ADVERSE EFFECTS OF MARINE POLLUTANTS ON THE OXYGEN BALANCE OF THE SEA

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I. INTRODUCTION

Dissolved oxygen in the ocean is of great importance and has been the subject of many investigations. It plays a basic role in biological activity, either in photosynthesis by plants or in respiration by the great majority of living organisms. Plant production by photosynthesis in the sea is of supreme importance not only because it supports the whole marine food chain, but also because it produces equivalent amounts of oxygen which then may be transferred to the atmosphere to contributre to the maintenance of terrestrial animal life.

Its distribution in the oceans, unlike that in the atmosphere, is highly variable. It is controlled, on the one hand, by the exchange with the air above the sea; on the other, by the mixing with the dense, cold, normally oxygen-poor, deep water, and is mediated by the biological and biochemical processes that take place in the sea water itself and in the underlying sediments. The subject of oxygen distributors is one of great complexity, as each process is linked with the others, giving rise to a delicate balance that may be easily disrupted.

The oxygen balance in natural marine systems is the result of an extremely delicate equilibrium between the rates at which the various processes take place. Seasonal changes as well as other lower and higher frequency fluctuations do occur in nature, but the overall pattern is the result of a harmonious sequence of disturbances that has influenced the evolution of the seas from the primigenious state up to the present time.

It is only in the last decades that human activities have developed the present vertigious rhythm after altering our heritage irreversibly. Man-induced changes that may contribute to the alteration of the distribution of dissolved oxygen in the sea are innumerable, interacting with each other in an unknown way: changes in coastal structure, changes in the amount and quality of the water discharged by the rivers, introduction of foreign, often harmful materials through the rivers and the atmosphere, or directly from land or from ships and other platforms.

Generally speaking, surface waters have a higher oxygen content than deep waters, due to the exchanges with the air above. At the sea surface, there is a layer, well mixed by the wind and extending down to the thermocline, in which the oxygen concentration is fairly uniform and high. If the water column is relatively stable, a subsurface maximum in the concentration of dissolved oxygen is frequently observed somewhere in the first 100m as a result of oxygen production by photosynthetic algae. The oxygen content is drastically reduced below the photsynthetic zone as the oxidation of organic matter takes place. If the oceans were not well stirred, we might expect the oxygen concentration to continue to fall off and the very deep waters to be anoxic and azoic. This is what happens in certain stagnant environments. But such circumstances are the exception rather than the rule due to the existence of great masses of oxygen-rich water that circulate beneath the Earth's major oceans ofter having sunk down from the polar regions. Hence the oxygen concentration does not continue to decrease with increasing depth but rather goes through a minimum and begins to increase.

II. DISSOLVED OXYGEN IN THE MEDITERRANEAN SEA

The oxygen distribution in the Mediterranean Sea is not substantially different from that of the major oceans except in that deep Mediterranean waters are oxygen-rich and often nearly at saturation. This is due to the oligotrophic character of the Mediterranean Sea with relatively low nutrient concentrations even in the deepest waters, especially in the Eastern Basin, and to the short residence time of the waters in the depths (in the order of 100 years)(UNEP, 1978).

In spite of this oligotrophic character, which has led many authors to consider this as an impoverished area as far as photosynthetic production is concerned, surface waters of the entire Mediterranean Sea have oxygen concentrations around and often above the saturation values. Various factors contribute to it:

1. In spring and fall, important phytoplankton blooms develop in the surface layers as a consequence of the increased availability of nutrients and of the existence of some degree of stratification, which allows the algae to remain in the euphotic zone for a sufficient length of time.

2. In winter, especially in large areas of the NW and NE Mediterranean Sea, vertical mixing develops and oxygenation of the deeper layers (sometimes down to 800 m or even more) therefore takes place in spite of a low rate of photosynthetic activity as a consequence of the short time spent by the algae in the euphotic zone.

3. In summer, in spite of the strong thermocline and halocline existing between about 30 and 75 m, a transfer of nutrients from the reserve in deeper waters to the shallower depths below the thermocline enables the existence of a plankton crop commensurate with other regions which have a larger reserve of nutrients but a reduced rate of supply (McGill, 1961). Under these circumstances, oxygen produced by photosynthesis below the thermocline remains trapped there as the exchange with the upper layers and the atmosphere is strongly hindered by stratification (Cahet et al., 1973).

4. Some areas around the larger rivers (Ebro, Rhone, Po, Nile, etc.) are also highly productive due to the nutrients discharged, although this kind of production reduces the amount of oxygen available in the waters below due to the sinking of large amounts of organic matter (Emara et al., 1973).

In most areas of the Mediterranean Sea, the oxygen concentrations decrease steadily downwards, although layers of higher saturation values may be found at intermediate depths. These layers constitute the remains of winter cold, oxygen-rich waters that have sunk from the surface (Furnestin, 1960). Layers of minimum oxygen concentration have also been described in both the Western and the Eastern basins, especially in the latter (Oren, 1970), but not of the kind normally encountered in the major oceans at equal latitudes developed by the sinking of organic matter from the highly productive surface layers.

According to Tchernia (1960), new, highly oxygenated deep water is formed in winter when the strong continental winds cause an increase in salinity and a drop in the temperature of the surface water, resulting in an increase in density. Mixing is then promoted and, because of the vertical homogeneity and instability, convective circulation occurs, giving rise to a mixed layer that may extend downwards to 800 m or even more in the very cold winters, with oxygen concentration nearly at saturation. This new deep water then spreads southwards, fills the greater depths of the Western Basin and, flowing through the Alboran Sea and the Straits of Gibraltar, spreads at intermediate depths over a large area of the Atlantic Ocean.

This process of deep-water formation has been considered to be restricted to some selected areas of the Mediterranean Sea (Gulf of Lyons, Adriatic Sea and Aegean Sea) although highly homogeneous winter water reaching considerable depths has been described in areas much wider than these, suggesting that the phenomenon may be far more extensive than is at present accepted. These same conditions have been observed in the Eastern Basin, in which cold surface water from the Adriatic Sea flows through the Strait of Otranto, after sinking to greater depths, along the western side of the Ionian Sea, and following the bottom of the basin, trapped in a counter-clockwise circulation, gradually rises to mid-depths along the southwestern shore, and finally flows into the Western Basin through the sills in the Sicilian Channel (McGill, 1961).

III. OXYGEN DYNAMICS

Various processes alter the concentration of dissolved oxygen in the sea water at a given location. Understanding of the role played by these processes on the distribution and production of oxygen in the sea is essential if the effect on the natural balance of introducing foreign materials and energy is to be understood. The processes are:

- Advection and eddy diffusion that alter the local concentrations of any dissolved constituent of the sea water in accordance with the principles of continuity and the theory of the distribution of the variables in the ocean (Sverdrup it al., 1943).

- Exchanges of gaseous substances with the atmosphere across the sea surface that occur in both directions, although the direction of the net transport will depend on the sign of the difference in the partial pressure of the gas in solution and that in the gas phase (Kanwisher, 1963).

- Chemical and biological changes that take place in the bulk of the sea, especially processes such as the photosynthetic production of oxygen by marine plants and respiratory consumption of oxygen by plants, animals and bacteria, which seem to be far more significant than reactions of oxygen with dissolved inorganic substances such as Fe(II), Mn(II), $S^{=}$, etc.

A. Diffusion and advection

Although dissolved oxygen concentrations are also modified by in situ processes which are primarily biological, and by interface processes, mainly exchanges with the atmosphere, diffusion and advection are perhaps the most important processes governing the oxygen distribution in the sea. A useful assumption in oceanography is that, in the couse of oceanic circulation, every speciment of sea water has, at some time in its history, been at the surface and in equilibrium with the gases of the atmosphere and that, between the time the water leaves the surface layers and the time it returns to them, advection and diffusion distribute the dissolved gases throughout the entire water mass (Richards, 1965).

The oxygen in the sea water at the surface tends to be in equilibrium with the oxygen in the atmosphere and the value of the concentration in this zone, provided it stays there long enough, is the saturation value. Surface saturation is not a general feature in the oceans. Undersaturated surface waters appear to be associated with areas of divergence in which deep, oxygen saturation values of 110 or 120 % and even higher, attributable to *in situ* photosynthetic production of oxygen, are common in large areas of the world's oceans.

The equilibrium solubility of a gas in a liquid is given by Henry's Law:

$$m = C \cdot p$$

where m is the molal concentration of the gas in the solution, C is a constant and p is the partial pressure of the gas above the solution. At atmospheric pressure, deviations from Henry's Law due to non-ideality of solutions are small. For oxygen, they remain within 1 to 3 % although, at elevated pressure, these deviations may become more appreciable (Horne, 1969).

B. Gas transfer across the air-sea interface

Knowledge of the state of equilibration of a gas in the surface layers of the ocean is uncertain. The thermodynamic equilibrium state will be approached, but the balance between the rate at which it is approached, the rate at which water is moved into and out of the surface layers, and the rates at which *in situ* processes alter the gas content of the water cannot be precisely evaluated. It is particularly difficult to evaluate the degree of equilibration of the surface layers in places with large thermal gradients (thermocline, fronts) due to the non-linearity of the relationship between solubility and temperature. It is even more so with oxygen because biological processes alter its concentrations rapidly.

If the partial pressure of the gas in the atmosphere is greater than the equilibrium partial pressure of the gas in the sea water (for given temperature and salinity), there will be mass transport of gas from the gaseous to the liquid phase; if less, then the sea water will release gas to the atmosphere. Large gradients in oxygen concentration can exist in the surface layers. Richards (1965) has reviewed the exchange of oxygen through a smooth surface layer. Eddy diffusion and advection bring the gas molecules to the surface boundary layers relatively rapidly; then, within these layers, the gas molecules are transported by molecular diffusion, this being the rate-limiting step. The flux of gas through the unit area is

$$\text{Flux} = D \cdot \Delta C/t$$

where ΔC is the gas concentration difference between the bottom and top of a layer of thickness t, and D is the diffusivity which, at 20 °C, has very nearly a value of 2×10^{-5} cm/sec for all the atmospheric gases. The concentration difference depends on the partial pressure and the solubilities of the gases and these vary considerably for the various atmospheric gases.

This process, limited by the rates of diffusion and replacement of the surface waters, is confined to a thin upper layer and is therefore sensitive to sea-state and wind. Laboratory experiments have shown that gas exchange depends on the state of agitation. The surface layer is estimated to be between 5×10^{-3} and 0.1 cm thick, with a value of 0.01 cm (corresponding to 10^5 molecule diametres) being a representative average. Agitation reduces the effective layer thickness. Strong stirring easily doubles the exchange rate. It also increases with wind after a critical value of 2 m/sec is reached. At higher velocities, exchange square of wind velocity. Bubbles carried below the sea surface under turbulent conditions may also increase the gas exchange by increasing the partial pressure of the gas by 10 % with every 1 metre of depth (Kanwisher, 1963).

Oil films have little effect on the rate until their thickness exceeds about 10^{-4} cm, but certain soluble surfactants can reduce the rate of solution (Downing and Truesdale, 1955).

C. Photosynthesis

The main in situ processes that alter oxygen concentrations are photosynthesis and respiration, including the biochemical oxidation of organic matter. By far the most important agents for marine photosynthesis, and probably for photosynthesis of our planet as a whole, is the group of microscopic organisms known collectively as phytoplankton, which are normally present in the euphotic zone, the surface layer of the ocean in which net oxygen production is accomplished by these organisms. The water layers in which photosynthetic production of oxygen exceeds respiratory consumption is called the photosynthetic zone and the depth at which they just balance is the compensation depth, which is often assumed to be roughly the depth at which 1% of the surface visible light energy remains. This depth depends largely on the amount of solar radiation reaching the sea surface and on the transparency of the water, varying from about 0.8 m in highly turbid inshore waters, to 15 m in moderately turbid coastal waters, to as much as 100 m in the clearest parts of the ocean, being shallower where plankton populations are denser as a consequence of attenuation by the microscopic organisms and other particles of the visible and near-visible radiant energy.

An account of the physics and biochemistry of the photosynthetic system would be out of place here, but a review of the physical and chemical factors having an effect on it should be attempted in order to determine the sensitivity of the system to marine pollutants.

The study of the process of oxygen production, linked to those of plant growth and nutrient utilization, requires a knowledge of the taxonomy and physiology of phytoplankton, but more special emphasis should be given to the role played by physical factors such as light and temperature, as well as by the chemical composition of the environment.

The rate of photosynthesis by algal cells is a function of the light intensity and increases with intensity until a "light saturation" value is reached. Most theoretical models of the role of light in photosynthesis lead to the formulation of hyperbolic curves for the relationship between the photosynthetic rate and the light intensity.

The solar energy reaching the surface of the sea depends on the angle of the incident radiation and cloud cover and on such factors as dust, water vapour and CO_2 contents of the atmosphere. There is little or no radiation with a wavelength of less than 300 nm or exceeding 3000 nm at the sea surface, and about one half of the total radiant energy from the sun is in the infra-red region of the spectrum. That which is able to penetrate the lower atmosphere is absorbed by a very thin layer at the surface of the sea.

The most important feature, as far as marine photosynthesis is concerned, is the vertical attenuation of light in sea water, which has a complex pattern and is affected by absorption and scattering by water molecules, dissolved organic matter and particulate organic and inorganic materials. Red light is strongly attenuated near the surface, and thus the weaker attenuation of blue-green light determines the depth down to which photosynthesis takes place (Jerlov, 1968). With increasing depth, the residual light in the sea has a progressively narrower spectral range with an intensity maximum between 500 and 550 nm, according to the water mass and meteorological conditions.

The presence of microscopic living or detrital material in the sea water has a strong effect on the attenuation of visible and near-visible radiant energy, a mechanism acting as a feed-back limitation for photosynthesis. The light energy used by plants in photosynthesis was originally thought to be solely that absorbed by chlorophyll. It is now accepted, however, that light absorbed by some of the carotenoids and other auxiliary pigments may also be effective, via an energy transfer within the chloroplasts (Haxo, 1960). Therefore, penetration of ultra-violet light may be of considerable ecological importance since its absorption by pure water is very small even at 360 nm and short wavelength components are only attenuated by scattering or absorption by dissolved organic matter.

The effects of temperature on the photosynthetic rate are generally small over a range of 3^{o}C or more on each side of the "optimum" temperature for each species, especially if the plant cells are allowed to adapt themselves for a day or two at the temperature concerned. At higher temperatures, there is an abrupt and generally irreversible decrease in photosynthesis, which may be brought about in part by a greatly increased demand for certain nutrients.

Temperature effects are greatest at high light intensities; in particular, the depression of photosynthetic rate by supra-optimal light intensity seems to be assisted by elevated temperatures. For reasons still not understood, the optimum growth temperatures for phytoplankton cultures nearly always seem to be many degrees higher than those which the species would normally be expected to encounter in their natural environments (Strickland, 1965).

In addition to radiant energy, plants need an adequate supply of nutrients if they are to grow. Some of the major elements contained in sea water, such as carbon, sulphur, sodium, potassium and calcium, are never in short supply and therefore have very little or no effect on the distribution of phytoplankton and production of oxygen. Nutrient shortages can arise with nitrogen, phosphorus and silicon, perhaps occasionally with certain of the B-group vitamins, and with some transitional elements such as iron, manganese, copper, cobalt, zinc and molybdenum.

The primary nutrients are present mostly in inorganic form as phosphate, nitrate and silicate ions, respectively. While regenerative processes may be important, especially during periods of stability, the major source of nutrients is the large reservoir that exists in the bulk of the ocean below the photosynthetic zone. Although small in comparison with this reservoir, the major exogenous source of phosphorus and silicon is land drainage. Nitrogen compounds are also introduced into the sea by land runoff, but the major proportion comes from the atmosphere, as a result of evaporation of ammonia from the land surface and from in situ fixation (Dugdale, 1976).

Nutrient concentrations in the euphotic zone are often extremely low due to the changes brought about by their uptake by phytoplankton. As a consequence of the large gradient generated in the vertical direction, their rate of supply is the result of advection and diffusion. The major difference between the various regions and seasons is in the physical mechanisms that supply nutrients to the euphotic zone. The use of the nutrient concentratrions to estimate the rate of the phytoplankton activity in the water column is uncertain, since this activity is related to the rates of nutrient turnover rather than to the standing stock concentration. One can view the ocean, even in the poorest region or season, as a system containing rather low standing crops of nutrients, plants and animals turning over at some non-negligible rate (Lorenzen, 1976).

IV RESPIRATION AND BIOCHEMICAL OXIDATION OF ORGANIC MATTER

The term "organic matter" is used in the chemical sense for decomposable matter. Shells and other hard skeletal parts of organic origin are not "organic matter". Most of the organic matter in the marine environment has its origin in the planktonic material forming relatively large aggregates, with the bacteria or faecal pellets sinking quickly to the bottom. Humic matter derived from the land is another minor source of organic compounds in the marine environment.

A. Oxygen consumption in sea water

The chain of animal life in the deeper waters has as its crucial links the rain of organic material from above as food, and the dissolved oxygen for the respiratory processes. Below the photosynthetic zone in the sea there is a net consumption of oxygen by the respiration of animals and the decomposition and biochemical oxidation of organic material. These processes are accompanied by regular changes in the CO_2 and nutrient contents of the water. Because these processes continue and predominate in the strata below that of active exchange with the atmosphere, good agreement between the consumption of oxygen and the regeneration of inorganic nutrients is more evident than the converse changes. The oxygen required to remineralise phytoplankton phosphorus and nitrogen, occurring in the ratio of their uptake, is normally calculated, on the basis of the final oxidation products, to be -276:16:1 (O:N:P) (Richards, 1965).

A useful term is the oxygen consumption or apparent utilization (AOU) given by the difference between the equilibrium saturation value and the actual oxygen saturation. This is used to estimate the changes in the oxygen concentration which have taken place since the water was equilibrated with the atmosphere. The rates of oxygen consumption estimated by Riley (1951), Wyrtki (1962) and Packard et al. (1977) tend to decrease exponentially with depth:

$$R = Ro \cdot \exp(-a \cdot Z)$$

with $Ro = 60$ to 140×10^{-10} ml/l/sec, and $a = 3$ to 4×10^{-5} cm^{-1}

In most of the world's marine waters, circulatory processes replenish the depths with oxygen-bearing water at rates such that the oxidative consumption does not exceed oxygen renewal, and these waters never lose all of their dissolved oxygen. However, in special circumstances, generally where circulatory processes are restricted, and frequently where the rates of organic production in the euphotic zones are high, the rate of oxygen consumption outstrips the rate of circulatory renewal of oxygen and anoxic conditions arise. Anoxic waters are well known in many marine environments, the largest and best known being the Black Sea. Anoxic basins and fjords represent sea water systems in which organic decomposition has completely removed dissolved oxygen because of the amount of organic matter introduced in the lower layers, and because these layers are only weakly circulating or stagnant.

Concurrent with anoxia, denitrification begins. During denitrification, nitrate ions supply the reducible substrate for the biochemical oxidation of organic matter. Because nitrate is generally formed in the biochemical cycle only in the presence of free dissolved oxygen, denitrification exhausts the supply of nitrate and nitrite ions and leads to the onset of sulphate reduction. During sulphate reduction, $S^{=}$ is produced and occurs in the water mainly as undissociated H_2S and HS^-. The introduction of sulphide ion into the environment is a nearly catastrophic event, since sulphides are highly toxic and thus eliminate all organisms except anaerobic bacteria from the ecosystem. In many of these anaerobic forms, sulphur plays the role normally taken by oxygen. Sulphides form highly insoluble compounds with many metal ions at the pH of sea water, and thus not only tend to strip the waters of ions of these metals but may enrich the sediments with precipitates of them. Anoxic waters are by no means azoic or devoid of life. Although familiar forms are missing, life persists even in these most inhospitable regions of the sea.

B. Oxygen consumption in marine sediments

Most of the organic matter in marine deposits occurs in a mixture with inorganic sediments and derives from planktonic material or humic matter from the land which have been trapped between particles of fine sediment in quiet parts of the sea floor. Below a thin cover of oxidized sediment, anaerobic conditions tend to develop, owing to bacterial activity and lack of oxygen supply by diffusion. However, various mud-feeding animals stir the surface stratum or burrow and plough through newly deposited sediment or seek protection by living below the surface. Plant roots (eg. mangroves) also disturb the lamination of sediments in shallow water. As a result, decomposition of organic matter is enhanced and disintegration of shell remains or disturbance of sedimentary structures take place.

Coarse sandy sediments tend to be poor in organic matter because they accumulate in agitated, well-ventilated waters, where the light organic matter is mostly washed away and the supply of oxygen is sufficient to result in swift decay. The organic carbon in coarse sediments is less than 1%. In finer deposits there is commonly a higher organic content, in many cases several percent because light organic remains and clay both tend to come to rest in quiet regions of the sea floor. This in turn implies poor ventilation of the bottom water and a low rate of exchange of oxygen with the sediment.

Many marine sediments are anoxic. Conditions favorable for the formation of sediments rich in organic matter are found in regions of upwelling water or near the river estuaries. In these areas, high primary production results in development of anaerobic conditions and much organic matter can thus be preserved, in spite of ventilation of the overlying waters. Contents of over 10% organic carbon in sediments are rare, however, and are associated only with anoxic conditions (Black Sea). With the reduction of the redox potential (Eh), the thermodynamic drive is diminished and organic materials tend to accumulate in the sediments rather than to be oxidized. Thus, sediments laid down under anoxic conditions are considerably richer (up to 10-fold) in organic matter than are sediments deposited under oxygen-bearing waters.

V. ALTERATIONS OF THE OXYGEN BALANCE IN THE MEDITERRANEAN SEA

Oil and petroleum products, synthetic organics, metals in excess of the amounts normally discharged, thermal or nuclear energy and many other categories of pollutants may have, and in fact do have, negative effects on the processes that control the oxygen balance. One of the most, if not the most, dangerous of all kinds of pollution, as far as oxygen is concerned, is eutrophication.

A. Eutrophication

Introduction of foreign organic matter or the enhancement of primary production by introducing plant nutrients, either in organic or inorganic form, result in a higher consumption of oxygen at depth which is not balanced by the extra amount of oxygen produced at the surface layers and is lost to the atmosphere. The final result of eutrophication is always an overall reduction of oxygen in the deep layers and in the sediments, which is often irreversible in enclosed areas or even in open coastal areas submitted to large discharges, at least on the human time scale.

The self-purifying capacity of the marine waters is directly connected to the processes that control the oxygen balance. This balance is easily upset and, when sewage is continuously discharged in excess of the capacity of self-purification into a coastal zone with restricted circulation, the zone rapidly becomes a nuisance, turbid and foul-smelling and devoid of natural life. Such a nuisance can be prevented by limiting the quantity of organic matter and nutrients discharged well below the capacity for self-purification of the water body receiving the discharge.

Oxygen deficiency develops from the increased respiratory demand of the saprobis microorganisms digesting the excess organic matter discharged into the sea by crude or partially treated sewage effluents. Moreover, the simultaneous discharge of nutrients promotes the production of plant material which contributes to the respiratory demand with increased amounts of detritus sinking to the bottom while oxygen produced by photosynthesis in the surface euphotic layer only, greatly reduced by turbidity, finds its way to the atmosphere and is lost to the system.

The oxygen cycle may then be broken into an oxygen-producing surface layer and an oxygen-consuming bottom layer with transport of this elelment in the downwards direction severely limited by restricted diffusion due to strong temperature and salinity gradients. Once the cycle is broken, the oxidation of organic matter proceeds through anaerobic pathways. The processes are then characterized by the production of foul-smelling compounds and gases (H_2S, CH_4) and by a failure to complete the oxidative process.

In the sediments underlying polluted waters, a lowering of their oxygen content is experienced due to the high biological and chemical consumption rates. If waters above are highly polluted, sediments may become completely anoxic. Even unpolluted waters, if they are eutrophic, can produce local deficiencies in the sediments by the decomposition of the decaying organic matter. Production of H_2S in the sediments may lead to lethal conditions for the fauna and flora in the overlying water. It also combines with the oxides of iron to form sulphides, which blacken the anaerobic layer. The blackened sulphide-containing sediments are of a widespread distribution, but the sulphides formed in the anaerobic conditions are oxidized rapidly in the presence of oxygen. The depth at which it occurs indicates the depth to which significant amounts of oxygen penetrate, either by diffusion processes or by the circulation of aerated water.

Mediterranean sediments have in general a low organic carbon content due to the presence of high oxygen concentrations in the deeper waters and to the low biological production of the overlying waters, except perhaps in the neighbourhood of the large rivers. Therefore, local oxygen deficiencies are always connected with eutrophicating zones due to the discharge of raw or treated effluents.

Sources of eutrophicating substances in the Mediterranean Sea have been identified and their effect estimated by UNEP (1978). Their distribution around the region is uneven with a maximum in the NW and in the Adriatic Sea and a minimum on the southern shores. Owing to the strong stratification of the surface waters, eutrophication is more acute in summer, when the ambient natural nutrient concentrations are low except in the eutrophic areas, and the oxygen transport through the thermocline is strongly reduced. However, winter mixing allows for the vertical transport of oxygen required to keep the deep waters and the sediments mostly oxidized all over the Mediterranean Sea.

B. Thermal pollution

It is difficult to generalise concerning the effects of increasing the temperature of sea water on the dissolved oxygen balance. The solubility of oxygen decreases with increasing temperatures, and the escape of oxygen through the sea-air interface is thus promoted by thermal pollution. If the water used for the cooling system is from above the thermocline, already warm and in equilibrium with the air above, heating will substantially decrease its density. Heated water will tend to remain at the surface and increase the stratification, therefore reducing the rate of supply of nutrients and of photosynthesis in the surface layers. If the water is from below the thermocline, it is very likely to have a higher salinity than the surface water and therefore tend to sink, creating an undersaturated, warm water layer below the surface mixed layer.

It is not easy to determine temperature effects alone on the rate of photosynthetic production of oxygen since there are several variables affecting the kinetics. Temperature effects depend on the duration as well as on the magnitude of the temperature changes, and they may be related more to the temperature extremes and their frequency than to their average value. For most warm water algae, the temperature for optimum growth is around 25°C, and at temperatures greater than about 30°C, species diversity decreases. Frequently, the natural temperature of the water is above the observed optimal growth conditions and the ambient temperatures of both the water and the air generally would be too high to allow rapid heat loss from large-scale hot water discharges (Yentsch, 1973).

Metabolic activity, and therefore respiration, is also related to temperature, increasing with rising temperature. The relationship is asymmetrical around the optimum, with skewness of the optimum toward high temperatures.

C. Oil and petroleum products

This group of products being in itself part of the "organic matter" described above, but with a slow rate of degradation by marine bacteria which renders it less important from this point of view, may still affect the oxygen balance in two ways: through inhibitory effects on the photosynthetic activity and through the reduction of the oxygen exchange across the air-sea interface. Although scientific references are scanty, the first effecthas been reviewed by UNEP (1978). The reduction of the oxygen produced by inhibition of photosynthesis and by killing (sometimes catastrophically) of marine organisms through coating or acute toxicity seems to be factual. There is evidence that concentrations of various petroleum products below 100 ppm produce inhibition or depression of cellular division, growth rate or photosynthetic activity in phytoplanktonic organisms.

The second effect, in spite of some alarming statements often put forward, does not seem to have any appreciable consequences except when the thickness of the oil layer is large enough (10^{-4}cm, according to Downing and Truesdale, 1955). This is probably never the case under open-sea conditions and no indication whatsoever has yet been reported to support any suggestion that the presence of oil layers, such as those that arise from pollution of the sea by oil, will give rise to a depletion of oxygen in sea water (UNEP, 1978).

D. Synthetic organic chemicals

The most important group of substances included under this heading should be DDT and the PCBs. Although very little information is available in scientific literature regarding the effect on the rates of such products, some work has been done on the subject and reviewed by UNEP (1978). It appears that the clearest effect on phytoplankton organisms is that of changing the rate of oxygen production and of nutient uptake. Dexter and Pavlou (1972) have examined the subject and come to the conclusion that growth rates of diatoms show an inhibition lag which was more apparent in ammonia-limited cultures, concluding that the toxic response may be enhanced under stresses encountered in the natural environment (e.g. light and/or nutrient limitation).

E. Heavy metals

Although some algal species might be affected to the extreme of disappearance, the observation of algal blooms in the most highly polluted marine areas is common. In one of these, the Golfe de Fos, one of the places where pollution reaches the top levels in the Mediterranean Sea, at least two species of phytoplankton occurred in appreciable abundance, apparently not affected by concentrations of 5μg Cd/1 and 10μg Pb/1 (UNEP, 1978).

VI. CONCLUSIONS

Some facts should be taken into account when considering the question of the oxygen balance in the protocol for the protection of the Mediterranean Sea against pollution from land-based sources:

1. Most pollutants (e.g. heavy metals, chlorinated hydrocarbons, petroleum hydrocarbons, thermal pollution, etc.) even though they may not have an important effect on the oxygen balance, have already been included in Annexes I and II of the draft protocol, as they have proven, for other reasons, to be harmful to man or to marine organisms and ecosystems.

2. Two groups of pollutants which have an important effect on the oxygen balance in the sea have not been included for other reasons in the draft , unless section 12 of Annex II is finally approved: eutrophicants (nutrients and organic matter) and suspended inorganic materials.

3. The first group is discharged into the sea mostly from land-based sources and affects primarily the coastal waters and sediments. Since their origin is mostly urban, they are released continuously and, being in dissolved or suspended forms, they are readily transported by coastal currents relatively large distances from the source.

4. Both organic matter and nutrients have approximately the same effects on the oxygen balance since, either directly discharged or through photosynthesis, increased organic matter is always the end-product. The deeper waters and the sediments are most affected, since the mixed surface layer is always at or near saturation.

5. The reduction of the compensation depth through turbidity created by the suspended inorganic material or by the organic matter and planktonic organisms should not be of great concern, as it would leave some unused nutrients at the base of the euphotic zone which would still be used at somewhat greater distances from the source.

Examining the characteristics of the Mediterranean Sea waters (oligotrophy during summer time, important mixing processes during the winter season and high rate of renewal through the Straits of Gibraltar) one tends to think, as has been stated, that artificially increasing the rather low rate of primary production of the region by the discharge of large amounts of nutrients, might be of interest to the human communities established around this sea. However, when the subject is given closer study, important drawbacks appear. Large scale effects should not be expected in the Mediterranean Sea as a whole, even if the natural increase in the human population is taken into account. However, anoxic sediments with abnormally high organic carbon content are now common in previously oxidated areas, and important changes have already occurred due to eutrophication in beaches and rocky shores along the highly populated areas and in the neighbourhood of tourist resorts. This fact may already be acting as a feed-back mechanism to reverse previously high trends of urban development in some critical areas and therefore should be taken into account by legislators who aim at maintaining the Mediterranean Sea, as far as possible, in the condition in which they received it from their parents.

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