1}$ . However, Froelich et al. [1982], in particular, point out that the evidence for this conclusion is not strong. Furthermore, there are indications that some of the particulate phosphorus may be adsorbed on iron oxides and that this component may be desorbed in sediments [e.g., Krom and Berner, 1981]. We therefore prefer to treat the river phosphorus concentration as an unknown and solve for it as above. Our result would require that of order 21% of the particulate phosphorus in Meybeck's [1982] summary be reactive.

The  $\text{PO}_4$  exchange through the Strait of Sicily is obtained by considering the  $\text{PO}_4$  balance for the Eastern Mediterranean, which gives a required net outward transport of  $55 \text{ mol s}^{-1}$ , and by using GEOSECS station 404 [Weiss et al., 1983] in the Ionian Basin to the east of the Strait of Sicily to characterize the  $\text{PO}_4$  concentration in the outflowing waters. Station 404 gives a  $\text{PO}_4$  concentration of  $0.21 \text{ } \mu\text{mol L}^{-1}$  in deep waters and in the base of the nutricline. This concentration, which is slightly larger than the value of  $0.19$  given by Bethoux [1980b], gives a  $\text{PO}_4$  export of  $146 \text{ mol s}^{-1}$  through the Strait of Sicily (Figure 3b). The inflow of  $\text{PO}_4$  must therefore be  $91 \text{ mol s}^{-1}$  which gives a concentration of  $0.126 \text{ } \mu\text{mol L}^{-1}$ , when divided by the water inflow. This concentration is in the range of surface concentrations in the various  $\text{PO}_4$  sections in McGill [1969]. It is higher than the

value of  $0.08 \mu\text{mol L}^{-1}$  of Bethoux [1980b], also obtained by balancing the  $\text{PO}_4$  budget, but using the UNEP [1977] river fluxes.

Returning to the concept of nutrient desert and nutrient trap circulation patterns illustrated in Figure 1, we see that in the Eastern Mediterranean the large net nutrient export through the Strait of Sicily, which very efficiently gets rid of inflowing nutrients, accounts for the very low nutrient concentrations presently observed in the Eastern Mediterranean.

The Western Mediterranean, on the other hand, is a nutrient trap with respect to the Eastern Mediterranean; but the dominant effect on its nutrient distribution is the large export of nutrients which occurs at the Strait of Gibraltar, so that, in effect, it also has the properties expected of a nutrient desert. Given that the water transports over the two sills in the Strait of Gibraltar and Sicily are approximately equal, the only way that the Western Mediterranean can be a net exporter of nutrients is if the difference in nutrient concentration between outflowing and inflowing waters is larger in the Strait of Gibraltar than in the Strait of Sicily. This fact, combined with the slightly higher nutrient content of the surface flow in the Strait of Gibraltar than in the Strait of Sicily, requires the higher deep nutrient content of the Western Mediterranean.

We shall see below that, during times when the Eastern Mediterranean nutrient content increases in connection with the anoxic episodes, it is difficult to keep the exchange over the Strait of Sicily from dominating the Western Mediterranean completely and driving it toward being a nutrient trap; unless, of course, the circulation there changes direction.

## 6. ANOXIA SCENARIOS

In all the scenarios we develop, we assume that the atmospheric input of phosphorus is reduced to a negligible amount due to the decreased aridity of the Sahara region. We also assume, for the present circulation pattern case, that the loss of phosphorus to the sediments is negligible. Allowing sediment loss to increase will make it more difficult to achieve anoxia. The large number of unknowns is further reduced by assuming that the inflow and outflow at the Strait of Gibraltar are

equal to each other, i.e.,  $T_1^C = T_2^C$ , as well as those at the Strait of Sicily, i.e.,  $T_1^S = T_2^S$ . This has the net effect of requiring that the salinity of inflowing waters equal that of the outflowing waters, i.e., that  $E-P-R-T^B=0$ , which is consistent with the freshening of the surface waters that is observed.

The simplest anoxic scenario we can develop is based on the present Mediterranean circulation pattern, with the assumption that the Western Mediterranean  $\text{PO}_4$  concentrations and river inflow remain unchanged from the present, and that the Strait of Gibraltar water exchange is the mean of the present inflow and outflow, i.e.,  $670 \text{ ML s}^{-1}$ . This then requires that  $E-P$  decrease to the value shown in Figure 4a, and that the net westward flux of  $\text{PO}_4$  from the Eastern Mediterranean across the Strait of Sicily be  $268-161-33=74 \text{ mol s}^{-1}$  (Figure 4b).

Setting the deep Strait of Sicily  $\text{PO}_4$  concentration for outflowing Eastern Mediterranean waters to the minimum anoxic value of  $1.37 \mu\text{mol L}^{-1}$ , and keeping the surface concentration of eastward flowing

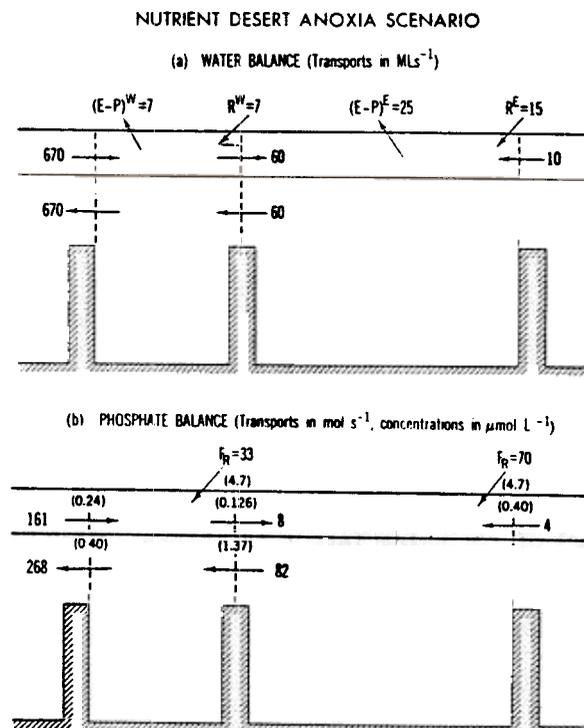


Fig. 4. Water and  $\text{PO}_4$  balance for nutrient desert anoxia scenario, which preserves the present circulation pattern.



Figure 5 shows our model for the case where the circulation in the Strait of Sicily changes direction such that the Eastern Mediterranean becomes a nutrient trap. Such a pattern is suggested by the lighter  $\delta^{18}\text{O}$  isotopic values of the Eastern Mediterranean during the most recent sapropel event [Vergnaud-Grazzini et al., 1986]. The input of  $\text{PO}_4$  by rivers cannot be balanced anymore by outflow at the Strait of Sicily, which now has a net inflow. The nutrient content will thus inevitably build up until the rate of loss of nutrients to the sediments can compensate for the inflow. What conditions must be met in order to obtain such high phosphorus preservation rates in the sediments? One can judge from situations such as the Black Sea that  $\text{PO}_4$  can go to very high concentrations of order  $7 \mu\text{mol L}^{-1}$  before preservation is large enough to account for inflow. This value is well above what is needed to bring on anoxia.

Once steady state is achieved, the phosphorus preservation rate in the sediments would be

$$\gamma^i F_p^i = R^i \text{PO}_4^i + (T_d^s \text{PO}_4^s - T_s^s \text{PO}_4^s) + T^b \text{PO}_4^b \quad (10)$$

where  $\text{PO}_4^s$  is, following our usual convention, equal to  $\text{PO}_4^v$ , and the symbols are as shown in Figure 5. One might expect the direction of  $\text{PO}_4$  transport at the Strait of Sicily to be out of the Western Mediterranean toward the east. We will assume this to be the case in our discussion below, though it should be kept in mind that the net  $\text{PO}_4$  flow might in fact be in the opposite direction if sufficient subsurface Eastern Mediterranean water gets entrained in the westward flowing upper waters. Removal of phosphorus to the sediments in the Eastern Mediterranean must therefore be large enough to account for the river inflow plus the net inflow through the Strait of Sicily. An order of magnitude estimate for the loss to the sediments of phosphorus is the present river input of  $42 \text{ mol s}^{-1}$ .

The sediment preservation for the nutrient trap case (Figure 5) can be compared with sediment preservation in the nutrient desert case (Figure 3)

$$\gamma^i F_p^i = R^i \text{PO}_4^i - (T_d^s \text{PO}_4^s - T_s^s \text{PO}_4^s) + T^b \text{PO}_4^b \quad (11)$$

which is small due to the fact that advection through the Strait of Sicily has a net outflow of  $\text{PO}_4$ .

The Western Mediterranean will, in the Eastern Mediterranean nutrient trap scenario, have no difficulty maintaining low nutrient levels since the circulation at the Strait of Sicily is now exporting nutrients to the east. Indeed, it is likely that the Western Mediterranean nutrient levels will drop in order to adjust to the new situation, unless the inflow of nutrients from rivers goes up.

Our scenario for the episodes of sediment anoxia in the Eastern Mediterranean is therefore that the circulation changes direction at the sill, probably as a result of the observed freshening of the surface waters within the basin. The sediment preservation rate of  $\text{PO}_4$  will initially be close to that of the nutrient desert case, equation (11), and there will therefore be a rapid accumulation of nutrients in the deep basin waters, associated with a decrease in oxygen levels. This increase in nutrients, with its associated decrease in oxygen, continues until the burial rate of organic phosphorus is equal to the total input and a new steady state is achieved. This model has none of the extreme constraints on exchange across the Strait of Sicily of the nutrient desert anoxia scenario. All that is required is that the circulation at the sill change direction.

Reversal of the west-east surface current direction during Eastern Mediterranean anoxic events has been previously suggested by a number of authors [Huang and Stanley, 1972; Muerdter, 1984], based on sedimentologic, isotopic and foraminiferal changes across the straits of Sicily at the appropriate time. We believe that the nutrient balance model presented above adds powerful support to these hypotheses, and look to data from cores to help us refine our understanding of the changes in Eastern Mediterranean circulation. The one prediction that our model in its present form makes is that the total phosphorus burial rate during episodes of anoxia ( $\gamma F_p^i$ ) must be considerably higher than the total burial during times when there is no

anoxia. This, then, is the critical information we must search for in the sediment record.

It is interesting to note, as in the previous anoxia scenario, that the nutrient trap anoxia scenario does not put a strict constraint on the biological production rate, which depends on both  $T^E$  and  $K^E$ , because  $K^E$  can vary independently. This is in direct contradiction to anoxia scenarios which require an increase in production to cause anoxia [e.g., Schrader and Matherne, 1981; Calvert, 1983].

What is the impact of the anoxia scenario on the sediment accumulation rate of carbon? The primary driving force of sediment accumulation is the surface new production, which, as noted above, can vary independently of the constraints that need to be met in order to obtain anoxia. On the other hand, carbon accumulation is also related to the level of oxidants present [e.g., Emerson et al., 1985], such that one would expect in general that a higher fraction of the organic carbon reaching the sediments would accumulate as the oxygen drops. Ryan and Cita [1977] made an estimate of carbon storage during an Eastern Mediterranean anoxic event of  $1.6 \times 10^{12}$  gC  $y^{-1}$ , assuming no change in sedimentation rate during sapropel deposition. This is a very high accumulation rate. Cita and Grignani [1982] and Ten Haven et al. [1987] cite evidence that most of this carbon is from marine as opposed to continental sources. If we assume that phosphorus is buried in Redfield ratio proportions of 1 mol phosphorus to 130 mol of carbon, then this carbon accumulation rate requires a very large loss of about 33 mol  $s^{-1}$  of phosphorus, or of the same order of magnitude as the current river input of phosphorus to the Eastern Mediterranean.

The estimate of phosphorus accumulation in the previous paragraph suggests that one of the major requirements of our nutrient trap anoxia model is met. However, it is difficult to evaluate how good an assumption the Redfield ratio is. Phosphorus can accumulate by processes [e.g., Froelich et al., 1982] different from carbon accumulation mechanisms such as those explored by Emerson et al. [1985]. Furthermore, Froelich et al. [1982] summarize measurements showing that the ratio of phosphorus to carbon in the sediments goes down with increasing carbon

accumulation rates. Clearly, we require direct measurements of the phosphorus accumulation rates to test the model.

## 7. DISCUSSION AND CONCLUSIONS

We suggest that it is very difficult to obtain anoxia in a reverse estuary/nutrient desert type circulation, such as that which exists in the Eastern Mediterranean at the present time, without placing unrealistic demands on exchange across the Strait of Sicily. An estuary/nutrient trap type circulation will inevitably go to low oxygen levels and it makes a great deal of sense to argue that a surface freshening, such as that observed in the Eastern Mediterranean during anoxic episodes, will provide the mechanism for such a reversal. The Red Sea, currently in an evaporative, nutrient desert configuration, also has had anoxic episodes in the past [Hsu et al., 1978] which probably were caused by a similar reversal in circulation across its sill. An important test of this model is that the loss of phosphorus to the sediments should be greatly increased, since it must account for the input from the rivers plus any other external inputs. If there is a significant imbalance it would require us to investigate further the possibility of a loss of  $PO_4$  from the basin by export in outflowing surface waters. What is needed most at this time, however, is further information on nutrient accumulation rates in the sediments.

There is a tendency in the literature to consider the oxygen budget independently of the budget of the limiting nutrient. Thus, for example, Jenkins and Williams [1984] make an argument that, if the Eastern Mediterranean were to stagnate, it would take 30,000 years to go anoxic at the present rate of oxygen utilization in the deep waters. This approach assumes that the productivity would remain unchanged during stagnation, whereas, in fact, such a stagnation would also lock up the limiting nutrient in the deep waters such that the productivity would drop and anoxia would never be achieved. Equation (3) clearly shows that the key to driving the oxygen down is to change the budget of the limiting nutrient. It further shows that the biological productivity and the rate of ocean circulation enter into the

problem only through their effect on the amount of limiting nutrient retained in the eastern basin. Southam et al. [1982] also noted this in reference to the Black Sea, which, as they point out, is not stagnant at the present time. Their explanation of the dynamics of anoxia is similar to ours in requiring an increase of the limiting nutrient concentration to bring on anoxia. However, while we do agree with their increased river supply scenario for the nutrient increase, we find difficulty in accepting their increased vertical exchange scenario, as discussed in Sarmiento et al. [1988].

One of the observations that a model for Eastern Mediterranean anoxia must account for is the rapid response of order a few kiloyears of the oxygen content to the orbital forcing [Rossignol-Strick, 1985]. The residence time of  $\text{PO}_4$  in the present Eastern Mediterranean is 290 years, and in the Western Mediterranean it is 190 years. These numbers are calculated by taking the mean deep  $\text{PO}_4$  of 0.21 and 0.40  $\mu\text{mol L}^{-1}$  for the Eastern and Western Mediterranean times their volumes of  $2.4 \times 10^6 \text{ m}^3$  and  $1.4 \times 10^6 \text{ m}^3$ , respectively, and dividing by the total inflow of  $\text{PO}_4$  into each basin taken from Figure 3. These residence times are very short indeed. It is worth pointing out that these residence times are the appropriate ones to consider in studying the response of the Mediterranean to increased anthropogenic sources of  $\text{PO}_4$ . However, for the anoxic case, the relevant response time is the residence time of  $\text{PO}_4$  in the anoxic ocean. This is longer due to the much higher quantity of  $\text{PO}_4$  present. For example, for the situation shown in Figure 4, the  $\text{PO}_4$  residence time in the Eastern Mediterranean calculated as above, but using 1.37  $\mu\text{mol L}^{-1}$  for the mean concentration, is 1410 years. This longer response time is still within the limits of the observations.

It is interesting to consider the implications of our Mediterranean river result for estimates of  $\text{PO}_4$  residence time in the global ocean. If applicable, our result of a mean  $\text{PO}_4$  concentration of 4.7  $\mu\text{mol L}^{-1}$ , would give a phosphorus residence time in the world ocean of order 20,000 years rather than the 70,000 year value given by Broecker and Peng [1982]. With such a short residence time, it is conceivable that phosphorus cycling might play an important role in short term

(order several thousand years) climate change through its impact on the carbon cycle, as suggested by Broecker [1982]. On the other hand, the work of Boyle [1988] suggests that oceanic  $\text{PO}_4$  levels have remained relatively stable through time.

**Acknowledgments.** The help of Carol Broccoli, Johann Callan, and Nancy Duprey Koehler, in preparing the manuscript, and of P. Tunison in drafting the figures is greatly appreciated. The original motivation for this work was an invitation by R. Berner to speak at a Gordon Research Conference on Chemical Oceanography held in early 1986. Discussions with him, and excellent reviews by E. Boyle and E. Suess are gratefully acknowledged. M. Zavattarelli and W. Stigliani discovered and kindly shared most of the references that were used to establish the present Mediterranean nutrient and water balance. Support was provided by the Carbon Dioxide Research Center, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Systems, Inc. (subcontract 19X-7405C with Princeton University) and by the National Science Foundation, Grant OCE-8711905. T. D. H. acknowledges a grant from the Petroleum Research Fund of the American Chemical Society.

#### REFERENCES

- Bergametti, G., Atmospheric input to the Western Mediterranean Sea-Geochemical and meteorological aspects, Ph.D. thesis, 296 pp., Univ. of Paris VII, 1987.
- Berger, W. H., Biogenous deep-sea sediments: Fractionation by deep-sea circulation, *Geol. Soc. Am. Bull.*, **81**, 1385-1402, 1970.
- Bethoux, J. P., Budgets of the Mediterranean Sea: Their dependence on the local climate and on the characteristics of the Atlantic waters, *Oceanol. Acta*, **2**, 157-163, 1979.
- Bethoux, J. P., Mean water fluxes across sections in the Mediterranean Sea, evaluated on the basis of water and salt budgets and of observed salinities, *Oceanol. Acta*, **3**, 79-88, 1980a.
- Bethoux, J. P., Le cycle du phosphore dans le bassin Occidental de la mer Méditerranée, modèle d'étude du devenir de rejets telluriques, *Ves Journ. Etud. Pollut. C.I.E.S.M.*, 997-1003, 1980b.

- Bethoux, J. P., Paléo-hydrologie de la Méditerranée au cours des derniers 20,000 ans, Oceanol. Acta, 7, 43-48, 1984.
- Boyle, E. A., Cadmium: Chemical tracer of deep water paleoceanography, Paleoceanography, in press, 1988.
- Bray, N. A., Thermohaline circulation in the Gulf of California, J. Geophys. Res., 93, 4993-5020, 1988.
- Broecker, W. S., Ocean chemistry during glacial time, Geochim. Cosmochim. Acta, 46, 1689-1705, 1982.
- Broecker, W. S., and T.-H. Peng, Tracers in the Sea, Eldigio, Palisades, N.Y., 1982.
- Bryden, H. L. and R. D. Pillsbury, Measurement of flow through the Strait of Gibraltar, in Proceedings of the International Conference on Computer Methods and Water Resources, Computer Mechanics Publications, Southampton, England, 1988.
- Bryden, H. L., and H. M. Stommel, Limiting processes that determine basic features of the circulation in the Mediterranean Sea, Oceanol. Acta, 7, 289-296, 1984.
- Calvert, S. E., Geochemistry of Pleistocene sapropels and associated sediments from the eastern Mediterranean, Oceanol. Acta, 6, 255-267, 1983.
- Cita, M. B., and D. Grignani, Nature and origin of late Neogene Mediterranean sapropels, in Origin of Cretaceous Organic Carbon-Rich Facies, edited by S. O. Schlanger and M.B. Cita, pp. 165-196, Academic, San Diego, Calif., 1982.
- Cita, M. B., C. Vergnaud-Grazzini, C. Robert, H. Chamley, N. Ciaranfi, and S. D'Onofrio, Paleoclimatic record of a long deep sea core from the eastern Mediterranean, Quat. Res., 8, 205-235, 1977.
- Coste, B., Echanges de sels nutritifs dissous entre la mer Méditerranée et l'océan Atlantique, Cah. Océanogr., 21, 943-963, 1969.
- Diester-Haas, L., No current reversal at 10,000 B.P. in the Strait of Gibraltar, Mar. Geol., 15, M1-M9, 1973.
- Duce, R. A., The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological activity, in The Role of Air-Sea Exchange in Geochemical Cycling, edited by, P. Buat-Ménard, pp. 497-529, D. Reidel, Hingham, Mass., 1986.
- Emelyanov, E. M., and K. M. Shimkus, Geochemistry and Sedimentology of the Mediterranean Sea, 554 pp., D. Reidel, Hingham, Mass., 1986.
- Emerson, S., K. Fischer, C. Reimers, and D. Heggie, Organic carbon dynamics and preservation in deep-sea sediments, Deep Sea Res., 32, 1-22, 1985.
- Fonselius, S. H., Phosphorus in Black Sea, in The Black Sea - Geology, Chemistry, and Biology, Mem. 20, edited by E. T. Degens and D. A. Ross, pp. 144-150, American Association of Petroleum Geologists, Tulsa, Okla., 1974.
- Froelich, P. N., M. L. Bender, N. A. Luedtke, G. R. Heath, and T. DeVries, The marine phosphorus cycle, Am. J. Sci., 282, 474-511, 1982.
- Graham, W. F., and R. A. Duce, Atmospheric pathways of the phosphorus cycle, Geochim. Cosmochim. Acta, 43, 1195-1208, 1979.
- Hopkins, T. S., Physical processes in the Mediterranean Basins, in Estuarine Transport Processes, edited by B. Kjerfve, 269-310, University of South Carolina Press, Columbia, 1978.
- Hsu, K. J., et al., Initial Rep. Deep Sea Drill. Proj., 42A, 1249 p., U.S. Government Printing Office, Washington, D.C., 1978.
- Huang, T. C. and D. J. Stanley, Western Alboran Sea: Sediment dispersal., ponding and reversal of currents, in The Mediterranean Sea, edited by D. J. Stanley, pp. 521-559, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1972.
- Huang, T. C., D. J. Stanley, and R. Stuckenrath, Sedimentological evidence for current reversal at the Strait of Gibraltar, Mar. Technol. Soc. J., 6, 25-33, 1972.
- Jenkins, J. A., and D. F. Williams, Nile water as a cause of eastern Mediterranean sapropel formation: Evidence for and against, Mar. Micropaleontol., 9, 521-534, 1984.
- Kidd, R. B., M. B. Cita, and W. B. F. Ryan, Stratigraphy of eastern Mediterranean sapropel sequences recovered during DSDP Leg 42A and their paleoenvironmental significance, Initial Rep. Deep Sea Drill. Proj., 42, 421-443, 1978.
- Knauss, F., Introduction to Physical Oceanography, 338 pp., Prentice-Hall, Englewood Cliffs, N.J., 1978.
- Krom, M. D., and R. A. Berner, The diage-

- nesis of phosphorus in a nearshore marine sediment, Geochim. Cosmochim. Acta, 45, 207-216, 1981.
- Lacombe, H., and P. Tchernia, Caracteres hydrologiques et circulation des eaux en Mediterranee, in The Mediterranean Sea, edited by D. J. Stanley, pp. 25-36, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1972.
- Lacombe, H., J. C. Gascard, J. Gonella, and J.P. Bethoux, Response of the Mediterranean to the water and energy fluxes across its surface, on seasonal and interannual scales, Oceanol. Acta, 4, 247-255, 1981.
- Manzela, G. M. R., G. P. Gasparini, and M. Astraldi, Water exchange between the eastern and western Mediterranean through the Strait of Sicily, Deep-Sea Res., 35, 1021-1035, 1988.
- McGill, D. A., A budget for dissolved nutrient salts in the Mediterranean Sea, Cah. Océanogr., 21, 543-554, 1969.
- Merz, A., Hydrographische Untersuchungen in Bosphorus und Dardanellen, Veroeff. Inst. Meeresk., 18, 1928.
- Meybeck, M., Carbon, nitrogen, and phosphorus transport by world rivers, Am. J. Sci., 282, 401-450, 1982.
- Miller, A. R., P. Tchernia, and H. Charnock, Mediterranean Sea Atlas, Woods Hole Oceanographic Institute, Woods Hole, Mass., 1970.
- Muerdter, D. R., Low-salinity surface water incursions across the Strait of Sicily during late Quaternary sapropel intervals, Mar. Geol., 58, 401-414, 1984.
- Olausson, E., Sediment cores from the Mediterranean and the Red Sea, Rep. Swed. Deep Sea Exped., 8(6), 337-391, 1961.
- Oppo, D. W., and R. G. Fairbanks, Variability in the deep and intermediate water circulation of the Atlantic Ocean during the past 25,000 years: Northern Hemisphere modulation of the Southern Ocean, Earth Planet. Sci. Lett., 86, 1-15, 1987.
- Rosignol-Strick, M., Mediterranean Quaternary sapropels, an immediate response of the African monsoon to variation of insolation, Palaeogeogr. Palaeoclimatol. Palaeoecol., 49, 237-263, 1985.
- Rosignol-Strick, M., W. Nesteroff, P. Olive, and C. Vergneaud-Grazzini, After the deluge: Mediterranean stagnation and sapropel formation, Nature, 295, 105-120, 1982.
- Ryan, W. B. F., Stratigraphy of late Quaternary sediments, in The Mediterranean Sea, edited by D. J. Stanley, pp. 149-169, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1972.
- Ryan, W. B. F., and M. B. Cita, Ignorance concerning episodes of oceanwide stagnation, Mar. Geol., 23, 197-215, 1977.
- Sarmiento, J. L., T. Herbert, and J. R. Toggweiler, Causes of anoxia in the world ocean, Global Biogeochem. Cycles, 2, 1988.
- Schrader, H., and A. Matherne, Sapropel formation in the eastern Mediterranean sea: Evidence from preserved opal assemblages, Micropaleontology, 27, 191-203, 1981.
- Shackleton, N. J., and N. D. Opdyke, Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V28-238: Oxygen temperature and ice volume on a 105 and 106 year scale, Quat. Res., 3, 39-55, 1973.
- Southam, J. R., W. H. Peterson, and G. W. Brass, Dynamics of anoxia, Palaeogeogr. Palaeoclimatol. Palaeoecol., 40, 183-198, 1982.
- Stanley, D. J., Ionian Sea sapropel distribution and late Quaternary paleoceanography in the Eastern Mediterranean, Nature, 274, 149-152, 1978.
- Takahashi, T., W. S. Broecker, and S. Langer, Redfield ratio based on chemical data from isopycnal surfaces, J. Geophys. Res., 90, 6907-6924, 1985.
- Tchernia, P., Descriptive Regional Oceanography, Pergamon, New York, 1980.
- Ten Haven, H. L., M. Baas, M. Kroot, J. W. de Leeuw, P. A. Schenck, and J. Ebbing, Late Quaternary Mediterranean sapropels, III, Assessment of source of input and palaeotemperature as derived from biological markers, Geochim. Cosmochim. Acta, 51, 803-810, 1987.
- Tixeront, J., Le bilan hydrologique et la mer Noire et de la mer Méditerranée, Cah. Océanogr., 22, 227-237, 1970.
- United Nations Environmental Programme (UNEP), Preliminary report on the state of pollution of the Mediterranean Sea, Rep. Unep/IG.11/INF. (4), pages 1-209, New York, 1977.
- UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, Pollutants from land-based sources in the Mediterranean. UNEP Regional Seas Reports and Studies No. 32, United Nations Environmental Programme (UNEP), 1984.

- Valiron, F., La pollution en Méditerranée: Situation actuelle, causes et remèdes. Prog. Water. Tech., 12, 427-440, 1980.
- Van der Zwaan, G. J., and L. Gudjonsson, Middle Miocene-Pliocene stable isotope stratigraphy and paleoceanography of the Mediterranean, Mar. Micropaleontol., 10, 71-90, 1986.
- Van Geen, A., P. Rosener, and E. Boyle, Entrainment of trace-metal-enriched Atlantic-shelf water in the inflow to the Mediterranean Sea, Nature, 331, 423-426, 1988.
- Vergneaud-Grazzini, C., W. B. F. Ryan, and M. B. Cita, Stable isotope fractionation, climate change and episodic stagnation in the eastern Mediterranean during the late Quaternary, Mar. Micropaleontol., 2, 353-370, 1977.
- Vergneaud-Grazzini, C., M. Devaux, and J. Znaidi, Stable isotope "anomalies" in Mediterranean Pleistocene records, Mar. Micropaleontol., 10, 35-69, 1986.
- Weiss, R. F., W. S. Broecker, H. Craig, and D. Spencer, GEOSECS Indian Ocean Expedition, vol. 5, Hydrographic Data, 1977-1978, National Science Foundation, Washington, D.C., 1983.
- Whitmarsh, R. S., et al., Initial Rep. Deep Sea Drill. Proj., 23, 1974.
- Williams, D. F., and R. C. Thunell, Faunal and oxygen isotopic evidence for surface water salinity changes during sapropel formation in the eastern Mediterranean Sea, Sediment. Geol., 23, 81-93, 1979.
- Wüst, G., On the vertical circulation of the Mediterranean Sea, J. Geophys. Res., 66, 3261-3271, 1961.
- Zahn, R., M. Sarnthein, and H. Erlenkeuser, Benthic isotope evidence for changes of the Mediterranean outflow during the late Quaternary, Paleoceanography, 2, 543-559, 1987.
- T.D. Herbert and J.L. Sarmiento, Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, NJ 08542.
- J.R. Toggweiler, Geophysical Fluid Dynamics Laboratory, National Oceanic and Atmospheric Administration, Princeton University, Princeton, NJ 08542.

(Received April 14, 1987;  
revised July 8, 1988;  
accepted August 8, 1988)