Alkalinity of the anoxic waters in the Western Black Sea

William T. Hiscock*, Frank J. Millero

Department MAC, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Cswy, Miami, FL 33149, USA

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Abstract

Measurements of total alkalinity and nutrients were made on samples from discrete depths, aboard the R/V Knorr, May 2001 in the Black Sea. Determination of macronutrient concentrations permits inclusion of these minor bases in alkalinity calculations and thus improved determination of the carbonate system. The permanent pycnocline maintains vertical separation of the oxic, suboxic and anoxic waters of the Black Sea. Results show an apparent excess in alkalinity and/or deficit in hydrogen sulfide from the stoichiometric ratio predicted from the sequential oxidation of Redfield organic matter by sulfate in the anoxic waters near the center of the western gyre. The lateral ventilation of the main pycnocline by Bosporus plume waters is responsible for consuming or removing sulfide from the anoxic zone. The removal of sulfide via intrusion of oxygen-enriched waters and generation of alkalinity and total inorganic carbon dioxide via dissolution of calcium carbonate results in differing stoichiometry between the upper and lower anoxic zones in the center of the western gyre. Changes in the distribution of nutrients and hydrogen sulfide are due to the oxidation of particulate organic matter apparently due to increased productivity in surface waters.

Keywords: Black Sea; Anoxic basin; Macronutrients; Biogeochemical cycle; Anoxic/oxic zonation

1. Introduction

The Black Sea is a residual basin of the ancient Tethys Sea; its present form is hypothesized to have emerged about 58 million years ago when structural upheavals in Anatolia split off the Caspian basin from the Mediterranean (Ryan et al., 1997). During the last glacial period, the Black Sea was a low salinity lake. About 7500 years ago (Ryan et al., 1997) saline water from the Mediterranean entered the Black Sea through the Bosporus Strait as a result of the rise in global sea level. The influx of saline waters led to a density stratification of the basin, with depletion of oxygen and development of sulfide in the deep water. Salinity gradually increased Black Sea until some 3000 years ago when the existing vertical salinity gradient became established (Deuser, 1974; Glenn and Arthur, 1985). At present, nearly 87% of the Black Sea waters are anoxic and contain high levels of sulfide.

A permanent halocline at a depth of 100–200 m separates the brackish, oxygenated surface waters from the saline, sulfide-rich deep waters (Sorokin, 1983; Kempe et al., 1990; Lyons et al., 1993), acting as a natural barrier and inhibiting vertical fluxes. A suboxic zone with undetectable levels of oxygen and

*Corresponding author. Tel.: 305 421 4710; fax: 205 421 4144.
E-mail addresses: whiscock@rsmas.miami.edu (W.T. Hiscock), fmillero@rsmas.miami.edu (F.J. Millero).

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hydrogen sulfide (H$_2$S) in the center of the Black Sea (Murray et al., 1989) further inhibits the downward flux of oxygen and all other advective and diffusive processes allowing interaction between the oxic/anoxic zones. The onset of hydrogen sulfide, on average, coincides with the permanent halocline at $\sigma_t \sim 16.2$. Due to internal waves and long-term changes in mean circulation, the actual depth of the onset of H$_2$S varies both spatially and temporally (Shaffer, 1986; Kempe et al., 1990; Lyons et al., 1993). However, there has been little change in the onset of H$_2$S in relation to density (Konovalov et al., 1999; Konovalov and Murray, 2001), despite the dramatic and well-documented changes observed at various levels of the Black Sea ecosystem (Gomoiu, 1992; Mee, 1992; Zaitsev, 1993; Bologa et al., 1995; Cociasu et al., 1996, 1997; Leppakoski and Mihnea, 1996). The Black Sea has evolved from a highly biodiverse ecosystem, rich in biological resources, to a low biodiversity ecosystem (Zaitsev and Mamaev, 1997). The changes have resulted from the intensive eutrophication of the ecosystem caused by anthropogenic perturbations in both the Black Sea waters and the drainage basins of its major supplying rivers (Mee, 1992; Mutlu et al., 1994; Leppakoski and Mihnea, 1996).

The sharp salinity gradient of the main pycnocline is maintained by the freshwater inflow in the surface layer from rain and rivers and the saline waters flowing in from the Bosporus Strait. The warm saline waters intruding the Black Sea are connected to the distant waters of the Atlantic Ocean by the succession of the narrow and shallow Bosporus Strait and Sea of Marmara, Dardanelles, Aegean Sea and the Mediterranean Sea (Fig. 1). All deep water in the Black Sea forms by mixing between the Bosporus outflow and overlying cold intermediate water (Cold Intermediate Layer (CIL)) (Murray et al., 1991). The residence time of the deep water with respect to this Bosporus Plume has been estimated from 387 (Murray et al., 1991) to about 2500 years (Ostlund and Dyrssen, 1986; Boudreau and LeBlond, 1989). The Bosporus is a two-layer system, carrying about 175 km$^3$ yr$^{-1}$ saline water ($S \sim 34$) from the Mediterranean to the Black Sea along the bottom and returning about 350 km$^3$ yr$^{-1}$ of low salinity water ($S \sim 18$) in the upper layer. The intrusions of Bosporus plume waters can be traced to a depth of 500–700 m (Murray et al., 1991; Oguz and Rozman, 1991; Ozsoy et al., 1991) and provide lateral injections of oxygen and other dissolved substances into the main pycnocline (Buesseler et al., 1991). The lateral ventilation of the main pycnocline dramatically affects the redox budget and results in the oxidation of H$_2$S (Konovalov et al., 2003).

The Black Sea environment provides a natural laboratory to investigate nutrient regeneration and respiratory processes in an anoxic system (Brewer and Murray, 1973; Smethie, 1987). In this paper, carbonate and nutrient measurements are reported from the 2001 Black Sea Expedition on the R/V Knorr and present new carbonate (pH, total alkalinity (TA) and total inorganic carbon dioxide (TCO$_2$)) and nutrient ($\text{PO}_4^{3-}, \text{Si(OH)}_4, \text{NO}_3^-, \text{NH}_4^+, \text{H}_2\text{S}$) measurements made at sea on samples collected near the Bosporus. The most extensive study to date of the carbonate system in the Black Sea (Goyet et al., 1991) was based on collected fixed with HgCl$_2$ and analyzed in the shore laboratory.
The addition of Hg\textsuperscript{2+} minimizes changes in the TCO\textsubscript{2} in the sample, but also precipitates the H\textsubscript{2}S that contributes to the TA of the waters. The corrections for the loss of H\textsubscript{2}S are difficult to calculate and lead to some uncertainties in the carbonate system. The determination of macronutrient concentrations permits inclusion of these minor bases in alkalinity calculations and thus an improved determination of the carbonate system. In addition, measurements near the Bosporus allow us to examine the effects of lateral intrusions of oxygen-enriched waters on the stoichiometry of the chemical reactions in the suboxic and anoxic waters. The Black Sea shows a dramatic range of chemical expression, and this investigation details the carbonate alkalinity (CA), total inorganic carbon and macronutrient distributions, across the interface, between (suboxic) and within the anoxic and oxic layers of the water column.

2. Materials and methods

Measurement of total alkalinity and nutrient parameters occurred aboard R/V Knorr, 21–31 May 2001. Samples were collected by hydrocasts throughout the water column using a rosette system with 10-L Niskin bottles. Repeat casts provided detailed sampling across the oxic/anoxic interface. This study, Leg 1 of the 2001 Black Sea Expedition, focused on the southwestern portion of the Black Sea, adjacent to the shallow Bosporus Strait. In total, 44 casts from 10 stations were sampled across the oxic/anoxic interface and in the deep waters (Fig. 1). Samples were drawn from the Niskin bottles into 500-mL borosilicate flasks using silicone tubing that fit over the petcock. Bottles were rinsed a minimum of two times and filled from the bottom, to avoid bubbles. Sample bottles were sealed with glass stoppers and Apezion\textsuperscript{R} grease and stored at room temperature for a maximum of seven hours. Periodically duplicate samples were drawn. Data obtained includes depth profiles of hydrographic properties, potentiometric pH\textsubscript{SWS}, total alkalinity, and the nutrient variables: silicic acid, phosphate, nitrate, ammonia and hydrogen sulfide. Hydrographic properties for these samples are tabulated in Appendix A. All cruise tracks, station locations, participants and data (hydrographic, oxygen/sulfide, nutrients) are available on the cruise web site at: www.ocean.washington.edu/cruises/Knorr2001.

2.1. Macronutrients

Phosphate (PO\textsubscript{4}\textsuperscript{3−}), silicic acid (Si(OH))\textsubscript{4}, nitrate NO\textsubscript{3}\textsuperscript{−}, nitrite NO\textsubscript{2}\textsuperscript{−}, ammonia (NH\textsubscript{3})\textsuperscript{+} and hydrogen sulfide (H\textsubscript{2}S) were measured utilizing novel liquid core waveguides (LCW). The colorimetric methods of Armstrong et al. (1967) and Bernhardt and Wilhelms (1967) were optimized for continuous flow analysis, and reaction products were heated to \(\sim 55^\circ\text{C}\) to enhance the color development. The automated colorimetric method for the analysis of hydrogen sulfide was similar to the method developed and investigated by Cline (1969). Absorbance measurements by individual Ocean Optics Spectrophotometers (S2000) were performed in custom length Teflon AF-2400 (Dupont) LCW. The range of linear response desired for the analysis of inorganic nutrient concentrations was customized for work in the high concentrations and the oxic/anoxic environments of the Black Sea.

Although sulfide exists predominately as ionized HS\textsuperscript{−} in seawater (pH\textsubscript{SWS} 7–8), it is discussed here as the total concentration of hydrogen sulfide and denoted as H\textsubscript{2}S. The interference of high H\textsubscript{2}S concentrations with measurement of phosphate, silicic acid and nitrate were overcome by sparging an acidified sample with nitrogen gas from a Balston N\textsubscript{2} generator. The acidified sample remaining after the alkalinity determination was utilized and a correction factor (~1%) was made for the dilution by hydrochloric acid. Secondly, the titrated sample was pre-equilibrated to a temperature of 25°C. Samples suspected of containing H\textsubscript{2}S were not analyzed for nitrate because H\textsubscript{2}S precipitates in the copperized cadmium reductor. Nitrite concentrations were not analyzed separately due to the uniformly low concentrations (<1.0 \(\mu\text{mol kg}^{-1}\)) found in previous investigations (Friederich et al., 1990; Codispoti et al., 1991). The sum of nitrite and nitrate were analyzed simultaneously, discussed here as the sum of nitrate and nitrite and hereinafter referred to as NO\textsubscript{3}\textsuperscript{−}, unless otherwise specified. The PO\textsubscript{4}\textsuperscript{3−} reagent potassium antimony tartrate \((K(SbO)C_4H_4O_6)\) has a known H\textsubscript{2}S interference. To minimize the interference of potassium antimony tartrate and H\textsubscript{2}S, the concentration of potassium antimony tartrate was increased. Samples from the deep anoxic waters with high concentrations of nutrients were diluted allowing spectrophotometric measurements to be performed over a smaller linear dynamic range. The detection limits for the measured values were: \(\pm 2.0 \mu\text{mol kg}^{-1}\) at low levels.
(<100 μmol kg⁻¹) and ±5.0 μmol kg⁻¹ at high levels (<350 μmol kg⁻¹) for Si(OH)₄; ±0.3 μmol kg⁻¹ at low levels (<25 μmol kg⁻¹) and ±1.3 μmol kg⁻¹ at high levels (<50 μmol kg⁻¹) for NH₄⁺; ±1.0 μmol kg⁻¹ at low levels (<150 μmol kg⁻¹) and ±7.5 μmol kg⁻¹ at high levels (<500 μmol kg⁻¹) for H₂S; ±0.07 μmol kg⁻¹ (<10 μmol kg⁻¹) for PO₄³⁻; and ±3.4 μmol kg⁻¹ (<20 μmol kg⁻¹) for NO₃⁻.

2.2. pH and total alkalinity

The total alkalinity of seawater (TA) was evaluated from the proton balance at the alkalinity equivalence point, pHeq = 4.5, and zero ionic strength in 1 kg of sample, utilizing a multi-point hydrochloric acid titration with seawater according to the definition of alkalinity of Dickson (1981). A program uses a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TA, TCO₂, pK₆⁺ and pHSWS from the potentiometric titration data (Millero et al., 1993). Samples containing high H₂S concentrations were examined first to prevent atmospheric contamination of the sample. The accuracy and precision of the titration system was examined throughout the cruise by making titrations on Certified Reference Material (CRM-Batch 38), and the measured values of TA agreed to ±2 μmol kg⁻¹. The values of TCO₂ were calculated from pHSWS and TA using the constants of Mehrbach et al. (1973) as reformulated by Dickson and Millero (1987). They should be reliable to ±3 μmol kg⁻¹.

3. Results and discussion

The thermohaline structure of the Black Sea is a defining characteristic and unique in comparison to its typical oceanic counterparts. The vertical structure is associated to the distribution of properties and processes in the Black Sea. The physical and chemical structure of the water column at the center of the western gyre is best described in terms of sigma-t (σt) values; typical distributions are depicted in Fig. 2. The salinity of the surface waters in the Black Sea is approximately half of the open-ocean water and similar in chemical composition (Goyet et al., 1991). A marked increase in salinity, up to 21, occurs at depths of ~50–170 m, below which the salinity increase is much more gradual. The increase in salinity is the main control on the pycnocline. There is a prominent temperature minimum characteristic of the CIL that occurs in the main pycnocline centered at σt ~14.5. The oxycline below the base of the oxic layer is a region of decreasing oxygen concentrations occurring between σt ~14.4–14.6 and σt ~15.6–15.9. Below the oxycline and the oxic layer is a zone of ~40 m, which is suboxic and has a lower boundary at σt ~16.2. Oxygen and hydrogen sulfide are both below limits of detection in the suboxic zone. The deepest parts of the Black Sea are characterized by T = 8.5–9.0 °C and S = 22.3, and are in steady-state on a time scale of centuries (Konовалov and Murray, 2001). The onset of H₂S and the upper boundary of the anoxic layer are generally accepted to occur at σt ~16.2 (Konovalov and Murray, 2001). Previous data confirms that the density of

Fig. 2. Temperature, salinity, oxygen and hydrogen sulfide versus density (σt) for selected hydrocasts near the center of the western gyre. The CIL is bounded by 8 °C isotherms, dashed vertical line. Its core is located at 2.5 < σt < 14.6. The main pycnocline is located between 2.5 < σt < 14.4 and 14.5 and is separated into upper and lower parts at σt ~15.5. The water column is divided vertically into three layers: oxic, suboxic, and anoxic. Within the oxic layer is the oxycline, which is located between 2.5 < σt < 14.4 and 14.5. The suboxic layer extends from about 15.6 to 16.2. The upper boundary of the anoxic layer is at 2.5 < σt.
the onset of H$_2$S has varied little over time (Vinogradov, 1991; Tugrul et al., 1992). Small fluctuations in the actual depth of the oxic/anoxic interface, both spatially and temporally, have been observed on the time scale of a century (Konovalov et al., 1999; Glazer et al., 2006; Yakushev et al., 2006). The oscillation of the depth, but not density, of the oxic/anoxic interface results from internal waves, long-term changes in mean circulation and exchange (Shaffer, 1986; Kempe et al., 1990; Lyons et al., 1993).

Near the Bosporus, warm and saline Mediterranean waters flow from the Sea of Marmara and intrude into the western gyre of the Black Sea. The salinity and temperature increase in deep water of the Bosporus to 36.5 and 14.5°C, in the Bosporus (Fig. 3) The oxygen-enriched water flowing out of the Bosporus entrains water from the overlying CIL and is laterally injected into the oxic, suboxic and anoxic zones of the Black Sea (Murray et al., 1991; Konovalov et al., 2003). This lateral process effectively controls the residence time of the main pycnocline and the deepest waters. The depth of injection of the Bosporus plume into the main pycnocline and below the colder, less saline CIL is dependant upon the entrainment ratio (Buesseler et al., 1991; Murray et al., 1991; Ozsoy et al., 1995a,b; Samodurov and Ivanov, 1998; Lee et al., 2002). The core of the CIL is centered at $\sigma_t \sim 14.5$ and by definition bounded by 8°C isotherms (Konovalov and Murray, 2001). The intrusion of the Bosporus plume shortens the residence time for the layer of the main pycnocline to a few years (Unluata et al., 1990; Buesseler et al., 1991) compared to several hundred years for the deepest layer (Murray et al., 1991). A comparison of profiles of physical and chemical properties from the southwestern shelf and the center of the western gyre is shown in Fig. 4, which emphasizes the effect of lateral injection of the Bosporus plume on the oxic/anoxic interface. The upper boundary of the profiles of H$_2$S from the southwestern shelf region differs significantly from those in the center of the western gyre. At the center of the western gyre the onset of H$_2$S is shallow, $\sigma_t \approx 16.2$ and depth $\sim 110$ m, compared to the deeper onset of H$_2$S, $\sigma_t \approx 16.4$ and depth greater than 170 m, near the southwestern shelf. Temperature and salinity measurements on the southwestern shelf reveal lateral processes connecting the intrusions of the Bosporus plume waters, which are identified by their warm and saline anomalies (Ivanov and Samodurov, 2001; Konovalov et al., 2003). The lateral intrusions and ventilation are observed only on the southwestern shelf and result in small-scale isopycnal and cross-isopycnal variability compared to the center of the western gyre of the Black Sea. The influx of the Bosporus plume waters is evident throughout the main pycnocline (Konovalov et al., 2003).

### 3.1. Macronutrients and alkalinity results

A number of hydrocasts were made near the center of the western gyre, at Station 6 and stations nearby. The profiles of measured variables are plotted against density in Fig. 5 and systematically compared to the decadal time series presented by
Konovalov and Murray (2001). As found in the nearshore stations, the fluctuations in the oxic/anoxic interface are believed to be at a minimum in the center of the western gyre (Codispoti et al., 1991).

The phosphate profile has two maxima. The shallow maximum is due to the typical regenerative and respiratory processes in the oxic zone. The deeper maximum reflects complex scavenging and desorption of phosphate associated with Mn and Fe recycling in the suboxic and anoxic zones (Brewer and Murray, 1973; Shaffer, 1986). Under aerobic conditions, bacteria accumulate and store phosphate when excess dissolved phosphate is available. Upon depletion of oxygen the stored phosphate is utilized as an energy source and is eventually released by bacteria to the surrounding solution (Carlton and Wetzel, 1988; Gächter et al., 1988; Toerien et al., 1990; Gächter and Meyer, 1993).

Phosphate is also absorbed onto iron and/or manganese oxides in oxic waters and released below the interface due to the reduction of Fe(III) and Mn(IV) by H2S. The maximum phosphate concentrations in the deep anoxic water reach approximately 9.5 μmol kg⁻¹. Modest increases of phosphate concentrations may have occurred due to eutrophication of the Black Sea (Konovalov and Murray, 2001); however, this trend is ambiguous due to the scatter in the temporal data.

The sum of nitrate and nitrite (NO₃⁻) increases to a maximum at σᵣ ~15.4–15.7 as a result of oxidative regeneration in a narrow layer located just above the suboxic zone. There is a nitrite maxima near the lower boundary of the NO₃⁻ maximum, corresponding to a zone of denitrification (Murray et al., 2005). Samples suspected of containing H₂S (σᵣ > 16) were not analyzed for nitrate because H₂S precipitates in the copperized cadmium reductor. Profiles of NO₃⁻ are similar to previous measurements (Codispoti et al., 1991; Tugrul et al., 1992; Konovalov et al., 1997), although the concentrations of NO₃⁻ at the maximum are higher, ~13.5 μmol kg⁻¹. The higher NO₃⁻ concentrations may result from small changes in fluxes of particulate nitrogen (Konovalov and Murray, 2001). The removal of NO₃⁻ occurs by denitrification in the suboxic layers above σᵣ ~16.0 and before the onset of H₂S. Denitrification can be represented by

\[
(\text{CH}_2\text{O})_{10}\text{(NH}_3)_4\text{(H}_3\text{PO}_4) + 84.8\text{HNO}_3 \\
\rightarrow 106\text{CO}_2 + 42.2\text{N}_2 + 148.4\text{H}_2\text{O} + 16\text{NH}_3 + 3\text{H}_2\text{PO}_4.
\]

(1)

Kuypers et al. (2003) showed that anammox (NO₃⁻ + NH₄⁺ = N₂ + 2H₂O) may also be active in the Black Sea. NO₃⁻ and NH₄⁺ concentrations both go to zero in the suboxic layer at the same density layer with little overlap. Ammonia concentrations increase uniformly with depth from the oxic/anoxic interface and attain maximum values of approximately 125 μmol kg⁻¹. In the suboxic zone nitrate is used as an oxidant, but there is no concomitant increase in ammonia.

Silicic acid uptake occurs in the euphotic zone and dissolution occurs at depth, similar to the open ocean. Silicic acid concentrations increase more or less uniformly with depth from below the euphotic zone and attain a maximum value of approximately 340 μmol kg⁻¹. Hydrogen sulfide concentrations increase below σᵣ ~16.2 at the center of the western gyre, with concentrations increasing with depth.
to values as high as 465 µmol kg\(^{-1}\) in the bottom waters. The sulfate (SO\(_4^{2-}\)) is reduced to H\(_2\)S from the metabolic oxidation of particulate organic matter (POM) with the stoichiometry represented by (Richards, 1965)

\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53\text{SO}_4^{2-} \rightarrow 106\text{HCO}_3^- + 53\text{H}_2\text{S} + 16\text{NH}_3 + \text{H}_3\text{PO}_4.
\]

While the depth of the onset of H\(_2\)S has varied little, the maximum concentrations of H\(_2\)S have increased by \(\sim 65 \mu\text{mol kg}^{-1}\) since 1992. The maximum concentration for deep waters increased from \(\sim 400 \mu\text{mol kg}^{-1}\) in 1992 (Konovalov and Murray, 2001) to our maximum concentration of 465 µmol kg\(^{-1}\). The observed increases for macro-nutrients, hydrogen sulfide and carbon relative to earlier investigations may be due to increased
oxidation of POM. There has been increased nutrient and organic material flux from the major rivers to the Black Sea. As a result there has been increased nutrient concentrations in the main pycnocline, increased primary production (Stelmakh et al., 1998), and eutrophication and degradation of the marine ecosystem. This has presumably resulted in a corresponding increase in the flux of POM reaching the anoxic zone.

Total alkalinity decreases with depth from the surface to the \( \sigma_t \sim 14.0 \) and then increases to the sulfide interface at \( \sigma_t \sim 16.2 \). This increase correlates well with the increase in salinity, phosphate and silicic acid concentrations (Fig. 5). Below the oxic/anoxic interface, TA increases rapidly due to bacterial anaerobic respiration of organic matter to bicarbonate and simultaneous reduction of sulfate to hydrogen sulfide.

3.2. Calculations of \( CA \)

The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point according to the definition of total alkalinity as defined by Dickson (1981)

\[
TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-]
+ [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{Si(OH)}_3\text{O}^-]
+ [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+]_f - [\text{HSO}_4^-]
- [\text{HF}] - [\text{H}_3\text{PO}_4].
\] (3)

\( TA \) is the concentration of all the bases that accept \( \text{H}^+ \) when a titration is conducted to the carbonic acid endpoint. For most waters \([\text{HCO}_3^-] , [\text{CO}_3^{2-}] \) and \([\text{B(OH)}_4^-] \) are the most important bases; however, in the anoxic waters of the Black Sea, \([\text{HS}^-] \) and \([\text{NH}_3] \) make significant contributions to the total alkalinity. Therefore to calculate \( CA \), the contribution of the aforementioned bases as well as the concentrations of \([\text{HPO}_4^{2-}] , [\text{PO}_4^{3-}] \), \([\text{Si(OH)}_3\text{O}^-] \), \([\text{HSO}_4^-] \), \([\text{HF}] \) and \([\text{H}_3\text{PO}_4] \) are required. The values of \( \text{TCO}_2 \) were calculated based on the \( pH_{\text{SWS}} \) at 25°C, \( CA \) and salinity using the carbonate constants given by Mehrbach et al. (1973) as reformulated by Dickson and Millero (1987). The visual basic program developed by Pierrot (2002), which improved the functionality of the original “\( \text{CO}_2 \) System” basic program written by Lewis and Wallace (1998), was modified to include \([\text{HS}^-] \) and \([\text{NH}_3] \) in addition to \([\text{HPO}_4^{2-}] , [\text{PO}_4^{3-}] , [\text{Si(OH)}_3\text{O}^-] , [\text{HSO}_4^-] , [\text{HF}] \) and \([\text{H}_3\text{PO}_4] \). The dissociation constants needed to make these calculations were presented by Yao and Millero (1995) and Millero (1995). The \( CA \) is defined by

\[
CA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]
\] (4)

and Fig. 6 shows the calculated \( CA \) and \( \text{TCO}_2 \) in relation to the measured total alkalinity and \( pH_{\text{SWS}} \). Hydrogen sulfide makes the largest contribution of the minor bases to total alkalinity in anoxic waters.

3.3. Production of \( TA \) and \( \text{TCO}_2 \)

The measured values of \( TA \) and \( pH_{\text{SWS}} \) and calculated \( \text{TCO}_2 \) and \( CA \) versus density are plotted in Fig. 6. The values of \( TA \) in the oxic surface waters (\( \sim 3500 \mu\text{mol kg}^{-1} \)) are higher than typical
oceanic values as a result of the low salinity and high total alkalinity of river waters entering the Black Sea (Dyrssen, 1985, 1986). The variations in TA are small in comparison to the change in calculated TCO$_2$ concentrations above the oxic/anoxic interface. The increase of TCO$_2$ below the surface water is indicative of oxidation of organic material by oxygen below the photic zone. The increase in TCO$_2$ coincides with a decrease in pH$_{\text{SW}}$. The oxidative degradation or aerobic respiration of bacteria is restricted to the oxic layer, but mineralization of organic matter is not restricted solely to the oxic layer. After oxygen is depleted, bacteria use other oxidants in a stepwise progression based on the decreased energy yield from the reactions. The sequence of oxidants is nitrate (NO$_3^-$), manganese dioxide (MnO$_2$), iron oxides (e.g., FeOOH) and sulfate (SO$_4^{2-}$), which are reduced to ammonia (NH$_4^+$), nitrogen (N$_2$), nitrous oxide (N$_2$O), dissolved manganese (Mn$^{2+}$), iron (Fe$^{2+}$) and hydrogen sulfide (HS$^-$), respectively.

The increasing concentrations in both TA and TCO$_2$ in anoxic waters reflect the net effect of all oxidation-reduction reactions on the carbon and proton balances. The increase of CA indicates that natural oxidants are progressively used for the oxidation of organic material and production of CA. The normalized TA (NTA = TA/35/S) and normalized TCO$_2$ (NTCO$_2$ = TCO$_2$/35/S) in the bottom waters of the Black Sea are $\sim$6950 $\mu$mol kg$^{-1}$ for NTA and $\sim$7100 $\mu$mol kg$^{-1}$ for NTCO$_2$, about 3 times greater than the open-ocean values 2350 and 2050 $\mu$mol kg$^{-1}$. The increases of TA and TCO$_2$ in the anoxic layer are due to oxidation of organic material by sulfate reduction. Assuming the stoichiometry of Eq. (2), the relationships between TA and TCO$_2$ to H$_2$S concentrations give slopes of

$$\frac{\Delta \text{TA}}{\Delta \text{H}_2\text{S}} \approx \left(\frac{106 + 16 - 2}{53}\right) = 2.3,$$

$$\frac{\Delta \text{TCO}_2}{\Delta \text{H}_2\text{S}} \approx \left(\frac{106}{53}\right) = 2.0.$$  

The linear correlation between these properties corroborates that TA and TCO$_2$ increase proportional to hydrogen sulfide release (Fig. 7). The observed TA:H$_2$S slope is $2.65 \pm 0.01$, which is greater than the theoretical value of 2.3. The difference between these values indicates there is either a deficit of sulfide and/or an excess of TA. Dyrssen (1985) suggested a small fraction of hydrogen sulfide is removed by iron sulfide without altering TA and TCO$_2$. In addition to sulfate reduction, bacterial formation of ammonia affects the proton balance and contributes to the increase of TA and TCO$_2$ in the anoxic, sulfide containing waters.
waters. Furthermore, Eq. (3) for total alkalinity does not take into account organic bases that may contribute to the alkalinity and thus the difference between the observed and theoretical ratios of TA:TCO₂. The nature of this organic fraction is still uncertain, but it has been suggested that the organic fraction consists of amino acids or humic substances. Since the true nature of the organic fraction has not been determined, there are still doubts about how it fits into the definition of alkalinity and how the data should be treated and normalized. The observed TCO₂:H₂S slope is 2.02±0.02, in agreement with the theoretical value of 2.0, indicating that the observed difference in the TA:H₂S represents a source in TA. The linear correlation between TA and TCO₂ in the anoxic waters shows a slope of TA:TCO₂ of 1.32±0.01, which is higher than the theoretical value of 1.13 and also suggests another contribution to the TA.

Values determined by Goyet et al. (1991) yielded an ratio of 3.05 for TA:H₂S (Table 1), which was higher than that found in this study. Elevated TA values could be due to the alkalinity generated by dissolution of CaCO₃ in the acidic CO₂-rich deep waters. The saturation coefficients of both calcite and aragonite \( \Omega_{\text{Cal}} \) and \( \Omega_{\text{Arg}} \) show under saturation at depth and support the hypothesis of dissolution of CaCO₃ (Fig. 8). The value of \( \Omega_{\text{Cal}} \) is less than 1 in

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**Table 1**

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<th>Model Black Sea 2001</th>
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<td></td>
<td>Anoxic⁵</td>
<td>Deep Anoxic⁵</td>
</tr>
<tr>
<td>TCO₂:H₂S</td>
<td>2.00</td>
<td>2.02±0.02</td>
</tr>
<tr>
<td>TA:H₂S</td>
<td>2.30</td>
<td>2.65±0.01</td>
</tr>
<tr>
<td>TA:TCO₂</td>
<td>1.13</td>
<td>1.32±0.01</td>
</tr>
<tr>
<td>PO₄³⁻:H₂S</td>
<td>0.019</td>
<td>0.011±0.001</td>
</tr>
<tr>
<td>NH₄⁺:H₂S</td>
<td>0.30</td>
<td>0.26±0.01</td>
</tr>
<tr>
<td>Si(OH)₄:H₂S</td>
<td>0.27b</td>
<td>0.53±0.01</td>
</tr>
<tr>
<td>C:N:P</td>
<td>106:16:1</td>
<td>190:25:1</td>
</tr>
<tr>
<td>Si:C:N</td>
<td>0.9:6:6:1⁶</td>
<td>2.0:7.7:1</td>
</tr>
</tbody>
</table>

⁵The stoichiometric ratios observed during the 2001 Black Sea Expedition are corrected for biases in the slope by calculating the geometric mean of Model I regressions of the variables with the axes reversed. Error values represent the standard error of the calculated slopes.

⁶Si:N for diatoms averages 0.90 in the open ocean Brzezinski (1985).

⁷Ratios for TCO₂ and TA to H₂S are from Goyet et al. (1991).


anoxic waters below $\sigma_t \sim 16.9$ (~400 m) and $\Omega_{Arg}$ is less than 1 in anoxic waters below $\sigma_t \sim 14.8$ (~60 m). The TA:H$_2$S ratio for this study is higher, TA:H$_2$S $= 2.78 \pm 0.06$, in the deep anoxic water below $\sigma_t \sim 17.1$ (~500 m) where calcite is under saturated and there is little influence from lateral influxes evident in the upper portion of the anoxic layer and main pycnocline. The TCO$_2$:H$_2$S ratio is also elevated in the deep anoxic water, TCO$_2$:H$_2$S $= 2.19 \pm 0.11$, and diverges from theory by approximately half of the divergence observed for the TA:H$_2$S ratio. The divergence in the TA:H$_2$S and TCO$_2$:H$_2$S ratios suggests dissolution of CaCO$_3$ in the deep anoxic waters. Goyet et al. (1991) relied solely on dissolution of CaCO$_3$ to explain their results. However, the difference between the anoxic water above and below $\sigma_t \sim 17.1$ (~500 m) indicates that lateral injection of oxygen rich Bosporus plume waters may produce the observed differences from the theoretical values. The lateral influx of oxygen (O$_2$) can directly affect the redox budget within the main pycnocline and upper portion of the anoxic layer, as shown in Konovalov and Murray (2001) (Fig. 4). Dramatic changes in the distribution of the main reduced redox species, H$_2$S, Mn$^{2+}$ and NH$_4^+$, were observed by Konovalov et al. (2003) to be a direct result of the lateral influx of O$_2$ associated with the Bosporus plume. Furthermore, the ratios of $\Delta$TA: $\Delta$H$_2$S are quite different depending on whether H$_2$S is oxidized by O$_2$ to sulfate (SO$_4^{2-}$), sulfite (SO$_3^{2-}$), thiosulfate (S$_2$O$_3^{2-}$) or elemental sulfur (S$^0$ or S$_8$). The change in $\Delta$TA: $\Delta$H$_2$S depends on the form of sulfur during sulfide oxidation and the ratios for SO$_2^{2-}$ $= 2$, SO$_3^{2-}$ $= 2$, S$_2$O$_3^{2-}$ $= 1$ and S$^0$ $= 0$. If sulfide is oxidized to SO$_4^{2-}$, SO$_3^{2-}$ or S$_2$O$_3^{2-}$ the total alkalinity would be lowered, whereas if the product is elemental sulfur or polysulfides the TA and TCO$_2$ would be unchanged but H$_2$S would be removed. In addition to direct oxidation of H$_2$S, Konovalov et al. (2003) present further details about mechanisms coupling the manganese cycle with the sulfide-elemental sulfur–sulfate cycle. The process begins in the oxic layer where dissolved Mn$^{2+}$ is oxidized to particulate Mn(III, IV) which then sinks into the anoxic layer where manganese oxide (MnO$_2$) acts as an oxidant of H$_2$S (Tebo, 1991; Konovalov et al., 2003).

$$\text{MnO}_2 + \text{HS}^- + 3\text{H}^+ \rightarrow \text{Mn}^{2+} + S^0(\text{S}_8) + 2\text{H}_2\text{O}. \quad (8)$$

The Bosporus plume water introduces a lateral flux of O$_2$ with the potential to affect the basin-wide distribution of sulfide and consume as much as $\sim 70\%$ of the sulfide sink (Konovalov and Murray, 2001). Therefore, injection of the Bosporus plume could result in consumption of sulfide and thus elevated TA:H$_2$S and TCO$_2$:H$_2$S ratios in the upper anoxic layer. Meanwhile, the classical generator of oceanic alkalinity contributes to the observed divergence of TA:H$_2$S and TCO$_2$:H$_2$S ratios for the deep anoxic waters.

The earlier results of Goyet et al. (1991) are less reliable due to the addition of mercuric chloride (HgCl$_2$) to the TA samples, which resulted in removal of H$_2$S from the samples. The alkalinity of the sample changes due to precipitation of mercuric sulfide (HgS) by the following reaction:

$$\text{HgCl}_2 + \text{H}_2\text{S} \rightarrow \text{HgS} + 2\text{H}^+ + 2\text{Cl}^-.$$ \quad (9)

The change in alkalinity for the anoxic deep waters due to this effect may represent up to 20% of the total alkalinity. In addition, Goyet et al. (1991) did not account for injection of Bosporus plume waters.

### 3.4. Stoichiometry and macronutrients

The stoichiometry of chemical reactions in oxic environments is frequently examined (e.g., Steinberg et al., 1998; Hiscock and Millero, 2005), using the Redfield ratio (Redfield et al., 1963). However, the stoichiometry of chemical reactions in the anoxic environment of the Black Sea and other anoxic basins utilizes the Richards Eq. (2) (Goyet et al., 1991; Zhang and Millero, 1993; Yao and Millero, 1995). The stoichiometric ratios for decomposition of organic matter and the associated release of nutrients during sulfate reduction can be used to examine concentrations of carbon (C), nitrogen (N), phosphorous (P), and sulfur (S) in this anoxic system, Table 1. The theoretical ratios from Eq. (2) are PO$_4^{3-}$: H$_2$S $= 0.019$ and NH$_4^+$: H$_2$S $= 0.30$. The ratio of Si(OH)$_4$ : H$_2$S depends on the relative abundance of silaceous phytoplankton. The stoichiometric ratios have been expanded to include silica (Si) and are typically referred to as the Redfield/Brzezinski proportion; Si:C:N $= 0.9:6.6:1$ (Brzezinski, 1985). Using the Richards equation yields a Si(OH)$_4$ : H$_2$S ratio of 0.27. The Si:N ratio in the open ocean ranges from 0.41 to 4.38 (Brzezinski, 1985; Dunne et al., 1999), and the resulting range for the ratio of Si(OH)$_4$ : H$_2$S is 0.12–1.3.
The stoichiometric values are given in Table 1, and the ratios of macronutrients to hydrogen sulfide versus depth are plotted in Fig. 9. The macronutrients; PO$_3^-$, NH$_4^+$ and Si(OH)$_4$, and the carbonate variables; TA and TCO$_2$, are corrected for initial values at the onset of the anoxic layer in Fig. 9. The vertical distribution of the values of macronutrients to hydrogen sulfide illustrates the variability associated with the upper portion of the anoxic layer (<500 m) as compared to the deeper anoxic layer (>500 m). In the deep anoxic waters, below $\sigma_t$ ~17.1 (~500 m), the macronutrient to hydrogen sulfide ratios are constant, as compared to the higher values found in the upper portion of the anoxic layer. The source of PO$_3^-$, NH$_4^+$ and Si(OH)$_4$ in the anoxic layer of the Black Sea is respiration of POM. A deficit of sulfide would result in elevated macronutrient to hydrogen sulfide ratios, and such a deficit may have resulted from removal of sulfide as a result of the lateral injection of oxygen-enriched waters of the Bosporus plume.

Macronutrients in the anoxic waters are plotted versus H$_2$S in Fig. 10. The observed ratios in the deep anoxic waters were PO$_3^-$ : H$_2$S = 0.017±0.001, NH$_4^+$ : H$_2$S = 0.28 ± 0.01 and Si(OH)$_4$ : H$_2$S = 0.41 ± 0.01 (Table 1). The fit for phosphate versus H$_2$S in the anoxic waters did not include data near the interface where phosphate is affected by the adsorption and desorption onto reactive Fe and Mn oxyhydroxides. The removal of H$_2$S in the upper portion of the anoxic layer due to injection of O$_2$ results in anomalies that prohibit fitting data throughout the entire anoxic layer. In addition, precipitation of hydrogen sulfide in the form of FeS$_2$ results in the removal of H$_2$S from the upper portion of the anoxic layer (Muramoto et al., 1991). The removal of H$_2$S in the upper portion of the anoxic layer by oxidation or sulfide formation results in particulate S$_8$ and FeS that can be transported to the deep waters. The theoretical ratio of Si(OH)$_4$ : H$_2$S from remineralization of biogenic silica (0.27) is lower than the observed value of 0.41 ± 0.01. The high observed ratios may indicate that silicic acid production is proportional to production of hydrogen sulfide.

The C:N:P ratios for the deep anoxic waters yield a stoichiometry of 130:16:1 (Table 1) for organic matter and a revised version of the Richards Eq. (2) can be given as

$$
(\text{CH}_2\text{O})_{130}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 65\text{SO}_4^{2-} \rightarrow 130\text{HCO}_3^- + 65\text{H}_2\text{S} + 16\text{NH}_3 + \text{H}_3\text{PO}_4.
$$

The values of Redfield/Brzezinski proportion yields Si:C:N ratio = 1.5:7.9:1, and values of the C:N ratio in POM for the Black Sea range from 7.5 to 9.6 (Burlakova et al., 1997; Yilmaz et al., 1998; Coban-Yildiz et al., 2006).

![Fig. 9. Ratio of phosphate, ammonia and silicic acid concentrations to hydrogen sulfide concentrations versus depth for the anoxic waters of the Black Sea. The dashed vertical lines represent the theoretical ratios for PO$_3^-$ : H$_2$S, NH$_4^+$ : H$_2$S, and Si(OH)$_4$ : H$_2$S. The solid horizontal line represents a depth of 500 m and $\sigma_t$~17.1.](image-url)
4. Conclusions

The inclusion of minor bases: borate, ammonia, phosphate, silicate and hydrogen sulfide has improved determination of the carbonate system in the oxic/anoxic waters of the Black Sea. The observed distribution of macronutrients, hydrogen sulfide and carbon has changed with respect to earlier investigations. The increase may be due to eutrophication and an increase in the primary production of the surface waters and increased export of POM into the anoxic region (Stelmakh et al., 1998). The lateral ventilation of the main pycnocline by Bosporus plume may be responsible for decreasing the concentrations of hydrogen sulfide in the anoxic zone. This sulfide removal may result in variation in the stoichiometric ratios between the upper and lower anoxic zones.

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References


Fig. 10. Silicic acid, ammonia and phosphate versus hydrogen sulfide in the anoxic waters. The dashed vertical lines represent isopycnal surfaces. The linear fits are corrected for biases in the slope by calculating the geometric mean of Model I regressions of the variables with axes reversed, results are in Table 1.


