Aquatic Geochemistry **5:** 13–27, 1999.

Climatic and Anthropogenic Variations in the Sulfide Distribution in the Black Sea

S. K. KONOVALOV, V. N. EREMEEV, A. M. SUVOROV, A. KH. KHALIULIN and E. A. GODIN
Marine Hydrophysical Institute, National Academy of Sciences of Ukraine, Kapitanskaya St., 2a, Sevastopol 335000, Crimea, Ukraine; e-mail: sergey@alpha.mhi.iuf.net, ksk123@ukrcom.sebastopol.ua

(Received 1 December 1997; accepted 16 July 1998)

Abstract. Information on the depth of the sulfide onset in the Black Sea has been analyzed for the period 1910–1995. Correlation between the depth of the sulfide onset and the density structure of the layer of the main pycnocline is significant for the entire period covered. Correlation coefficients (R) between the depth of the sulfide onset and the position of isopycnal surfaces in the layer of the main pycnocline vary, on average, 0.71–0.88. The average value of density (σ_t) at the depth of sulfide onset, defined as a sulfide concentration equal to 3 μM, is close to 16.17. Oscillations in the average depth of the sulfide onset range over 24 m and indicate that a steady-state trend does not occur. The period of these oscillations may occur over a century timescale. The dataset for the period 1960–1995 has been used to analyze temporal variations in concentrations of sulfide inside the anoxic zone of the Black Sea. The results of isopycnal analysis demonstrate that possible temporal variations in the average position of sulfide onset versus density (σ_t) scale do not exceed 0.15, which is close to the limit of uncertainties for data obtained before 1988. In contrast, a prominent increase in sulfide concentration, as well as nutrient levels, within the anoxic zone is shown and is related to anthropogenic impact.

1. Introduction

The presence of a sharp permanent pycnocline (halocline) in the Black Sea water column is the main reason for weak ventilation of deep waters and for the permanent presence of sulfide below 100–200 m depth (Skopintsev, 1975). The concentration of sulfide increases with depth and is as high as 350-400 μM near the bottom. No other biological forms, beside sulfate reducing bacteria, can survive under these conditions. The future of the Black Sea depends on the balance of oxic and anoxic waters. For this reason the questions of temporal variation in sulfide distribution has taken an important place in the long history of Black Sea oceanographic investigations, that started with the first publication in 1890 (Andrusov, 1890). These questions are even more important now because anthropogenic impact is so strong, is easily observed and is well documented for the Black Sea environment (Mee, 1992; Cociasu et al., 1996).

Temporal variations in the position of sulfide onset were discussed intensively in the 1980s. The possibility of fast shoaling of the oxic/anoxic interface was declared in a number of publications. Faschuk et al. (1986) discussed the upward rise of the sulfide onset separately from changes in other properties. However, Murray et al. (1989), who compared the data of R/V ATLANTIS (1969) and R/V KNORR (1988), demonstrated an upward shift of the oxic/anoxic transition zone that was attributed to temporal changes in both the physical and chemical structure of the Black Sea. Interestingly, this possible upward rise of the sulfide containing waters and other changes in the Black Sea environment were primarily attributed to the results of human activity, and not to any climatic changes. The idea of fast shoaling of the sulfide onset was first argued by Bezborodov et al. (1991) and Vinogradov et al (1991). Bezborodov et al (1991, 1993) compared the results of different decades (1920s and 1980s), and they demonstrated the absence of a permanent trend in the depth of the first appearance of sulfide in Black Sea waters as well as a wide interval of seasonal and interannual variations in the depth of sulfide onset. These variations can differ greatly from one location to another. Thus, Bezborodov and Eremeev (1993) used the data of 20 cruises from 1982 to 1992 to demonstrate the shallowest position (95–110 m) of the sulfide onset for the central part of the main cyclonic gyres and the deepest position (150–190 m) for the region of anti-cyclonic gyres at the periphery of the deep part of the sea. Their analysis indicated spatial variations can reach 100 m. This value is normally higher for spring during an annual cycle. Temporal variations in the depth of the sulfide onset for individual locations on multiannual, seasonal and mesoscales are as much as 5–25, 10–30 and 15–50 m respectively. The difference in the depth of the sulfide onset between the 1920s and 1980s (Bezborodov and Eremeev, 1993) does not exceed 20 m for the central part of the sea, and 50 m for individual locations, these data are close to the range of temporal variations observed in the 1980s.

In contrast to Bezborodov et al. (1991, 1993) and Vinogradov et al. (1991), Tugrul et al. (1992) analyzed possible variations in the position of the sulfide onset versus density scale rather than depth. They analyzed the data of R/V ATLANTIS (1969), R/V KNORR (1988) and R/V BILIM (1991), and showed temporal stability of the sulfide onset with density for at least a 20-year period (Tugrul et al., 1992).

The possible temporal variations in distribution of sulfide have resulted not only in the a number of important conclusions, but in several interesting questions:

- Are there any temporal variations in the average depth of sulfide onset over a century timescale, even though the depth of sulfide onset for individual locations is mainly a function of changes in the intensity of water dynamics on meso- and seasonal scales (Bezborodov and Eremeev, 1991)?
- Is correlation between the position of sulfide onset and the density structure of water significant for a longer period or, is this true for only the last 20–30 years (Tugrul et al., 1992)?

- Is the sulfide distribution inside the anoxic zone stable, as declared for the thermohaline structure of the deep layer of the Black Sea waters (Skopintsev, 1975)?

2. Material and Results

Two datasets of different type have been prepared to answer the above questions on the possible climatic and anthropogenic variations in the sulfide distribution in the Black Sea. One of them contains all available information on sulfide distributions, along with temperature and salinity data, in the Black Sea from 1910–1995. The main sources of this information are the following institutions and cruise-based datasets:

- Marine Hydrophysical Institute (MHI), National Academy of Sciences of Ukraine;
- Institute of Biology of Southern Seas, National Academy of Sciences of Ukraine;
- State Oceanographic Institution;
- Southern Institution of Fishery;
- Hydrographic Service of the Black Sea Navy ;
- Oceanographic Data Center;
- Archives of the Office Hydrography;
- Institute of Oceanology of Russian Academy of Sciences;
- Moscow State University;
- Datasets of international cruises in the Black Sea (R/V ATLANTIS, R/V KNORR, etc.).

The total number of oceanographic stations with information on sulfide vertical distributions is 4301, while the number of stations with the information on the vertical distribution of temperature and salinity is 22,587 for the same period.

Raw data on sulfide distribution versus depth were filtered (3σ-filter) and then the data were verified for the presence of “unexpected” values in the distribution of sulfide versus other physical and chemical properties. Points that differ greatly from the average value were compared with data for adjacent locations (stations) and deleted from the dataset if “unexpected” values did not fit regional patterns. The yield was transformed into a data base, where individual data were aggregated in squares of $40'$ along latitude and $60'$ along longitude (about 40×40 nautical miles). General information on the amount and spatial distribution of the data is shown at Figure 1. A number of digital maps were prepared as a joint atlas to analyze temporal variations in the position of the sulfide onset with the thermohaline properties of the Cold Intermediate layer and the layer of the main pycnocline. A printed version of this atlas is available from Eremeev et al. (1996, 1998), while an electronic version is available from suvorov@alpha.mhi.iuf.net. Only a small part of this atlas, related directly to the subject of present discussion, is used in this article.

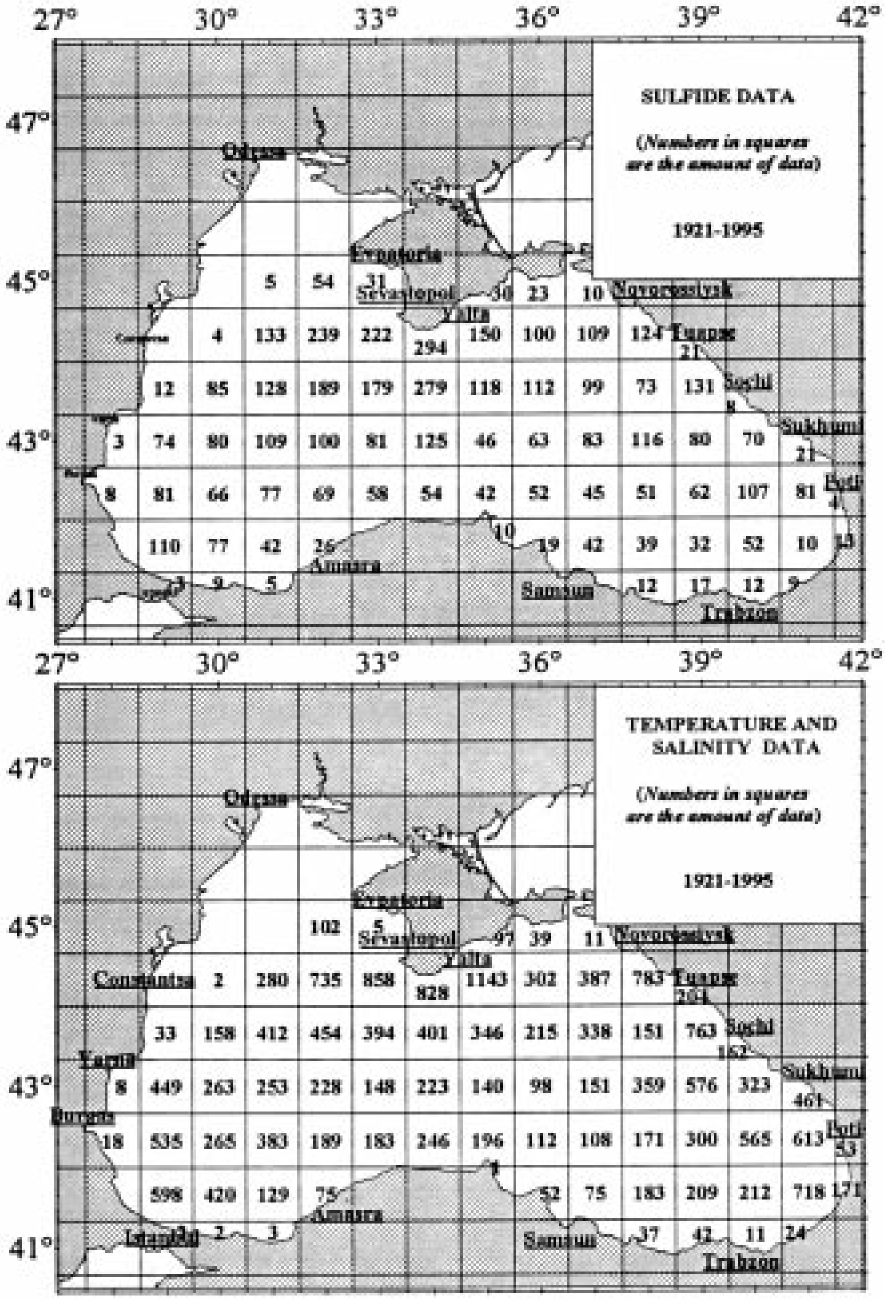

Figure 1. The number of oceanographic stations for different regions of the Black Sea from 1910–1995. Numbers in squares represent the amount of vertical profiles of measurements of (a) sulfide concentration; and (b) temperature and salinity.

The depth of the sulfide onset is defined as a sulfide concentration of 3 μM, which can be readily determined by iodometric titration and/or the Cline spectrophotometric method (1969). Nanomolar concentrations of sulfide can be determined by voltammetric methods (Luther et al., 1991) which showed a greater than two orders of magnitude increase in sulfide (1–150 nM) over 9 m. This rapid rise has been confirmed by researchers from MHI (Zaburdaev, personal communication) using a potentiometric sulfide electrode on a CTD rosette system. Because these data have been collected only in the last decade, it is not possible to make a historical comparison, which is possible with the 3 μM concentration.

Thus, the depth of sulfide onset (3 μM) was interpolated from the data using a polynomial equation of the order 3–5. These equations were adjusted every time to fit individual distributions of sulfide versus depth for individual stations. The possible errors of interpolation were estimated for cruise-based datasets, where vertical resolution was high (R/V KNORR, 1988, and the recent cruises of MHI). The error in depth was never $>$10 m, and is typically $<$5 m. We realize that spatial and temporal resolution are not appropriate to analyze variations in the position of sulfide onset, as are the physical properties of water. Thus, the data have been averaged on an annual scale before the middle of the 1980s, and plots have been prepared for individual decades (Figure 2) (Eremeev et al., 1996, 1998).

In addition, this dataset has been used to analyze variations in the average depth of sulfide onset from 1924–1995 (Figure 3). To get this plot, the results of interpolation have been averaged for every available cruise dataset and the line on Figure 3 is the result of smoothing as a running average with 10-year intervals.

The second dataset represents properties of the *anoxic zone* of the Black Sea from 1960 to 1995. Improved spatial and vertical resolution is the main difference between the first and the second dataset. The data used to form this dataset are listed in Table I. To plot and analyze sulfide distributions as well as other properties of the hydrochemical structure of the Black Sea for the period from 1960–1995, the data were averaged versus depth (when the depth is 1000 m or more), or density scale at intervals of 100 m depth or 0.1 of density, respectively. Dynamic properties of the anoxic zone are shown in Figure 4, while temporal variations in sulfide concentration for individual isopycnal surfaces and depth levels are shown in Figure 5.

3. Discussion

Analysis of spatial variations in the depth of sulfide onset for the 1980s (Figure 2) confirms the presence of a strong correlation between the depth of the first appearance of sulfide and the position of the main pycnocline. This question was discussed intensively in the beginning of the 1990s by Bezborodov and Eremeev (1993), Tugrul et al. (1992) and Vinogradov and Nalbandov (1990), but based on our analysis of recent results, this correlation occurs for other decades of this century. The correlation coefficient (R) between the depth of sulfide onset and the

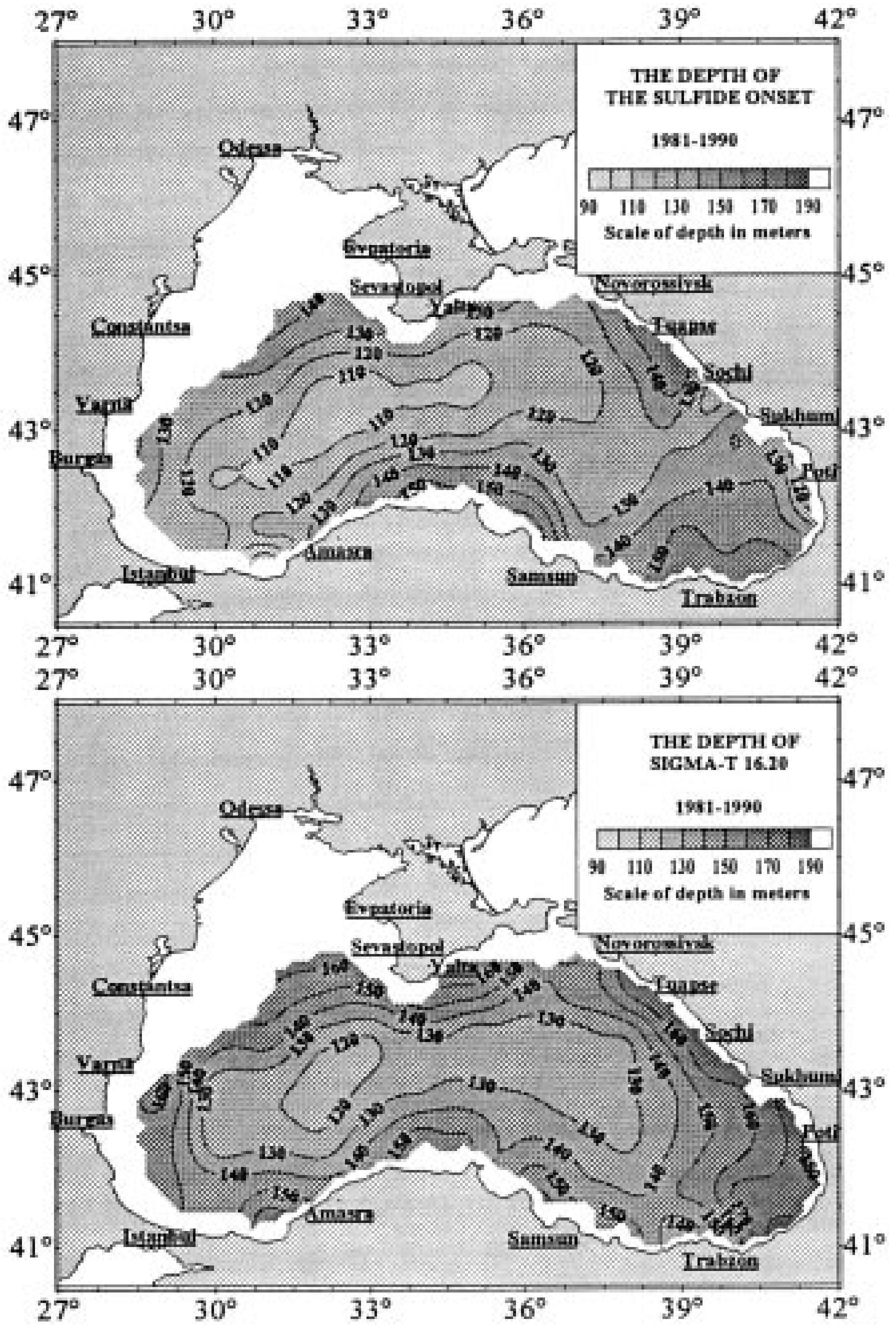

Figure 2. (a) Spatial variations in the depth of the sulfide onset; and (b) the position of the isopycnal surface 16.2 in 1980s. Initial data have been averaged for individual 40×40 nautical mile squares within decades.

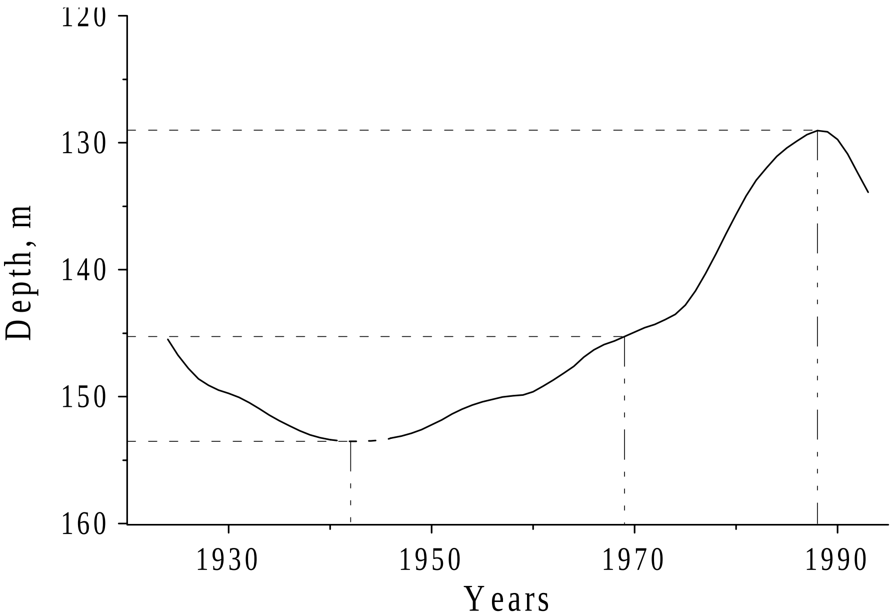

Figure 3. Temporal variations in average depth of the sulfide onset in the Black Sea from 1924–1995. Data have been averaged for every individual cruise dataset and the line is the result of smoothing as a running average with 10-year intervals. Dashed lines represent the lowest value, 129 m in 1988, the highest value, 153 m in 1942, and the value (145 m) in 1969, the year of the R/V ATLANTIS expedition.

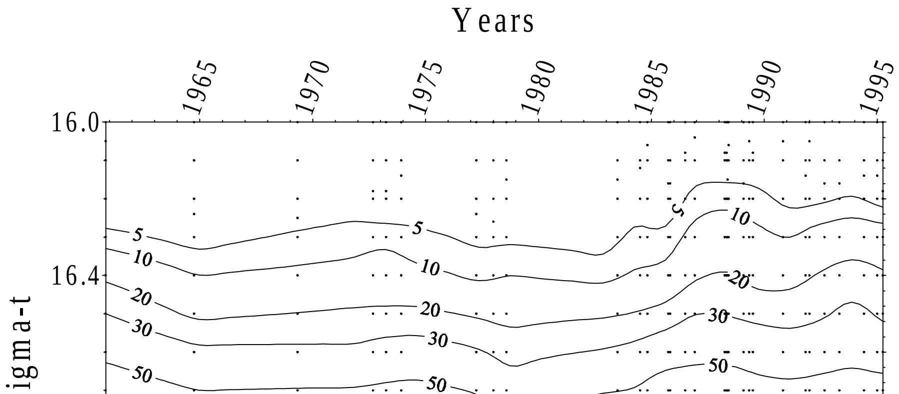

Figure 4. Changes in sulfide concentration inside the anoxic zone of the Black Sea from 1960–1995. Data of individual cruises averaged for 0.1 intervals of density (σ_t) scale, dots at plot, have been used to plot this figure.

Table I. General information on the cruise datasets used for analysis of temporal variations in chemical properties of the Black sea from 1960–1995

No.	O_2	H_2S	Time	Ship/cruise No.
1	787	538	October, 1960	ML-09
2	258	114	August–September, 1964	ML-16
3	382	364	March–April, 1969	ATLANTIS
4	571	501	June–August, 1972	AV-06
5	303	212	March–April, 1973	AV-07
6	218	229	November, 1973	AV-08
7	43		April–August, 1976	ML-30
8	190		September–December, 1976	AV-14
9	218	202	March, 1977	AV-14/1
10	372	350	October, 1977–February, 1978	ML-33
11	263	470	July–August, 1978	ML-35
12	359		December, 1980–May, 1981	AV-23
13	248	225	May–June, 1983	AV-27
14	129	194	June–July, 1984	AV-29
15		231	September, 1984	ML-43/1
16	479	710	July–August, 1985	ML-44/1
17	107	100	October, 1985	ML-44/4
18	405	444	June–July, 1986	AV-34
19	380	448	November–December, 1986	PK-14/2
20	945	1001	March, 1988	ML-49/1
21	408	463	April, 1988	AV-37/1
22	83	6959	April–June, 1988	KNORR
23	619	365	April–May, 1988	PK-18
24	655	438	November, 1988–March, 1989	PK-20
25	1511	991	March–May, 1989	PK-21
26	628	296	June–July, 1989	PK-22
27	607	581	November–December, 1989	ML-51
28	2438	2666	September–November, 1990	ML-53a
29		353	June–July, 1991	PK-27
30	1398	1161	September–October, 1991	PK-28
31	1524	1386	November–December, 1991	ML-54
32	1441	1014	July–August, 1992	PK-29
33	167	153	September–November, 1992	ML-55
34	827	336	April, 1993	PK-30
35	243	64	November, 1993–January, 1994	PK-31
36	466	138	May, 1994	GIDROOPTIK
37	695	459	December, 1994	PK-32
38	811	190	March–April, 1995	PK-33

Numbers in table represent the amount of measurements.
Abbreviations: ML, RV MIKHAIL LOMONOSOV; AV, RV ACADEMICIAN VERNADSKIY; PK, RV PROFESSOR KOLESNIKOV; and GIDROOPTIK, RV GIDROOPTIK are research vessels of Marine Hydrophysical Institute (MHI), National Academy of Sciences of the Ukraine; ATLANTIS, RV ATLANTIS; and KNORR, RV KNORR, research vessels of Woods Hole Oceanographic Institution.

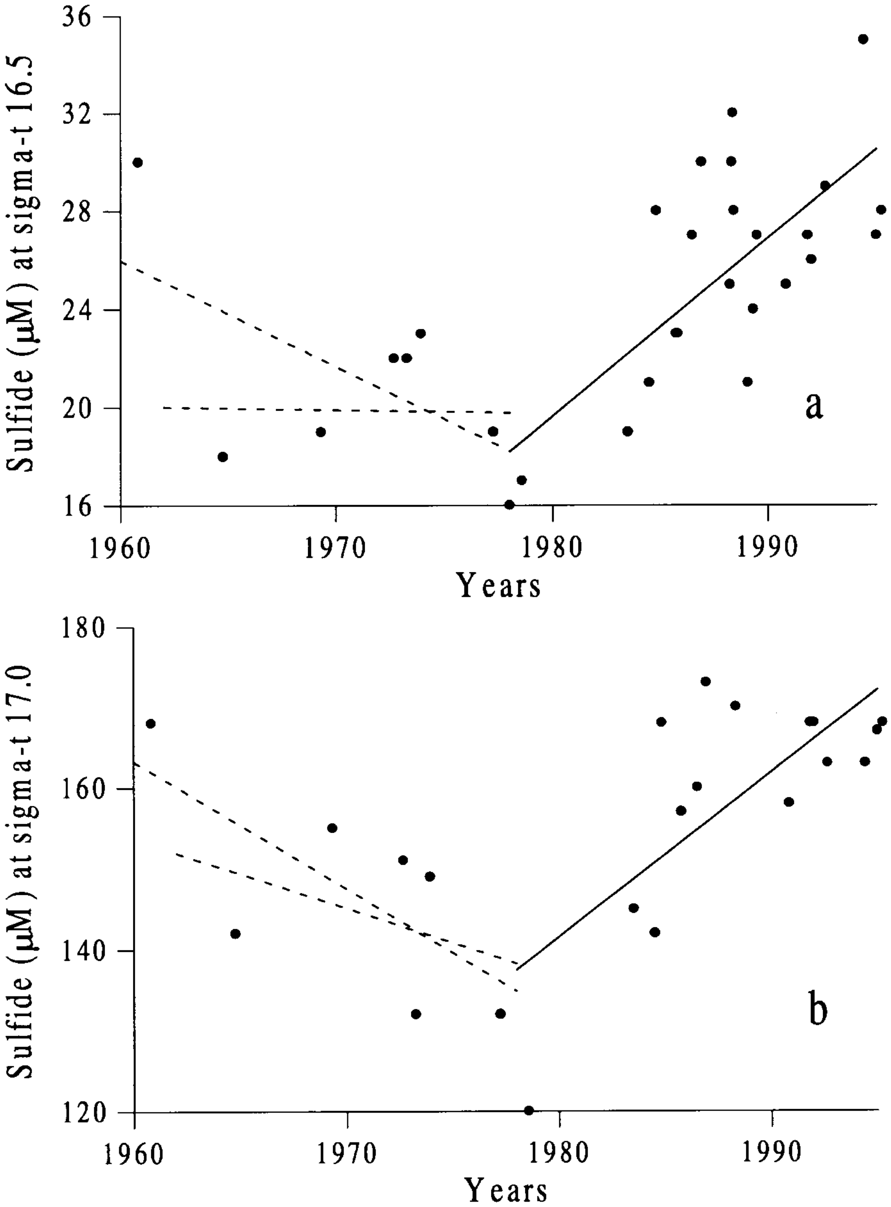

Figure 5. Variations of sulfide concentration at individual isopycnal surfaces (a–b) and depth levels (c–d) from 1960–1995. Dots represent data of individual cruises, Table I, averaged for 0.1 intervals of density (σ_t) scale or 100 m intervals of depth.

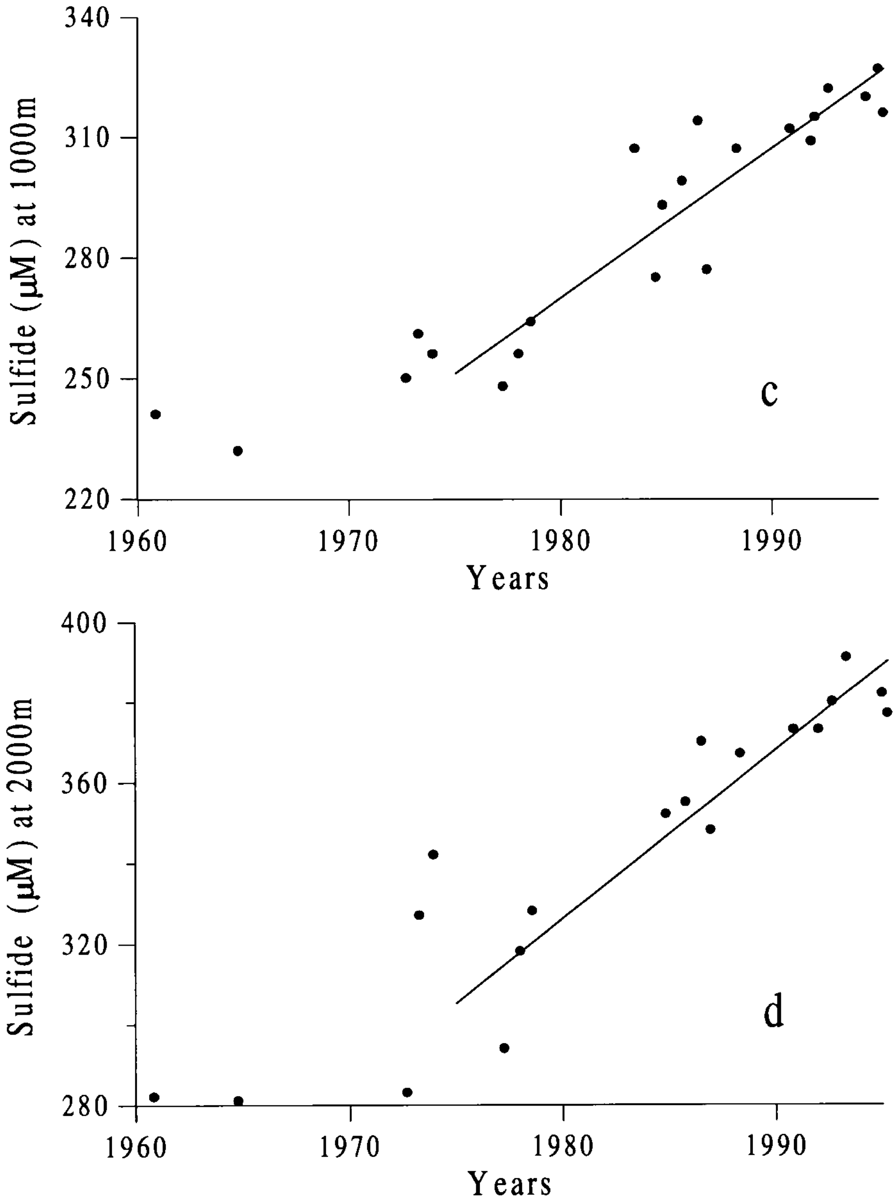

Figure 5 continued.

position of σ_t at 16.2 = 0.71 for the entire dataset of the 1980s, and this value is even higher and equals 0.88 for the central part of the sea. We have calculated values within the same range of 0.71–0.88 for all the other decades in this century. There is no information on the processes responsible for this unique value of density that is close to 16.17 at the depth of sulfide onset. In general, this value of density corresponds to the lower edge of the main pycnocline. This layer is a natural barrier that prevents both downward flux of oxygen, and upward flux of sulfide in the Black Sea and all the possible variations in the position of sulfide onset versus density are suppressed by the presence of the strong pycnocline. For this reason, correlation between the depth of sulfide onset and structure of the main pycnocline can be used to fill any gaps in the chemical information for this century.

Taking into account the presence of significant correlation between the position of sulfide onset and the density structure of the Black Sea water column, temporal variations in the depth of the first appearance of sulfide can be demonstrated as shown in Figure 3. The range of these variations is about 24 m from the beginning of the 1940s to the end of 1980s and trends are stable at subscale intervals (for example, from 1942–1988, Figure 3). The average depth of sulfide onset shifted upward about 16 m from 1969–1988, as suggested by Murray et al. (1989). So, the only reason for the “unexpected” changes they observed was the unavailability of an extended historical dataset at the end of the 1980s. The reason for those variations in the average depth of sulfide onset was mainly the change in the position of the main pycnocline, but the position of the sulfide onset versus the density scale was quite stable, as proposed by Saydam et al. (1993).

The deepest position of the sulfide onset was in the beginning of the 1940s (1942) and the average depth was close to 153 m, while 1988 was the year of the most shallow position of the first appearance of sulfide when the average depth was about 129 m (Figure 3). On the other hand, temporal variations in the position of the sulfide onset are more complex than a simple steady-state upward shift of it, as suggested by Bezborodov et al. (1993). Actually, temporal variations in the average depth of the sulfide onset can be inferred from the data of Figure 3 as an oscillation on a century timescale because the trough and crest in Figure 3 are 50 years apart. More importantly these changes are mainly the result of variations in the position of the main pycnocline, but not in the position of the sulfide onset versus density scale. These oscillations in the position of the main pycnocline and, consequently, in the depth of the first appearance of sulfide, cannot be explained by regulation of fresh water discharge. There were no prominent changes in river discharge regulation at the end of the 1980s, but changes in trends of the position of the sulfide onset are obvious (Figure 3). Thus, temporal changes in the depth of the sulfide onset are most probably the result of natural trends in the density structure of the water column due to climatic changes related to the intensity of evaporation, precipitation, river discharge and exchange of water between the Black Sea and other seas.

The stability of the position of the sulfide onset versus density scale, suggested by Saydam et al. (1993) for the 1980s and shown above for other decades in this century, can be distinguished from other observations of dramatic changes in the chemical, optical and biological structure of the Black Sea. General degradation of the Black Sea ecosystem (Mee, 1992) has been observed, in particular, as an increase in nitrate concentrations (Tugrul et al., 1992), the appearance or broadening of the suboxic zone (Murray et al., 1989), and a decrease in the transparency of surface layer water (Vladimirov et al., 1997). These changes are due to anthropogenic impact that has been taking place since the early 1970s. To understand this problem one has to look at Figures 4 and 5, where temporal variations in the distribution of sulfide versus density scale are shown for the entire anoxic zone and individual surfaces (density or depth) from 1960 to 1995. This period represents both the time when anthropogenic impact was minor (when the intensity of climatic processes were primarily responsible for chemical changes) and the time when anthropogenic influence grew substantially and perhaps to some dangerous level. The data in Figure 4 show that the above variations in the average position of the sulfide onset versus density do not exceed 0.15 units of σ_t, which is close to the vertical resolution and the level of uncertainties in the datasets obtained before 1988.

While the position of the sulfide onset was quite stable versus the density scale, the data in Figures 5 and 6 reveal dramatic temporal variations in the chemical structure of the anoxic zone. The concentration of sulfide changed versus both the density (Figure 5a, b) and depth (Figure 5c, d) scales. The range of these changes exceeds any possible analytical errors, and the stable trend of the average values confirms that the values represent real changes in the sulfide distribution from 1960 to 1995. This period can then be divided into two subperiods with a breakpoint that corresponds to the middle of the 1970s. This breakpoint represents a dramatic moment in the evolution of the Black Sea. Prior to this breakpoint, there is lower sulfide production (or increased sulfide utilization / precipitation), whereas, after the breakpoint an increase in sulfide production occurs inside the anoxic zone (Figure 5).

The increase of sulfide concentration in the anoxic zone from the mid-1970s corresponds to the beginning of intense anthropogenic pollution, that is primarily recognized as an increased discharge of nutrients with river waters and from other coast-based sources (Cociasu et al., 1996; Humborg et al., 1997). Thus, the increase in the sulfide concentration (Figure 5) in the 1980s is a result of escalating anthropogenic eutrophication. Moreover, the coincidence of increasing sulfide concentration in different layers of the anoxic zone supports the suggestion that the only significant source of sulfide is the process of bacterial sulfate reduction (Sorokin, 1982). This process can take place at any depth under anoxic conditions, as long as there is a source of organic matter. Evidently, the increase in nutrient discharge led to an increase in production of particulate organic matter and, consequently, its flux into the anoxic zone. The flux of particulate organic matter can intensify sulfate reduction at any depth of the anoxic zone on a week-to-month timescale. The residence time of sinking particulate organic matter is fairly short, when compared with the residence time of the water mass of the anoxic zone which is stagnant due to lack of ventilation.

The growth of sulfide concentrations, explained by intense anthropogenic eutrophication, should correspond to changes in other chemical properties of the anoxic zone, because the flux of particulate organic matter must lead to increases

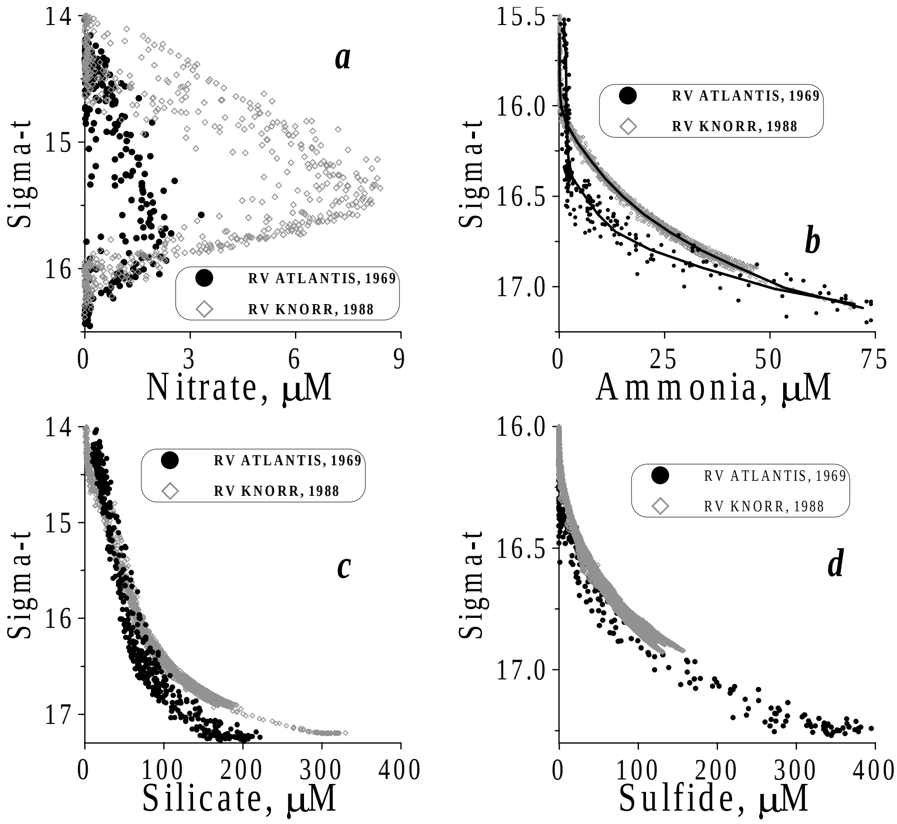

Figure 6. Vertical distributions of (a) nitrate; (b) ammonia; (c) silicate; and (d) sulfide in 1969 (data of R/V ATLANTIS) and 1988 (data of R/V KNORR). In plot (d), the 1988 sulfide dataset is at a smaller σt than the 1969 dataset. The large 1988 dataset overlaps so well that the unfilled diamonds appear filled. The 1988 dataset is from the pump profiler system which only was operated below 300 m (Murray et al., 1989).

in sulfide and nutrient concentrations. The data of Figure 6 confirm this suggestion demonstrating an increase in nitrate concentrations (Tugrul et al., 1992), along with increases in concentrations of ammonia and silicate. Thus, temporal increases in sulfide and nutrient concentrations demonstrate the same trend (Figure 6) and confirm that the increase in sulfide concentrations is the result of intense anthropogenic eutrophication.

The growing concentrations of sulfide in the 1980s (Figure 5) shows a general scheme for the evolution of the Black Sea. It demonstrates that the intensity of anthropogenic eutrophication has reached the level, where man-induced activities are comparable with or overshadow climatic processes in the Black Sea.

4. Conclusion

Analysis of the dataset representing chemical properties of the Black Sea from 1910 to 1995 has led to the following conclusions:

1. Oscillations rather than a steady-state trend are prominent for long-term changes in the average depth of the sulfide onset (Figure 3). The range of these oscillations is about 24 m from the beginning of 1940s to the end of 1980s. The period of these oscillations may occur on a century timescale.
2. The depth of the sulfide onset and the density structure of the water column correlate for the entire period covered with the available data. The average value of density (σ_t) at the depth of sulfide onset (3 μm) is close to 16.17. Average values of the correlation coefficient (R) vary from 0.71 to 0.88 for all the different decades. Temporal variation in the average depth of the sulfide onset is mainly the result of climatic changes in the density structure of the water column. The position of the sulfide onset versus density (σ_t) scale does not exceed 0.15 and is close to the limit of uncertainties for data obtained prior to 1988.
3. Temporal increases in sulfide distribution inside the anoxic zone over the last two decades are disturbing and reveal the following conclusions. First, the anoxic zone shows human induced changes in the chemical structure quickly (Figures 5 and 6). Second, there is a strong imbalance between sources and sinks of sulfide that has resulted in a dramatic growth of sulfide concentrations inside the anoxic zone (Figure 5). Lastly, anthropogenic impact is now comparable or even more important for the evolution of the Black Sea's chemical structure than are climatic changes. Abatement of anthropogenic impacts is required, or further undesired changes in the chemical and biological structure of the Black Sea may occur.

Acknowledgments

This work has been supported by the National Council of the USA (COBASE Program of the Office for Central Europe and Eurasia, Grant in 1997 to J. Murray), by the National Science Foundation (Grant NSF OCE-9314349 to G. Luther) and by the Research Support Scheme (Grant No. 867/1996).

References

Andrusov, N. I. (1890) Preliminary report on the Black Sea cruise. Izvestiya imperatorskogo Russkogo geographicheskogo obschestva (News of the Russian Royal Geographic Society), **26**(5), 398–409 (in Russian).

Bezborodov, A. A. and Eremeev, V. N. (1991) The hydrogen sulphide boundary in the Black Sea in the 1920s and 1980s. *Soviet J. Phys. Ocean.* (A cover-to-cover translation of Morskoi Gidrofizicheskii Zhurnal) **2**(5), 407–410, Utrecht, The Netherlands, Tokyo, Japan.

Bezborodov, A. A. and Eremeev, V. N. (1993) Chernoe more. Zona vzaimodeistviya aerobnikh I anaerobnikh vod. (Black Sea. The oxic/anoxic interface). Sevastopol, MHI ASU, 299 pp (in Russian).

Cline, J. E. (1969) Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Ocean*. **14**, 454–458.

Mee, L. D. (1992) The Black Sea in a crisis: a need for concentrated international action. *Ambio* **21**, 278–285.

Cociasu, A., Dorogan, L, Humborg, C., and Popa, L. (1996) Long-term ecological changes in the Romanian coastal waters of the Black Sea. *Mar Pollut Bull*. **32**, 32–38.

Eremeev, V. N, Suvorov, A. M., Godin,E. A., and Khaliulin, A. Kh. (1996) Statistical analysis of the location of the upper boundary of the hydrogen sulfide zone from multiannual data. In: *Hydrochemistry and Dynamics of Hydrogen Sulfide Zone in the Black Sea* (ed. R. C. Griffiths), Part IV, pp. 59–107. UNESCO Reports in Marine Sciences, UNESCO.

Eremeev, V. N, Suvorov, A. M., Khaliulin, A. Kh., and Godin, E. A. (1998) *Climatic Atlas of the Location of the Hydrogen Sulfide Contamination Zone Upper Boundary in the Black Sea*. MHI, Sevastopol, 80 pp (Russian/English version).

Faschuk, D. Ya. and Aizatulin, T. A. (1986) A possible Transformation of the Anaerobic Zone of the Black Sea. *Oceanology* **26**(2), 171–178.

Humborg, C., Ittekkot, V., Cociasu, A., and Bodungen, B. v. (1997) Effect of Danube River dam on Black Sea biogeochemistry. *Nature* **386**, 385–388.

Luther, III, G. W., Church, T. M., and Powell, D. (1991) Sulfur speciation and oxidation in Black Sea Waters. *Deep-Sea Res.* **38** (Suppl. 2A), S1121–S1137.

Murray, J. W., Jannasch, H. W., Hojo, S., Anderson, R. F., Reeburgh, W. S., Top, Z., Friederich, G. E., Codispoti, L. A., and Izdar, E. (1989) Unexpected changes in the oxic/anoxic interface in the Black Sea. *Nature* **338** (6214), 411–413.

Saydam, C., Tugrul, S., Basturk, O., and Oguz, T. (1993) Identification of the oxic/anoxic interface surfaces in the Black Sea. *Deep-Sea Res.* I, **40**(7), 1405–1412.

Skopintsev, B. A. (1975) *Formirovanie sovremennogo khimicheskogo sostava vod Chernogo morya (Formation of the Present Chemical Structure of the Black Sea*). Leningrad, Gidrometeoizdat, 336 pp (in Russian).

Sorokin, Yu. I. (1982) *Chernoe more: priroda i resursi (The Black Sea: The Nature and the Resources*). Moscow, Nauka, 217 pp (in Russian).

Tugrul, S, O. Basturk, C. Saydam and A. Yilmaz (1992) Changes in the hydrochemistry of the Black Sea inferred from water density profiles. *Nature* **359**, 137–139.

Vinogradov, M. Ya. (1991) The upper boundary of the hydrogen sulfide zone in the Black Sea and trends in its position. *Oceanology* **31**(3), 299–303.

Vinogradov, M. E. and Nalbandov, Yu. R. (1990) Effect of changes in water density on the profiles of physicochemical and biological characteristics in the Pelagic ecosystem of the Black Sea. *Oceanology* **30**(5), 567–573.

Vladimirov, V. L., Mankovsky, V. I., Solov'ev, M. V., and Mishonov, A. V. (1997) Seasonal and long-term variability of the Black Sea optical parameters. In: Sensitivity to Change: Black Sea, Baltic Sea and North Sea (eds. E. Ozsoy and A. Mikaelyan). Kluwer Academic Publishers, Dordrecht, NATO ASI Series, 2, *Environment* **27**, 33–48.