

Introduction: Redox Interfaces in Marine Waters

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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

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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 *chemotropy* 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 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 $2 \text{ mg O}_2 \text{ L}^{-1}$ ($\sim 63 \text{ } \mu\text{M O}_2$ i.e. [31]) or $2 \text{ ml O}_2 \text{ L}^{-1}$ ($\sim 89 \text{ } \mu\text{M O}_2$ i.e. [1, 32]). The threshold of tolerance, stress responses and morbidity of pelagic and benthic

animals is usually in the range of $1\text{--}4\text{ mg O}_2\text{ L}^{-1}$ (e.g. [32–34]), which corresponds to a threshold molar concentrations of $\sim 75\text{ }\mu\text{M O}_2$.

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 $4.5\text{ }\mu\text{M O}_2$ [36] to $15\text{ }\mu\text{M O}_2$ [37]. A value of $10\text{ }\mu\text{M}$ [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 $\sim 15\text{ }\mu\text{M O}_2$ 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 $\sigma_\theta \sim 15.3\text{ kg m}^{-3}$ for the Black Sea [41]. The lower boundary of this layer corresponds to the disappearance of oxidised manganese species, $\sigma_\theta \sim 16.15\text{ kg m}^{-3}$ 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

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