Introduction: Redox Interfaces in Marine Waters

E.V. Yakushev and A. Newton

Abstract The typical features of the structure of the redox layers in a marine water column are described. The oxic, hypoxic, suboxic and anoxic layers are discussed with respect to the definitions of terms. A classification of the redox conditions is proposed based on processes typical of the redox conditions appearing during the different stages of oxygen depletion.

Oxygen depletion events are connected with anthropogenic forcing such as eutrophication. However, climatic forcing may further stimulate the formation of oxygen-depleted zones. The redox interfaces and oxygen depletion events studies will therefore require an interdisciplinary approach, which the present book reflects.

Keywords Baltic Sea, Black Sea, Oslo fjord, Redox zone

Contents

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Abbreviations

DO	Dissolved oxygen
OM	Organic matter

1 Preface

During the last decades, many studies have focused on the oxygen depletion of coastal and oceanic waters in the context of the series of projects and programmes, i.e. INCO-Copernicus, NATO, FP6 and FP7 programmes Bonus, HYPOX and SESAME. The results obtained have been published in numerous articles and monographs, many of which are listed in the reference section. This new book is well timed and urgent. It presents the “state of the art” of our knowledge and understanding of the nature of redox interfaces, structures and oxygen depletion. It synthesises the joint response of the global scientific community to the challenge of global changes in the “oxygen condition” of marine waters, new developments in observation techniques, such as the introduction of new analytical methods, and the analysis of data to identify thresholds of change using new models. Nevertheless, there are still gaps in our knowledge about the cycling of chemical elements in changing redox conditions. An understanding of the processes involved is fundamental to assess the impacts and effects of global and climatic changes and to enable an ecosystem approach of adaptive environmental management for the coastal seas and ocean basins.

2 Occurrence and Hydrophysical Structure

The occurrence of oxygen-depleted and anoxic water depends on the combined influence of eutrophication (organic matter and nutrient loads) and hydrodynamics (intensity of mixing and water renewal). Oxygen depletion zones form when there is an imbalance between the supply of organic matter (OM) and the supply of dissolved oxygen (DO) for its decomposition. This may occur when a hydrophysical structure, such as temperature stratification, restricts the aeration of the water column. The existence of low-oxygen structures can be temporary or permanent, correspondingly creating zones of temporary or permanent hypoxia and anoxia.

Oxygen depletion and anoxia in the water column are increasingly common features observed in the World Ocean, inland seas and coastal areas. Observations show a decline in the dissolved oxygen concentrations at continental margins in many regions, and these are related to both an increase in anthropogenic nutrient loadings and a decrease in vertical mixing (e.g. [1–3]). Observations of decreases in oxygen are also reported in the tropical oceans [4–9]. Low-oxygen “dead zones” have spread exponentially since the 1960s [1]. The decrease in DO throughout the open ocean basins may be a long-term, nonperiodic trend related to climate change, or the result of natural cyclical processes, or a combination of both [6]. Within the marine science community, there is increasing interest to these events in recent years because of their global character.

The scales of processes that affect the formation of each system's hydrophysical structure vary from molecular diffusion to climatic variability. However, in lakes and fjords, some processes, such as transport of water with geostrophic currents or mesoscale eddies, are unimportant, leading to less intense mixing than under marine conditions. Therefore, the chemical structure of redox interfaces in fjords and lakes is characterised by sudden changes in redox conditions and steep chemical gradients. In comparison to lakes and fjords, oxidation–reduction features at marine redox interfaces are characterised by gradual gradients, and gradually varying temporal changes as well. For example, the boundary of anoxic zone of the Cariaco Basin is influenced by mesoscale eddies that periodically supply dense water with high oxygen content to the anoxic zone [10]. In the Baltic Sea, under certain winter weather conditions in particular years, there is an influx of oxygen-rich saline northern Sea waters to the deep anoxic layers [11, 12]. The Black sea oxic/anoxic interface appears to be more stable, because the Bosphorus plume waters influence only the south-western part of the Black Sea. The central and peripheral Black Sea are characterised by the stability of the chemical features (i.e. maximum positions, onset levels) in the density field [13, 14]. Such a *chemotropicity* implies that there are no horizontal gradients of chemical variables along the same density surface, supporting the use of a 1D model for describing the processes responsible for the maintenance of the redox-layer chemical structure.

3 Global Distribution

Permanent anoxic conditions are observed in numerous lakes, lagoons, fjords, seas and also in some regions of the World Ocean. They include examples of very different systems under the simultaneous influence of saline and brackish waters and suffering from restricted ventilation [15]. The most notable and stable example is in the Black Sea [16, 17]. Other examples include the Cariaco Trench of Venezuela [10, 18], the Gotland Deep of the Baltic Sea [19, 20], Drammensfjord [21], Framvaren [22], Hemmelsdorfer See [23], Gulf of Mexico [2], coastal salt ponds along the US coast [24], Saanich Inlet (Vancouver Island) [25], Elefsis Bay [26] and meromictic lakes in the Vestfold Hills in Antarctica (e.g. [27]).

4 Effects on Chemistry, Biochemistry and Ecosystem Function

The redox interface is a layer where oxic and anoxic conditions are adjacent. It is very complex because of the many chemical reactions and biogeochemical mineralisation processes that can be oxic, suboxic and anoxic. The decline in DO concentration therefore affects the biogeochemical cycles of N, P, S, as well as the carbonate system and trace metals equilibria. Water layers that are already depleted with respect to DO may be close to the threshold between suboxic and anoxic conditions and are the water bodies most vulnerable to the effects of the globally observed deoxygenation trend [28]. It is necessary to better understand the physical processes leading to anoxia, the biogeochemical structure of the oxic/anoxic interfaces and the ecological consequences of oxygen depletion in order to predict the possible effect of global changes in oxygen conditions.

Oxygen depletion significantly affects the water quality and ecosystem function. Absence of oxygen impairs the oxic ecosystem both directly and indirectly. Increased occurrence and volumes of anoxic water threaten the functioning of healthy aerobic ecosystems and thereby have a direct impact to human welfare and ecosystem services. There can be an additional, indirect impact at the water–sediment interface, where redox equilibria control the rate of supply of phosphorus from the sediments and the release of hazardous substances, e.g. methyl mercury.

There is a normal sequence or succession of processes during the transition from oxic to anoxic. The bacterial decomposition of organic matter is an oxidative process. If there is an excess of organic material to be decomposed once the DO has been used, bacterial activity will substitute the DO with a series of other electron acceptors that usually ends with reduction of sulphate, a major constituent in seawater. This last process produces hydrogen sulphide, which is toxic to aerobic life forms. Conversely, the oxidation of reduced inorganic compounds in the anoxic zone also fuels the microbial production of OM via chemosynthesis [17, 29, 30]. It is necessary to emphasise that the synthesis of organic matter happens in all the oxygen conditions via photosynthesis (oxic and anoxygenic) or chemosynthesis.

5 Terminology, Definitions, Boundaries and Thresholds

The oxygen condition of natural waters is an important element of water quality legislation, e.g. in the Water Framework Directive (EC 2000). However, there are several terms that are in use to describe the changes in oxygen condition, i.e. *oxic*, *oxygen-deficient*, *hypoxic*, *suboxic*, *anoxic*, but these are not be precisely defined. The terms reflect different DO conditions and the associated processes. For example, the term “oxygen-deficient” is widely used for a wide range of low oxygen concentrations, from below 80% saturation to suboxic levels. Nevertheless, the boundaries in terms of oxygen concentrations are rather arbitrary, and therefore, there are several problems to the currently used definitions. Biochemical thresholds provide less arbitrary boundaries.

A frequently used boundary between *oxic* and *hypoxic* conditions is set at 2 mg O_2 L^{-1} (~63 μM O_2 i.e. [31]) or 2 ml O_2 L^{-1} (~89 μM O_2 i.e. [1, 32]). The threshold of tolerance, stress responses and morbidity of pelagic and benthic animals is usually in the range of 1–4 mg O_2 L^{-1} (e.g. [32–34]), which corresponds to a threshold molar concentrations of ~75 μM O_2.

The boundary between *hypoxic* and *suboxic* conditions is also arbitrary, and there has been opposition to the use of the term "suboxic" once oxygen is no longer present [35]. In the Black Sea, for example, the reported suboxic values range from 4.5 μM O_2 [36] to 15 μM O_2 [37]. A value of 10 μM [13] is often used, which corresponds to the water layers with enhanced nitrification due to an upward flux of ammonia [28]. However, this boundary should correspond to the biochemical threshold after which the dominant electron acceptors are oxidised ions of N (nitrate, nitrite) or oxidised species of metals [Mn(IV), Fe(III)], whereas DO becomes an auxiliary oxidant.

The *suboxic* layer may be further divided into "suboxidised" layer, where DO is present, and "subreduced" layer, where DO is absent [38]. The *suboxidised* layer is therefore a layer where DO is present with a threshold molar concentration of ~15 μM O_2 as an "upper" boundary. The *subreduced* layer, where there is no longer any DO but H_2S is not yet present, should correspond to the conditions necessary for the onset of processes such as anammox [39] or formation of Mn(III) [40], that are inhibited by both oxygen and hydrogen sulphide.

Once the oxidised species of nitrogen, manganese or iron and DO is completely depleted, OM microbial decomposition uses sulphate as the next electron acceptor for oxidation. This is the appropriate threshold for the term *anoxic*.

The main biogeochemical processes change in intensity dependent on the oxygen conditions as summarised in Table 1. A schematic of the corresponding layers and different redox conditions with respect to the distributions of DO, H_2S, speciation of Mn and N is shown in Fig. 1.

6 The Redox Layers in a Marine Water Column

The transition layer between the oxic and anoxic conditions in the water column is often called "redoxcline" or "redox layer". The redox boundaries in the water column are established and controlled by two opposite fluxes: the upward flux of reduced chemical species and the downward flux of oxidised chemical species. The redox layer covers the layer of transformation from the oxic conditions to anoxic. A nitrate maximum can be taken as the upper boundary of the redox layer. This corresponds to σ_θ ~ 15.3 kg m^{-3} for the Black Sea [41]. The lower boundary of this layer corresponds to the disappearance of oxidised manganese species, σ_θ ~ 16.15 kg m^{-3} for the Black Sea.

In the stratified water bodies, these counter fluxes generate a wide range of redox potentials within narrow zones in the water [42]. The biogeochemical processes occur in a predictable sequence according to their redox potential (i.e. [13]) and the products of these reactions appear in the water according to the laws of thermodynamics. The vertical distributions of the chemical compounds result from the

Table 1 Basic biogeochemical processes and corresponding oxygen condition

Oxygen conditions	Oxic	Hypoxic	Suboxic		Anoxic
			Suboxidised	Subreduced	
DO concentration	>75 µM	15–75 µM	0–15 µM	0 µM	
H_2S concentration					>0 µM
Oxic mineralisation of OM and nitrification	+	+			
Oxidation with DO of reduced species of S, Mn, Fe, C, N		+	+		
Denitrification and mineralisation of OM with metals			+	+	
Anammox, accumulation of Mn(III)				+	
Reduction of oxidised species of S, Mn, Fe, C				+	+
Sulphate reduction, methanogenesis					+
Increased mortality		+	+	+	+
Synthesis of OM	+	+	+	+	+

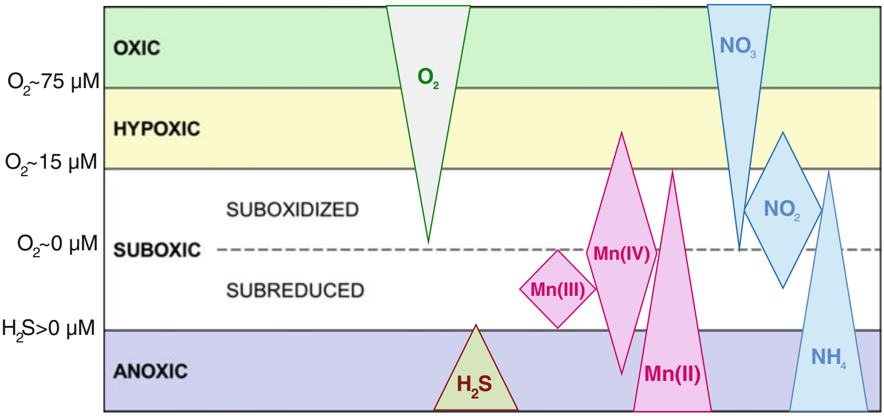

Fig. 1 A redox framework for the structure of the oxygen condition of a water column with respect to the distributions of DO, H_2S and indicative speciation of Mn and N

reactions that can occur in narrow layers, i.e. 2–5 m in the Black Sea [43] and several dm in the fjords.

There are common features of the water column redox interfaces for the different marine basins [44]. These characteristics are:

- A nitrate maximum is observed at the depth where the vertical gradient of oxygen decreases (lower part of oxycline).
- Onset depths of concentrations of ammonia and dissolved manganese correspond to oxygen depletion and the position of the “shallow” phosphate minimums.
- Hydrogen sulphide appears in deeper waters, about 10 m in the Black Sea.

Organic matter is the main reducing agent in the redox zone [45]. It is a product of photosynthesis and is transported downwards from the euphotic zone. Organic matter is also generated in the redox zone by chemosynthesis. Organic matter serves as a carbon source for the reduction of DO and thereafter, nitrate, nitrite, Mn oxide, Fe oxide and sulphate.

The biogeochemical structure of the water column redox layer is characterised by an absence of overlap between dissolved oxygen and hydrogen sulphide [13, 46–48]. Reduced and oxidised forms of several elements (N, S, C, Mn, Fe) can be observed in the redox layer, which reflects the complexity of the chemical processes. The role of the biogeochemical cycles of the different elements in the formation and support of the redox-layer structure is still not clear.

Oxygen disappears at a depth where the onset of ammonia and dissolved manganese is observed, while hydrogen sulphide appears deeper (approximately 5–10 m in the Black Sea).

The depth at which H_2S is first observed also depends on the equilibrium between the transport of electron acceptors and organic matter (e.g. [28, 49, 50]).

The suboxic (subreduced) zone phenomenon where both oxygen and hydrogen sulphide are absent [13] is not clearly understood. It may be due to the peculiarities of the manganese cycle: the formation of a significant amounts of the particulate Mn(IV) that can precipitate from the depth at which it is formed due to the reaction between oxygen and dissolved Mn(II) [51, 52]. Mn(III) has been observed in the marine environment [40]. It is an important intermediate product of the Mn cycle that could be formed both by Mn(II) oxidation [53] and by Mn(IV) reduction [54, 55]. This dissolved, oxidised Mn(III) could explain the distribution of other elements at redox interfaces, such as phosphate. Mn(III) permits the formation of P-containing complexes [53]. Studies of this oxidised and dissolved species of Mn are recent (Luther, p.c. [56]). This species was not represented in previous suboxic zone models that seek to describe the flow of primary nutrients such as nitrogen, phosphate and carbon as well as heavy metals through the oxic/anoxic boundary.

7 Modelling

The study of the processes responsible for the maintenance of redox interfaces should combine field observations and experimental measurements. These should be supplemented by modelling to allow a joint analysis of the complex processes studied by the different scientific disciplines. Models are oversimplifications of real system, sometimes overemphasising particular characteristics, as in a caricature. Nevertheless, modelling seems to be appropriate for use as a diagnostic tool. Models can be used to test the hypothesis of which processes are responsible for the observed distributions. Thus, modelling and observations mutually complement each other.

Nutrient cycling in the oxic conditions can be described for individual elements, and it is possible to use the Redfield ratios to estimate the other elements changes. However, the modelling of oxic/anoxic transformation requires the parameterisation of cycles of several elements simultaneously [52, 57].

In contrast to modelling in the typical oceanic and marine waters oxic conditions, the modelling of the oxic/anoxic transformation cannot only give numerical estimates but can reveal the mechanisms of the main processes occurring. This is particularly useful because there are still many knowledge gaps. The main goal of oxic/anoxic modelling is therefore to use the knowledge of events, processes and systems to analyse and understand the observed situation and distribution of observed chemical species.

The choice of list of variables and complexity of a model should depend on the time and space scale of the studying event. Nevertheless, the model should at least parameterise all those listed in Table 1 processes. The model should also establish the thresholds that provide the boundaries or "switches" between the different redox processes.

8 Structure of the Monograph

This monograph is characterised by the following features. First of all, it is multidisciplinary since it deals with the principal processes that form the physical, biogeochemical and biological structures of the redox interfaces. Secondly, it assesses the issues connected with predicting the development interannual oxygen depletion and mathematical modelling.

The book consists of 11 chapters, which may be conventionally joined into the sections devoted to the general features of the redox-layer biogeochemical and microbiological structure (3 chapters), cycling of selected elements (2 chapters), interannual estimates (3 chapters) and modelling (3 chapters).

Thus, this book presents a description of the knowledge accumulated to date (2012) on pelagic redox interfaces. Nevertheless, it is not a collection of individual papers but rather a monograph written by a team of scientists joined by a common understanding of the complicated phenomena and processes that are connected with the redox-interfaces structure formation and oxygen depletion development. The publication is based on numerous observational data, collected by the authors of the chapters during sea and shore expeditions, on the archive data of P.P. Shirshov Institute of Oceanology RAS, Winogradsky Institute of Microbiology, Water Problems Institute RAS, Faculty of Biology, Lomonosov Moscow State University (Russia), Norwegian Institute for Water Research (Norway), Leibniz Institute for Baltic Sea Research, Warnemuende, Helmholtz-Zentrum Geesthacht, Max Planck Institute for Marine Microbiology (Germany), Hellenic Centre for Marine Research, Institute of Oceanography (Greece), Baltic Nest Institute, Stockholm University (Sweden) and others, as well as on a wide scientific literature. These data are complemented by the results of a series of national and international projects listed below, where an extensive research was carried out over the past decades.

This book is addressed to the specialists working in various fields of physical oceanography, marine chemistry, pollution studies and biology and studying a cascade of problems from regional climate to mesoscale processes and from remote sensing of the sea to numerical and laboratory modelling. It may also be useful to the students and postgraduates specialising in the oceanographic research of the seas. The editors and authors expect that this monograph would help the readers to complement the information on the nature of the oxygen depletion and the redox interfaces phenomena. More information on special issues may be derived using the reference lists contained in each chapter.

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References

1. Diaz R, Rosenberg R (2008) Spreading dead zones and consequences for marine ecosystems. Science 321:926–929
2. Rabalais NN, Turner RE, Weisman WJ Jr (2002) Gulf of Mexico hypoxia a.k.a. "The dead zone". Annu Rev Ecol Syst 33:235–263
3. Richardson K, Jørgensen BB (1996) Eutrophication: definition, history and effects. In: Jorgenson BB, Richardson K (eds) Eutrophication in coastal marine ecosystems. Coastal and Estuarine studies, vol 52. AGU, Washington, pp 1–19
4. Deutsch C, Brix H, Ito T, Frenzel H, Thompson L (2011) Climate-forced variability of ocean hypoxia. Science 333(6040):336–339
5. Emerson S, Watanabe YW, Ono T, Mecking S (2004) Temporal trends in apparent oxygen utilization in the upper pycnocline of the North Pacific: 1980–2000. J Oceanogr 60:139–147
6. Falkowski PG, Algeo T, Codispoti L, Deutsch C, Emerson S, Hales B, Huey RB, Jenkins WJ, Kump LR, Levin LA, Lyons TW, Nelson NB, Schofield OS, Summons R, Talley LD, Thomas E, Whitney F, Pilcheret CB (2011) Ocean deoxygenation: past, present, and future. Eos Trans AGU 92(46):409–420
7. Keeling RE, Kortzinger A, Gruber N (2010) Ocean deoxygenation in a warming world. Annu Rev Mar Sci 2:199–229
8. Paulmier A, Ruiz-Pino D (2009) Oxygen minimum zones (OMZs) in the modern ocean. Prog Oceanogr 80:113–128

9. Whitney FA, Freeland HJ, Robert M (2007) Persistently declining oxygen levels in the interior waters of the eastern subarctic Pacific. Prog Oceanogr 75:179–199
10. Scranton MI, McIntyre M, Taylor GT, Muller-Karger F, Fanning K, Astor Y (2006) Temporal variability in the nutrient chemistry of the Cariaco Basin. In: Neretin LN (ed) Past and present water column anoxia, NATO Sci Ser. Springer, Amsterdam, pp 139–160
11. Feistel R, Nausch G, Wasmund N (eds) (2008) State and evolution of the Baltic Sea, 1952–2005. Wiley, New Jersey
12. Schneider B, Nausch G, Kubsch H, Peterson I (2002) Accumulation of total CO_2 during stagnation in the Baltic deep water and its relationship to nutrient and oxygen concentrations. Mar Chem 77:277–291
13. Murray JW, Codispoti LA, Friederich GE (1995) Oxidation–reduction environments. The suboxic zone in the Black Sea. In: Huang CP et al (eds) Aquatic chemistry: interfacial and interspecies processes. ACS Adv Chem Ser 244:157–176
14. Vinogradov ME, Nalbandov YR (1990) Oceanology 30:769
15. Ström TE, Klaveness D (2003) Hennebont: a seawater basin transformed by natural and anthropogenic processes. Estu Coast Shelf Sci 56(5–6):1177–1185
16. Andrusov NI (1890) Predvaritelnii otchyot ob uchastii v Chernomorskoi glubomernoi ekspiditsii 1890 g (preliminary report on participation in the 1890 Black Sea fathometer expedition). Izvestiya Russkogo Geograficheskogo Obschestva (Proc Russ Geogr Soc) 26 (5):398–409 (in Russian)
17. Sorokin Yu I (2002) The Black Sea. Ecology and oceanography. Backhuys Publishers, Leiden, p 875
18. Deuser WG (1973) Cariaco trench: oxidation of organic matter and residence time of anoxic water. Nature 242:601–603
19. Fonselius S (1981) Oxygen and hydrogen sulphide conditions in the Baltic Sea. Mar Pollut Bull 12:187–194
20. Kautsky L, Kautsky N (2000) The Baltic Sea, including Bothnian Sea and Bothnian Bay. In: Sheppard CRC (ed) Seas at the millennium: an environmental evaluation, vol 1, Regional seas: Europe, The Americas and West Africa. Elsevier Science Ltd./Pergamon Press, Oxford, pp 121–133
21. Richards FA (1965) Anoxic basins and fjords. In: Riley JP, Skirrow G (eds) Chemical oceanography. Academic, London, pp 611–645
22. Skei JM (1988) Framvaren – environmental setting. Mar Chem 23:209–218
23. Halbfass W (1923) Grundzüge einer vergleichenden Seenkunde. Borntraeger, Berlin, p 354
24. Conover RJ (1961) A study of Charlestown and Green Hill ponds, Rhode Island. Ecology 42:119–140
25. Grant Gross M, Gucluer SM, Creager JS, Dawson WA (1963) Varved marine sediments in a stagnant fjord. Science 141:918–919
26. Pavlidou A, Kontoyiannis H, Anagnostou Ch, Siokou-Frangou I, Pagou K, Krasakopoulou E, Assimakopoulou G, Zervoudaki S, Zeri Ch, Chatzianestis J, Psyllidou-Giouranovits R (2010) Biogeochemical Characteristics in the Elefsis Bay (Aegean Sea, Eastern Mediterranean) in Relation to Anoxia and Climate Changes. In: Yakushev EV (ed) Chemical structure of pelagic redox interfaces: observation and modelling. Springer, Heidelberg. Hdb Environ Chem. doi:10.1007/698_2010_55
27. Gallagher JB, Burton HR, Calf GE (1989) Meromixis in an Antarctic Fjord: a precursor to meromictic lakes on an isostatically rising coastline. Hydrobiologia 172:235–254
28. Jost G, Pollehne F (2011) The energetic balance of microbial exploitation of pelagic redox gradients. In: Yakushev EV (ed) Chemical structure of pelagic redox interfaces: observation and modelling. Springer, Heidelberg. Hdb Environ Chem. doi:10.1007/698_2011_104
29. Canfield DE, Thamdrup B, Kristensen E (2005) Aquatic geomicrobiology. In: Southward AJ, Tyler PA, Young CM, Fuiman LA (eds) Advances in marine biology, vol 48. Elsevier Academic Press, Amsterdam, p 640

30. Nealson KN, Stahl DA (1997) Microorganisms and biogeochemical cycles: what can we learn from layered microbial communities? In: Banfield JF, Nealson KN (eds) Reviews in mineralogy, vol 35, Geomicrobiology: interactions between microbes and minerals. Mineralogical Society of America, Washington, p 5
31. CENR (2000) Integrated assessment of hypoxia in the Northern Gulf of Mexico. National Science and Technology Council Committee on Environment and Natural Resources, Washington, 58 pp
32. Savchuk O (2010) Large-scale dynamics of hypoxia in the Baltic Sea. In: Yakushev EV (ed) Chemical structure of pelagic redox interfaces: observation and modelling. Springer, Heidelberg. Hdb Environ Chem. doi:10.1007/698_2010_53
33. Diaz RJ (2001) Overview of hypoxia around the world. J Environ Quality 30:275–281
34. Vaquer-Sunyer R, Duarte CM (2008) Thresholds of hypoxia for marine biodiversity. Proc Natl Acad Sci USA 105:15452–15457
35. Canfield DE, Thamdrup B (2009) Towards a consistent classification scheme for geochemical environments, or, why we wish the term “suboxic” would go away. Geobiology 7:385–392
36. Lam P, Jensen MM, Lavik G et al (2007) Linking crenarchaeal and bacterial nitrification to anammox in the Black Sea. Proc Natl Acad Sci USA 104:7104–7109
37. Zubkov MV, Sazhin AF, Flint MV (1992) The microplankton organisms at the oxic-anoxic interface in the pelagial of the Black Sea. FEMS Microbiol Ecol 101:245–250
38. Stunzhas PA (2005) Application of continuous oxygen profiles to redox zone studies in a coastal anticyclonic eddy. Oceanology 45:S93–S101
39. Kuypers MMM, Sliekers AO, Lavik G, Schmid M, Jorgensen BB, Kuenen JG, Sinnenghe Damste JS, Strous M, Jetten MSM (2003) Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. Nature 422:608–611
40. Trouwborst RE, Brian GC, Tebo BM, Glazer BT, Luther GW III (2006) Soluble Mn(III) in suboxic zones. Science 313:1955–1957
41. Yakushev EV, Lukashev YuF, Chasovnikov VK, Chzhu VP (2002) Modern notion of the vertical hydrochemical structure of the Black Sea redox zone. In: Zatsepin AG, Flint MV (eds) Complex investigation of the Northeastern Black Sea. Nauka, Moscow, pp 119–132 (in Russian)
42. Lewis BL, Landing WM (1991) The biochemistry of manganese and iron in the Black Sea. Deep-Sea Res II 38:S773–S803
43. Volkov II, Kontar EA, Lukashev Yu F, Neretin LN, Niffeler F, Rozanov AG (1997) The upper boundary of hydrogen sulfide and redox nefeloid layer in water of the Caucasian slope in the Black sea. Geochemistry 7:540–550
44. Yakushev EV, Chasovnikov VK, Murray JW, Pakhomova SV, Podymov OI, Stunzhas PA (2008) Vertical hydrochemical structure of the Black Sea. In: Kostyanoy AG, Kosarev AN (eds) The handbook of environmental chemistry, vol 5, The Black Sea environment. Springer, Heidelberg, pp 277–307
45. Rosanov AG (1995) Redox stratification of the Black Sea water. Oceanology 35:544
46. Konovalov SK, Tugrul S, Basturk O, Salihoglu I (1997) Spatial isopycnal analysis of the main pycnocline chemistry of the Black Sea: seasonal and interannual variations. In: Ozsoy E, Mikaelyan A (eds) Sensitivity to change: Black Sea, Baltic Sea and North Sea, NATO ASI, 2/27. Kluwer Academic Publishes, Dordrecht, pp 197–210
47. Lukashev YuF, Yakushev EV (1999) Dissolved oxygen content measurements on the border of the sulfide zone of the Black Sea . In: PACON-99 symposium, abstracts, Russian Academy of Sciences, Moscow, 23–25 June 1999,167 pp
48. Stunzhas PA (2000) On the structure of the interaction zone of aerobic and anaerobic water in the Black Sea on the base of measurements by membrane-free oxygen sensor. Oceanology 40:503–509
49. Grote J, Labrenz M, Pfeiffer B et al (2007) Quantitative distributions of *Epsilonproteobacteria* and a *Sulfurimonas* subgroup in pelagic redoxclines of the central Baltic Sea. Appl Environ Microbiol 73:7155–7161

50. Vetriani C, Tran HV, Kerkhof LJ (2003) Fingerprinting microbial assemblages from the oxic/anoxic chemocline of the black sea. Appl Environ Microbiol 69:6481–6488
51. Yakushev EV, Debolskaya EI (2000) Particulate manganese as a main factor of oxidation of hydrogen sulfide in redox zone of the Black Sea. In: Oceanic fronts and related phenomena. Konstantin Fedorov Memorial Symposium. Pushkin, Saint-Petersburg. 18–22 May 1998. Proceedings. IOC Workshop Report No. 159. Kluwer Academic Publisher, pp 592–597
52. Yakushev EV, Pollehne F, Jost G, Umlauf L, Kuznetsov I, Schneider B (2007) Analysis of the water column oxic/anoxic interface in the Black and Baltic seas with a redox-layer model. Mar Chem 107:388–410
53. Webb SM, Dick GJ, Bargar JR, Tebo BM (2005) Evidence for the presence of Mn(III) intermediates in the bacterial oxidation of Mn(II). Proc Natl Acad Sci USA 102:5558–5563
54. Ali K, Ashiq U (2004) Study of the kinetics and activation parameters of reduction of Mn(III) to Mn(II) by SO_3^{2-} ion in $(MnSiW_{11}O_{40}H_2)_{5-}$ heteropoly ion. J Iran Chem Soc 1:122–127
55. Kostka JE, Luther GW III, Nealson KH (1995) Chemical and biological reduction of Mn(III)-pyrophosphate complexes: potential importance of dissolved Mn(III) as an environmental oxidant. Geochim Cosmochim Acta 59:885–894
56. Pakhomova SV, YakushevEV (2011) On the role of iron and manganese species in the formation of the redox-interface structure in the Black Sea, Baltic Sea and Oslo Fjord. In: Yakushev EV (ed) Chemical structure of pelagic redox interfaces: observation and modelling. Springer, Heidelberg. Hdb Environ Chem. doi:10.1007/698_2011_98
57. Yakushev EV (2012) Redox layer model: a tool for analysis of the water column oxic/anoxic interface processes. In: Yakushev EV (ed) Chemical structure of pelagic redox interfaces: observation and modelling. Hdb Environ Chem. doi:10.1007/698_2012_145