CHARACTERISTIC CHEMICAL FEATURES AND BIOGEOCHEMICAL CYCLES IN THE BLACK SEA

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Abstract

In this report, temporal and spatial variabilities in the biochemical and biological sectors of the Black Sea are reviewed, based on the long-term chemical and biological data collected by the Black Sea riparian countries and USA. Past and present biochemical data, starting from R/V J. Elliott Pillsbury August-1965 cruise till R/V Bilim July-1997 cruise, were compared in terms of density dependent profiles for the dynamically different regions of the Black Sea. Observed changes in the ecosystem of the Black Sea during recent decades are reviewed in conjunction with the alterations and modifications in the wide range of environmental controls. Recent physical and biochemical measurements such as nutrients, dissolved oxygen, hydrogen sulfide have also been evaluated for describing the possible routes and mechanisms of transport of coastally trapped pollutants into the offshore, deep-basin waters through meandering rim current system, and the redox mechanisms controlling the sub-oxic zone located between oxic and anoxic layers.

1. Introduction

The Black Sea, the most isolated and the largest inland sea permanently occupied by anoxic water below 100-200 meters, possesses various oceanographic features which make it distinctively different from other basins. What make the Black Sea different from the other basins are its topography in which the interacting coastal and deep ecosystems are contained in the same enclosure, and the presence of cyclonically meandering rim current along the peripheries of the basin. The Black Sea is further unique in having very narrow shelf zone along more than half of its margin, except northwestern shelf area. Detrital particulate organic and inorganic matter of both allochthonous and autochthonous origin is partly assimilated within the coastal waters and partly transported to the offshore waters through transient eddies and jet filaments derived by the abrupt changes in the marginal topography. Because of the absence of bioturbation, delicate laminae of sediments are generally well preserved in the abyssal

bottom sediments as a result of the establishment of anoxic conditions in the water column throughout the last 5,000 years [1]. Detectably thick transition zone, so-called suboxic zone where DO <10 μM) and H_2S $<1\mu M$ [2], located between the upper oxygenated and the deep anoxic layers, is another unique feature that makes it distinct from other anoxic basins, such as Framvaren Fjord [3] and Tyro and Bannock Basins of the Mediterranean [4] where there is a sharp boundary between oxic and anoxic waters. Complicated biogeochemistry and related redox processes within the suboxic zone (SOZ) has been of great interest to chemical oceanographers and modellers.

The upper, oxic layer, comprising about 10-15 % of the total volume of the Black Sea [5], supports the necessary energy to derive the biological cycles ranging from microbiological up to higher trophical levels. It receives wide spectrum of industrial, agricultural and domestic wastes of about 160 million population occupying a catchment area of 2×10^6 km^2, nearly five times larger than its total surface area of 423×10^3 km^2 (Figure 1).
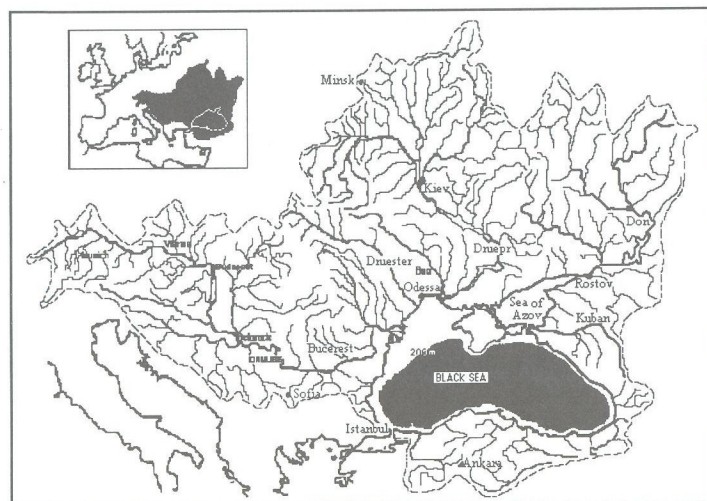

Figure 1. Total catchment area of the rivers discharging into the Black Sea basin.

Majority of the riverine discharges are located on the northern and north-western shelf area which comprises 35% of the total surface area of the basin [6]. The Danube River alone, with its about 200 km^3/y water discharge, represents 3/4 of the north western river run off and 2/3 of the total riverine input (370 km^3/y) into the basin [7, 8], and carries wastes amounting more than the total discharge to the North Sea [9]. Dnyester (9.3 km^3/y) and Dnyeper (54 km^3/y) are the second group of fresh water inputs to the basin which were strongly regulated after 1955 [10, 11]. The total fresh water contribution of Turkish rivers, none of which are regulated, is being only 35 km^3/y [12]. However, annual sedimentary loads of Turkish rivers, being 32.1×10^6 tons, exceed all

other rivers discharging into the basin, except Danube which brings 83×10^6 tons of sediments. On the other hand, annual particulate organic matter load of Turkish rivers (0.275×10^3 tons/yr) is 1/3 of that of Danube (0.913×10^3 tons/y) and discharges of all other rivers on the northern part of the Black Sea(0.977×10^3 tons/y) [13].

2. Materials and methods

The data obtained during the R/V J. Elliott Pillsbury August-1965, R/V Atlantis April-March-1969 and R/V Knorr August-1988 cruises were taken from technical reports [14, 15, 16]. Other data were taken during the various cruises of R/V Bilim since September-1991 till July, 1997. Water samples were collected by a Sea Bird model CTD probe, equipped with a Rosette type sampling system and insitu light transmissometer, at selected density surfaces. Nutrients were analysed on board R/V Bilim by using a two channel Technicon Autoanalyser, whereas dissolved oxygen was measured by Winkler method modified for low level oxygen concentrations. Hydrogen sulfide concentrations for September-1991 period were measured by iodometric technique whereas those for other cruises by colorimetric methylene blue technique. Positions of stations and transects used in the discussions are displayed in Fig. 2.
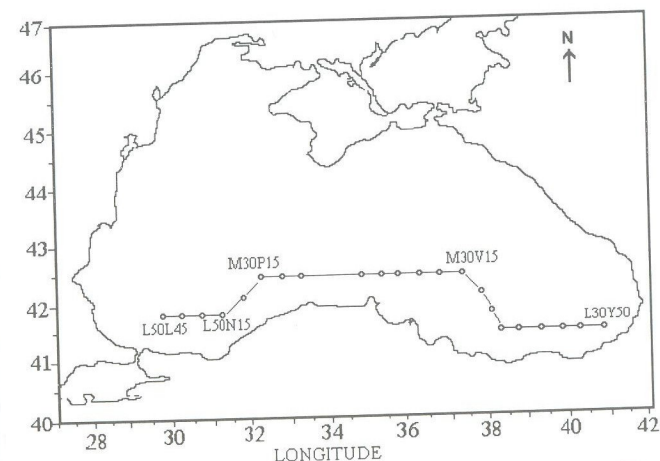

Figure 2. Locations of stations along the southern transect for September,1991

3. Results and Discussions

It is well known that coastal ecosystems of semi-enclosed seas act as natural filters for the open ocean waters by assimilating the major fraction of organic and inorganic inputs into the basin via absorption/desorption, fast sedimentation, and/or complex redox processes in the water column before their detrimental effects are fully transmitted to offshore waters. The remaining fraction of the materials of terrestrial origin are

transported to the offshore areas of the basin where they are further converted into particulate organic and inorganic matter. 10-15% of the particulate organic matter in the open ocean is exported to the deep benthic layer where it is permanently buried in sediments for further diagenesis. However, when the coastal ecosystems of such basins are forced to survive under diverse and intense man-made stress, firstly their ecosystem shifts from natural, well balanced state to a less stabilised state which is more sensitive to further perturbations. Present ecosystem of the Black Sea is suffering such modifications and considered to have little resistance to destabilisation.

3.1. EUTROPHICATION PROBLEMS AND THEIR ECOLOGICAL IMPLICATIONS

Scientific evidence clearly indicated that profound changes have occurred in the Black Sea ecosystem during last three decades [2, 6, 9, 17, 18, 19, 20, 21]. The most dramatic changes have been detected on the north-western shelf area in the form of a decrease in taxonomic diversity of hydrobionts, as very intense blooms of some species to the detriment of others, decline in water transparency, and hypoxia in the benthic layer which influenced the benthic ecosystem [22]. Deterioration of the Black Sea ecosystem has been the consequence of the increased organic pollution through river discharges, even though the inflow of fresh water by the major rivers has been reduced by 25-50% since late 1970's [6, 8, 23]. The amplitude of seasonal variations in the water discharges of these rivers has been reduced significantly [10, 24].

These external modifications, in turn, has resulted in an increase in the annual loads of labile organic matter and nutrient elements through agricultural usages, but a decrease in that of silicate [8, 27] due to increased sedimentation in the upstream dams. Annual nitrate and phosphate discharges of the Danube have increased from 143×10^3 and 12.5×10^3 tons in 1950's to about 740×10^3 and 30×10^3 tons, respectively, whereas that of reactive silicate has decreased by 30-50% from about 800×10^3 tons to 330×10^3 tons in late 1980's [8, 20, 23, 27]. Winter concentration of silicate in Romanian coastal waters decreased from 55 μM before the construction of the "Iron Gate Dam" to 20 μM in 1992 [8]. Correspondingly, strong reduction in the Si:N ratio from 42 to about 2.8, and an increase in the N:P ratio has been detected [8, 18].

Main ecological problems of the Black Sea encountered today are considered to be induced by these large scale, man-made diversions for agricultural and power production purposes in the catchment area of the Black Sea (see Figure 1), and possibly by the decadal variations in the climatic field [24]. Relative contributions of these factor are not clearly defined yet. Most probably, man-made modifications are imposed on the climatic variations as suggested by Niermann and Greve [25] and Tiit [26]. Artificial interferences together with the introduction of opportunistic invaders to the Black Sea ecosystem [9] forced the system to attain a new ecological state in which regular late winter-early spring and autumn blooms have been replaced by late spring-summer blooms with extended periods during last 2-3 decades. In the mean time, the mean value of secchi disk decreased from 20-21 m in 1920s down to 6-8 m in 1990-92 after which its value started to increase gradually to about 14 m in 1995 [28].

3.2. CHANGES IN THE BIOCHEMICAL PROPERTIES OF THE UPPER LAYER

It has long been known that the depth of the oxic-anoxic interface in the Black Sea varies both in space and time, being shallower (70-80m) in the interior of cyclonic gyres in the central basin, and deeper (150-200m) at the peripheries of the main cyclonic circulation and in the anti-cyclonic eddies located between the cyclonically meandering rim current and the coastal zone [29, 30, 31]. September-1991 data collected by R/V Bilim (IMS-METU) were used to show the affects of water circulation on the vertical distributions of biochemical properties of the southern Black along an east-west transect (Fig. 2). Water circulation characteristics of the basin, in terms of biochemical properties, for this period were discussed in some detail by Baştürk et al. [32, 33]. Some of these stations, along the transect, fall into the rim current frontal zone (RCFZ), some in peripheries of the cyclonic gyres and some in the anti-cyclonic eddies.

Depth dependent variation of the potential density surfaces along the E-W transect (Figure 3) implies that the upper ($\sigma_\theta = 15.8$) and lower ($\sigma_\theta = 16.15$) boundaries of the SOZ approach to each other at the frontal zone between cyclonic gyres and the RCFZ. On both sides of these regions SOZ thickness increases again. 5 μM H_2S isoline approaches to that of 10 μM DO surface (Fig. 4) where the suboxic layer becomes very thin (≈ 10 m) as compared to other regions (30-40 m). In parallel to the deepening of isopycnal surfaces towards the east-end of the transect, DO and H2S contours deepen. Primary PO_4 minimum within the SOZ, as was shown by Baştürk et al. [32, 34] for the cyclonic gyres, is clearly evident at these locations (Fig. 5a). However, at the peripheries of these stations, deep PO_4 minimum layer disappears due to the increased vertical and diapycnal mixing between oxic and anoxic surfaces. PO4 concentrations attain higher values (1.0-1.2 μM) compared to those measured at the central stations (0.2-0.3 μM).
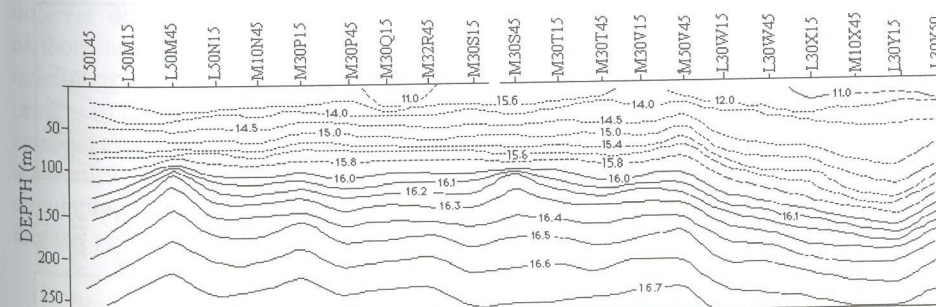

Figure 3. Depth dependent variation of potential density along an east-west transect in the southern Black Sea in September, 1991
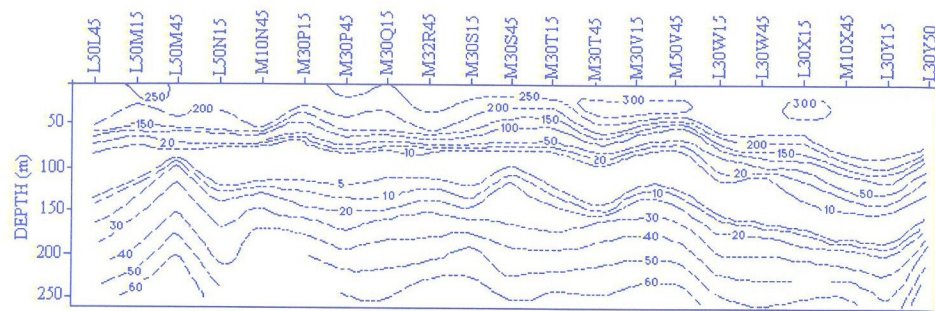
Figure 4. Depth dependent variations of dissolved oxygen and hydrogen sulfide, in µM, along the east-west transect in southern Black Sea in September,1991.

Similarly, the peak concentrations of TNO_x ($NO_3 + NO_2$) at the peripheral stations are higher ($\approx$ 7-8 µM) than those of stations located in the cyclonic gyre ($\approx$ 5 µM) where isopycnal surfaces are sandwiched in a narrow zone (Fig. 5b). Details of vertical profiles of biochemical properties were given for cyclonic, anticyclonic and rim current regions by Baştürk et al. [32]. All these features imply that the sandwiching of the isopycnal surfaces, which is observed frequently in the regions where abrupt changes in the bottom topography couples with the RCFZ, increases the concentration gradients of biochemical elements within the SOZ, which ,in turn, increases the material diffusion between oxic and anoxic layers. These redox sensitive elements are then transported laterally and cyclonically towards the peripheries of gyres. This process is important for the introduction of reduced elements into the upper layer through SOZ.
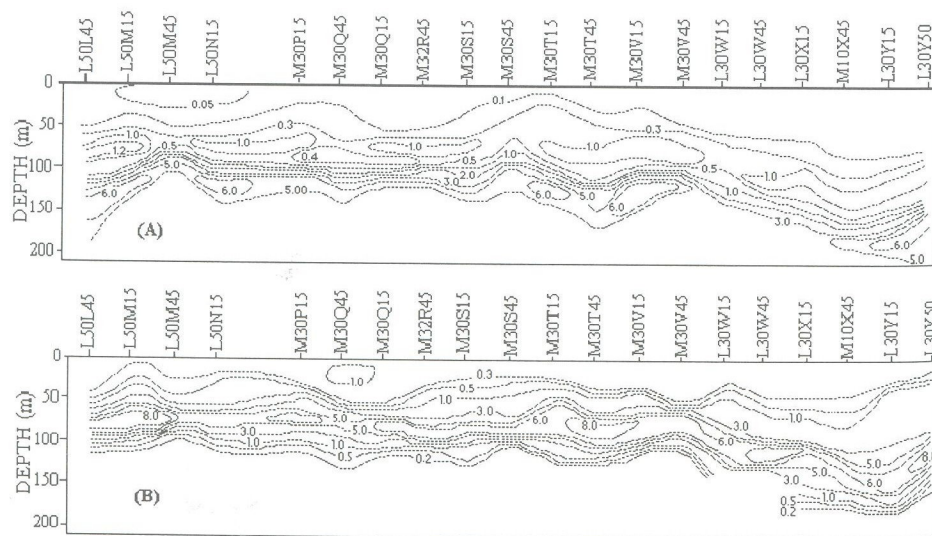

Figure 5. Depth dependent variations of phosphate (A) and total oxidized nitrogen (B) along the southern E-W transect in Black Sea (all are in units of µM)

Difficulties in determining the trace levels of dissolved oxygen and hydrogen sulfide in the transition zones between oxic, suboxic and anoxic zones together with the spatial and temporal variability in the biochemical structure of the upper layer, have led to conflicting conclusions when the comparisons were made in terms of depth profiles even from the similar locations. Researches also derived conflicting conclusions about the long-term changes in the depth of chemical boundaries of the oxic/anoxic interface [2, 5, 8, 19, 25, 36, 37, 38, 39, 40, 41, 42]. The chemistry of the entire basin as a function of water density - rather than depth - has been examined by numerous investigators recently [19, 42, 43] to define the chemical boundaries of the transition zone. All these investigators have shown that the distinct chemical features in the oxic/anoxic transition layer are consistently formed at certain density surfaces, independent of geographical location.

Ecological changes in the photic layer of the Black Sea observed in the form a shift from productive diatom based state to consumptive, organic rich state have led an upward expansion of the upper boundary of the suboxic zone, but not that of sulfidic layer [2, 19, 40, 43] in the Black Sea. The first redox sensitive element that had responded to these shifts is the dissolved oxygen within the oxycline. When the density dependent variation of dissolved oxygen for different years within the western cyclonic gyre of the Black Sea are examined, it will be recognised that the DO gradient zone in 1960's was much broader than in 1990's in terms of density surfaces (Fig. 6). Ventilation of the oxycline down to 15.3-15.4 density surfaces during the winter mixing and horizontal advection processes is also evident. It is also evident seen that 25 µM DO concentration measured at about 15.8-15.9 σ_θ surface in 60's has shifted upward by 0.3-0.4 density units in 1990's. All these changes clearly indicated that in parallel to changes in the coastal zones, the offshore regions of the Black Sea has also undergone detectable biochemical and ecological deteriorations.

Inter-annual as well as intra-annual variations within the basin can be triggered by different driving forces which affect the general circulation and hence the coastal-offshore interactions, horizontal advection and the vertical mixing processes between oxic/suboxic/anoxic layers [33]. These interactions influence the depth dependent profiles of biochemical properties down to the lower boundary of SOZ [33]. However, episodic events, like the one observed in July-1992, may induce pronounced changes in the vertical distributions of chemical properties due to changes in the climatology and circulation characteristics which affected the vertical mixing intensity and hence induced intense planktonic blooms in mid-summer (Fig. 7).
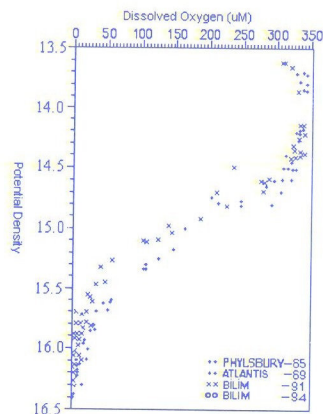
Figure 6. Potential density dependent variations of dissolved oxygen in the western interior of the Black Sea for different periods.
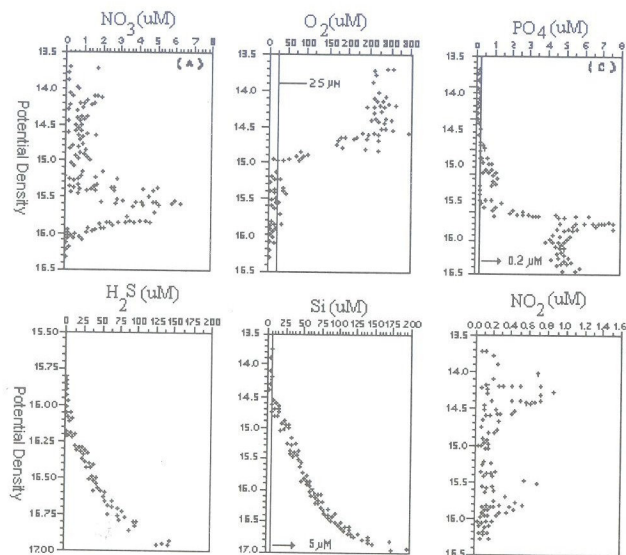

Figure 7. Potential density dependent plots of biochemical properties during the abnormal July,1992 period

During July-1992 period, DO, PO_4 and TNO_x concentrations in the oxycline were greatly reduced down to 15.4 surface where normal, well established TNO_x peak was positioned. This erosion of upper nutricline can not be due to simple dilution effect of vertical mixing, because there should be an increase in the DO concentration in parallel to the reduction in TNO_x concentration due to the entrainment of oxic waters. If these types events are repeating regularly or randomly at about decadal frequency, then the low TNO_x concentrations measured in 1960s can be attributed to such episodic events

which may influence nearly the whole basin in 1960's; even though the event observed in July-1992 was confined to offshore waters of the southern Black Sea. The hydrochemical details of these events and the factors and mechanism(s) responsible for this type events are still poorly understood and debates more process oriented, detailed surveys.

Upper and lower gradients (μM property/m) of the total oxidised nitrogen (TNO_x) were calculated from the depth integrals of chemical properties given by Baştürk et al. [34] for September-1991. When the measured and the calculated gradients for the water layer between 14.2 and 15.4 σ_θ surfaces, which denote the nitracline onset and nitrate maximum, are compared, practically no difference is observed between two gradients. However, 0.03-0.04 unit differences between the values for anticyclonic region and rim current frontal zone implies that more nitrogen species accumulated in these zone, probably due to less intense denitrification. On the other hand, measured lower gradient of NO_x was found to be lower than the gradient calculated from *in situ* O:N:P ratios measured within the sub-oxic layer of the Black Sea for September, 1991. The difference, in contrast to upper gradient, becomes larger in lower gradient of cyclonic gyres (-0.354 μM/m). This large difference between the measured and calculated gradients of NO_x, suggests that nearly half of the NO_3 is utilized by the reduced species diffusing into the narrow sub-oxic zone of the cyclonic gyres.

3.3. SUB-OXIC LAYER

The layer of co-existence (C-layer), in which DO and H_2S were suggested to coexist [35, 44] was shown to be analytical artefacts in sampling and analysis procedures [2, 19, 40]. Co-existence of DO and H_2S is proved to be unrealistic when one considers the rapid dynamics of the reaction between them [45, 46]. At least 10 times faster H_2S oxidation rates in deep Black Sea compared to surface waters with added H_2S, and the similarities between the rates of oxidation of filtered and unfiltered samples under oxic (150-200 μM DO) [47] and suboxic oxygen levels (DO<50 μM) [48] imply that the oxidation of H_2S is mostly abiotic in nature and O_2 is not a direct oxidant for H_2S. Instead, it may be oxidized by the coupling of Mn and Fe cycles involving dissolved and particulate forms of them.

Insitu H_2S oxidation rates within the suboxic zones of the dynamically different regions of the Black Sea were shown to be different [48]; faster removal rates ($t_{1/2}$ =2.5-3.4 hr) within the suboxic layers of the western cyclonic gyre compared to those in anticyclonic eddies ($t_{1/2}$=2.3-15.4 hr), and even faster rates within the RCFZ ($t_{1/2}$ =1.2-1.3 hr) due to the catalytic actions of particulate forms of iron and manganese oxides resuspended from the shelf-slope zone by strong rim current. Tebo [49] measured nearly two orders of magnitude higher Mn(II) residence time in the SOZ of the central parts of the basin (30-90 days) compared to that at the near-shore waters (0.6-1.0 day). At offshore stations no overlapping of NO_3 and NH_4 gradients was evident whereas they overlapped at the near-shore stations [49]. 5 μM DO concentration was shown to penetrate down to 16.0 density surface at the near-shore stations whereas the same level was observed at 15.4 density surface of the interior of the basin.

In order to understand the redox processes and mechanisms of hydrogen sulfide removal within the sub-oxic zone of coastal frontal zones, a process oriented joint survey was conducted during July, 1997 cruise of R/V Bilim along a transverse transect where stations were located 5 nm apart in the offshore direction in the region close to Sakarya Canyon which is located at the south western Black Sea. This area is characterised by an abrupt change in the topography from about 200 m to more than 1000 m along the coast and covers an anticyclonic eddy and strong rim current at its offshore boundary. A detailed sampling strategy was followed along a transect vertical to the coastline. Here we will present anomalous distributions of some chemical parameters at a station (St. L29M46) which was located within the Sakarya Canyon (Fig. 8).

Deep light transmission minimum layer, called as Fine Particle Layer (FPL) [50], weakly observed within the lower boundary of the SOZ of offshore waters intensifies within that of coastal shelf zone but at deeper density surfaces (down to 16.6 density surface). This layer commences at 15.9 density surface and expands down to the 16.4 surface in coastal shelf zone. At the Sta. L29M46 (Fig. 8), the onsets of NH_4 and Mn(II) were observed at the same density surface (15.85) and have similar profiles. However, dissolved oxygen concentration less than 10 μM, on contrary to its frequently observed basin-wide position (DO< 10 μM at σ_θ = 15.6-15.8), was measured down to 16.4 density surface below which sulfidic layer has known to be started (H_2S> 1 μM at σ_θ = 16.15-16.20). About 20 μM DO concentration was measured at 16.2 density surface which was accepted as the onset of sulfidic layer. The well established SOZ layer is very narrow at this station compared to previous boundaries [43]. Even under the intense erosion conditions within the upper zone of the sulfidic layer and thus oxygenation down to the 16.4 density surface, oxic and anoxic layers still do not overlap with each other. In other words, the C-layer does not exist even under intense mixing conditions.

At the station at about 5 nm north of the coastal station (not shown here), the FPL starts to be sliced intermittently by horizontal intrusions of sulfidic water masses from the surrounding in the offshore direction. There is no single and broad FPL as was observed at coastal station, but rather a series of minimum. Additionally, lower boundary of the FPL deepens from 16.4 surface down to 16.7 density surface at this station. Vertical distributions of DO and H_2S at that station followed sequentially each other, never being overlapped. When there is a DO peak, H_2S concentration drops to below detection limits (<1 μM) or wise versa. Additionally, 50 μM DO concentration was detected at around 16.4 surface, followed again by a sulfidic zone. At the interfaces of these oxic/anoxic zones no overlapping of the layers are detectable.
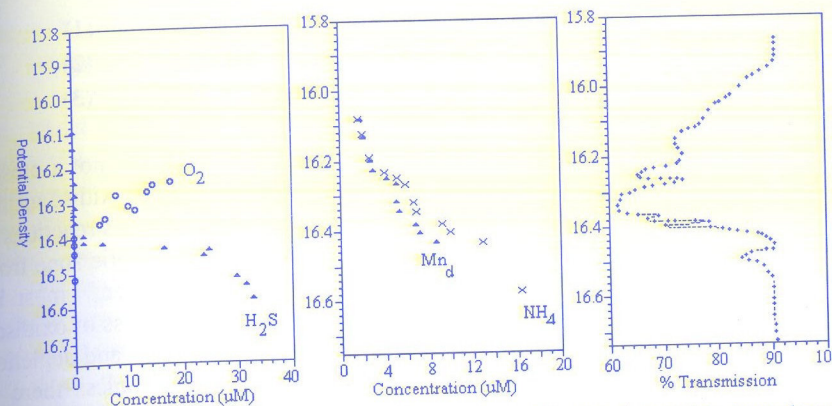
Figure 8. Anomalous distributions of biochemical parameters within deep fine particle layer observed at Sta. L29M46 located within the Sakarya Canyon region (R/V Bilim, IMS-METU July,1997 cruise)

Comparison of the vertical O_2 and H_2S gradients in the suboxic zone of the Black Sea, and the insufficiency of the O_2-electron gradient to compensate the electron concentration required for the oxidation of H_2S diffusing upward, have led Murray et al. [43] to suggest three alternative processes.
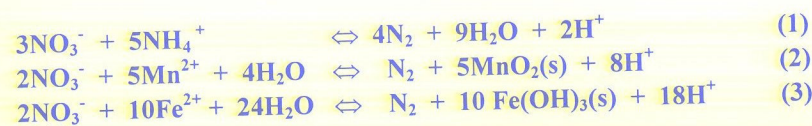
1. Sulfide is oxidized by the settling particulate $MnO_2(s)$ [47, 51], and possibly by iron oxyhydroxides [FeOOH(s)] formed by bacteria in shallower oxic waters [47]. Manganese cycle may be the key process for maintaining the broad suboxic zone; oxidised Mn may oxidised reduced sulfur while reduced Mn(II) may consume dissolved oxygen, as was suggested by Tebo [49]. However, vertical electron equivalent gradients of Mn(II) and Fe(II) were shown to be much less than that of the sulfide gradient [43].

2). Another explanation is the anaerobic oxidation of sulfide associated with the phototrophic reduction of CO_2 to organic carbon as suggested by Jannash [52] and Jorgensen et al. [53], as also supported by the findings of Repeta et al. [54] who measured considerable quantities of bacteriochlorophyll pigments below the suboxic zone.

3). Horizontal as well as vertical ventilation processes may supply sufficient DO. However, it was shown by Lewis and Landing [55] that horizontal mixing of oxygen could provide the necessary oxygen to account for Mn oxidation, but probably not that of sulfide and other reduced species.

Since NO_3, NH_4, Mn(II) and Fe(II) all decrease to low concentrations at about the same density levels (σ_θ =15.95, 15.95, 15.85 and 16.00, respectively), equivalence of upward and downward electron gradients have led Murray et al. [43] to hypothesise that NO_3 is the main account for the oxidation of reduced species diffusing upward from the anoxic layer. The following reactions were suggested by Murray et al. [43] to occur within the suboxic-anoxic boundary:

$$3NO_3^- + 5NH_4^+ \quad\Leftrightarrow\quad 4N_2 + 9H_2O + 2H^+ \tag{1}$$

$$2NO_3^- + 5Mn^{2+} + 4H_2O \Leftrightarrow N_2 + 5MnO_2(s) + 8H^+ \tag{2}$$

$$2NO_3^- + 10Fe^{2+} + 24H_2O \Leftrightarrow N_2 + 10 Fe(OH)_3(s) + 18H^+ \tag{3}$$

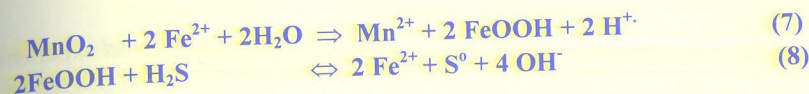When one examines the suggested model of Murray et al. [43], it is not a closed redox cycle since it needs constant input of NO_3 into the redox layer to oxidise all the reduced species diffusing into suboxic zone. One important output of theses reactions is that, under steady-state conditions, no new nitrogen would reach the euphotic zone from deeper layer, and hence the sinking flux of particulate organic nitrogen, must be sustained by the riverine and atmospheric inputs. However, the constant loss of oxidised nitrogen species through denitrification will lead, in long-term, the erosion and depletion of nitracline and thus the upward rising of sulfidic layer boundary, unless there is constant inputs from surrounding water masses through isopycnal mixing.

Luther et al [56] have suggested two thermodynamically favourable reactions between manganese and nitrogen species: the first one is the reduction of NO_3^- to N_2 through the oxidation of $Mn(II)$ to $MnO_2(s)$ (rxn 4), the second one is the oxidation of $Mn(II)$ in the presence of O_2 to $MnO_2(s)$ (rxn 5) which oxidises NH_4^+ and organic nitrogen to N_2 (rxn 6). Mass-balance calculations show that the oxidation of NH_4 and organic-nitrogen by MnO_2 may be the dominant process producing N_2 in Mn-rich continental margin sediments. Above pH 6.8, the reaction between $Fe(III)$ species and NH_4^+ to form N_2 was shown to be thermodynamically unfavourable [56]. On the other hand, Rozanov [57] has stated that oxygen is the main and direct oxidant of all reduced species diffusing from the anoxic layer in the suboxic zone.
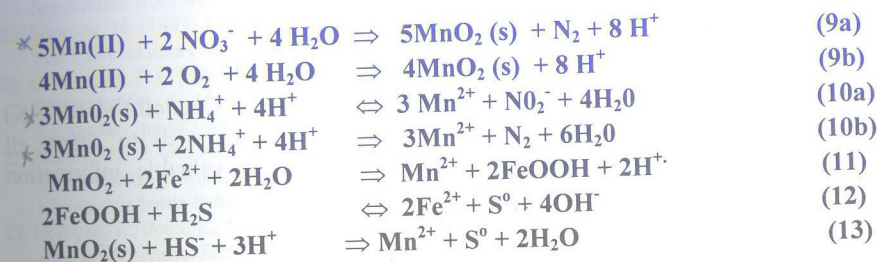
$$5 Mn^{2+} + 2 NO_3^- + 4 H_2O \Rightarrow 5 MnO_2 + N_2 + 8 H^+ \tag{4}$$

$$2 Mn^{2+} + 4 OH^- + O_2 \Rightarrow 2 MnO_2 + 2 H_2O \tag{5}$$

$$2 NH_3 + 2 MnO_2^- + 6 H^+ \Leftrightarrow 3 Mn^{2+} + N_2 + 6 H_2O \tag{6}$$
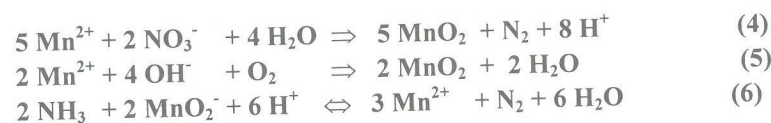
NO_2 maximum ($\sigma_t = 15.85$) was shown almost always to coincide with the zone of denitrification and with the zone of Particulate Mn maximum ($\sigma_t = 15.85$) [43]. Coincidence of Mn-Oxide maximum surface with that of NO_2, and positioning of particulate manganese layer between the layer of NO_3 minimum, suboxic levels of DO, and particulate Fe oxides suggest that particulate manganese oxide couples the redox processes in the upper layer of the suboxic zone with those in the lower layer by carrying the oxidation potential of nitrate and oxygen to the lower section of SOZ where ammonia is oxidised to N_2 and/or to NO_2 plus reduces NO_3 to NO_2 and/or N_2 while itself is oxidised. On the other hand, it was shown that $Fe(II)$ in the form of pyrite reduce MnO_2 rapidly (rxn 7) to form iron(hydr)oxides, which in turn oxidises H_2S to S^o and $S_2O_3^=$ (rxn 8) [58, 59]. Particulate manganese is also suggested to be involved in the oxidation of hydrogen sulfide by Nealson et al. [60] (rxn 13).

$$MnO_2 + 2 Fe^{2+} + 2H_2O \Rightarrow Mn^{2+} + 2 FeOOH + 2 H^+ \tag{7}$$

$$2FeOOH + H_2S \quad\Leftrightarrow\quad 2 Fe^{2+} + S^o + 4 OH^- \tag{8}$$

Field studies and surveys suggested that NH_4 is oxidised basically by the particulate MnO_2, probably, to N_2 or NO_2. Observed decrease in the $Mn(II)$ concentration within the oxygenated water layers (see Fig. 8) is proposed to be due to the oxidation of $Mn(II)$ back to $MnO_2(s)$ by oxygen, which in turn oxidises NH_4^+ to N_2 or NO_2, and indirectly the H_2S by coupling with iron oxidation.

By considering the reaction types suggested by different researchers, the following reaction schemes are suggested as possible redox reactions within the oxic/suboxic/anoxic interfaces. In the given order, particulate manganese plays a key role and acts as an electron carrier, or a catalyst, for the electrons given by O_2 and NO_3^- to the NH_4^+ and H_2S diffusing from the anoxic layer.

$$5Mn(II) + 2 NO_3^- + 4 H_2O \Rightarrow 5MnO_2 (s) + N_2 + 8 H^+ \tag{9a}$$

$$4Mn(II) + 2 O_2 + 4 H_2O \Rightarrow 4MnO_2 (s) + 8 H^+ \tag{9b}$$

$$3MnO_2(s) + NH_4^+ + 4H^+ \Leftrightarrow 3 Mn^{2+} + NO_2^- + 4H_2O \tag{10a}$$

$$3MnO_2 (s) + 2NH_4^+ + 4H^+ \Rightarrow 3Mn^{2+} + N_2 + 6H_2O \tag{10b}$$

$$MnO_2 + 2Fe^{2+} + 2H_2O \Rightarrow Mn^{2+} + 2FeOOH + 2H^+ \tag{11}$$

$$2FeOOH + H_2S \Leftrightarrow 2Fe^{2+} + S^o + 4OH^- \tag{12}$$

$$MnO_2(s) + HS^- + 3H^+ \Rightarrow Mn^{2+} + S^o + 2H_2O \tag{13}$$

4. Conclusions and Suggestions for Future Studies

The chronology of the catastrophic events related to the ecological deteriorations in the basin during the last 2-3 decades in the Black Sea can be summarised as;

a - Substantial increase in annual nutrient loads (N,P) even though the river discharges has been reduced on contrary to that observed for silicate load.

b - Changes in the relative proportions of nutrient elements within the photic layer have induced a shift from regular late winter-early spring and autumn blooms to late-spring-early summer blooms with extended periods and remarkable changes in the taxonomic composition of bloom-producing planktonic species.

c - Collapse of the Black Sea pelagic and benthic ecosystems has been followed by a decrease in relative abundance of diatoms, and an increase in the low-food value planktons, especially dinoflagellates during 1980-1990 period [20, 62, 63]. Formation of large hypoxic areas was recorded in 1973 on NW shelf which later became frequent due to the increased sedimentation of organic matter produced in the photic layer or introduced from land-based sources.

d - These changes, together with the invasion by opportunistic organisms such as *Mnemiopsis leidyi* have put additional stress on the ecosystem of the Black Sea which induced drastic changes in the taxonomic composition of the zooplankton species which

were serving as food for the fish larvae. Thus a detectable decrease has experienced in fish stocks and catches in conjunction with the reductions in the diets of fish larvae.

e - modifications of the organic matter cycle within the upper layer of the water column have induced changes in the vertical distributions of the biochemically active elements which were detected as an upward expansion of oxic/anoxic interface with respect to density surfaces. Nearly two-fold increase in the nitrate content of the oxycline, detectable decrease in that of silicate, and removal of ammonia which was at detectable levels in 1960s were the overall outcome of all these modifications.

f- In coastal zones, removal of ammonia, hydrogen sulfide and dissolved iron(II) and manganese(II) are probably following biochemical cycles that differ from those in the interior of the basin as suggested by Murray et al. [43]. Therefore, manganese cycle and its impact on the distributions of reduced species diffusing into suboxic zone should be studied in future.

Acknowledgements

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