

Investigating hypoxia in aquatic environments

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# Investigating hypoxia in aquatic environments: diverse approaches to addressing a complex phenomenon

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## Abstract

In this paper we synthesize the new knowledge on oxygen and oxygen-related phenomena in aquatic systems, resulting from the EU-FP7 project HYPOX (“In situ monitoring of oxygen depletion in hypoxic ecosystems of coastal and open seas, and land-locked water bodies”, [www.hypox.net](http://www.hypox.net)). In view of the anticipated oxygen loss in aquatic systems due to eutrophication and climate change, HYPOX was set up to improve capacities to monitor hypoxia as well as to understand its causes and consequences.

Temporal dynamics and spatial patterns of hypoxia were analysed in field studies in various aquatic environments, including the Baltic Sea, the Black Sea, Scottish and Scandinavian fjords, Ionian Sea lagoons and embayments, and in Swiss lakes. Examples of episodic and rapid (hours) occurrences of hypoxia as well as seasonal changes in bottom-water oxygenation in stratified systems are discussed. Geologically-driven hypoxia caused by gas seepage is demonstrated. Using novel technologies, temporal and spatial patterns of water-column oxygenation, from basin-scale seasonal patterns to meter-scale submicromolar oxygen distributions were resolved. Existing multi-decadal monitoring data were used to demonstrate the imprint of climate change and eutrophication on long-term oxygen distributions. Organic and inorganic proxies were used to extend investigations on past oxygen conditions to centennial and even longer timescales not resolved by monitoring. The effects of hypoxia on faunal communities and biogeochemical processes were also addressed in the project. An investigation of benthic fauna is presented as an example of hypoxia-devastated benthic communities that slowly recover upon a reduction in eutrophication in a system where natural and anthropogenic hypoxia overlap. Biogeochemical investigations reveal that oxygen intrusions have a strong effect on microbially-mediated redox cycling of elements. Observations and modeling studies of the sediments demonstrate the effect of seasonally changing oxygen conditions on benthic mineralization pathways and fluxes. Data quality and access are crucial in hypoxia research. Therefore, technical issues are addressed, including the availability of suitable sensor technology to resolve gradual

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changes in bottom-water oxygen that can be expected as a result of climate change in deep-sea waters. Using cabled observatories as examples, we show how the benefit of continuous oxygen monitoring can be maximized by adopting proper quality control. Finally, we discuss strategies for state-of-the-art data archiving and dissemination in compliance with global standards and how ocean observations may contribute to global earth observation attempts.

## 1 Introduction

Oxygen concentrations in the open ocean and in coastal areas are decreasing worldwide (Diaz, 2001; Diaz and Rosenberg, 2008). Ocean models predict declines of 1 to 7% in the global ocean oxygen inventory over the next century (Keeling et al., 2010) and analysis of open ocean oxygen recordings already indicate a decrease of oxygen in the ocean interior (Stramma et al., 2008). Oxygen depletion and “hypoxia” develop wherever the consumption of oxygen by organisms or chemical processes exceeds the supply of oxygen from adjacent layers of water or from the atmosphere.

Natural as well as anthropogenic drivers may be responsible for oxygen depletion. Specific hydrodynamic conditions, i.e., enclosed and semi-enclosed water bodies with limited water exchange and long water retention times, wind-shielded fjords and lakes or freshwater lenses in coastal seas near river mouths may make aquatic systems naturally prone to oxygen depletion. In addition, oxygen decline is often related to the respiration of organic matter and reduced substances, to a lack in oxygen supply due to density stratification, and to advective intrusion of oxygen-poor waters from deeper layers or adjacent water bodies. Geologically-driven hypoxia or anoxia by the release of gases (e.g., methane and carbon dioxide) is less common but has been reported from African lakes, the Cariaco Basin, from offshore Namibia, from the Gulf of Mexico and from tectonically active areas of western Greece (Nayar, 2009; Ward et al., 1987; Kessler et al., 2005, 2011; Monteiro et al., 2006; Etiope et al., 2006).

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Warming induced by climate change adds to oxygen depletion as it reduces the solubility of oxygen in water, and enhances microbial activity. Warming of the upper water column and the increase in precipitation strengthens water-column stratification, impeding mixing and hindering the transport of oxygenated water to greater ocean depths. In lakes analogous processes occur. Global warming also results in rising lake surface water temperatures (Adrian et al., 2009) and an increase in the intensity and duration of thermal stratification (Stefan et al., 1998; Peeters et al., 2002; Livingstone, 2003). During winter and spring – when temperate lakes typically undergo deep mixing – shorter or even absent periods of homothermy will reduce or inhibit deep-water renewal, resulting in lower deep-water oxygen concentrations (Stefan et al., 1996; Livingstone, 1997; Peeters et al., 2002; Jankowski et al., 2006; Rempfer et al., 2009, 2010). Climate warming is therefore likely to lead to an increase in the occurrence of hypoxia in lakes (Stefan and Fang, 1994; Jankowski et al., 2006). Locally, however, global change may give rise to opposite effects. For example, increasing winds enhance mixing in the water column of marine as well as freshwater systems. Alterations in the freshwater balance may reduce density gradients (Neumann, 2010).

Anthropogenic drivers, e.g., agriculture, industry, and urbanization impose pressures upon aquatic ecosystems, like the pollution of coastal seas with fertilizers and sewage leading to persistent algal blooms (“eutrophication”), and affect both the supply and uptake of oxygen. Planktonic photosynthesis may temporarily increase oxygen concentrations in the upper water layers until the organic matter eventually settles from the sunlit surface layer. Upon microbial degradation of the organic material below the euphotic zone and at the seafloor oxygen is utilized and deep-water oxygen concentrations decrease. If bottom-water oxygen drops significantly, ecosystems undergo successive deterioration, eventually turning into permanently anoxic environments where microorganisms replace all higher life. This collapse of aquatic communities leads to a dramatic decline in ecosystem function and services such as biodiversity, fisheries, aquaculture and tourism (Levin et al., 2010; Zhang et al., 2010). In many systems, effects of warming and eutrophication may coincide. In the Baltic Sea, for example, the

projected decrease in oxygen concentrations is expected to be caused by a reduced oxygen supply from the atmosphere due to increasing temperatures in combination with intensified nutrient availability from runoff and internal cycling (Meier et al., 2011).

Oxygen availability may affect the behaviour, physiology and mortality of organisms of any size and has an influence on the activity of microorganisms and the prevailing biogeochemical processes (Levin et al., 2010; Middelburg and Levin, 2009; Riedel et al., 2012). Hypoxia thus substantially affects ecosystem functioning, with strong implications for all ecosystem components, biodiversity, biologically-mediated cycling of matter and ecosystem services such as fisheries and tourism. In general, oxygen-stressed ecosystems tend to have less diverse abundance of long-lived species and reduced trophic complexity, and instead show a shift towards smaller opportunistic species (Pearson and Rosenberg, 1978; Nilsson and Rosenberg, 2000). Because of the plurality of ecosystem components and their individual reactions it is evident that the term “hypoxia” has to refer rather to a process- or biota-specific grade of low-oxygen stress than to some general concentration threshold. Vaquer-Sunyer and Duarte (2008) showed that oxygen depletion induces significant mortality when concentrations are 2.3 times higher than the threshold of  $62.5 \mu\text{molL}^{-1}$  conventionally used in the literature. This indicates that organisms may be suffering from oxygen limitation in areas not presently designated as hypoxic. It has been suggested that thresholds for hypoxia in coastal ecosystems are higher than previously thought and are not static, but regulated by local and global processes, being particularly sensitive to warming (Steckbauer et al., 2011), and also dependent on levels of other parameters such as  $p\text{CO}_2$  (Brewer et al., 2009; Hofmann et al., 2011). In this paper, term “hypoxia” is not assigned to a specific concentration threshold but rather to an environmentally significant degree of oxygen depletion that depends on the effect or process studied.

The importance of long-term monitoring of oxygen concentrations has been recognized for many decades. The earliest systematic records of coastal hypoxia from Europe and North America date back to the 1910s (Zhang et al., 2010; Petersen, 1915; Sale and Skinner, 1917).

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Oxygen monitoring is typically carried out annually, seasonally or monthly during ship-based surveys. Long-term time-series measurements are critical for identifying the influence of climate variability vs. anthropogenic pressures. On the other hand, ship-based monitoring cannot cover the spatial extent of hypoxia nor temporal dynamics on shorter time-scales or stochastic and episodic low-oxygen events. Ecosystem responses, however, depend on frequency, duration, spatial extent and severity of hypoxia events, and thus require continuous monitoring of oxygen. The need for an improved and continuous monitoring of oxygen is even more pronounced due to the prediction of generally declining oxygen concentrations in the future (Keeling et al., 2010). Observations with an improved spatio-temporal coverage also facilitate the identification of hypoxia drivers and help constrain numerical models. The need to develop new observational tools and models to support integrated research of biogeochemical dynamics and ecosystem behaviour that will improve confidence in remediation management strategies for coastal hypoxia has been highlighted also by the SCOR working group 128 on natural and human-induced hypoxia and consequences for coastal areas (Zhang et al., 2010).

The core objective of the EC-FP7 project HYPOX (“In situ monitoring of oxygen depletion in hypoxic ecosystems of coastal and open seas, and land-locked water bodies”, www.hypox.net) was to better understand the causes of hypoxia formation and improve the predictive capacity of models. To this end, HYPOX initiated a comprehensive and state of the art programme for monitoring of oxygen and related parameters in a variety of aquatic systems that differ in oxygen

status or sensitivity towards change. HYPOX working areas (Fig. 1 and Table 1) are subject to a large variety of natural and anthropogenic causes of oxygen depletion and show a wide range in the severity of oxygen deficiency. They are located in coastal and open seas including the North Atlantic–Arctic Ocean transition (Fram Strait), three contrasting sites in the Black Sea (Bosporus outlet area, Romanian Shelf, Crimean Shelf), as well as two Baltic Sea sites (Gotland Basin and Boknis Eck in Eckernförde Bay). Several lagoons and embayments in the subtropical/Mediterranean Greek Ionian

Sea were also studied, as well as fjord systems (Koljoe Fjord in Sweden and Loch Etive in Scotland). Swiss lakes were investigated as examples of land-locked freshwater water systems. For several of the sites, including North Atlantic, Boknis Eck, Lake Zurich, Koljoe Fjord, and Loch Etive, multi-decadal long-term monitoring data exist for oxygen and related parameters, e.g., Bange et al. (2011) (Boknis Eck), Zimmermann et al. (1991) (Lake Zurich), [http://produkter.smhi.se/pshark/datamap\\_bohuskusten.php](http://produkter.smhi.se/pshark/datamap_bohuskusten.php) (Koljoe Fjord area).

To gain deeper insights into the various drivers and mechanisms of hypoxia formation, the core part of the HYPOX project was dedicated to the development of monitoring strategies for oxygen and associated parameters tailored to the types of oxygen depletion found at the respective sites. In addition, we looked for fingerprints of past hypoxia in the sediment record using organic and inorganic biomarkers. In order to extend the gained knowledge in space (i.e., generalization of the findings) as well as in time (i.e., extrapolation of current observations into the future) modeling was an intrinsic part of our approach. These generalizations and forecasting capabilities facilitate an examination of the effects of future climate and eutrophication scenarios on oxygen availability and ecosystem functioning. Observations of oxygen availability and the response of animal communities and ecosystems to hypoxia are needed, not only to improve our understanding of the potential loss of ecosystem functions and services as a consequence of global warming and eutrophication but also to identify early warning indicators and tipping points in the wider ecosystem.

This paper is arranged in seven chapters. Following this introduction (chapter one), chapter two briefly introduces the study sites. In chapter three we describe our approaches to observe hypoxia at appropriate scales with a focus on temporal dynamics and spatial scales of hypoxia. Chapter four reports on investigations of long-term changes in present and past hypoxia. Chapter five is dedicated to effects of hypoxia on faunal patterns and biogeochemical processes. Chapter six tackles how to improve data quality and access of the monitoring data as well as data dissemination. Finally,

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conclusions and recommendations from three years of hypoxia research in HYPOX are provided in chapter seven.

## 2 Description of study sites

### 2.1 Open and shelf seas

5 In the Baltic Sea our focus of work was in the Gotland Basin on temporal dynamics of the oxic–anoxic interface between low-density surface waters and more dense and saline deep waters that originate from climate-controlled inflow events of North Sea waters. Additional investigations focused on the effect of hypoxia on the release of reduced substances, e.g., phosphorus, from the sediments in Boknis Eck. Currently, the  
10 release of phosphorus from sediments is estimated to be an order of magnitude larger than the anthropogenic input (Conley et al., 2009), and may be an important driver of harmful algal blooms and subsequent oxygen depletion at depth. The Baltic Sea is the second largest brackish water system of the world: It has a mean depth of 52 m (max. 460 m), an area of  $\sim 413\,000\text{ km}^2$  and a volume of  $\sim 22\,000\text{ km}^3$  (Feistel et al., 2008).  
15 The Baltic Sea consists of several deep basins (Arkona Basin, Bornholm Basin, Eastern and Western Gotland Basin, Gulf of Finland, Gulf of Bothnia, Bothnian Bay) which are separated by shallow sills (e.g., Drodgen Sill and Darss Sill). The sills restrict the propagation of North Sea saline waters at depth and deep-water exchange between the basins. In particular the largest basin (i.e., Gotland Basin) is thus naturally prone to a permanent haline stratification, long residence times, and oxygen deficiency in the deeper water layers. In the Baltic Sea basins, hypoxia has been naturally occurring  
20 intermittently since its formation 8000 yr BP during several periods in the Holocene, including the medieval warm period (Leipe et al., 2008), while anthropogenic eutrophication increased the spatial extent and intensity of oxygen depletion (Conley et al., 2009).  
25 This situation is exacerbated by the large drainage basin and anthropogenic nutrient surplus (Feistel et al., 2008). The Baltic Sea is surrounded by industrialized countries

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with intensive agricultural activity and, with a catchment area of  $> 1\,700\,000\text{ km}^2$ , experiences significant freshwater runoff over the entire basin. The Baltic Sea is thus affected by both natural and anthropogenic drivers and pressures, and is very sensitive to eutrophication (HELCOM, 2009). Nutrient concentrations peaked during the 1980s and have since declined due to successful efforts to reduce nutrient loads from land. However, only 13 areas (2 open basins and 11 coastal) in the Baltic Sea are classified as “areas not affected by eutrophication”, whereas 176 areas (15 open basins and 161 coastal sites) remain “areas affected by eutrophication” (HELCOM, 2009). Nutrient input from the sediments (“internal nutrient loading”) is also a serious problem and more significant than terrestrial inputs in the Gulf of Finland (Pitkanen et al., 2001) and the Baltic Proper (Viktorsson et al., 2013). In addition, projected climatic changes are stronger for the Baltic Sea than the global average (BACC, 2008), affecting both the freshwater balance and the seasonal extent of ice in the northern part.

Bottom waters in the central part of the Gotland Basin (a on panel I of Fig. 1) have been hypoxic and anoxic for more than half of the past 50 yr. Since the late 1970s, major salt-water inflow events of oxygenated saline water from the North Sea have resulted in only two short ventilation episodes in 1993 and 2003. Yet, the resupply of saline water leads to a stabilization of the permanent stratification and slight uplift of the halocline, which results in an extension of the area exposed to hypoxic conditions (Conley et al., 2009). Some of the shallower, yet mostly stratified basins of the Baltic Sea (i.e., the Bornholm and Arkona Basin) encounter hypoxic or anoxic conditions on shorter time-scales with clear seasonality (Feistel et al., 2008). The Baltic Sea thus provides an ideal natural laboratory to study the impact of intermittent oxygen deficiency on different time-scales.

Boknis Eck is a narrow channel located at the northern entrance of Eckernförde Bay in the southwestern Baltic Sea ( $54^{\circ}31' \text{ N}$ ,  $10^{\circ}20' \text{ E}$ , b on panel I of Fig. 1), and has a maximum water depth of about 28 m. The hydrography of Boknis Eck is dominated by regular inflow of North Sea water through the Kattegat and the Danish straits while riverine input is negligible. Higher salinity of the inflowing North Sea water in combi-



nation with temperature increase at the surface lead to a pronounced summer stratification and the development of a pycnocline at about 15 m water depth. Phytoplankton blooms in autumn (September–November) and spring (February–March) are followed by pronounced sedimentation of organic material (Smetacek et al., 1984). While stratification restricts vertical mixing, organic matter supply causes an increase in benthic activity and oxygen demand in the deep layer (Graf et al., 1983). These factors cause pronounced seasonal hypoxia and, in more recent times, anoxia during late summer (Hansen et al., 1999). In addition, low-oxygen conditions are accompanied by elevated benthic fluxes of phosphate and ammonium (Balzer et al., 1983; Dale et al., 2013). Storms and a decrease in surface-water temperature cause a mixing of the water column and ventilation of the deeper water in autumn (Hansen et al., 1999).

The Black Sea suffers from combined effects of anthropogenic eutrophication, overfishing and climate forcing (Oguz and Gilbert, 2007; Mee et al., 2005), and thus allows to study many aspects of natural and man-made hypoxia. Consequently, Black Sea studies within HYPOX included investigations of oxygen fluctuations in bottom waters (Romanian shelf, Crimean shelf), effects of oxygen on benthic fauna and biogeochemical cycles (Bosporus outlet area, Romanian shelf, Crimean shelf), ecosystem recovery following a reduction in anthropogenic nutrient load (Romanian shelf), and studies of past redox conditions (Bosporus outlet area, Fig. 1).

The Black Sea is a semi-enclosed basin and contains the world's largest volume of natural permanently anoxic waters at depths below approximately 200 m since ca. 7500 yr BP (Jones and Gagnon, 1994). The sea is climatologically strongly influenced by the North Atlantic Oscillation (NAO) (Oguz et al., 2006) and there is a strong link between climate forcing and biological productivity (Oguz and Gilbert, 2007). The basin is largely isolated from the world ocean and only limited water exchange with the Mediterranean takes place via the Bosporus Strait and the Sea of Marmara. Precipitation and evaporation are roughly balanced. The Black Sea receives strong freshwater input by river runoff that mainly enters the surface layers on the western shelf by the Danube, Dnieper and Dniester rivers, and by numerous smaller rivers discharging in the south,

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east and north. The freshwater input leads to a strong natural thermohaline stratification which restricts vertical transport and is responsible for lack of oxygen at depth. The rivers collect wastewater from more than 100 million people in the catchment which has led to elevated nutrient inputs from the major rivers and resulted in high-productivity regimes (Oguz and Gilbert, 2007). The Black Sea has been recognized as a natural laboratory for studying various effects of climate forcing and anthropogenic drivers and pressures over the last decades. Before the onset of eutrophication, changes in the distribution of oxygen were attributed to seasonal variations in the solubility of oxygen and in the depth of the upper boundary of the sulfidic layer (Skopintsev, 1975). Apart from the inflow of Mediterranean water, the Bosphorus outlet area (c on panel I of Fig. 1) is characterized by a rim current at the shelf margin and hypoxia below ca. 100 m water depth. The mean annual inflow of Mediterranean water through the Bosphorus has been estimated from salt and water budgets to be  $310 \text{ km}^3 \text{ yr}^{-1}$  (Ünlüata et al., 1990). Field studies (Latif et al., 1991) suggest a continuous inflow of Mediterranean water, which is occasionally interrupted for short durations (2–3 days) under strong and persistent northerly winds. The oxic, warm, and saline Mediterranean water cascades down the continental shelf to greater depths where it mixes with the adjacent anoxic waters, detaches from the slope and forms the so-called “Bosphorus Plume”. After oxygen is consumed, the Bosphorus Plume waters can still be detected by temperature anomalies, which have been measured up to  $\sim 80$  nautical miles off the Bosphorus mouth (Konovalov et al., 2003).

The Romanian shelf is part of the broad western shelf and receives most of the river runoff (d on panel I of Fig. 1). The freshwater input leads to strong natural thermohaline stratification and also to seasonally restricted ventilation of deeper water layers on the shelf. This represents a natural driver for hypoxia and makes the western shelf prone to oxygen deficiency near the seafloor, particularly during summer. During autumn and winter, the thermohaline stratification is eroded by frequent storms and the water column is re-oxygenated. Strong small-scale anticyclonic eddies that are present at the shallow shelf (Beckers et al., 2002) keep nutrient-rich water in the area and allow for

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high primary productivity. Oxygen depletion as a consequence of anthropogenic eutrophication seriously affected the shelf from the early 1970s to the mid-1990s (Mee, 1992; Zaitsev, 1992; Tolmazin, 1985). More frequent and intense algal blooms (particularly of non-siliceous species as a result of the construction of damming, e.g., Humborg et al., 1997), red tides (i.e., *Noctiluca*, *Prorocentrum cordatum* blooms) and changes in phytoplankton species composition led to deposition of surplus organic matter on the seafloor, causing frequent hypoxic and even anoxic events during the summer for more than 20 yr with serious consequences for pelagic and benthic ecosystem structure and functioning as well as living resources, tourism and recreation (BSC, 2008; Mee et al., 2005). During eutrophication-induced hypoxia, the sediments on the western shelf released half as much phosphorus as the entire input from the Danube River in the same period of time (Friedrich et al., 2002), thereby internally fuelling eutrophication. Statistical models indicate that eutrophication and climate explain a similar amount of the hypoxia inter-annual variability (Capet et al., 2013).

The western shelf benthic ecosystem showed a significant reduction in species diversity, an increase in the abundance and biomass of zoobenthic populations due to invasive species (*Mya arenaria*, *Rapana venosa*), a reduction of biofilter strength due to the loss of filter-feeder populations (e.g., *Mytilus galloprovincialis*), as well as the flourishing of opportunistic species such as worms and ascidians. Following the economic collapse in the eastern European countries during the 1990s, riverine nutrient loads decreased and the ecosystem is showing signs of slow recovery, such as a decrease in the frequency and duration of hypoxic events (Langmead et al., 2009). Yet, the estimated load of nutrients and phytoplankton biomass remained high in the 1990s, as compared to the pre-eutrophication period (Yunev et al., 2007).

At the Crimean shelf (e on panel I of Fig. 1) the position and structure of the chemocline is strongly influenced by anticyclonic gyres that are located outside of the main Rim Current as well as by internal waves and synoptical variability of the Black Sea circulation pattern (Filonov, 2000). Quasi-periodical and incidental vertical fluctuations of the oxycline and the oxic–anoxic interface have been observed to occur at the Crimean

shelf (Luth et al., 1998). The temporal changes in the depth of the oxygen–sulfide interface cover a range of 130 to 165 m corresponding to lateral intrusions of up to 1 km distance along the shelf sea floor. This may occasionally aerate the seafloor below the average pycnocline depth, or flush the lower part of the oxic seafloor areas with anoxic waters. The temporal dynamics and intensity of these disturbances, as well as their intermediate effect on benthic communities and biogeochemical processes, remain poorly resolved.

Long-term monitoring of oxygen in the deep-sea at the North Atlantic/Arctic transition in the Fram Strait is crucial to understand the effects of global warming and changes in deep-sea circulation (Soltwedel et al., 2005) and their potential effects on oxygenation of the deep ocean. The Fram Strait is the only deep connection between the central Arctic Ocean and the Nordic Seas, where exchange of intermediate and deep waters take place (Rudels et al., 2000; Fahrbach et al., 2001). The so-called “HAUSGARTEN” area in the Fram Strait west of Spitsbergen (f on panel I of Fig. 1) is characterized by the inflow of relatively warm and nutrient-rich Atlantic Water into the central Arctic Ocean (Manley, 1995). Recent years exhibited a strong increase in the annual mean net heat transport within West Spitsbergen Current waters, with the strongest increase in the Yermak Branch (Schauer et al., 2004). Circulation patterns in the Fram Strait result in a variable sea-ice cover, with permanent ice-covered areas in the west, permanent ice-free areas in the south-east, and seasonal varying ice conditions in central and north-eastern parts, i.e., in the wider HAUSGARTEN area. The dramatic decrease in summer sea-ice extent observed over the last decades will cause an on-going northward shift of the ice-edge related primary production. Satellite remote sensing over the last 30 yr revealed a continuous decrease of the Arctic summer minimum sea ice area by approximately 10 % per decade attributed to global warming. Further alterations in sea ice cover, water temperature and primary production are expected, but the consequences for the wider ecosystem are largely uncertain (Weslawski et al., 2009). In order to understand the impact of large-scale environmental changes on the Arctic marine ecosystem, the German Alfred Wegener Institute for Polar and Marine Research

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(AWI) established the deep-sea observatory HAUSGARTEN in 1999 (Soltwedel et al., 2005). Today, the observatory includes 17 permanent sampling sites along a bathymetric transect covering water depths between 1000–5500 m, and along a latitudinal transect following the 2500 m isobath. Multidisciplinary research activities at HAUSGARTEN cover almost all compartments of the marine ecosystem from the pelagic zone to the benthic realm. Although the marine ecosystem in Fram Strait system is far from being classified as hypoxic, the observatory serves as a model site to study a possible link between climate change, bottom-water circulation changes, and oxygen supply in the open ocean.

## 2.2 Land-locked water bodies

Loch Etive is a 0.2–2 km wide and 30 km long Scottish fjord with 6 shallow sills of 7–13 m water depth and a glacially deepened hollow in its inner part (Figs. 1 and 9, g on panel I). Located on the Scottish west coast, it is well exposed to the Northern Atlantic and characterized by relatively low industrial and agricultural pressure. Previous modeling studies suggested that the oxygen depletion occurring in the inner deep basin of Loch Etive is mainly dominated by naturally driven factors (Edwards and Edlesten, 1977). Tidally forced exchange through a complicated geometry of narrow straits combined with water-column stratification generates nonlinear 3-D dynamical features such as reversing tidal jets with V-shape leading edges, standing lee waves and internal tides. The interaction of several factors such as current velocity, stratification, sill geometry and tidal oscillation frequency is required to displace the isopycnals to depths below the interface that separates deep stagnant waters from the upper well mixed layer. Renewal events only take place if the density of arriving water intrusions is higher than the density of the resident bottom waters in the inner part of the basin. Investigations in Loch Etive, and the Swedish Koljoe Fjord described below, aimed to resolve temporal dynamics and drivers of episodic water-renewal events that occasionally aerate stagnating and hence oxygen-depleted deep waters. In both systems, deep-water exchange was known to be partly wind-driven but the processes controlling

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ventilation events had not been entirely resolved (Nordberg et al., 2001; Edward and Edelsten, 1977).

Koljoe Fjord is a fjord basin within the Orust-Tjörn fjord system on the Swedish west coast (h on panel I of Fig. 1). It is sandwiched between the open Skagerrak in the west and the adjacent fjord basin Havstensfjord in the east. Havstensfjord itself is connected to a series of basins further south that eventually also open up to the Skagerrak. Narrow sills of intermediate depth separate Koljoe Fjord from the other water bodies. The deepest part of the basin reaches 45 m. The fjord is stratified with an approximately 10 m thick surface layer. A halocline at 13 m water depth prevents wind induced mixing to oxygenate the water below. Oxygen concentrations in the deep water are therefore quickly reduced after renewal events, and the fjord is prone to long stagnation periods with hypoxic or anoxic conditions (e.g., Nordberg et al., 2001). Sinking organic matter from terrestrial sources, runoff and algal blooms worsen the situation. A coastal monitoring program has been in place for several years in the fjord system. Stations are located at three places within the fjord system, and at the southern entrance. Since 1990, monitoring has generally been undertaken on a monthly basis.

In Greek lagoons along the Ionian coast of western Greece, locally constrained low-oxygen zones are observed to occur episodically around gas seepages. The Ionian coast represents the main petroliferous area in Greece. Active tectonics and salt diapirism induces important onshore and offshore gas and oil seepages (Papatheodorou et al., 1993; Hasiotis et al., 2002; Etiopé et al., 2006; Karakitsios and Rigakis, 2007; Kamberis et al., 2000). We hypothesize that gas seepage represents a geogenic driver for hypoxia events. Investigations carried out at these sites focused on gas seepages and on the combined effects of hydrographic setting, sewage and fertilizer input and the release of reduced compounds from the sediments on the occurrence of seasonal and permanent anoxia. We focus on three lagoons: Amvrakikos Gulf, Aetoliko Lagoon, and Katakolo Bay (panel VI of Fig. 1).

Aetoliko Lagoon is situated at the northern part of Messolonghi-Aetoliko Lagoon complex (b on panel VI of Fig. 1). It represents the largest and most important wet-

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land area in Greece and is protected under the Ramsar convention (Dassenakis et al., 1994). Fishery is a traditional activity in the lagoons and fundamental for the local economy. The southern part of the lagoon is connected with the open sea (Patras Gulf) through the shallow Messolonghi lagoon. The northern part of Aetoliko lagoon represents the deepest part of the lagoon complex. The lagoon exhibits permanent thermohaline stratification due to low water circulation and limited exchange with the open sea. Below the well oxygenated surface water layer the water is permanently anoxic with hydrogen sulfide concentrations of up to  $176 \mu\text{mol L}^{-1}$ .

Amvrakikos Gulf is a shallow marine, seasonally anoxic embayment connected to the open Ionian Sea by narrow and shallow straits (a on panel VI of Fig. 1). It is considered to be the only Mediterranean-type fjord (Ferentinos et al., 2010; Kountoura and Zacharias, 2011). The seafloor of the gulf is covered by fine-grained sediments and a thin veneer of black muddy sediments. The vertical distribution of dissolved oxygen seems to be largely controlled by the density stratification of the water column that divides into a brackish surface layer and a saline bottom layer (Ferentinos et al., 2010). Gas seepage-related hypoxia from pockmarks in the southeastern part of the gulf (Amphilochia Bay) has been investigated as part of this study.

Katakolo Bay is an open embayment which is located at the western coast of Peloponnesus (c on panel VI of Fig. 1) and hosts one of the largest offshore thermogenic methane seeps in Europe (Etiopé et al., 2013). Gas seepage is obvious by widespread plumes of bubbles that occur over a shallow,  $94\,200 \text{ m}^2$  area (5.5 to 16 m water depth) and may lead to localized and episodic hypoxia.

The Swiss lakes addressed in our study (panel I of Fig. 1) are deep, wind-shielded water bodies which are typically monomictic; i.e., they mix completely once a year. Recent climate change has caused shifts towards less frequent mixing (oligomixis) (Livingstone, 1993), which can result in deep-water hypoxia (Livingstone, 1997; Rempfer et al., 2010) and the release of phosphorus from the sediment (North et al., 2013b). Current conditions in the lakes, as well as the impact of climate change and the history of hypoxia, were addressed by a combination of measurements and time-series

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analyses. Many lakes on the Swiss Plateau underwent strong eutrophication in the early 1970s as a result of phosphate input from detergents and agricultural runoff. The trophic status of most deep Swiss lakes has improved markedly over the past few decades as a result of measures to combat anthropogenic eutrophication. However, global warming is leading to increased lake surface temperatures worldwide (Schneider and Hook, 2010), which can affect many aspects of lake ecosystems (Adrian et al., 2009). For example, less vigorous mixing paired with a longer duration of stratification (Livingstone, 2003) is likely to result in lower hypolimnetic oxygen concentrations and an increase in the thickness of the hypoxic zone (Livingstone and Imboden, 1996). These climate effects might counteract the benefits of the measures introduced to improve lake trophic status. In Switzerland, the availability of long, high-quality lake profile data, especially from Lake Zurich, allows attempts to be made to quantify the effect of recent climate change on deep-water oxygen concentrations (e.g., Livingstone, 1997; Jankowski et al., 2006; Rempfer et al., 2009, 2010; North et al., 2013b).

Lake Zurich is a medium-sized perialpine lake with a surface area of 65 km<sup>2</sup>, a volume of 3.3 km<sup>3</sup> and a maximum depth of 136 m (Livingstone, 2003). Although typically monomictic, Lake Zurich can also behave as a dimictic or oligomictic lake depending on the winter weather (Rempfer et al., 2010). The recent shift towards oligomixis, a situation in which the lake does not mix completely in some years (Livingstone, 1993), has resulted in some occurrences of extremely low deep-water oxygen concentrations (Livingstone, 1997). Lake Zurich underwent strong eutrophication until the early 1980s. As a consequence of the construction of wastewater treatment plants in the 1970s and 1980s, and the nationwide banning of phosphates in detergents in the 1980s, the total phosphorus concentration in the lake decreased rapidly and the lake is now considered to be weakly eutrophic or mesotrophic (Jankowski et al., 2006).

Lake Rotsee is a small monomictic, eutrophic lake with a surface area of 0.46 km<sup>2</sup>, a volume of 3900 m<sup>3</sup> and a maximum depth of 16 m. During most of the year the water column exhibits a highly stable stratification with a chemocline located between about 6 and 10 m depth (Schubert et al., 2010). Since around 1850, the trophic state in-



creased as a result of sewage input, and in 1920 the lake was classified as polytrophic (Bloesch, 1974; Stadelmann, 1980). Numerous blooms of *Planktothrix rubescens* were observed, which turned the lake water red (Züllig, 1985). In an attempt to restore the lake, a canal to the Reuss River was constructed in 1922 to increase the input of fresh water to the lake (Kohler et al., 1984). However, because of the continued supply of nutrients from a nearby disposal site, the occasional drying up of the canal, and the inability of the water inflow from the canal to initiate mixing (Bachmann, 1931; Stadelmann, 1980), the trophic status of the lake barely changed. Recovery of the lake started slowly after the construction of an interceptor sewer in 1969 and a sewage treatment plant in 1974 (Stadelmann, 1980).

### 3 Observing hypoxia at appropriate temporal and spatial scales

The oxygen concentration of aquatic systems, in particular in areas with strong oxygen gradients, may vary over different temporal and spatial scales. Temporal scales include periodic seasonal or hydrodynamic effects (e.g., tides or internal waves), but can also be of episodic nature, e.g., due to meteorologically triggered intrusions or overflow events. Spatial variability may occur over large areas, such as entire basins and water bodies, or affect the distribution of oxygen and redox-sensitive species on cm-scales within perturbed pelagic redoxclines. Changes in oxygen concentrations might involve the full scale from well-oxygenated to almost anoxic conditions, or be restricted to a narrow range between anoxic conditions and the availability of trace amounts of oxygen. Such minute changes may still have severe implications for marine biota, as for many aquatic organisms oxygen can be either mandatory or toxic. In this chapter, we report on investigations of oxygen distribution that address these different scales. Special emphasis is given to the description of the measurement/monitoring strategies and the chosen methodological and technological approaches.

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### 3.1 Short-term changes of oxygen in the pelagic redoxcline – the example of the Baltic Sea

Strong stratification of the deep Baltic Sea water column results in the formation of a pelagic redoxcline – a transition zone with strong vertical redox gradients. Similar situations are observed in the Black Sea and other stratified marine systems (e.g., many fjords). Oxygen and other major electron acceptors (e.g., nitrate) that are abundant in the upper water layer oxidize reduced species (e.g., sulfide and reduced metal species) that accumulate in deeper waters. Consequently, pelagic redoxclines are prime locations of biogeochemical redox transformations that depend on vertical transport of reduced and oxidized species across this layer. Traditionally, redoxclines have been viewed as gradually evolving layered systems with steady turbulent diffusion as the sole mechanism for vertical solute transport. There is increasing evidence, however, that redoxcline systems in the Baltic and the Black Sea show more complex structure and variability on short time-scales (Dellwig et al., 2010; Konovalov et al., 2003; Glazer et al., 2006). Direct observations of the dynamic properties of pelagic redoxclines cannot be addressed by traditional ship-based monitoring but require continuous measurements. For this reason, a profiling mooring was built within the framework of HYPOX (Prien and Schulz-Bull, 2011) which allowed, for the first time, the temporal evolution of redox conditions in the water column of the central Eastern Gotland Basin to be observed (left panel of Fig. 2). An underwater winch equipped with a positively buoyant instrumentation platform was moored at a depth of about 185 m (a on panel II of Fig. 1). At regular time-intervals the winch released the cable and the instrumentation platform ascended, recording profiles of oxygen, standard oceanographic parameters, as well as chlorophyll *a*, fluorescence, turbidity, oxidation reduction potential, and pH. The right panel of Fig. 2 shows the dissolved oxygen concentration assembled from 171 profiles recorded every eight hours over a 56 day winter deployment. The measurement series reveals not only fast changes in oxygen concentrations of more than  $5 \mu\text{molL}^{-1} \text{h}^{-1}$  in a layer several tens of meters thick between the oxycline and the

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anoxic deep layer, but also frequent intrusions of oxygenated water into deeper water layers with low oxygen concentrations. This high temporal variability is indicative of a complex three-dimensional structure of the redoxcline created by lateral import of different water masses due to complex hydrodynamic processes (e.g., baroclinic and barotropic inflows, breaking internal waves, upwelling, and boundary mixing; Reissmann et al., 2009).

These complex and dynamic conditions have important implications. Increased turbulent mixing of, for example, oxic or nitrate-bearing waters with sulfidic waters will most likely enhance biogeochemical transformation processes and alter microbial community composition. Large changes in redoxcline stability and structure may lead to strong shifts in the nitrogen as well as manganese cycle (Hannig et al., 2007; Dellwig et al., 2010). At the same time these processes will determine major transport schemes across the oxic–anoxic boundary. One example is the transport of phosphate from deeper waters towards the sunlit surface layer of the Baltic where it may facilitate blooming of cyanobacteria. Based on these findings the redoxcline appears as a dynamic and three-dimensional system, controlled or strongly modified by intermittent lateral transport processes rather than by continuous vertical diffusion. This provides an exciting new perspective for explaining observations that have so far remained enigmatic such as the absence of microbial communities under favourable growth conditions and the occurrence of chemical intermediates in the water column that are decoupled from the redox conditions at the time of observations.

### 3.2 Fast redox fluctuations at the seawater sediment interface – examples from the Gotland Basin (Baltic Sea) and the Crimean shelf (Black Sea)

Where temporally dynamic and spatially complex redoxclines impinge the seafloor (see previous section), bottom-water oxygen conditions are likely to show similarly pronounced short-term fluctuations. Such fluctuations can be expected to have a strong impact on sessile benthic fauna. Even under spatially uniform redox conditions in a stratified water column hydrodynamic displacement of isopycnal interfaces may

cause rapid changes in oxygen availability at the seafloor. Oxygen time-series data were collected in the lowermost water column in the eastern Gotland Basin (a on panel II of Fig. 1) and the south-western Crimean shelf (d on panel III of Fig. 1) to investigate the variability of bottom-water oxygenation in permanently stratified systems.

Stand-alone benthic observatories (left panel of Fig. 3) were deployed at the seafloor of the Gotland Basin at the depth of the redoxline (90 m). The right panel of Fig. 3 shows persistent fluctuations in the range of 17 to 28  $\mu\text{molL}^{-1}$  as they occurred in summer 2010 in the eastern Gotland Basin during calm weather. Measurements obtained at the same station during turbulent meteorological conditions in autumn 2009 depicted much larger fluctuations with episodic oxygenation events of up to 200  $\mu\text{molL}^{-1}$ . Similar conditions were observed at the south-western Crimean shelf during calm weather in April–May 2010. Here, oxygen concentrations 1 m above the seafloor were generally highly variable and occasionally dropped from  $> 150 \mu\text{molL}^{-1}$  to almost anoxic condition within less than two hours (Fig. 4b). A compilation of oxygen measurements carried out by various instruments showed that sediments at water depths of 130 to 145 m on the south-western Crimean shelf were exposed to bottom waters alternating between oxic, hypoxic, and anoxic conditions. Variations in oxygen concentration and water density were strongly correlated, revealing that the observed changes in bottom-water oxygen were indicative of dynamic shifts of the pycnocline. In general, the driving forces behind the variability can be manifold ranging from small- to large-scale processes such as internal waves, the passage of mesoscale eddies, Ekman pumping, atmospheric pressure oscillations and tides. The stronger the gradients in the pycno- and oxycline, the greater are the impact of their vertical displacement on benthic oxygen conditions. Although tidal sea level changes are only a few centimeters in the Black Sea, the up and down shifts of the water column caused an oxygen variability of up to 20  $\mu\text{M}$  in the oxycline at the Crimean shelf.

The examples from the Gotland Deep and Black Sea show that continuous recordings at high frequency are needed in order to accurately characterize benthic oxygen

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levels in stratified waters at the depth of the redoxcline. The pronounced oscillations in bottom-water oxygenation are expected to have severe effects on the inhabiting benthic communities and may affect organic matter remineralization and redox cycling of major elements as well as the associated nutrient release from the underlying sediments.

### 3.3 Fine structure of the lower oxycline – the example from Swiss lakes

The Baltic Sea profiling mooring described in Sect. 3.1 revealed the strong spatio-temporal dynamics of redoxclines in stratified marine basins. Of particular significance for redox cycling is the oxic–anoxic interface since the rates of many biogeochemical processes are determined by the presence or absence of oxygen (e.g., Canfield et al., 2005). Standard oxygen sensors are not able to detect oxygen down to the trace concentrations required to fully understand the distribution of biogeochemical processes and redox species in the environment (Stolper et al., 2010; Thamdrup et al., 2012). To resolve redoxcline oxygen distributions at the relevant scales of concentration and time, oxygen sensors need to be sensitive and respond quickly. The recently developed self-calibrating switchable trace oxygen (STOX) sensor resolved the problem of drift in amperometric oxygen sensors and lowered the detection limit to trace levels ( $2 \text{ nmolL}^{-1}$ ) (Revsbech et al., 2009). However, the time needed for calibration cycles (15 s in especially fast cycling sensors, few minutes for regular sensors; Revsbech et al., 2011) limits speed or vertical resolution in profiling applications. Investigations within HYPOX revealed that standard (i.e., non-switchable) amperometric as well as optical oxygen microsensors are suitable to fully characterize the fine-scale structure of the oxic/anoxic interface in stratified water columns (right panels of Fig. 5). Utilizing the deep anoxic water layer as an in situ calibration point solved issues of drift and offset for the amperometric sensors. Combined with novel signal amplification techniques this allowed the reduction of the detection limit to  $< 10 \text{ nmolL}^{-1}$  at a signal resolution of  $< 0.1 \text{ nmolL}^{-1}$  per bit (for detailed method description see Kirf et al. 2013a). The optical microsensor also showed a good performance without any measurable drift, a detection limit of  $< 20 \text{ } \mu\text{molL}^{-1}$ , and smallest increments of  $4 \text{ nmolL}^{-1}$ . During par-

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allel use the two independent sensor systems recorded virtually identical profiles and proved both able to resolve submicromolar oxygen concentrations at the bottom of the oxycline. The sensor systems were integrated into the custom-built “Profiling Analyzer” (PIA) platform to combine high-resolution in situ sensing and sampling capabilities with online data transfer (left panel of Fig. 5).

The application of the new sensor-array to the water column of the permanently stratified Swiss Lake Zug revealed hitherto unobserved extensive meter-scale submicromolar zones (right panels of Fig. 5). The existence of these extended layers of trace oxygen concentrations are not resolved with traditional CTD surveys using standard electrochemical or optical macro sensors. Similarly, extrapolation from the upper part of the oxycline (e.g., between 200 and 10  $\mu\text{molL}^{-1}$ ) to zero oxygen underestimates the true thickness of the layer of trace oxygen concentrations and cannot account for the observed small-scale variability. In Lake Zug and Lake Rotsee the depth of the oxic–anoxic interface as well as the spatial distribution of oxygen concentrations in the low micromolar to submicromolar range varied between casts and within a single cast between sensors separated laterally by as little as 25 cm. This indicates pronounced small-scale variability in redoxcline conditions. Given the low diapycnal mixing in the two lakes this small-scale variability can persist over time-scales relevant for microbial processes and may create transitional habitats where specific microorganisms can thrive. The significance of trace oxygen concentrations for microorganisms and, hence, biogeochemical processes was confirmed by parallel sampling at the lower end of the oxycline (Kirk et al., 2013b) that indicated a clear separation of redox processes taking place at trace oxygen levels from those occurring at anoxic conditions below the true oxic–anoxic interface. Results obtained in the water column of the Swiss lakes are again challenging the traditional view of the pelagic oxycline as a stable and uniform habitat with a sharp, stationary, and two-dimensional oxic–anoxic interface (see also Sect. 3.1). Investigations at appropriate scales are needed for improved understanding of the spatio-temporal nature of the lower oxycline.

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### 3.4 Seasonal changes in oxygen – examples from the Western Black Sea shelf and western Baltic Sea

To monitor the seasonal evolution of bottom-water hypoxia on the Western Black Sea shelf, a stand-alone benthic mooring was deployed at 28 m water depth off Constanta (Romanian shelf) from May to August 2010 (c on panel III of Figs. 1 and 6c). This provided the first long-term in situ time-series of bottom-water oxygen, temperature, turbidity, salinity, and current velocity on the Western shelf and allowed biological and hydrophysical controls on oxygen to be identified. During cold weather until May and June in 2010, along with low biological activity, bottom-water oxygen remained constant (Fig. 6a), and CTD profiles revealed the absence of a thermocline (data not shown). From mid-June to mid-July, oxygen decreased from 230 to 100  $\mu\text{M}$ , while bottom-water turbidity remained low. The presence of a thermocline likely reduced bottom-water ventilation. Small peaks in bottom current speed were accompanied by increases in bottom-water temperature (Fig. 6b) and by small increases in oxygen superimposed on the general downward trend in bottom-water oxygen. In late July, oxygen and turbidity increased and then sharply decreased. This could be explained as (i) the sinking of a senescent phytoplankton bloom leading to the initial increase in turbidity and oxygen, and (ii) subsequent sedimentation and decomposition of the detrital material giving rise to the oxygen consumption and decrease in turbidity. From mid-August, oxygen concentrations appeared to be again dominated by hydrophysical controls. Warm, low-salinity and probably low-oxygen water from the Danube plume was transported to the target area by strong south-westward currents (data on currents direction not shown), which resulted in bottom-water hypoxia. This short, intense mixing event led to slight ventilation and, hence increases in oxygen. When stratification was restored, oxygen in the bottom water decreased again to about 100  $\mu\text{M}$ . These results show that for monitoring of seasonal hypoxia in shallow waters, long-term moorings consisting of optodes, CTD, current meters and turbidity sensors, and ideally, ADCP for vertical velocities and a fluorometer for chl *a*, are appropriate tools to resolve short-term

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temporal variability in oxygen and to identify both physical and biological drivers. The study of Capet et al. (2013) stresses the urgent need for dedicated oxygen monitoring on the northwestern shelf, since the recovery process had been overestimated due to spot measurements in areas and months not typically affected by hypoxia. Our new high-resolution oxygen time-series during the summer season represent the first step to improve the understanding of hypoxia dynamics and realistic assessment of the recovery process on the northwestern shelf.

A longer time-series of bottom-water oxygen concentrations was collected by monthly CTD casts in 2010 as part of the HYPOX project at the long-term monitoring station Boknis Eck in the western Baltic Sea (b on panel II of Figs. 1 and 7). The overall seasonal trend in this data set is clear, although short-term fluctuations in oxygen as observed on the Romanian shelf may well be missed by monthly sampling. The major oxygen and temperature dynamics in 2010 reflect ventilation of bottom waters in winter due to wind-induced mixing and thermal stratification and oxygen consumption in summer. Similar seasonal patterns are also found in long-term time-series of oxygen and associated parameters obtained from the monthly sampling program established at Boknis Eck in 1957 (Bange et al., 2011). On decadal time-scales the data show a general increase in the number of summer anoxic events with bottom-water oxygen concentrations  $< 2 \mu\text{mol L}^{-1}$  as well as increasing sea surface temperatures (Bange et al., 2011). While only one anoxic event was recorded during the period 1957–1983, ten events occurred between 1986 and 2010. Annual mean bottom-water oxygen concentrations are also decreasing year-on-year. These features may result from (i) eutrophication and intensified nutrient recycling (see also Sect. 5.2.2), (ii) enhanced and prolonged summer stratification due to the warming of the surface waters and a shift of strong wind events and breakup of stratification from autumn to winter/early spring for the period 1988–2007 (Lehmann et al., 2011). Thus, both local (i.e., eutrophication) and global processes (i.e., North Atlantic Oscillation) may affect the inter- and intra-annual trends in oxygen concentration at this site (Bange et al., 2011).

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### 3.5 Large-scale patterns in water-column oxygenation – example from the Black Sea

Argo floats are autonomous profiling sensor platforms that drift with oceanic currents at pre-programmed depths ([www.argo.net/](http://www.argo.net/)). They are able to change their buoyancy by modifying the total volume of the device, which enables vertical displacements within the water column. The fleet of floats currently profiling the world's oceans largely improved our understanding of physical oceanography and it has been suggested earlier to add oxygen sensors to extend the scope towards ocean biogeochemistry (Gruber et al., 2007). However, of the more than 3000 profiling Argo floats presently drifting in the world's oceans, only ca. 200 are equipped with oxygen sensors. Because the Black Sea is a deep basin, the use of Argo floats is an optimal solution not only for physical variables (Korotaev et al., 2006), but also for oxygen.

The data used in this study were collected with the Navigating European Marine Observer (NEMO) profiling floats. These are Argo type floats that were manufactured by Optimare Sensorsysteme AG (Bremerhaven, Germany) and equipped with oxygen optodes (type 3830, AADI, Bergen, Norway). During cruise leg MSM15/1 of R/V *MARIA S. MERIAN*, NEMO floats 0144 and 0145 were deployed as the first oxygen sensor equipped profiling floats ever operating in the Black Sea (Stanev et al., 2013). Deployments took place on 7 May 2010 in the northern Black Sea at 44°0.02' N, 32°4.92' E (NEMO-0144) and 44°10' N, 32°30.01' E (NEMO-0145). NEMO-0144 ended operations end of December 2011, while NEMO-0145 continued measurements until end of November 2012. The trajectories of two floats departed rapidly one from another after the deployment (e on panel III of Fig. 1). NEMO-0144 (blue dots) entered the open Black Sea, while NEMO-0145 (pink dots) followed the upper continental slope. Both floats were programmed to rise from 500 m depth to the sea surface at intervals of five days and transmit the conductivity, temperature, pressure, and oxygen measurements that were collected during the ascent by Short Burst Data (SBD) packages via the IRID-

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IUM satellite system. In between profiles measurements were carried out twice a day at the parking depth of 450 m.

About 120 000 observations of oxygen in the Black Sea, taken between 1910 and 1999, are available via the MEDiterranean ACCess based system for exploration and visualization of the marine cast data (MEDACC; <http://isramar.ocean.org.il/isramar2009/medacc/>). Most of the measurements are restricted to the upper water layer and recorded irregularly in time and space and often lack proper quality control. The oxygen observations collected by the deployment of NEMO-0144 and 0145 amounted to about 1/5 of the total number of oxygen data available today. The data are plotted in Fig. 8 and demonstrate the power of continuous observations for understanding oxygen dynamics in the coastal and open ocean areas. Surface maxima of oxygen were formed in winter in parallel with the cold intermediate water. However, later in the year the core of the oxygen maximum was observed in the upper 50 m while the core of cold intermediate water in the Black Sea is usually below this depth. There are further indications that the evolution of oxygen and temperature was governed by different processes, i.e., that oxygenation of the upper water column was decoupled from the formation of cold intermediate water. Consecutive temperature profiles show that the penetration of cold water into the intermediate layer represents a convective process, which appears only during short periods of time in winter. The penetration of oxygen on the other hand is rather controlled by diffusive fluxes leading to a continuous increase in the oxygen content of the upper water layer until waters start to warm up in late spring. The progressive decrease in oxygen content of the surface mixed layer in summer is explained by the increase in temperature resulting in reduced oxygen solubility. Just below the surface, however, an oxygen maximum evolves in summer with concentrations exceeding values observed at the surface in winter. This could indicate that the enhanced photosynthetic productivity in the photic layer acted as a major oxygen source in summer. Similar sub-surface features in the oxygen distribution were revealed by Argo floats in other ocean basins (Riser and Johnson, 2008). The Black Sea

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subsurface oxygen maximum persisted until the seasonal thermocline disappeared in October/November.

Characteristics and dynamics of oxygen distribution differed strongly between the upper continental slope (NEMO-0145, Fig. 8b) and the open Black Sea (NEMO-0144, Fig. 8a). The oxygenated layer in the open basin was about two times thinner than at the upper continental slope, and the temporal variations of its thickness were very small (about 20 m). In contrast, the depth of the oxic–anoxic water interface around the continental slope (represented by the  $5 \mu\text{molL}^{-1}$  isoline) underwent changes of more than 75 m within a period of a few weeks only. These changes closely tracked the vertical displacement of the pycnocline which was dominated by mesoscale oscillations. Therefore, the “bursts” of low- or high-oxygen waters manifested the importance of mesoscale processes for the oxygen dynamics.

### 3.6 Episodic hypoxia and ventilation in fjords – the example of Loch Etive

Fjord systems are characterized by silled entrances and limited exchange with the neighboring water bodies. This often results in density stratifications, prolonged residence times of deep waters and the development of hypoxic conditions at depth, thus similar to the conditions characteristic of the Black Sea and the Baltic. For this reason, investigations in Koljoe Fjord and the fjord-like Loch Etive serve as model studies for deep-water renewal in stratified systems with topographically restricted exchange to the open ocean. Cabled observatories with power supply from land and online data access were installed in both Koljoe Fjord and Loch Etive (c on panel II and a on panel V of Fig. 1, respectively). The availability of real-time data allowed for concurrent numerical modeling studies.

This section focuses on monitoring and modeling carried out in Loch Etive (panel V of Fig. 1). Some of the results obtained in the geographically and hydrographically more complex Koljoe Fjord system are covered in Sect. 6.2. Density and oxygen time-series recorded at 124 m in Loch Etive show that stagnant periods with gradually decreasing oxygen concentrations represent the standard case for the deep water in the inner

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basin of Loch Etive (period after July 2010 in the lower panel of Fig. 9). In Loch Etive, exchange with the neighbouring sea as well as vertical mixing is largely controlled by tides. Under normal conditions, tidal forcing is unable to induce deep mixing or to push saline deep waters across the main sill (“Bonawe Sill”, see b on panel V of Fig. 1) into the deep inner basin and only a slight mixing with oxic and shallow low-salinity waters occurs. The mixing is visible as a slow decrease in deep-water salinity and density but oxygen intrusions do not balance consumption, leading to almost hypoxic conditions at depth towards the end of the recording period (oxygen concentrations  $< 62.5 \mu\text{mol L}^{-1}$ , light grey area in the lower panel of Fig. 9). In winter and early summer 2010, however, three bottom-water renewal events appear as sudden increases in oxygen and density (black dashed vertical lines in Fig. 9). Analyzing tides and weather data for the respective periods and feeding them into a 3-D hydrodynamic model (a localized version of the Finite Volume Coastal Ocean Model FVCOM; Chen et al., 2003) revealed that specific meteorologic and oceanographic conditions are needed for deep-water renewal events to occur. All events happened at spring tide and coincided with a drop in air pressure of 30–50 hPa that led to an additional sea level rise of 0.3–0.5 m. This inverse barometer effect exaggerated the tidal oscillations and helped to force dense waters upwards and across the sill. Reduced freshwater input due to low precipitation and low discharge from a nearby hydroelectric station as well as a frequent occurrence of temperatures below the freezing point during winter minimized the outflow of brackish surface water from the inner fjord. These exceptionally dry and cold conditions facilitated the accumulation of dense saline and oxic waters at the entrance of Loch Etive in the Lynn of Lorne/Ardmucknish Bay (d on panel V of Fig. 1). This important precondition for deep-water renewal in the upper basin was captured with high accuracy by the FVCOM model (Fig. 10). Inflow events were further supported by east-south-easterly “down-fjord” winds (Bell, 1973) that pushed stratified surface layers away from the lower Loch, thereby enhancing estuarine circulation and the delivery of dense water toward the entrance of the inner basin. After the deep-water renewal events the weather reverted back to the long-term average conditions with higher temperatures

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and more precipitation. This resulted in the presence of a pool of low-salinity water at the entrance of Loch Etive (Fig. 10c, d) and impeded further renewal events from summer 2010 until the end of the recorded data series in winter 2011/2012.

Continuous fixed-point observations proved feasible to track hypoxia evolution at depth and to detect rare bottom-water renewal and ventilation events. Online data access facilitated concurrent analysis of the hydrographic conditions that invoke inflow. Furthermore it allows the implementation of hypoxia early warning tools for the deep Loch Etive which is considered to be particularly prone to hypoxia (Gillibrand et al., 2006). Application of numerical simulations allowed the identification of the hydrodynamic mechanisms that govern inflow events and demonstrated the complexity of the conditions required to bring about deep-water renewal. By applying the knowledge gained from combined online monitoring and modeling, it may be possible to manually provoke inflow events by reducing the freshwater supply from the hydro-electric power station at times of favourable natural conditions and thereby mitigating deep-water hypoxia.

### 3.7 Hypoxia driven by gas seepage – examples from Greek lagoons and embayments

In Katakalo Bay, Amvrakikos Gulf and Aetoliko Lagoon on the Ionian coast of western Greece (panel VI in Fig. 1) hypoxia was studied in relation to geogenic drivers, i.e., the seepage of reducing gases from the seafloor ( $\text{CH}_4$  and  $\text{H}_2\text{S}$  originating from deep sedimentary rocks). Two different observation systems were used: the benthic Gas Monitoring Module (GMM) for time-series monitoring (Marinero et al., 2004) and the towed Module for Environmental Deep Under Sea Analysis (MEDUSA) for spatial surveys (Marinero et al., 2011). GMM and MEDUSA were equipped with a CTD and sensors for oxygen,  $\text{CH}_4$  and  $\text{H}_2\text{S}$ . In addition, GMM carried turbidity and current sensors, while MEDUSA was equipped with video camera and altimeter.

Katakolo Bay is affected by a considerable active and permanent seepage of methane and sulfide from thermogenic origin along a series of faults (Etioppe et al.,

2006; Etiope et al., 2013). MEDUSA was used for a thorough survey of the Katakolo Bay gas bubble fields. Based on the survey GMM was then deployed very close to a shallow seep field at ca. 8 m water depth for a 101 day monitoring of oxygen and reducing gases. Drops in oxygen concentration were observed to coincide with elevated concentrations of dissolved CH<sub>4</sub> due to seepage from the seabed. This trend of oxygen decrease and CH<sub>4</sub> increase was observed both by spatial surveys (oxygen decrease upon passage of the MEDUSA module over bubble seeps) and in time-series data obtained with the GMM observatory. Figure 11b and d shows one example from each instrument. In Katakolo Bay, seepage of gas apparently acted as a geogenic driver that was able to decrease oxygen concentrations even under relatively exposed hydrographic conditions and in the absence of strong stratification or a permanent oxycline.

In Amvrakikos Gulf and Aetoliko Lagoon where strong stratification and fertilizer input from land results in seasonal or even permanent anoxia at depth, no clear indication for seepage-related oxygen depletion was observed. In the south-eastern sector of Amvrakikos Gulf, MEDUSA surveys indicated weak seepage at a large, apparently fault-controlled pockmark while no seepage was detected in the rest of the Gulf. Some pockmarks were identified in Aetoliko Lagoon but isotopic gas analyses suggest that sulfide and methane were of microbial origin and thus most likely not indicative of seepage but a product of sulfate reduction and methanogenesis taking place in anoxic sediments.

In conclusion, the results from the Greek locations provide evidence for the potential of strong gas seepage to act as a geogenic driver that reduces oxygen availability even at relatively exposed sites. Similar processes may also take place in other areas with intense gas seepage. At conditions of low and episodic gas seepage, hypoxia in the Ionian Sea lagoons and embayments seems to be mainly controlled by oceanographic and anthropogenic drivers although a weak oxygen depletion of bottom waters by local seepage cannot be ruled out (Fig. 12). The combination of temporal monitoring and spatial surveys proved to be an effective approach to study seepage related hypoxia.

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## 4 Investigating long-term changes in present and past hypoxia

In this section, we demonstrate ways of investigating long-term trends in oxygen in aquatic systems. Trends and variability in the occurrence of hypoxia on a decadal time-scale are addressed by analyzing existing monitoring data from two very different systems – the permanently stratified water column of the Black Sea, and the deep Lake Zurich in which mixing of variable intensity regularly occurs in winter. Similar to conditions in the Baltic Sea (see Sect. 3.4 and Feistel et al., 2008), both the Black Sea and Lake Zurich (along with many other lakes) have been affected by variability in climate forcing and long-term eutrophication. Temperature and oxygen profiles, which have been measured for several decades at these sites, are used to separate out the confounding effects of climatic forcing and eutrophication. During the last few decades, nutrient availability in the Black Sea has increased while it has declined in the Lake of Zurich. Similar to the western Baltic Sea (see Sect. 5.2.2.), Lake Zurich shows a general trend toward increasing stratification as a result of the warming of the upper water column. For the Black Sea, oscillations in climatic conditions and winter vertical mixing were found to control the downward flux of oxygen, while the dramatic shoaling in the upper boundary of the hypoxic zone seems to be associated mainly with eutrophication. To look further into the history of oxygen and hypoxia, inorganic and organic proxies from the sediment record were studied in some Swiss lakes and in the Bosphorus outflow area of the Black Sea. Manganese, in combination with sulfur and/or iron, proved to be suitable as a proxy for past oxygenation for both deep Lake Zurich and the Bosphorus outflow area. In the Bosphorus outflow area, manganese profiles in sediment cores revealed the history and dynamics of the Mediterranean inflow and its ventilation effects on the seafloor over the past several thousand years. Biomarkers provided valuable insights into past hypoxia and the eutrophication of Swiss lakes.

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## 4.1 Multidecadal hypoxia trends in stratified basins – the example of the Black Sea

In recent years, much insight has been gained on biogeochemical and physical processes driving the oxygen distribution and its variations in the Black Sea (e.g., Konovalov and Murray, 2001; Konovalov et al., 2003, 2005, 2006; Glazer et al., 2006). Among the still open questions concerning long-term (decadal) variations in oxygen distribution is the identification of the main drivers and the discrimination between the influence of climate change and direct anthropogenic pressure (eutrophication). Profiles of oxygen distributions for the Black Sea are relatively scarce (in total 3240 profiles until 2011), but date back to 1923 and have been collected systematically since 1955. This analysis focuses on long-term variations in the depth of the upper boundary of the suboxic zone (UBSOZ) and on the identification of the respective roles of climate and eutrophication in these variations. In agreement with earlier work (Konovalov and Murray, 2001) the UBSOZ is defined as the  $20 \mu\text{mol L}^{-1}$  isopleth.

The basin wide distribution of the UBSOZ depth shows a temporarily variable but spatially consistent “bell-shaped” pattern (Fig. 13). For the entire period covered by oxygen measurements (i.e., 1923–2011) the mean depth of the UBSOZ generally increases from 80 m in the central Black Sea to 165 m at the shelf slope, with a maximum depth in the Bosphorus Strait region. In addition, the depth of the UBSOZ exhibits seasonal fluctuations of up to 50 m, synoptic fluctuations of up to 25 m and diel fluctuations of up to 15 m (data not shown). Despite this variability on shorter temporal scales, pronounced changes on decadal time-scales can clearly be recognized (Fig. 13). During the period of relatively low eutrophication in 1955–1976, the UBSOZ depth generally ranged between 95–220 m (Fig. 13a). After 1976, the suboxic zone has shoaled progressively, exposing shallower seafloor areas to hypoxia. By the most recent period (1987 to present), characterized by high productivity levels and intense climatic variability, it had risen further to 60–160 m (Fig. 13b). Hence, for the major part of the Black

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See the long-term decrease in the depth of the UBSOZ from 1955 onwards is in the range of 20–50 m.

To recognize the nature of these changes it is necessary to discriminate between the influences of biogeochemical and physical processes. The temporal evolution of oxygen concentrations in the core of the main pycnocline ( $\sigma_t = 15.4$ ) as a function of temperature allows to trace temporal trends in basin oxygenation while eliminating the influence of changes in water-column stratification (Fig. 14). The pycnocline temperature can be regarded as a proxy for the climate driven intensity of vertical ventilation in winter and, hence, oxygen supply. Consequently, at least within the observed range of temperatures, the oxygen concentration in the main pycnocline is expected to scale approximately linearly and inversely with temperature as long as the rate of oxygen consumption stays largely constant. This is the case for the low eutrophic period 1955–1976 and – at generally lower pycnocline oxygen concentrations – also for the high eutrophic period 1987–2011. High concentrations of oxygen in the main pycnocline during 1955–1976 agree to the particularly deep oxygen penetration in that period (Fig. 14) while low pycnocline oxygen concentrations in the period 1987–2011 are reflected in the shallowest depth of the UBSOZ (Fig. 13). This is in agreement with a change from relatively low rates of primary production and nutrient supply in the first period to high trophic conditions in more recent times (e.g., Sorokin, 1964; Cociașu et al., 1996; Konovalov and Murray, 2001; Yunev et al., 2002). The intermediate period of the most intense eutrophication from the late 1970s to the second half of the 1980s is characterized by a completely different pattern in pycnocline oxygenation (Fig. 14). In these years relatively stable temperatures indicate a steady rate of ventilation of the Black Sea but the associated oxygen supply was clearly insufficient to compensate for the increasing oxygen consumption. Consequently, concentrations of oxygen in the main pycnocline dropped by about  $80 \mu\text{mol L}^{-1}$ . This decrease at largely constant temperatures reveals a strong impact of eutrophication while the effect of climate forcing was less pronounced. However, it seems that the higher eutrophication level increased the sensitivity of the system to changes in climate. Compared to the situation before

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1976, the slope of the quasi linear response of the pycnocline oxygenation to changing temperatures substantially increased. As the result, the range of oxygen variability is about two-fold for the same range of temperatures and oxygen concentrations show an excursion to almost anoxic conditions from 2005 to 2011.

5 In summary, the analysis of long-term monitoring data allows the quantification of spatial and temporal changes in the distribution of oxygen and the respective effects of eutrophication and climate change on oxygen conditions. The identified long-term trends combined with seasonal and diel fluctuations are expected to impact redox conditions at the shelf slope at depths ranging from 100 to 250 m at different time-scales. 10 Consequently, bottom waters as well as the upper sediment layers and the inhabiting faunal communities at these depths are expected to experience variable redox conditions of oxic, suboxic and even anoxic/sulfidic environments. When the effects of eutrophication and climate changes are resolved (Fig. 14), projections of climate driven trends become possible. For example, the very cold winter of 2011–2012 may have 15 caused an increase in the depth of oxygen penetration and the stock of oxygen in the Black Sea. Yet, variations in eutrophication are presently hard to predict. Thus, long-term monitoring remains crucial and new tools for timely warning of dramatic changes, in particular the development of hypoxia, are of utmost importance.

## 4.2 Multidecadal trends in lake hypoxia – the example of Lake Zurich

20 From the approximately 70-year time-series of monthly instrumental data from Lake Zurich, the period 1972–2010 was selected for analysis. During this period, monitoring was carried out consistently by the City of Zurich Water Supply, with measurement accuracies of 0.1 K and  $10 \mu\text{mol L}^{-1}$  or better for temperature and oxygen, respectively (O. Köster, personal communication, 2012). For details on the Lake Zurich data set 25 see Zimmermann et al. (1991), Livingstone (2003), Jankowski et al. (2006), and North et al. (2013a, b). Water-column profiles of temperature and concentrations of oxygen, total phosphorus and soluble reactive phosphorus were measured at the location of the deepest point of the lake (136 m). A two-stage process using linear and cubic spline

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interpolation was used to transform the measured profiles into spatially and temporally uniform data with depth intervals of 1 m and time intervals of 1 month. From these interpolated data, mean temperatures and concentrations of oxygen, total phosphorus and soluble reactive phosphorus (volume-weighted for different layers of the lake) were calculated, as well as the thickness of the hypoxic zone (from  $62.5 \mu\text{mol O}_2 \text{L}^{-1} / 2 \text{mg L}^{-1}$  down to the maximum depth of the lake) and the Schmidt stability (a measure of the lake's thermal stability; Schmidt, 1928; Idso, 1973).

Minimum oxygen concentrations at depth – and consequently also the maximum thickness of the hypoxic zone – are typically reached at the end of the summer stratification period in September (Jankowski et al., 2006). Based on the temporal evolution of deep-water oxygen concentrations and the thickness of the hypoxic zone in September (Fig. 15a and b) the study period can be divided into three segments<sup>1</sup> (North et al., 2013b). In Segment I (1972–1987), with the exception of the first two years, the mean deep-water oxygen concentration (i.e., below 120 m water depth) is generally at or above  $62.5 \mu\text{mol L}^{-1}$  and the hypoxic zone is rarely thicker than 11 m. By contrast, in Segment III (2000–2010), the hypoxic zone is consistently thicker than 11 m. Segment II (1988–1999) represents a transitional phase during which deep-water oxygen concentrations and the thickness of the hypoxic zone are extremely variable. The long-term decrease in deep-water oxygen concentrations and the increase in the extent of the hypoxic zone clearly cannot be the result of eutrophication: the decrease in mean total phosphorus concentration from  $> 3 \mu\text{mol L}^{-1}$  in the early 1970s to  $< 1 \mu\text{mol L}^{-1}$  in the past decade shows that Lake Zurich underwent oligotrophication during the study period (Fig. 15d).

To a large degree, the mean deep-water oxygen concentration in September mirrors that in the preceding April (Fig. 15b), when deep-water oxygen concentrations in deep Swiss perialpine lakes are generally at their annual maximum after mixing and ventilation in winter and spring (Livingstone and Imboden, 1996). This tight coupling implies that minimum deep-water oxygen concentrations in September are directly related to

<sup>1</sup> Here we adopt the common hypoxia threshold of  $2 \text{mg L}^{-1} / 62.5 \mu\text{mol L}^{-1}$ .

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the intensity of mixing, and hence climatic forcing, in winter and spring (Livingstone and Imboden, 1996). Computation of the Schmidt stability confirmed that the thermal stability of the water column in winter and spring increased from Segment I to Segment III, inhibiting deep mixing in the lake. This was primarily due to an increase in water temperature in the uppermost 20 m of the lake (Fig. 15c), which reflects a similar increase in regional air temperature in winter and spring. Most of the increase in both water and air temperatures occurred abruptly from 1987 to 1988 as a result of the late 1980s climate regime shift (CRS) (North et al., 2013a), which is known to have affected temperatures in oceans (e.g., Conversi et al., 2010) and lakes (e.g., Anneville et al., 2004; Anneville et al., 2005), and which appears to have resulted ultimately from a shift in the Arctic Oscillation (Rodionov and Overland, 2005). Thus the reason for the long-term increase in the extent of hypoxia appears to be at least partially associated with changes in the large-scale climatic regime (North et al., 2013b).

One clear impact of the increase in the extent of hypoxia has been on the soluble reactive phosphorus concentration in the deep water of the lake, which exhibited an abrupt increase from Segment II to Segment III despite a fairly consistent decline in the mean total phosphorus concentration in the lake since the early 1970s (Fig. 15c). This indicates that the increase in the extent of hypoxia apparent in Segment III is likely to have resulted in an increase in the dissolution of phosphorus from the sediment; i.e., in an increase in internal phosphorus loading that is ultimately the result of a long-term change in climatic forcing (North et al., 2013b).

Despite the success achieved in fighting eutrophication in Swiss lakes, the recent increase in hypoxia in Lake Zurich demonstrates that the effects of climate warming might slow down or even reverse this process. An increase in deep-water hypoxia as a result of less vigorous lake mixing is in itself a negative ecological development, but this is likely to be compounded by a concomitant increase in internal phosphorus loading. More detailed research in various lakes is needed to fully understand how reduced mixing affects internal phosphorus loading. Long-term monitoring data are essential to address this question as well as many other aspects of the impact of climate and other

non-stationary drivers on lake ecology. Lake monitoring thus needs to be continued and where possible intensified – especially in case of lakes that already have long historical data sets or are sources of drinking water (to over 1 million people in the case of Lake Zurich). The recent trend toward decreasing the frequency of monitoring in some

5 Swiss lakes for financial reasons needs to be reversed if we want to understand how – and how fast – lake systems are changing.

### 4.3 Long-term oxygenation history – examples from Swiss lakes and the Bosphorus outflow

10 Organic and redox-sensitive inorganic markers in the sediment enable the reconstruction of environmental conditions related to hypoxia farther back into the past than is possible using only multi-decadal instrumental time-series. In lakes and semi-enclosed seas, seasonal to millennial redox changes in the hypolimnion strongly modify the cycling of Fe and Mn (Davison, 1993). Reducing conditions become established, for instance as a result of oxygen consumption during the remineralization of organic matter, leading to the release of Fe and Mn (Nealson and Saffarini, 1994; O’Sullivan and Reynolds, 2005). After oxygenation at the chemocline following partial or total mixing of the water column, Fe and Mn precipitates are deposited and can potentially be preserved in the sediment (Haworth et al., 1984; Schaller and Wehrli, 1996). The concentration and types of biomarkers in the sediment relate to shifts in plankton and microbial communities in the water column, depending on environmental conditions. Here we present the Mn/Fe ratio as a semi-quantitative proxy for the intensity of past spring oxygenation, and lipid biomarkers for reconstructing eutrophication and hypoxia in Swiss lakes. The redox-sensitive elements Fe, Mn, and S are employed to reconstruct the history of the Mediterranean inflow to the Black Sea and its role in ventilating the Bosphorus outflow area.

25 Seasonal hypolimnion oxygenation events in Lake Zurich from the past century were reconstructed based on a core 110 cm long from the deepest area of the lake. The core was analyzed with an Avaatech X-ray fluorescence (XRF) core scanner (30 s at 10 and

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30 kV at 0.3 mm spatial resolution). The age model was based on organic varve counting, where the minima in the calcium signal occur in winter, and are attributed to the beginning of each calendar year. The laminated part of the core (Fig. 16) spanned the period 1895–2010, which could be resolved seasonally by the XRF analysis. The relative trace metal concentrations determined in the core were compared with the oxygen concentrations measured in the water column to assess the potential of trace metals as indicators of deep-water hypoxia. Manganese (Mn) peaks in the sediment clearly tend to occur in late winter and spring, coinciding with the spring deep-water oxygen maxima, whereas iron (Fe) exhibits peaks in autumn and winter (Naeher et al., 2013b, and references therein). Naeher et al. (2013b) showed that the Fe signal is mainly governed by calcite dilution. The maximum Mn XRF counts, when normalized by the Fe XRF data measured at the same depth, correlated well with the maximum three-month running mean oxygen concentrations in the water column at 135 m (Fig. 16). Although some deviation exists between predicted and monitored oxygen concentrations, the Mn/Fe ratio clearly represents a semi-quantitative proxy for reconstructing spring maximum oxygenation from the sedimentary record. This proxy was also applied to the period between 1895–1936 in order to reconstruct bottom-water oxygenation for the period before time-series oxygen monitoring began in Lake Zurich (Naeher et al., 2013b). Limitations to the Mn/Fe method come from the fact that sediment and geochemical focusing limits its application to the deepest point of the lake. In addition, there are some instances of especially low Mn/Fe ratios at high oxygen concentrations that suggest that the supply of Mn to the sediment in the hypolimnion water may diminish after several consecutive years of high deep-water oxygen concentrations (Naeher et al., 2013b).

Lipid biomarkers in the sediments of the Swiss Lake Rotsee were used to reconstruct eutrophication and hypoxia over the last 150 yr, based on a 56-cm-long core taken at 16 m water depth at the deepest point of the lake (Naeher et al., 2012). The procedures and analytical instruments used for the determination of lipid biomarkers are reported in Naeher et al. (2012). Eutrophication in the lake led to an increase in

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total organic carbon (TOC) accumulation rates in the 1920s and 1960s (green curve in Fig. 17) which indicate a higher productivity (Naeher et al., 2012). Higher abundances of anaerobic bacteria at times of higher productivity (based on  $C_{16:1\omega7}$  fatty acid; the purple curve in Fig. 17) indicate that the supply of organic matter to the sediment also led to an increase in organic matter mineralization rates and oxygen demand, which resulted in hypoxic/anoxic conditions. The increase in the abundance of tetrahymanol since the 1920s (turquoise curve in Fig. 17) might have been associated with intensified stratification in line with observations at other sites (Sinninghe Damsté et al., 1995). The presumed increase in the supply of organic matter also led to a higher biomass of methanogens (based on glycerol dialkyl glycerol tetraethers,  $\delta^{13}C$  values of cleaved ethers and microbial data), followed by a temporal delay of aerobic methanotrophic bacteria (based on  $17\beta$ - $21\beta$ -bishomohopanoic acid, diploptene,  $\delta^{13}C$  values) (Naeher et al., 2013c). More robust markers for hypoxia originate from phototrophic sulfur bacteria (Chromatiaceae, Chlorobiaceae; Brocks and Summons, 2003), which live under photic-zone euxinia and anoxia. In Rotsee, the detection of isorenieratene, okenone, methyl-isobutyl-maleimide and methyl-*n*-propyl-maleimide indicated the presence of Chromatiaceae and Chlorobiaceae, implying the occurrence of photic-zone euxinia in Rotsee (Naeher et al., 2013a). In conclusion, lipid biomarkers in sediments can indicate past environmental changes, such as for instance eutrophication, productivity, organic matter mineralization/degradation, stratification and oxygen depletion based on microbial community changes and/or the adaptation of microorganisms to the changed environmental conditions.

Fe and Mn, in conjunction with S, were also applied as inorganic proxies to reconstruct oxygenation events by Mediterranean water in the Bosphorus outlet area of the Black Sea on time-scales of several millennia. Sediment cores taken in 2009 from R/V ARAR and in 2010 from R/V MARIA S. MERIAN (Leg MSM15/1) along transects from 75 m to 307 m water depth on the shelf and upper slope (a on panel IV of Fig. 1) were analyzed by Itrax XRF core scanner and dated by the radiocarbon method using Acceleration Mass Spectrometry (AMS). Manganese proved to be a good proxy for the

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warm, saline, oxygen-bearing Mediterranean water mass in sediment cores (Fig. 18). The sedimentary record of the Mediterranean water ventilation effect on the seafloor can be observed throughout the entire length of Core MSM015-192 in the eastern part of the outlet area down to at least 307 m (depth limit of the transects, b on panel IV of Fig. 1), as shown by high Mn counts on the XRF scanner profile (Fig. 18a). Such Mn anomalies in upper slope cores, not associated with Fe and S anomalies, are most probably formed by deposition of Mn(II) from the water column during oxic conditions. High Mn counts throughout the core from the eastern site indicate oxic bottom-water conditions during the deposition of the core sequence (Fig. 18a). The core located in the western part of the outflow area (MSM015-311, c on panel IV of Fig. 1) shows high Mn counts in the period older than 5.3 kaBP, which indicates the prevalence of oxic bottom-water conditions then (Fig. 18b). Such geochemical evidence, in combination with seafloor morphological features, indicate that the Mediterranean inflow initially also used the north-west trending main channel, transporting oxygenated waters to the western part of the area. At 5.3 kaBP, this western transport of Mediterranean water shifted completely eastward, leading to the occurrence of bottom-water anoxia in the western area. In addition to Mn anomalies, the transition from oxic to anoxic conditions in the western part are shown by lithological changes in mud color from grey-green through grey and dark grey to black, as well as by a transition to lower densities in the radiographic image at 5.3 kaBP (Fig. 18b). CTD surveys obtained during the same cruises indicate that today's Bosphorus plume is still located to the east of the Bosphorus channel (see Sect. 5.2.1). Our study in the Bosphorus outlet area has shown that we can use Mn as an effective proxy for investigating the history and changing dynamics of the inflow of Mediterranean water into the Black Sea.



## 5 Effects of hypoxia on faunal patterns and biogeochemical processes

### 5.1 Effects on faunal patterns

Rapidly changing oxygen concentrations and the occurrence of hypoxia impose stress on aquatic organisms, and the physiological responses and survival strategies of the biota are very complex (Vaquer-Sunyer and Duarte, 2008; Zhang et al., 2010; Levin, 2003; Ekau et al., 2010). When oxygen concentrations decrease, pelagic organisms may escape vertically, develop migration strategies to avoid hypoxic areas, or develop adaptation mechanisms (Ekau et al., 2010). Benthic invertebrates may initially show aberrant behavior before they finally undergo mass mortality (Zhang et al., 2010). All these responses lead to changes in community structure and functioning, and typically to a reduction in species diversity accompanied by the dominance of a few oxygen-tolerant species (Levin, 2003). Recent studies indicate that water-column oxygenation determines the diel vertical migration patterns of zooplankton. This, in turn, may intensify oxygen depletion, especially in oxygen minimum zones (Bianchi et al., 2013). Hypoxia affects ecosystem functions related to macrofauna, such as bio-irrigation and bioturbation (Middelburg and Levin, 2009), which may indirectly affect benthic biogeochemical processes that depend on fauna-mediated oxygen transport (e.g., denitrification). Ecosystem responses to hypoxia and pathways of recovery from hypoxia are typically non-linear and may be characterized by specific thresholds of hypoxia duration and severity, by the sudden collapse of communities and functions, and by extended and complex pathways of recovery if oxygen conditions improve. In most cases the ecosystem is affected by a combination of several stressors that accompany hypoxia (Zhang et al., 2010). In this section we show the effects of hypoxia based on the examples of fish kills in the north-western Black Sea (Romanian shelf) and in Greek lagoons, and on the examples of benthic ecosystem decline and pathways of recovery on the Romanian Black Sea shelf. We also focus on changes in the species distribution of benthic organisms along depth gradients and rapidly varying oxygen concentrations in the Bosphorus outlet and on the Crimean shelf.

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### 5.1.1 Fish kills are drastic effects of hypoxia – examples from the north-western Black Sea and Greek lagoons

The most drastic effect of hypoxia is the mass mortality of pelagic and benthic organisms. When oxygen levels drop, animals relocate, show reduction in growth and reproduction, or die (Levin et al., 2010). The response depends on the species and on the severity and spatial extent of hypoxia. The paleontological record reveals an extreme example of this: during a warm period 250 million years ago a drastic drop in oxygen levels resulted in the extinction of more than 90 % of all marine species (Benton, 2005). Fish kills are the most obvious signs of “dead zones”. We report here exemplarily on the mass mortalities of pelagic and benthic organisms caused by hypoxia resulting from geogenic, hydrological, meteorological, and anthropogenic drivers in the north-western Black Sea and in Greek lagoons.

In the north-western Black Sea (c on panel III of Fig. 1), mass mortalities of benthic organisms, including demersal fish, were most dramatic during a period of anthropogenically driven eutrophication in the 1980s and 1990s. Today, such mass mortalities still occur occasionally during hot summers when water-column stratification prevents ventilation of the bottom water. The construction of a large number of littoral defense works to protect beaches and to stop coastal erosion along the beaches created so-called “littoral cells” where eutrophication thrives during the summer. In the early years of eutrophication, demersal fish kills occurred following blooms of *Procentrum cordatum* that reached 10 to 50 million cells L<sup>-1</sup> in the Romanian coastal sea off the Danube Delta (Skolka and Cautis, 1971; Gomoiu, 1977). The fish died as a result of blocking of their respiratory apparatus; i.e., from clogging of the gills by algae and detritus in suspension and from asphyxiation due to hypoxia. The species most affected by hypoxia were *Neogobius melanostomus* (75.5 % mortality), *Gobius niger* (7.5 %), *Mesogobius batrachocephalus* (1.5 %), *Pomatoschistus microps* (2.5 %), *Symphodus ocellatus* (3 %), *S. tinca*, *S. cinereus* (1 %), *S. roissali* (0.5 %), *Parablennius sanguinolentus* (5 %), and *P. tentacularis* (2 %). The most dramatic hypoxia-related fish kills along the

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Romanian coast were recorded in 1969, 1975 and 1989. Despite recovery from large-scale eutrophication during the past 10 yr, major benthic fauna kills were reported in the Romanian Black Sea littoral in 2001, 2005, and 2010 (Fig. 19a). Severe hypoxia was observed in 2001 and 2010 during summer heat waves, when oxygen solubility was reduced by up to 50%. Water temperatures of up to 30 °C coupled with salinities of less than 10 psu associated with high discharge from the River Danube resulted in strong stratification and a rapid development of diatoms such as *Leptocylindrus danicus* and *Cerataulina pelagica*, and of the dinoflagellate *Prorocentrum minimum*. Hypoxia effects were also registered on macrobenthic crustaceans such as Isopoda, Decapoda and Tanaidacea, and on fish populations. Migration of macrobenthic species (Isopoda, Decapoda, Amphipoda) was observed from the deeper levels towards shallow water, where oxic conditions allowed them to survive. A drastic decrease in the number of worms changed the structure of the epibiotic system (Teaca et al., 2006). In the hot summer of 2010, despite diminishing eutrophication, oxygen concentrations as low as 34  $\mu\text{mol L}^{-1}$  were recorded in the Constanta coastal area. The fishes affected belonged to communities that typically inhabit hard bottom regions (especially *Blenniidae*) and sediments (*Gobiidae*) (Fig. 19a). The main species affected were: *Neogobius melanostomus*, *Pegusa lascaris*, *Mullus barbatus ponticus*, *Gaidropsarus mediterraneus*, *Ophidion rochei*, *Scorpaena porcus*, and *Syngnathus* sp. Approximately 3 t of dead fish were collected from the beaches according to the local authorities.

In the Greek lagoons, historical records on fish kills date back to the 17th and 18th centuries. The fish kills were observed following stormy weather, and there was evidence of elevated concentrations of hydrogen sulfide, such as the intense odor of “rotten eggs” (Meletios, 1807). For Aetoliko Lagoon (b on panel VI of Fig. 1) it has been reported that during such an event, silverware turned black, gardens withered, and masses of dead fish were washed up onshore (Moller and Anders, 1986). Seven major events have been observed in the 20th and 21st centuries: in 1963, 1990, 1992, 1995, 1998, 2001, and 2008 (Dassenakis et al., 1994; Dimitriou et al., 2010; Gianni and Zacharias, 2011). For example, in 1992 after a storm, a “milky yellow” plume ap-

peared following the shoaling of sulfide-rich bottom water and the generation of free sulfur. This plume then spread over the lagoon, and severe oxygen depletion took place in the surface water layer accompanied by high hydrogen sulfide concentrations (> 100 ppm) (Dassenakis et al., 1994). Approximately 100 t of dead fish (mostly *Mugilidae* and *Dicentrarchus labrax*) were washed ashore or sank to the floor of the lagoon (Leonardos and Sinis, 1997). Three months later the system had almost returned to its normal state. Dassenakis et al. (1994) suggested that the meteorological conditions (S-SW winds) caused the mixing of well-oxygenated surface water with anoxic, sulfide-rich bottom water, resulting in the catastrophic anoxic event. Similar events of fish kills due to mixing of H<sub>2</sub>S into surface water have occurred for instance in dead-end canals (Luther III et al., 2004). Although the main drivers of anoxia and fish kills in Aetoliko Lagoon seem to be oceanographic and anthropogenic, gas seepage cannot be excluded as a geological driver (see Sect. 3.7). Fish kills related to gas seepage and gas-charged sediments have been also reported in the nearshore environment of the Namibian shelf (Emeis et al., 2004).

The case of Amvrakikos Gulf (a on panel VI of Fig. 1) shows impressively how disregarding the hydrological setting can lead to the failure of large fish farms. In 1998, the rise of the hypoxic/anoxic interface caused the sudden death of 1000 t of fish (Ferentinos et al., 2010, Fig. 19b). Potential mechanisms were the massive intrusion of dense seawater through the straits from the open sea, driven by differences in density or by the formation of a gravity-driven hyperpycnal flow at the mouth of the Arachthos River opposite the fish farms. High-density water filled the deeper parts of the eastern basin of the Gulf, thus uplifting the anoxic bottom layer. The inability of fish in fish cages to escape from anoxic water makes them particularly vulnerable to such events.

### 5.1.2 Response of benthic communities to eutrophication-driven hypoxia – the example of the north-western Black Sea shelf

The combination of existing data with HYPOX data collected on the north-western Black Sea shelf off the coast of Romania (b on panel III of Fig. 1) enabled changes in

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the benthic community, and hence the current state and trends in recovery of the shelf ecosystem, to be assessed. During eutrophication in the 1970s and 1980s, seasonal hypoxia developed in the water column below the surface mixed layer. This resulted in vast hypoxic areas that extended offshore to water depths of up to 40 m (Fig. 20a, upper panel) and led to a dramatic reduction in benthic biodiversity. In hot summers like that of 2010, hypoxia still occurs in nearshore areas due to stratification, albeit with a shorter duration and a smaller spatial extent (Fig. 20a, lower panel). Mud worms like *Melinna palmata* were the winners in this situation of eutrophication and hypoxia, whereas filter feeders like *Mytilus galloprovincialis* and *Acanthocardia paucicostata* decreased in abundance and spatial coverage (Fig. 21). An increase in the accumulation of detritus in the sediments during the 1970s and 1980s supported a massive development of mud worm populations. Bivalve communities became unable to cope with the sudden food supplies from heavy blooms and detritus at some point. Although mussel communities are able to withstand short periods of severe hypoxia by glycogen metabolism, they lose their filtering capacity (Mee et al., 2005) and succumb to persistent hypoxia. Compared to the pre-eutrophication period (Gomoiu, 1992), abundances of epibenthic species (crustaceans and some mollusks) decreased, while a massive development of endobenthic detritophagous organisms was observed. The expansion of the population of small organisms resulted in a diminution of biomass and impoverishment of the trophic base for demersal fishes (turbot, sole, mullet). A new benthic community dominated by mud worms became established along the Romanian coast, forming a sub-coenosis in the areas inhabited by the typical *Mytilus* community. In the Sf. Gheorghe area off the southern Danube branch we found a spectacular population development of the polychaete worms *Prionospio multibranchiata*, *Capitella capitata*, *Polydora cornuta*, and *Dipolydora quadrilobata*, the latter being a new species for the Romanian coast (Begun et al., 2010). These are opportunistic species on soft sedimentary and hard bottom substrates. In general, integrated over all key taxonomic groups, we found a decrease in the diversity of benthic macrofauna during the period of anthropogenic eutrophication (1970–1990) (Fig. 20b). The area affected by sum-

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mer hypoxia extended from 3500 km<sup>2</sup> in 1973, its first major recorded appearance, to 20 000 km<sup>2</sup> by the 1980s (Tolmazin, 1985). An ecological regime shift transformed the highly productive and eutrophic ecosystem into a less productive and degraded ecosystem during the early 1990s. For example, benthic communities that were spatially well distributed in the 1960s have become reduced and fragmented during the past 40 yr (e.g., *Phyllophora* biocenosis; Zaitsev, 1992), and others have been suppressed by invasive species which occupied their habitats. *Mya arenaria* and *Anadara inaequalvis* have modified the indigenous mollusk community comprising *Lentidium* and *Cerastoderma* (Gomoiu, 2001). Over the last 10 yr we have observed a slight recovery in the macrobenthic community structure in terms of species numbers in the Romanian pre-Danubian sector (Fig. 20b). On the path to recovery, however, fast-growing opportunistic species are occupying newly formed niches; e.g., ascidians are replacing filter-feeding mussels, and filamentous algae like *Polysiphonia* are hindering the recovery of macroalgae like *Phyllophora* by overgrowing. The recent data reveal a still fragile macrobenthic ecosystem that differs from the pre-eutrophication state and is susceptible to anthropogenic and environmental impacts. The combination of oxygen monitoring data with benthic community data gathered within HYPOX confirms that the western coastal ecosystem has recuperated to some extent from an ecological collapse marked by excessive eutrophication, oxygen depletion and mass mortality, and has now reached a new, albeit fragile, stage of ecosystem recovery.

### 5.1.3 Oxygen gradients shaping benthic communities – examples from the Bosphorus outflow and the Crimean shelf

The convergence of the low-salinity surface waters of the Black Sea with the more saline waters of the Mediterranean, and the resulting rapid transition from oxic conditions to hypoxic and anoxic conditions, creates an ecological system that requires the organisms that prevail there to adopt special adaptation strategies. During cruise 15/1 of RV MARIA S. MERIAN in 2010 at the Bosphorus outlet of the Black Sea (covering

water depths of 80 to 170 m) and on the Crimean shelf (covering water depths of 70 to 146 m), the main objective was to study changes in macrobenthic community structure with depth, and hence along oxygen gradients.

In the Bosphorus area (a on panel III of Fig. 1) we found two distinct ecological communities, *Modiolula phaseolina* and *Amphiura stepanovi*–*Terebellides stroemi*, located to the north-east and the north-west of the outlet. The species richness and abundance of the macrobenthos diminished with decreasing oxygen content in the bottom water (Fig. 22). No fully established bottom communities were found at oxygen concentrations below  $10 \mu\text{molL}^{-1}$ . At stations with low oxygen concentrations, the macrobenthos was composed of only a few species of annelids. These included two polychaete species (*Nephtys hombergii*, *Heteromastus filiformis*) as well as oligochaete species. Both *Heteromastus filiformis* and *Nephtys hombergii* inhabited almost all depths studied, while the brittle star *Amphiura stepanovi* was restricted to oxygen concentrations higher than  $10 \mu\text{molL}^{-1}$ .

While the benthic habitat at the Bosphorus outlet is characterized by strong vertical gradients in oxygen, the Crimean shelf slope (depth 70–146 m, d on panel III of Fig. 1) is additionally affected by more rapid temporal changes in oxygen concentration (see Sect. 3.2). At the Crimean slope the only community-forming species we found was the bivalve *Modiolula phaseolina*. In terms of abundance, this K-strategist made up 77 % of the community at water depths of 70–90 m and oxygen concentrations of approximately  $290 \mu\text{molL}^{-1}$ , while smaller r-strategists, such as annelids, contributed only 14 %. The predominance of *M. phaseolina* at these depths agrees with earlier reports of mollusks or K-strategists as typical community-structure forming species in the Black Sea under stable oxic conditions (Pianka, 1970, 1978). At the 100–150 m depth level, the oxygen concentration decreased to  $140 \mu\text{molL}^{-1}$  and the community structure changed: the proportion of annelids and other r-strategists increased to 42 %, whereas *M. phaseolina* made up only 29 % of the benthic community. However, *M. phaseolina* is found over a large depth range in the Black Sea, including deeper areas where oxygen is becoming depleted. Comparing key species presently inhabiting the oxic–anoxic tran-

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sition zone at the Crimean shelf to those in the 1950s reveals a decrease in the average size of the individuals. This occurred along with a strong decrease in biomass – from  $43 \text{ gm}^{-2}$  in 1957 (Kiseleva and Slavina, 1964) to  $28 \text{ gm}^{-2}$  in 2010 – while the abundance of the dominant species remained unchanged. This may indicate a rise in the depth of the oxic–anoxic transition zone in addition to the rapid temporal changes that have occurred.

## 5.2 Effects on biogeochemical processes

When oxygen deficiency occurs in a stratified water column, a segregation of redox-sensitive substances and biogeochemical transformations becomes established along redox gradients. When bottom-water oxygen decreases to hypoxic levels, early diagenetic processes in the sediment shift from aerobic to anaerobic pathways and the nature and magnitude of sediment-water exchange changes (Middelburg and Levin, 2009). Organic matter may be less degraded in systems with high organic matter rain rates due to the lower efficiency of anaerobic decomposition processes or the enhanced conservation of sedimentary bacterial biomass in the absence of eukaryotic grazers (e.g., Lee, 1992; Hartnett and Devol, 2003). Reduced substances may accumulate during longer periods of hypoxia, with dramatic feedback to benthic and pelagic organisms. We provide examples of pelagic biogeochemical processes in the Bosphorus outflow ventilation area, and of benthic early diagenetic processes in the Romanian Black Sea shelf and Baltic Sea.

### 5.2.1 Biogeochemical implications of oxygen intrusions in the redoxcline – the example of the Bosphorus outflow

In aquatic systems with frequent or permanent anoxia, such as the Baltic Sea, the Black Sea, and enclosed fjords, enhanced mixing of anoxic and oxic waters may occur; e.g., because of the breaking of internal waves, during inflow events that inject oxic water into anoxic layers, or at the intersection of the oxycline with the sediment. The impact

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of mixing events on biogeochemical cycling and on the microbial community, which has not been well studied, was addressed in the Bosphorus outflow area (a on panel IV of Fig. 1).

In Sect. 3.1 it was demonstrated that, even in highly-stratified systems, redoxclines can be highly complex and dynamic in space and time. It was reasoned that the associated intense mixing of oxic and anoxic waters, and of their related microbial communities, might affect the biogeochemical conversion processes taking place at the redoxcline. The Bosphorus outflow area in the south-western Black Sea offers a unique opportunity to study the effect of intrusions of oxic waters into anoxic water layers on water-column biogeochemistry. In this area, oxic saline water from the Mediterranean leaves the Bosphorus Strait and, due to its excess density, cascades down the continental shelf to greater depths, where it mixes with the adjacent anoxic waters. Even after the oxygen has been consumed, these “Bosphorus plume” waters can still be detected by temperature anomalies measured up to ~ 80 miles off the mouth of the Bosphorus (Konovalov et al., 2003). Studies carried out within HYPOX focused on the competition between abiotic and microbially mediated redox processes and the effect of this on the position and magnitude of chemical gradients. In November 2009 and in April 2010, a custom-built pump CTD was deployed to obtain continuous concentration profiles of redox-active elements at a vertical resolution of up to 0.5 m based both on sensor data and on wet-chemical analyses of samples delivered through a hose into the ship’s laboratory. In contrast to other pump CTD systems (e.g., Friederich et al., 1990), the free-falling pump CTD used in this study was able to descend by its own negative buoyancy, which allowed samples to be obtained undisturbed by the ship’s motion (Fig. 23e).

In November 2009, oxic Bosphorus plume water was detected down to 350 m depth at several stations to the north-east of the Bosphorus outlet (Fig. 23a). The water layers affected by the oxic plume were up to 250 m thick. In contrast to this, no Bosphorus plume inflow was detected during the entire seven-day sampling campaign in April 2010 (Fig. 23b), although the moderate easterly winds that prevailed at that time are not

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considered likely to prevent the inflow of Mediterranean water through the Bosphorus Strait (Latif et al., 1991). High-resolution nutrient profiles obtained in November 2009 revealed that the first appearance of reduced ions, such as ammonium and sulfide, in the Bosphorus plumes was 25–100 m lower than at a nearby reference station where oxic plume water was not detected (Fig. 23c, d). Increased nitrite concentrations at the plume station indicated significant nitrogen turnover in both the oxic and anoxic layers. Using  $^{15}\text{N}$ -labeling experiments, nitrification rates of  $4\text{--}20\text{ nmolL}^{-1}\text{ d}^{-1}$  were measured in the oxic plume water, whereas very high  $\text{N}_2$  production rates ( $> 150\text{ nmolL}^{-1}\text{ d}^{-1}$ ) were found to coincide with the first appearance of sulfide at greater depths, suggesting the occurrence of denitrification coupled with sulfide oxidation (Fig. 23 d). The presence of old, deoxygenated plume water at the reference station was indicated by temperature anomalies at 220 m depth. Again, microbial activity in this layer was reflected in higher nitrite concentrations, which coincided with lower concentrations of sulfide and ammonium.

Our results show that oxygen intrusions in the Bosphorus outlet area cause a shift in the position of the oxic/anoxic interface and of the redoxcline. This suggests that lateral mixing plays a significant role in maintaining a permanent suboxic zone in the Black Sea, as hypothesized by Murray et al. (1995) and Konovalov and Murray (2001). Lateral intrusions initially mix oxic compounds and reduced compounds or ions such as oxygen, nitrate and sulfide, which usually do not meet in quasi-diffusive horizontally layered systems.

While high-resolution profiles proved highly suitable for identifying and localizing the processes that occur in complex redoxclines, incubation experiments are necessary to quantify turnover conversion rates, as lateral advection complicates the calculation of fluxes and rates from concentration gradients. The elevated rates of nitrogen loss found in the plume waters once the oxygen was depleted may have important implications for large-scale nitrogen cycling. However, the sequence of microbial and chemical processes favored by the injected oxidizing potential and the associated reaction rates, and especially the amount of nitrogen that is lost from the ecosystem via denitrifica-

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tion, need further investigation. The unexpected absence of Bosphorus plume waters in April 2010 emphasizes the fact that the regulation of the Bosphorus inflow is not yet fully understood.

### 5.2.2 Benthic nutrient regeneration under seasonally changing oxygen conditions – the examples of the north-western Black Sea shelf and the western Baltic Sea

To illustrate the impact that dissolved-oxygen variability can have on benthic nutrient exchange fluxes, we return to the sites that are subject to seasonal hypoxia (Sect. 3.4). In many respects, the benthic environments of the Romanian Black Sea shelf and Boknis Eck in the western Baltic Sea are similar, despite the differences in geographic setting and coastal morphology. Both sites are shallow-water sites ( $\sim 30$  m water depth) with sediments rich in organic carbon (2 and 5 wt%), and at both sites bottom-water temperatures range from  $< 5^\circ\text{C}$  in March to  $11^\circ\text{C}$  in September, with bottom-water hypoxia developing in late summer (Figs. 6 and 7).

Total oxygen utilization (TOU) and nutrient fluxes were measured on the Romanian Black Sea shelf (Portita site, 28 m water depth, c on panel III of Fig. 1) using in-situ benthic flux chambers and ex-situ whole-core incubations. Under normal oxic conditions ( $225\ \mu\text{molL}^{-1}$   $\text{O}_2$  in the bottom water in May 2010), the measured TOU ( $11.7\ \text{mmolm}^{-2}\ \text{day}^{-1}$ ) was lower than during the hypoxic conditions that prevailed in September 2010 ( $18.9\ \text{mmolm}^{-2}\ \text{day}^{-1}$ ; Fig. 24). Previous studies at the same location during eutrophication in May 1997 reported comparable in situ oxygen uptake rates of  $13.8\ \text{mmolm}^{-2}\ \text{d}^{-1}$  (Friedrich et al., 2002). No release of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  was detected in May 2010, but concentrations of these ions became elevated in September when the bottom-water oxygen concentration was  $< 150\ \mu\text{molL}^{-1}$ .  $\text{Si(OH)}_4$  fluxes were higher in September than in May ( $p = 0.046$ , which is marginally significant). In contrast,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  showed no significant difference between seasons.

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Broadly similar nutrient fluxes and seasonal patterns were observed at Boknis Eck (b on panel II of Fig. 1) during 2010 (based on fluxes calculated from porewater gradients; Dale et al., 2013). At the Romanian Black Sea shelf, the higher  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  fluxes in September 2010 can be attributed to a larger amount of fresh organic matter deposited on the sediment surface and to the occurrence of exceptionally high water temperatures during the summer of 2010, which resulted in higher bacterial metabolic activity. For Boknis Eck, Dale et al. (2013) identified additional processes and mechanisms to account for elevated nutrient fluxes in late summer. They suggested that the efflux of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  from the sediments in later summer may be enhanced by the ebullition of methane gas bubbles, which acts as a pseudo-irrigation process (Dale et al., 2013). Using a non-steady state 1-D numerical reaction-transport model, Dale and coauthors further proposed that the phosphate-storing sulfide-oxidizing *Beggiatoa* bacteria that are present in the sediments at Boknis Eck (Preisler et al., 2007) release large amounts of  $\text{PO}_4^{3-}$  to the porewater when oxygen concentrations fall to low levels ( $< 10 \mu\text{mol L}^{-1}$ ), thus enhancing the mobilization of  $\text{PO}_4^{3-}$  from the sediments. The release of significant amounts of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  can be expected to fuel primary productivity in the water column and exacerbate bottom-water hypoxia, thus providing positive feedback to benthic nutrient release at both the Black Sea shelf and Boknis Eck.

A more generic representation of the benthic response to seasonal hypoxia in coastal sediments can be obtained using the above-mentioned non-steady-state model developed for Boknis Eck (Dale et al., 2013). This model considers the transport and reaction of solutes and solids such as oxygen,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , particulate organic matter (POM), and iron-bound phosphorus in the sediments. Simulated POM degradation occurs via several pathways, including aerobic respiration and denitrification, through which organic N and P are mineralized as dissolved  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . Seasonal changes in water-column temperature, salinity, dissolved oxygen, POM flux to the seafloor, bio-turbation, and bioirrigation are used to drive the model. Whole-core incubation experiments show that bioirrigation falls essentially to zero when irrigating fauna are exposed

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to hypoxia, but plays an important role in benthic nutrient exchange for the rest of the year (Dale et al., 2013). For the present discussion, the model is run until a seasonally-cycling steady state in concentrations and reaction rates is achieved. To reduce the complexity of the model and to make it more relevant to other seasonally-hypoxic sites, the modulation of dissolved P dynamics by sulfide-oxidizing *Beggiatoa* bacteria and the enhancement of solute transport by rising gas bubbles are both omitted from the model.

The model results (Fig. 25) demonstrate that under seasonally recurrent hypoxia the major pathways of POM mineralization switch between aerobic respiration in winter and spring and sulfate reduction in summer and autumn. Denitrification, iron reduction, and methanogenesis play a minor role in this example, but may be much more important at other locations (e.g., Martens and Klump, 1980; Canfield et al., 1993; Middelburg et al., 1996). Oxygen fluxes in the sediment are high in winter (January–March), when bioirrigating fauna are most active. Benthic oxygen uptake diminishes through spring and summer as bioirrigation rates and bottom-water oxygen concentrations decrease concomitantly until severely hypoxic conditions ( $O_2 \sim 2 \mu\text{mol L}^{-1}$ ) are established in September. Benthic aerobic respiration increases again in October–November, when wind-induced mixing ventilates the bottom waters (Hansen et al., 1999). Trends in  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations are different to the trend in oxygen concentration. The near-constancy of the porewater concentrations in the upper 10 cm in winter, at values equal to those in the bottom waters, is due to the non-local exchange of porewater with bottom water by bioirrigation. Solute pumping by indwelling fauna ameliorates the classic fingerprint of organic matter degradation in the surface sediment layers and accounts for the bulk of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  flux from the sediment in winter. As bioirrigation rates decrease in spring and summer,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  begin to accumulate in the porewater. The absence of a surface oxidized layer in September and October, or the reduction in its thickness, reduces the rate of nitrification and sequestration of  $\text{PO}_4^{3-}$  into iron oxyhydroxide minerals, and hence also reduces the retention capacity of the sediment for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  (e.g., McManus et al., 1997).

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The high diffusive flux rates of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  into the water column during hypoxia corroborate the benthic measurements performed at Portita (Fig. 24) and demonstrate that sediments underlying seasonally hypoxic waters are important sites of preferential nutrient regeneration and return to the water column, as previous investigators have shown (Conley and Johnstone, 1995; Cowan and Boynton, 1996; Rozan et al., 2002). Importantly, the results show that diffusive losses of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  are important during hypoxic conditions, whereas irrigation fluxes are more important under the oxygenated conditions found in winter. An understanding of the intensity and depth of bioirrigation at seasonally hypoxic sites is thus critical for evaluating the potential impact of enhanced nutrient release to the water column when bioirrigation is diminished.

## 6 Improving data quality and data access

### 6.1 Challenges in resolving gradual oxygen changes in the deep sea – the example of the Fram Strait

Water-column studies at HAUSGARTEN include the assessment of various physical and chemical parameters. Dissolved-oxygen concentrations in the near-bottom zone were monitored in situ by means of optical oxygen sensors (“optodes”, AADI, Bergen, Norway) attached to moored, free-falling systems (bottom-landers, similar to the system shown in the left panel of Fig. 3) deployed at the central HAUSGARTEN site (2500 m water depth, f on panel I of Fig. 1), and ex situ by the Winkler titration of water samples taken at all permanent sampling sites during the annual summer expeditions to HAUSGARTEN. Whereas Winkler titrations have been conducted regularly since 2000, continuous optode measurements with single-sensor and multi-sensor instruments did not begin until the summer of 2004 (no data are available from July 2005 to July 2006).

Despite the well-documented good performance of optodes (e.g., Tengberg et al., 2006; Uchida et al., 2008), the HAUSGARTEN data showed a number of puzzling



characteristics that make them difficult to interpret (Fig. 26). Probably the most striking feature in the data is the episodic occurrence of significant drops in oxygen concentration (up to  $100 \mu\text{mol L}^{-1}$ ) that can last for minutes to days. Similar anomalies have been reported for optode deployments in the deep central Atlantic and the north-western Mediterranean Sea (Lo Bue et al., 2011). The detailed analysis of optode and current meter data performed by Lo Bue et al. (2011) showed that the drops in measured oxygen concentration correlated with low current speeds ( $< 10\text{--}12 \text{ cm s}^{-1}$ ) and stochastic flow direction patterns. In low-current regimes, the corrosion of metallic material in the vicinity of the oxygen sensors (e.g., bottom-lander frame, ballast weights) best explains the conspicuous drops in dissolved oxygen (Lo Bue et al., 2011). Optodes mounted 0.9 m above the seafloor, with an almost equal distance to the ballast weights and the ring of floats on top of the bottom-lander, always showed the lowest fluctuations. In agreement with the rather turbulent flow patterns that exist around the bottom-lander frame, not all the sensors of the multi-sensor instrument show the anomalies in parallel.

Another prominent feature of all optode measurements is a well-attenuated settling of the registered oxygen values within the first few weeks of the long-term deployments, indicating that the sensors need a long time to adapt to the high pressure at 2500 m water depth and/or the extremely low water temperatures at the central HAUSGARTEN station ( $\sim -0.8^\circ\text{C}$ ). However, whereas the multi-sensor instrument deployed between 2007 and 2008, and between 2008 and 2009, showed an initial drop in measured oxygen concentrations, single-sensor optodes deployed at the shallowest and the central HAUSGARTEN sites (1250 and 2500 m water depth, respectively) between 2009 and 2010 surprisingly exhibited the reverse phenomenon, with increases in measured oxygen concentration occurring immediately after deployment (Fig. 26).

Moreover, although all sensors were always thoroughly calibrated, optode measurements from different annual cycles often showed conspicuous offsets in oxygen concentration (up to  $20 \mu\text{mol L}^{-1}$ ) that were clearly not attributable to natural variation. Neglecting all the conspicuous features mentioned above (i.e., episodic drops in oxygen concentration, the adaptation phase of the sensors, offsets between deployments), op-

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5 tode data from the different deployments between 2004 and 2011 showed only a very low variation in oxygen concentration (a maximum of  $2 \mu\text{molL}^{-1}$  over one year). Sensor records showed slightly decreasing oxygen concentrations overall between 2007 and 2009, but a slight increase between 2009 and 2010 (Fig. 26). This observation makes it difficult to deduce whether the minor long-term trends registered by the optodes are real or the result of sensor drift.

10 Despite the good performance of the Aanderaa optodes in short-term and shallow-water applications, long-term deployments at the HAUSGARTEN Arctic deep-sea observatory indicate that this sensor type is probably not suitable for making long-term measurements in deep, polar waters, and in low-current environments in general. The various sensor peculiarities portrayed above apparently impede the resolution of minor variations in dissolved oxygen of the magnitude expected in the deep ocean. Oxygen concentrations determined by the Winkler titration of bottom-water samples during the expeditions to the HAUSGARTEN observatory are merely spot measurements and therefore, unfortunately, cannot help to verify the optode data. Continuous study of the temporal evolution of dissolved-oxygen concentrations in the deep ocean thus remains a big challenge, and one that apparently necessitates the development of new, improved sensors.

### 20 6.2 Quality control of online oxygen monitoring data – the examples of Koljoe Fjord and Loch Etive

25 The stochastic nature of deep-water renewal events in the fjord systems studied in HYPOX (see Sect. 3.6) called for continuous monitoring in Koljoe Fjord (Sweden) (c on panel II of Fig. 1) and Loch Etive (Scotland) (a on panel V of Fig. 1). Both these sites are easily accessible, allowing cabled online observatories to be deployed. The experience gained with regard to appropriate instrumentation and the safeguarding of data quality is presented here to provide guidance for the future monitoring of coastal and land-locked sites.

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Both the Koljoe Fjord and the Loch Etive observatories consist of multi-sensor instruments (type “Seaguard” and “RDCP600”; AADI, Bergen, Norway) connected by an underwater cable to a station on land, and comprise custom-built communication and power supply systems supplied by Develogic (Hamburg, Germany). The two observatories are illustrated schematically in Figs. 27 (Koljoe Fjord) and 9 (Loch Etive). Measurements are obtained at sub-hourly resolution using sensors manufactured by AADI (Bergen, Norway) and include oxygen (optode type 3830, 4330, and 4835) and standard oceanographic parameters (conductivity, temperature, sea level), as well as horizontal currents and 3-D current profiles (acoustic Doppler current velocimeters and profilers). The Koljoe Fjord observatory also served as a platform for the field testing of a new optical CO<sub>2</sub> sensor (data not shown). Both observatories are equipped with automated real-time data retrieval to the PANGAEA database, as well as web-based data display and quality control systems (some details are provided in the next section and in Fig. 28).

Quality control of the time-series data obtained was recognized as vital to distinguish environmental trends from sensor artifacts. In the case of Koljoe Fjord, data for validation originate from the nearby coastal monitoring station, which is visited monthly by the Swedish Meteorological and Hydrological Institute ([http://www.smhi.se/oceanografi/oce\\_info\\_data/SODC/download\\_sv.htm](http://www.smhi.se/oceanografi/oce_info_data/SODC/download_sv.htm)). Reference data at several discrete depths are provided for oxygen (Winkler titration), salinity, temperature, and a wide range of additional parameters. For the Loch Etive observatory, occasional water samples, and oxygen, conductivity, and temperature profiles measured by the Scottish Association for Marine Science, provide reference data. Wind measurements and additional weather data are available from nearby weather stations in the case of Koljoe Fjord, and from a shore station in the case of Loch Etive. Apart from temporary malfunctioning of the underwater hub and a lightning strike at the Loch Etive shore station, the sensors proved to work reliably on time-scales of several months to years. Figure 27 shows that the sensors were able to detect dynamic changes in oxygen concentration (especially at intermediate depths) that stan-

5 dard monitoring approaches would not be able to resolve even if monitoring was carried out monthly, as is the case for Koljoe Fjord (the data obtained at the Loch Etive observa-  
tory are presented in Sect. 3.6). Signal drift caused by biofouling, however, turned out to  
be an issue at both sites. Biofouling affected mainly the conductivity sensors (i.e., salin-  
10 ity measurements), but also the oxygen sensors in the upper part of the water column  
(down to  $\sim 11$  m). When the sensors were retrieved for maintenance purposes, severe  
biofouling, involving mainly mussels and tunicates, was apparent, especially in sum-  
mer. The effect of biofouling on the conductivity and oxygen readings was determined  
by comparing the sensor data with the corresponding reference data (e.g., oxygen  
15 recordings from 4 and 8 m water depth in July and August 2011, and in July and Au-  
gust 2012) and by the changes in sensor reading before and after cleaning. The effect  
of biofouling on conductivity readings resulted in the true salinity being underestimated  
by as much as 6–10 units. For oxygen, readings were typically lowered by approxi-  
mately  $150\text{--}200\ \mu\text{mol L}^{-1}$  when severe biofouling was encountered in late summer. In  
20 contrast, occasional excursions to higher concentrations (up to  $600\ \mu\text{mol L}^{-1}$ ) were ob-  
served at midday at both Koljoe Fjord (May 2012 at 4 m) and Loch Etive (June 2010  
at 14 m; data not shown). We attribute these to the growth of biofilms of photosynthe-  
sizing algae on the sensors. No indication of drift was observed during the two-year  
observation period for the temperature sensors or for any sensors deployed at 16.5 m  
or deeper. At these depths biofouling was slight or absent, probably due to the limited  
availability of oxygen for respiration ( $< 90\ \mu\text{mol L}^{-1}$ ). In general, the effect of biofouling  
in Koljoe Fjord and Loch Etive agrees with previous reports on the performance of oxy-  
gen optodes and conductivity sensors (e.g., ACT, 2004, 2009; Tengberg et al., 2006;  
Martini et al., 2007; Jannasch et al., 2008).

25 Sensor readings and reference data agree well for sensors deployed either at the  
surface or in the deep water. For sensors installed at intermediate depths (10–20 m) in  
Koljoe Fjord, quality control was complicated by the extremely strong natural variability  
(up to  $8^\circ\text{C}$ , 5 salinity units, and  $200\ \mu\text{mol O}_2\ \text{L}^{-1}$  within a period as short as 6–12 h;  
see Fig. 27, October 2011 and September 2011). These changes are associated with

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aspects of fjord hydrodynamics (i.e., wind-induced mixing and the vertical motion of density surfaces induced by tides and internal waves) that occur on time-scales not accounted for by traditional monitoring. This impedes the use of monitoring data obtained by the Swedish authorities nearby for quality control purposes. Contamination with air is probably the reason for the small amounts of oxygen detected in some deep-water (> 30 m) reference samples; at these depths sensor readings clearly indicate the presence of anoxic conditions after the oxygen was depleted in November 2011.

In summary, continuous measurements were found to add valuable information to standard monitoring, which is a prerequisite for the successful monitoring of bottom-water renewal events and for obtaining an in-depth understanding of the hydrodynamics of the system (see also Sect. 3.6). Although the relevant technologies appear to be fairly mature, the installation of permanent observatories involves a long-term commitment of resources and personnel, especially in shallow-water systems with high biological activity, as frequent maintenance cruises are necessary to keep systems and sensors running properly. At both sites, and in other stratified systems, profiling observatories similar to the system deployed in the Gotland Basin (see Sect. 3.1) could solve the biofouling problem by retracting the sensors to deep waters with low oxygen concentrations between profiles. As suggested by Glenn et al. (2000), observatories should be regarded as supplemental to existing standard monitoring programs, which are always needed to supply validation data, rather than a substitute for such monitoring programs. On the other hand, slight modifications to established monitoring programs at stations providing validation data for the observatories can provide a large amount of added value for a negligible amount of additional effort.

### 6.3 Strategies for data dissemination and contribution to global earth observation

The benefits provided by ocean and lake observations such as those obtained within HYPOX, and by the knowledge derived from these observations, depend crucially on how accessible these data are to potential users, both within and outside the scientific

community. That is, these benefits depend on the appropriateness of the data-sharing and dissemination procedures adopted. One of the major motivations for setting up the HYPOX project was the perceived necessity of outlining procedures to integrate ocean and lake observations into global earth observation initiatives and to demonstrate the benefits of data sharing to the aquatic science community. Impediments to open and timely data dissemination are technological and scientific, but also cultural. The collection of data on aquatic systems is driven by scientists with approaches and information needs that are both highly diverse and specific. Even in a well-focused project like HYPOX, the processes being investigated were targeted on many spatio-temporal observation scales. The diversity of scientific approaches fosters a culture of data dissemination that is still largely focused on individual publications, while the value of data sharing and the publication of citable data sets is only now beginning to be valued by the aquatic science community. Consequently, institutions and individual scientists often have reservations about sharing their data, so that data are often not made generally accessible for long periods of time. To be made full use of, these data must be fully integrated into global earth observation activities, meaning that additional technical requirements need to be met.

HYPOX is typical of third-party funded, aquatic sciences projects in that it involved multiple partners from different disciplines working together for a limited period of time. Approaches that proved suitable for HYPOX may therefore also serve as an example for other projects and consortia. To harmonize data sharing and dissemination, a common data policy for the work carried out within the HYPOX project and beyond was established. This included agreement on granting open access to data not later than two years after collection, and the immediate provision of a basic set of parameters (temperature and salinity) to the EU project EGIDA<sup>2</sup> for use in pioneering attempts on the integration of earth observations. From a technical point of view the most important data-sharing issues were the adoption of common standards and protocols and the establishment of agreement on standard workflows for data processing, in-

<sup>2</sup>EU-FP7 project (EGIDA project: <http://www.egida-project.eu/>).

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cluding the implementation of protocols for the quality control and quality assurance of continuous real-time data (see previous section). To facilitate this, the HYPOX consortium agreed to use the established data infrastructure system PANGAEA<sup>3</sup> as a data archive. PANGAEA served as the central hub for the collection and dissemination of data and metadata, and formed the interface with the global earth observation initiative GEOSS<sup>4</sup> via the so-called GEOSS Common Infrastructure (GCI)<sup>5</sup>. The global initiative GEOSS was started in 2005 with the aim of merging earth-related observations to provide a common information base. To this end, GEOSS acts as an information broker for the earth sciences, interfacing with different information systems and data providers. Fig. 28 shows the basic architecture of the data infrastructure that was established jointly by HYPOX and PANGAEA. The data retrieval and access system makes use of standards that comply with the principles and concepts of Spatial Data Infrastructures (SDI). According to Kuhn (2005), an “SDI is a coordinated series of agreements on technology standards, institutional arrangements, and policies that enable the discovery and use of geospatial information by users and for purposes other than those it was created for”. For HYPOX, data management system standards like ISO19115<sup>6</sup>,

<sup>3</sup> Information system for geo-referenced earth system data hosted by the Alfred Wegener Institute, Bremerhaven, and MARUM, the Center of Marine Environmental Sciences, Bremen, Germany (<http://www.pangaea.de>).

<sup>4</sup> International initiative by the Group on Earth Observation (GEO) ([www.earthobservations.org/geoss.shtml](http://www.earthobservations.org/geoss.shtml)).

<sup>5</sup> A collection of registries for services and data formats that allows GEOSS and other brokering services to access registered data sets ([http://www.earthobservations.org/gci\\_gci.shtml](http://www.earthobservations.org/gci_gci.shtml)).

<sup>6</sup> International standard for the description of metadata ([www.iso.org/iso/catalogue\\_detail.htm?csnumber=26020](http://www.iso.org/iso/catalogue_detail.htm?csnumber=26020)).



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Sensor Web Enablement<sup>7</sup>, the standard service OGC-CSW<sup>8</sup>, and OAI-PMH<sup>9</sup> were implemented, and relevant guidelines, like INSPIRE<sup>10</sup>, were taken account of to ensure interoperability with GCI and GEOSS, as well as with other major data service providers. Four HYPOX services have been registered and are publicly available via the GEOSS registry portal: a geo-referenced news feed (HYPOX GeoRSS), an open archive initiative (OAI) service for harvesting the metadata of all HYPOX data sets in PANGAEA, and two sensor observation services for direct access to data from the cabled observatories of Koljoe Fjord and Loch Etive. In addition to these central data services, individual web portals have been established to serve the particular scientific needs of experts. As an example, the University of Gothenburg has set up a web page to continuously display incoming data from the Koljoe Fjord observatory<sup>11</sup> in order to follow the evolution of fjord oxygenation and to validate observational results and decide whether processes like biofouling are affecting the measurements (see previous section).

In conclusion, a central data management system has been built up within HYPOX that fulfills the requirements of diverse data sets ranging from biological to physical data, and from discrete individual measurements to continuous streams of sensor data in real-time. The HYPOX data management system provides a sustainable service to

<sup>7</sup> Open Geospatial Consortium standard describing a sensor data acquisition standard ([www.opengeospatial.org/projects/groups/sensorwebdwg](http://www.opengeospatial.org/projects/groups/sensorwebdwg)).

<sup>8</sup> Open Geospatial Consortium standard for catalog services that implements search functionalities and engines for spatial data using their metadata ([www.opengeospatial.org/standards/cat](http://www.opengeospatial.org/standards/cat)).

<sup>9</sup> Protocol for metadata harvesting ([www.openarchives.org/pmh/](http://www.openarchives.org/pmh/)).

<sup>10</sup> EU directive published in 2007 (<http://inspire.jrc.ec.europa.eu/>).

<sup>11</sup> Data access and plotting web tool for Koljoe Fjord data, run by Mikhail Kononets at the University of Gothenburg (<http://mkononets.dyndns-home.com:8080/> and [http://mkononets.dyndns-home.com:8080/cgi-bin/recent\\_data\\_plots.script](http://mkononets.dyndns-home.com:8080/cgi-bin/recent_data_plots.script)).

data providers, project members, and associated initiatives, as well as to the end-users of the data.

## 7 Conclusions

Comprehensive observational studies of oxygen depletion were carried out in open seas, coastal waters, and land-locked water bodies within the three-year project HYPOX. The various temporal and spatial scales of hypoxia in these aquatic ecosystems were addressed by appropriate monitoring strategies in order to arrive at a mechanistic understanding of the dynamics of hypoxia and to make a proper assessment of its consequences for the different ecosystem compartments. A variety of different approaches for monitoring oxygen concentration and associated parameters were tested and optimized as a first step towards setting up a multidisciplinary oxygen observation network. Our study demonstrates the capabilities, but also the limitations, of currently available technologies to monitor oxygen depletion at the spatial and temporal scales that are required to fully address the complexity of the phenomenon of hypoxia. The monitoring of present-day conditions was extended into the past by studying long-term instrumental time-series, and sedimentary proxies for past oxygen conditions. In addition to hypoxia, the ecosystem response to hypoxia was studied, focusing not only on the response of higher organisms but also on biogeochemical processes in the water column and in the sediments.

Time-series obtained using the profiling instrumentation platform GODESS and mooring arrays allowed a thorough characterization of oscillating redoxclines in the central Baltic Sea and the Black Sea off the south-western Crimean Peninsula. The redoxclines at these sites turned out to be temporally dynamic, three-dimensional systems that are controlled or strongly modified by intermittent lateral transport processes rather than by uniform and continuous vertical diffusion. These new insights improve our understanding of diapycnal mixing processes and biogeochemical processes in stratified marine water columns. Similarly complex characteristics, albeit on a much

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smaller spatial scale, were also observed in the water column of a permanently stratified Swiss lake. Optimized amperometric microsensors and trace level microoptodes revealed an extended and spatially and temporally dynamic zone with submicromolar oxygen concentrations at the lower end of the oxycline, and allowed the oxic/anoxic interface to be exactly localized. These findings challenge the traditional view of oxyclines as stable and uniform habitats with sharp, stationary, two-dimensional oxic–anoxic interfaces. This has important implications for biogeochemical processes in the water column that are involved in redox-cycling, as well as for their vertical zonation.

Extending the temporal scale to seasonal phenomena, stand-alone static moorings equipped with optical oxygen sensors, current meters, and turbidity sensors proved useful tools for characterizing the evolution of summer hypoxia. Ideally, to fully address the respective contributions of biological and physical processes, fluorometers for the determination of photopigment concentrations, and ADCPs that extend current measurements to the entire water column, should be added. A 3 month continuous time-series from the north-western Black Sea shelf identified summer hypoxia to be a highly-dynamic process, and provided insights into what controls the occurrence of hypoxia. At this location, seasonal bottom-water hypoxia occurs as the consequence of multiple factors, including the sedimentation of spring and summer phytoplankton blooms and the formation of a stable thermocline that decreases ventilation, resulting in stagnant bottom water. This implies that the hydrodynamic setting makes the shelf naturally prone to hypoxia. Brief occurrences of bottom-water hypoxia during the warm season may therefore have been a common phenomenon on the north-western Black Sea shelf even before eutrophication set in.

For the first time, ARGO-type profiling floats equipped with oxygen sensors were deployed in the Black Sea. These proved to be powerful tools for investigating seasonal changes in patterns of water-column oxygenation on large spatial scales. The data obtained emphasize the importance of mesoscale processes for the distribution of oxygen in the Black Sea basin. Our observations revealed enhanced photosynthetic productivity in the upper mixed layer to be a major source of oxygen to the waters of

the Black Sea in summer, and provided evidence of short-term vertical displacements of the lower boundary of the suboxic zone by up to 75 m.

To assess the potential role of gas seepage as a geogenic driver of oxygen depletion, a combination of time-series monitoring at benthic observatories and spatial surveys with towed sensor platforms proved effective. Investigations carried out in Greek lagoons identified the high-volume, continuous seepage of CH<sub>4</sub> and H<sub>2</sub>S of deep thermogenic origin as a potential driver of oxygen depletion, whereas in systems with low, episodic gas seepage, the occurrence of hypoxia was governed by the hydrodynamic setting and anthropogenic factors.

The investigation of long-term trends in aquatic systems requires long-term time-series measurements. The thorough analysis of long time-series data (e.g., monthly CTD casts) from monitoring programs can reveal the presence of multidecadal and seasonal trends. Thus, although monthly sampling fails to resolve high-frequency (daily to weekly) variations in oxygen concentration, standard long-term monitoring programs still provide essential information on hypoxia and its drivers on multi-decadal time-scales. Such time-series data allow the effects of climatic forcing and eutrophication on oxygen depletion to be distinguished from one other, as was demonstrated in this study for Boknis Eck in the western Baltic Sea, the Black Sea basin, and Lake Zurich. For the western Baltic Sea, analysis of time-series data since the 1950s identified both local processes (i.e., eutrophication) and global processes (i.e., the NAO) as drivers of year-to-year decreases in bottom-water oxygen concentration. The situation in the Black Sea basin is similar. Measurements taken in the central Black Sea over the last 90 yr reflect the shoaling of the suboxic zone and a general decrease in pycnocline oxygenation since the 1970s. While some of the changes could be attributed to climate variability (i.e., the NAO), eutrophication could be identified as a main driver for the oxygen content in the Black Sea interior – especially in the period from the late 1970s to the second half of the 1980s. For Lake Zurich, analysis of the 70 yr time-series indicated that, despite recent oligotrophication as a result of reduced phosphate input, deep-water oxygenation continued to decline because of an increase in the thermal

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stability of the water column brought about by climate-driven warming. Deep-water hypoxia, in turn, leads to an increase in the release of phosphorus from the sediments and rising deep-water phosphate concentrations.

Organic and inorganic proxies in sediments proved to be powerful tools for reconstructing the oxygenation history of aquatic systems up to geological time-scales. In stratified Swiss lakes and in the Black Sea, the general patterns of eutrophication and hypoxia over the last century were reconstructed using lipid biomarkers in the sediment. The concentration and composition of such sediment biomarkers are related to shifts in the plankton and microbial communities in the water column, which are induced by changes in the prevailing environmental conditions. However, such sediment proxies cannot be used to obtain high-resolution information on the duration and spatial extent of hypoxia. The sedimentary Mn/Fe ratio was recognized as a semi-quantitative proxy for reconstructing oxygen maxima during turnover in Lake Zurich, whereas the manganese record in the sediments of the Bosphorus outflow area proves to be an effective proxy for tracing the inflow of Mediterranean water into the Black Sea, and its dynamics, during the Holocene.

Rapid changes in oxygen concentrations and hypoxia impose stress on marine fauna and flora. Records of mass mortality of pelagic and benthic fauna and flora, with carcasses being washed ashore, is presented as the most drastic consequence of oxygen depletion. For the Greek lagoons it is shown that if the natural hydrological disposition for the occurrence of episodic anoxia is disregarded, the economic consequences for fish farms can be severe. The combination of high-resolution oxygen time-series measurements with surveys of benthic communities proved successful in assessing ecosystem status with regard to hypoxia. The results of this assessment confirmed that the coastal benthic ecosystem of the western Black Sea has overcome the earlier ecological collapse that was marked by excessive eutrophication, oxygen depletion, mass mortality of organisms, and the appearance of invasive species, and has now reached a new, fragile stage of ecosystem recovery with a shift in the baseline relative to pre-eutrophication conditions. The oxygen-generating seagrass beds and macroal-

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gae (*Phyllophora*) communities as well as filter-feeding mussels have largely vanished, to be replaced by opportunistic species with short life cycles (e.g., fast-growing filamentous algae, worms, and ascidians). In areas with naturally changing oxygen conditions, such as the Crimean shelf and the Bosphorus outlet, the established benthic communities are adapted to low and fluctuating oxygen conditions.

Rates and pathways of biogeochemical processes typically depend on redox conditions, i.e., on oxygen availability, and substantial effects are to be expected when oxygen is introduced into anoxic waters. The cycling of redox-active elements at dynamic oxic/anoxic interfaces cannot be investigated with sensors alone, but requires additional sampling at high-resolution. Continuous deep profiles of oxygen and redox-sensitive elements down to 300 m depth have been obtained in the Bosphorus outflow area of the Black Sea using a custom-built pump CTD. Based on these data, we were able to show that the supply of oxygenated Mediterranean Sea waters to the Black Sea is not continuous, but is restricted to specific periods in time. Oxic compounds and ions such as oxygen and nitrate, and reduced ions such as sulfide, which usually do not meet in quasi-diffusive, horizontally layered systems, are mixed by lateral intrusions. In the plumes of oxygenated water that penetrate into the anoxic deep waters of the Bosphorus outlet area, suboxic processes result in increased nitrogen loss rates. Furthermore, oxic plume waters are shown to have caused a significant depression in the onset of reduced substances such as sulfide and ammonium. Studies of fluxes at the sediment–water interface carried out in the western Baltic Sea and the south-western Black Sea shelf confirm that sediments underlying seasonally hypoxic waters are preferential sites for the regeneration of nutrients (e.g.,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) that are released to the water column. The combination of benthic flux estimates from in situ flux chambers, ex situ porewater gradients and non-steady-state 1-D numerical reaction-transport modeling applied to seasonally hypoxic settings revealed a general pattern in which diffusive losses of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  are important during hypoxic conditions, whereas irrigation fluxes are more important during oxic conditions found in winter. An understanding of the intensity and depth of bioirrigation at seasonally-hypoxic sites is

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critical for the evaluation of the potential impact of enhanced nutrient release on water-column processes and hypoxia over an annual cycle.

The reliability of the oxygen measurements obtained during monitoring is a necessary prerequisite for their use. The monitoring of gradual changes in bottom-water oxygen concentration at the long-term, deep-sea observatory HAUSGARTEN in Fram Strait was used as a particularly challenging example to test the reliability of current state-of-the-art oxygen sensing technology. Although optical oxygen sensors (optodes) perform well in shallow waters, our results indicate that this sensor type is of limited suitability for conducting long-term measurements in deep waters, especially at low current speeds. Continuous observation of the temporal development of oxygen concentrations in the deep ocean (e.g., in order to identify the gradual trends that might be expected to occur in response to global change) remains a big challenge, necessitating the development of improved sensors with better temporal stability.

Cabled observatories, such as those installed in Koljoe Fjord and Loch Etive, proved to be highly suitable for the monitoring of systems with episodic changes in bottom-water oxygenation where the main drivers are either unknown or where there is a complex interplay of several drivers. Combining online observations from the Loch Etive cabled observatory with numerical simulations allowed the hydrodynamic mechanisms that govern stagnation and overturning/ventilation events to be identified, in turn allowing the prediction of deep-water oxygenation. Furthermore, online access to oxygen data may facilitate measures to mitigate hypoxic conditions and to monitor the efficiency of such measures. The installation of permanent observatories, however, involves a long-term commitment of resources and personnel for maintenance, especially in shallow-water systems with high biological activity. Due to the inevitable need for validation data, observatories should always be regarded as supplemental to existing standard monitoring programs rather than as a substitute for such programs.

The benefits of ocean data obtained within HYPOX and similar projects depend crucially on the accessibility of these data to users; i.e., on putting appropriate data-sharing and dissemination procedures into place. For the cabled observatories, data-

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flow procedures were established that allow automated, near real-time data access. PANGAEA served as the central hub for the collection and dissemination of all HYPOX data, including continuous data and all manner of individual multidisciplinary observations along with their associated metadata. PANGAEA also functioned as the interface to the earth observation initiative GEOSS (Global Earth Observation System of Systems).

Despite the use of state-of-the-art technology by a network of experts, the research performed within HYPOX revealed a variety of unresolved technological, scientific, and logistic challenges that will need to be addressed in the future. These challenges include, but are not limited, to: (1) the continuation of existing long-term time-series monitoring programs and the set-up of additional programs; (2) the installation of continuous cabled and autonomous observatories to complement standard monitoring programs; (3) a proper validation of observatory data using data from reference stations; (4) the development and application of oxygen sensor technologies for monitoring water column oxygen distributions down to trace levels, and for monitoring gradual changes in oxygen concentration in the micromolar range; (5) the integrated assessment of the response of ecosystems to hypoxia, including community patterns, the adaptive behavior of organisms, and biogeochemical processes; (6) the development of model-based forecasting tools; and (7) the setting-up of readily accessible databases for the dissemination of oxygen observations and the integration of these observations into global aquatic system observation initiatives. The success and efficiency of any long-term monitoring effort, be it autonomous observatories or classical monitoring, requires the long-term commitment of human and financial resources. Nevertheless, our comprehensive study within the three-year HYPOX project was able to address many aspects of hypoxia in aquatic systems, and revealed the vital need for dedicated oxygen monitoring at appropriate spatial and temporal scales using appropriate technologies. The variety of characteristics and consequences of hypoxia that were identified at the different HYPOX target sites emphasizes the need to conduct oxygen measurements at

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carefully selected locations and periods of time in order to adequately address the risk of occurrence of hypoxia and the subsequent ecosystem response.

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**Table 1.** HYPOX study sites, drivers of oxygen depletion, investigated processes and monitoring approach.

| Location                        | Natural driver  | Anthropogenic driver  | Frequency and duration  | Processes studied  | Type of in-situ observatory/ monitoring approach   |
|---------------------------------|---|---|---|--|--|
| Black Sea Crimean shelf         | Permanent thermohaline stratification, oscillations of the chemocline depth (eddies, internal waves), interactions with local shelf bathymetry, locally CH <sub>4</sub> seepage | Locally eutrophication, long-term trends in chemocline depth  | Oscillating, from hours to weeks, maybe also longer   | Benthic oxygen uptake, mineralization pathways, distribution of benthic communities  | CTD profiles with Clark-type O <sub>2</sub> sensors, static mooring arrays, areal surveys (manned submersible, towed observatories), benthic observatories (benthic chambers, micro profilers, BBL studies) with O <sub>2</sub> optodes and Clark-type micro sensors, seafloor mapping |
| Black Sea North-western shelf   | Seasonal thermohaline stratification due to freshwater-seawater confluence  | Agriculture, coastal urbanization, fisheries, eutrophication due to nutrient input from Danube River and non-point sources            | Seasonal bottom-water hypoxia   | Pathways of benthic organic matter mineralization at changing O <sub>2</sub> , formation of bottom-water hypoxia, consequences of hypoxia for benthic ecosystem  | Static 3 month mooring with O <sub>2</sub> optodes, benthic flux chambers  |
| Black Sea Bosphorus outflow     | Permanent thermohaline stratification, hypoxic conditions in otherwise anoxic deep waters due to inflow of saline water of Mediterranean origin                                 | Wastewater/nutrient input from NW shelf and Bosphorus may influence water-column biogeochemistry                                      | Episodic oxygen injections into permanently anoxic deep waters  | Water-column biogeochemical processes at permanent redoxcline and in oxio/hypoxic "Bosphorus plume" waters at ca. 300 m depth, consequences of O <sub>2</sub> depletion for benthic fauna along depth/oxygen transect                        | Pump-CTD casts, with Clark-type electrodes   |
| Central Black Sea               | Density-driven stratification between saline deep waters and less saline surface waters, interactions with local shelf topography   | Interplay of climate variability and eutrophication leads to rising of the sub-oxic zone  | Persistent anoxia below pycnocline  | Seasonal and local variability of the chemocline position and fine structure, long-term trends   | Drifting ARGO-type profiling observatories with O <sub>2</sub> optodes, 90 yr of O <sub>2</sub> time-series observations based on CTD casts with Clark-type O <sub>2</sub> sensors and Winkler titration   |
| Baltic Sea Gotland basin        | Density-driven stratification, baroclinic or barotrophic inflows and breaking internal waves  | Climate warming stabilizes stratification   | Persistent anoxia > 200 m, during stagnation periods anoxia > 110 m, wind driven oxycline dynamics at time-scales of hours to weeks | Short-term fluctuations at pelagic redoxcline, three-dimensional system, fast redox fluctuations at the sediment-water interface, organic matter mineralization and nutrient release at the seafloor at changing bottom-water O <sub>2</sub> | Profiling mooring GODESS and benthic observatories with O <sub>2</sub> optodes, benthic flux chambers, seafloor mapping  |
| Baltic Sea Boknis Eck           | Summer stratification   | Eutrophication due to anthropogenic nutrient input and nutrient recycling at the seafloor, climate warming stabilizes stratification, | Seasonal bottom-water hypoxia   | Long-term trends in O <sub>2</sub> and nutrients, Pathways of benthic organic matter mineralization and nutrient fluxes at changing bottom-water O <sub>2</sub>  | 50 yr time-series based on monthly CTD casts with Clark-type O <sub>2</sub> sensors and Winkler titration, pore water geochemistry, ex situ core incubations   |
| Swedish west coast Koljöe Fjord | Density-driven stratification due to freshwater-seawater confluence   | Global change related changes in wind and precipitation patterns will influence inflow events   | Long stagnation periods with hypoxia or anoxia, episodic deep-water renewal events due to wind-induced inflow of saline waters      | Physical processes of mixing, hydrophysical and meteorological prerequisites of inflow events  | Time-series since 1935 with Clark-type O <sub>2</sub> sensors and Winkler titration, cabled observatory with O <sub>2</sub> optodes  |

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**Table 1. Continued.**

| Location  | Natural driver   | Anthropogenic driver  | Frequency and duration   | Processes studied  | Type of in-situ observatory/ monitoring approach  |
|---|--|---|--|--|---|
| Scotland<br>Loch Etive<br>(Upper basin/<br>Bonawe deep,<br>lower Basin/<br>Airds Bay) | Density-driven stratification due to freshwater-seawater confluence, strong tidal influence  | Global change related changes in wind and precipitation patterns will influence inflow events, anthropogenic regulation of river runoff | Long stagnation periods with hypoxia or anoxia, episodic deep-water renewal and oxygenation only at low freshwater input, spring tides, and favourable winds | Hydrophysical and meteorological prerequisites of inflow events  | Cabled observatory with O <sub>2</sub> optodes, long-term bottom moorings   |
| Switzerland<br>Lake of Zurich   | Seasonal/multiannual thermal stratification  | Climate warming is impeding overturning in winter, counteracted by decreasing eutrophication  | Long-term trend from monomictic to oligomictic, seasonal to annual stagnation with bottom-water hypoxia  | Effect of climate variability on stratification stability and bottom-water O <sub>2</sub> . Internal loading of deep water with P release from sediments during bottom water hypoxia, bottom-water oxygenation history | 70 yr monthly time-series based on weekly CTD casts with Clark-type O <sub>2</sub> sensors and Winkler titration, time-series analysis, redox sensitive metals in the sediment record   |
| Switzerland<br>Lake Rotsee  | Thermal stratification, wind-shielded  | Eutrophication due to fish farms and fertilizer runoff from agriculture in the past   | Monomictic, annual stagnation and bottom-water anoxia  | Fine structure of the submicromolar oxic-anoxic interface at nanomolar resolution, eutrophication and oxygenation history  | Optimized amperometric O <sub>2</sub> sensing with Clark type sensors, fiberoptical trace optodes, biomarker in the sediment record   |
| Greek lagoons<br>Amvrakikos Gulf  | Mediterranean-type fjord, seasonal thermohaline stratification, limited exchange with open sea, low and episodic gas seepage from pockmarks        | Eutrophication due to fish farms and fertilizer runoff from agriculture   | Seasonal anoxia  | Drivers of hypoxia and anoxia, role of gas seepage   | Areal surveys with towed observatory MEDUSA (CTD, O <sub>2</sub> , CH <sub>4</sub> and H <sub>2</sub> S sensors), organic biomarkers, benthic foraminifera  |
| Greek lagoons<br>Aetoliko Lagoon  | Semi-enclosed lagoon, limited exchange with open sea, persistent thermohaline stratification, low and episodic gas seepage from pockmarks          | Increased freshwater discharge, limited water exchange due to technical works   | Persistent bottom water anoxia   | Temporal and spatial dynamics of gas seepage, gas origin, seasonal dynamics in pycnocline depth, relation of meteorological conditions to fish kills   | Areal surveys with towed observatory MEDUSA (CTD, O <sub>2</sub> , CH <sub>4</sub> and H <sub>2</sub> S sensors)  |
| Greek lagoons<br>Katakolo Bay   | Gas seepage from tectonically active area (geogenic driver), permanently strong seepage of thermogenic methane and H <sub>2</sub> S from pockmarks |   | Hypoxia around seepage sites (physical O <sub>2</sub> stripping – maybe also oxidation of reduced gases)   | Temporal and spatial dynamics of gas seepage and its relation to hypoxia   | Areal surveys with towed observatory MEDUSA (CTD, O <sub>2</sub> , CH <sub>4</sub> and H <sub>2</sub> S sensors), 3 month deployment of benthic observatory GMM (with CTD, O <sub>2</sub> optode, CH <sub>4</sub> and H <sub>2</sub> S sensors) |
| North Atlantic<br>Fram Strait   |  | Potentially decrease in deep-water oxygen due to global warming and changes in deep-water formation/thermohaline circulation            | Oxic conditions, potentially slight long-term O <sub>2</sub> decrease  | Impact of large-scale environmental changes on the Arctic marine ecosystem (benthic activity/oxygen uptake)  | Long-term moorings with O <sub>2</sub> optodes, Winkler titration, time-series of oxygen microprofiles  |

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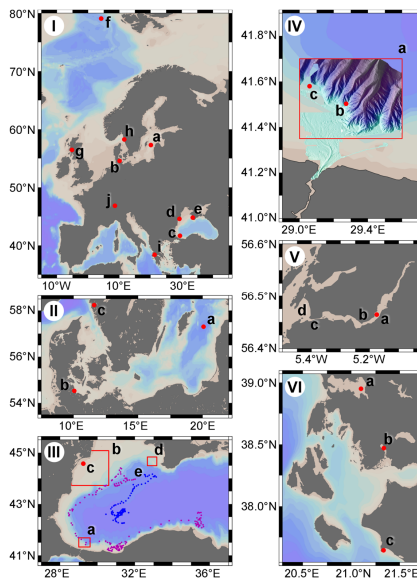
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**Fig. 1.** Panel I: study area overview; (Ia) Gotland Basin, (Ib) Eckernförde Bay/Boknis Eck, (Ic) Bosphorus outlet, (Id) Northwestern Black Sea shelf, (Ie) western Crimean shelf, (If) Fram Strait/HAUSGARTEN observatory, (Ig) Loch Etive, (Ih) Koljoe Fjord, (Ii) Ionian Sea lagoons and embayments, (Ij) Swiss lakes. Panel II: Baltic Sea and adjacent study area; (IIa) Gotland Basin observatory, (IIb) Eckernförde Bay/Boknis Eck time series station, (IIc) Koljoe Fjord observatory. Panel III: Black Sea study area; (IIIa) Bosphorus outlet study area, (IIIb) Northwestern shelf study area, (IIIc) Portita Bay/Northwestern shelf observatory (IIId) Western Crimean shelf study area, (IIIe) deployment area of Nemo Floats 144 and 145 (profiling locations/drift track: blue and purple dots). Panel IV: Bosphorus outlet study area; (IVa) coring and water sampling area, (IVb) core MSM015-192, (IVc) core MSM015-311. Panel V: Loch Etive study area; (Va) Loch Etive cabled observatory, (Vb) Bonawe Sill, (Vc) sill “Falls of Lora”, (Vd) Ardmucknish Bay. Panel VI: Ionian Sea study sites; (VIa) Amvrakikos Gulf, (VIb) Aetoliko Lagoon, (VIc) Katakolo Bay.

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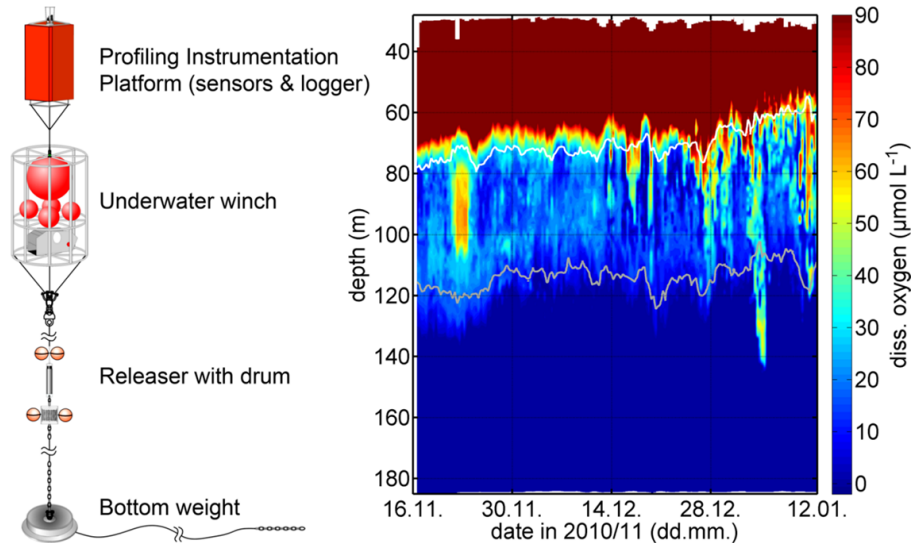
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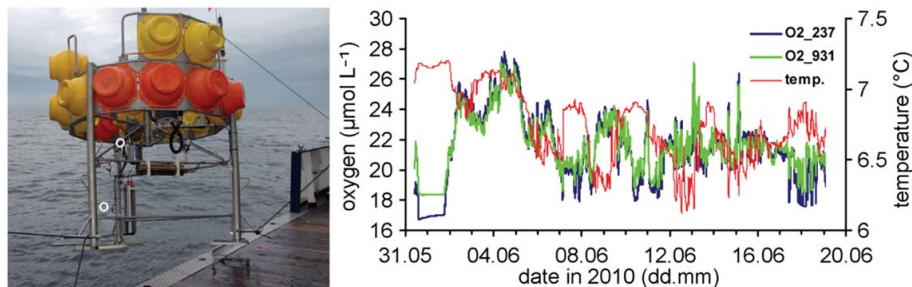


**Fig. 2.** Left panel: sketch of the profiling mooring GODESS with profiler, underwater winch, releaser with recovery line and bottom weight (from top to bottom) in the Gotland Basin. Right panel: dissolved-oxygen concentration for a 56 day deployment in the central Eastern Gotland basin (16 November 2010 to 11 January 2011). All concentrations above  $90 \mu\text{mol L}^{-1}$  are plotted in red. White and gray lines denote the  $8.0 \text{ kg m}^{-3}$  and  $9.5 \text{ kg m}^{-3}$  isopleths of density anomaly, respectively.



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**Fig. 3.** Left Panel: photograph of the GEOMAR benthic observatory. White circles denote oxygen optodes attached 0.3 and 1 m above the seafloor. Right panel: time-series of bottom-water oxygen concentration and temperature measured 0.3 m above the seafloor at a 90 m deep station in the Gotland Basin during summer 2010 (Alkor cruise AL355).

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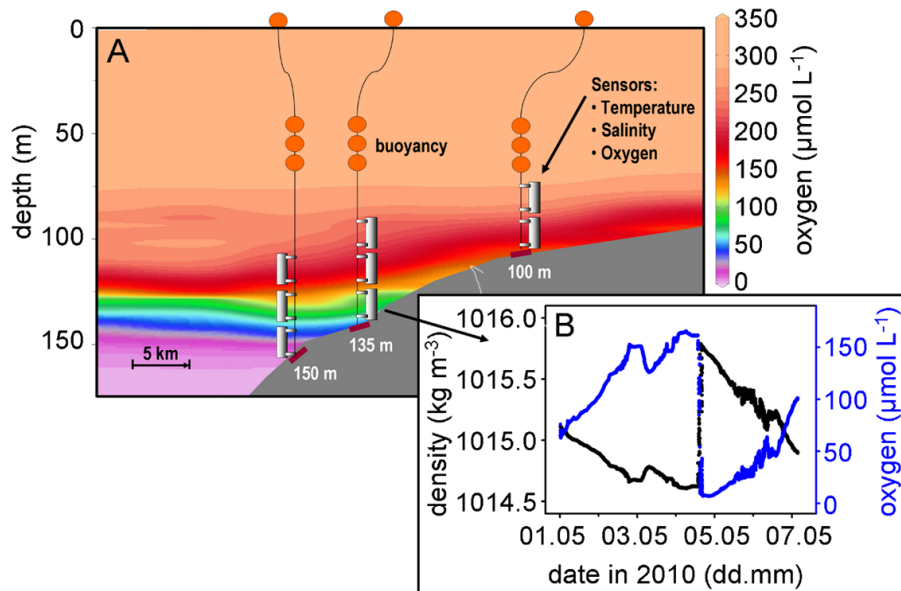
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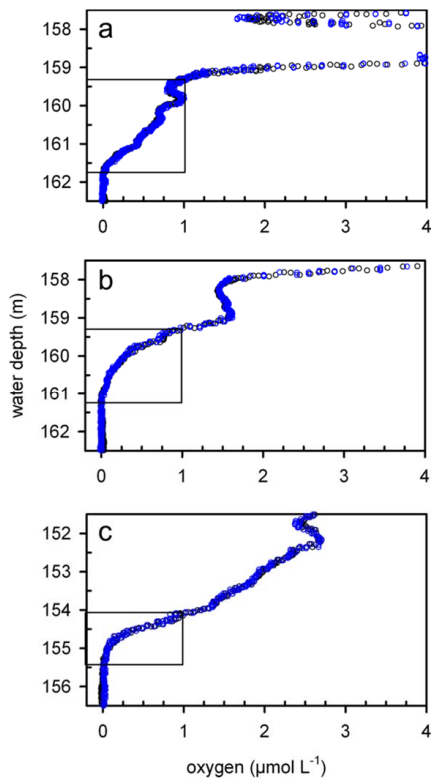
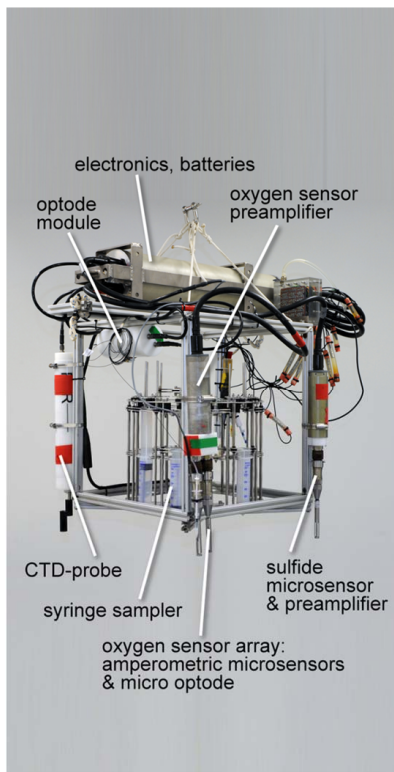


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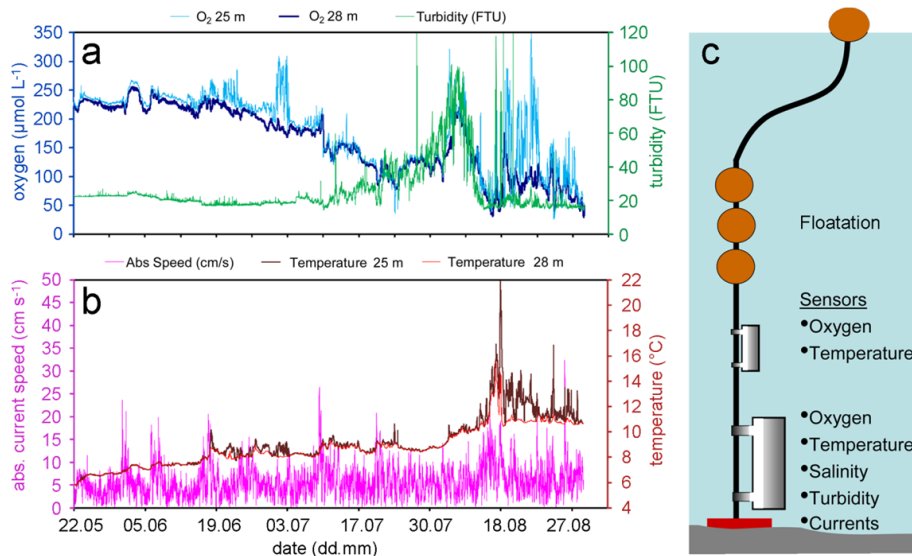
**Fig. 4. (A)** Three moorings were deployed from 1 to 7 May 2010 at 100, 135 and 150 m depth, measuring temperature, salinity and oxygen concentration. The average distribution of oxygen is compiled from 16 CTD profiles taken between 24 April and 7 May. **(B)** Time-series of density and oxygen of the lowermost CTD at 135 m depth. Oxygen correlates with density showing a gradual increase in oxygen over several days followed by a sudden drop of oxygen concentration of more than  $150 \mu\text{mol L}^{-1}$  within two hours.



**Fig. 5.** Left panel: sampling platform “PIA” for high-resolution measurements of nano-molar oxygen concentrations. Right panel: three examples of high-resolution oxygen-profiles measured within 3 h on the 7 July 2010 in the south basin of Swiss Lake Zug. Oxygen concentrations were derived in parallel from a microoptode (blue) and an amperometric microsensor (black, after in-situ recalibration based on optode-data). Boxes indicate submicromolar oxygen concentrations.

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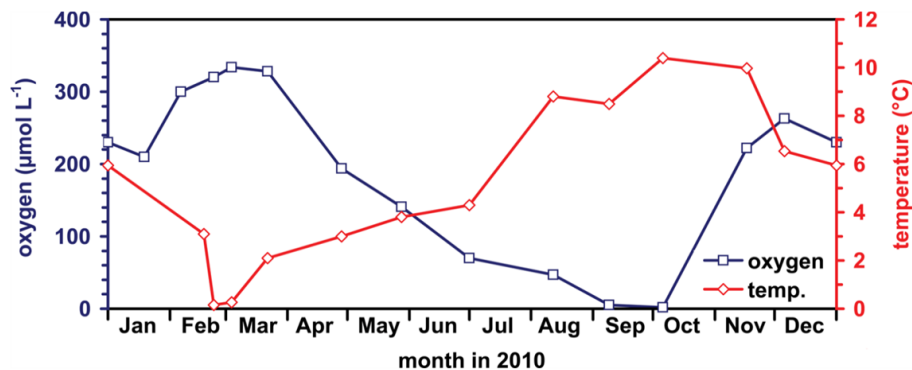
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**Fig. 6.** Left Panel: Time-series of **(a)** oxygen concentrations ( $\mu\text{M}$ ) and turbidity (Formazin Turbidity Units, FTU), and **(b)** temperature ( $^{\circ}\text{C}$ ) in 25 m and 28 m water depth and absolute current speed ( $\text{cm s}^{-1}$ ) above the sea floor. Data were collected May to August 2010 on the Romanian Black Sea shelf ( $44^{\circ}34.681' \text{ N}$ ,  $29^{\circ}14.620' \text{ E}$ ) with a recording current meter (Type RCM9, AADI, Bergen, Norway). Right Panel **(c)**: Schematic of the mooring.

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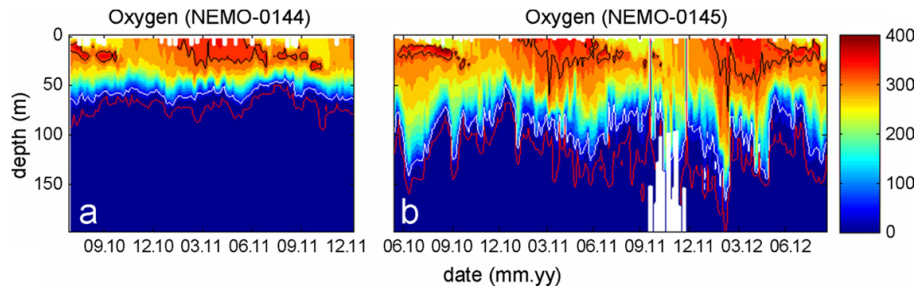


**Fig. 7.** Time-series of temperature and dissolved oxygen in the bottom water (25 m) measured at Boknis Eck in 2010.

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**Fig. 8.** Temporal evolution of oxygen (in  $\mu\text{mol L}^{-1}$ ) as observed by NEMO-0144 (**a**) and NEMO-0145 (**b**). These plots illustrate the evolution of subsurface oxygen maximum and the mesoscale variability of the interface between oxic and anoxic waters. The white and red isolines depict oxygen concentrations of 50 and  $5 \mu\text{mol L}^{-1}$ , respectively. Note that in the basin interior (NEMO-0144) the temporal evolution of the depth of isopycnals is very small. White vertical strips illustrate missing data due to either malfunction of sensors or reaching bottom.

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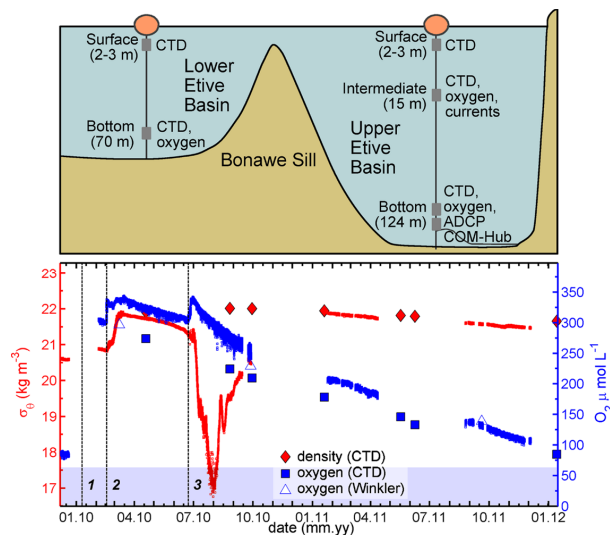
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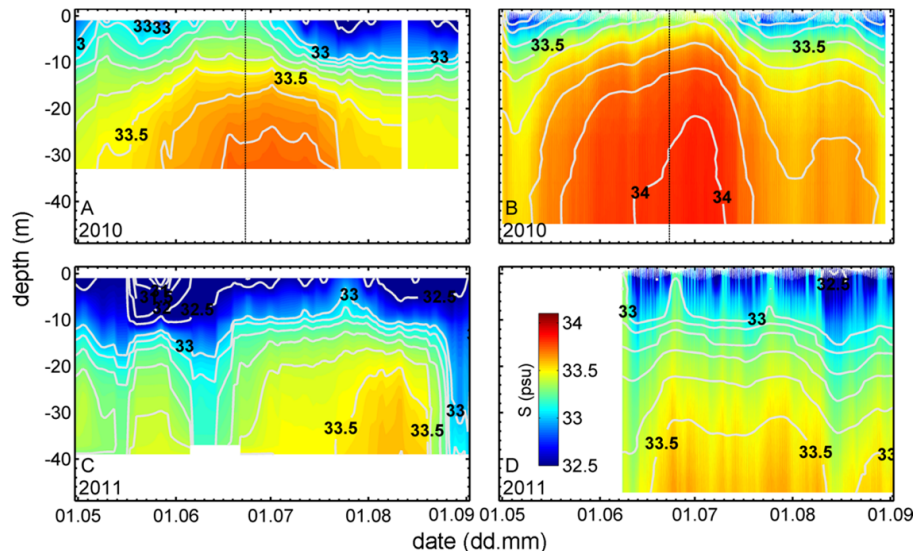


**Fig. 9.** Upper panel: schematic of the Loch Etive Cabled Observatory (“LECO”, right mooring) and the autonomous installation installed in the lower basin seawards of Bonawe Sill. Time-series in the lower panel originate from LECO’s lowermost sensor unit. Lower panel: potential density (red line) and dissolved oxygen measured with an oxygen optode (type 3835, AADI, Bergen, Norway; blue line) in the upper Loch Etive at the HYPOX mooring site at 124 m water depth. Blue squares and red diamonds represent validation data from CTD casts obtained with various instruments (SBE19+, SBE16, SBE9, equipped with SBE oxygen sensors, Seabird Electronics, Bellevue, WA, USA). The blue triangles represent oxygen concentrations of samples measured by Winkler titration. The three overturning events observed (~ 10 January, 17–23 February, 23–30 June 2010) are indicated by dashed vertical lines. The gaps in records are due to cable connection/instrument failure, repair and re-deployments. During the 3rd renewal event vertical stratification was destroyed and surface waters were delivered to the bottom (little). Stratification recovered with heavy rains in early July, however, bio-fouling in the conductivity cell lead to the apparent extended presence of low-density waters at depth. The grey area denotes hypoxic conditions with oxygen concentrations below  $62.5 \mu\text{mol L}^{-1}$ .



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**Fig. 10.** Weekly time-series of salinity profiles at Lynn of Lorne in Ardmucknish Bay ( $56^{\circ}28.91' \text{ N}$ ,  $5^{\circ}30.10' \text{ W}$ ) from CTD casts (left) and calculated with the FVCOM model (right) in summer of 2010 (**a, b**) and 2011 (**c, d**). The onsets of the overturning events in the Loch Etive deep basin are indicated by dashed vertical lines. The presence of a pool of high-density (salinity) water at the entrance to Loch Etive in 2010 and its absence in 2011 is well reproduced by the model.

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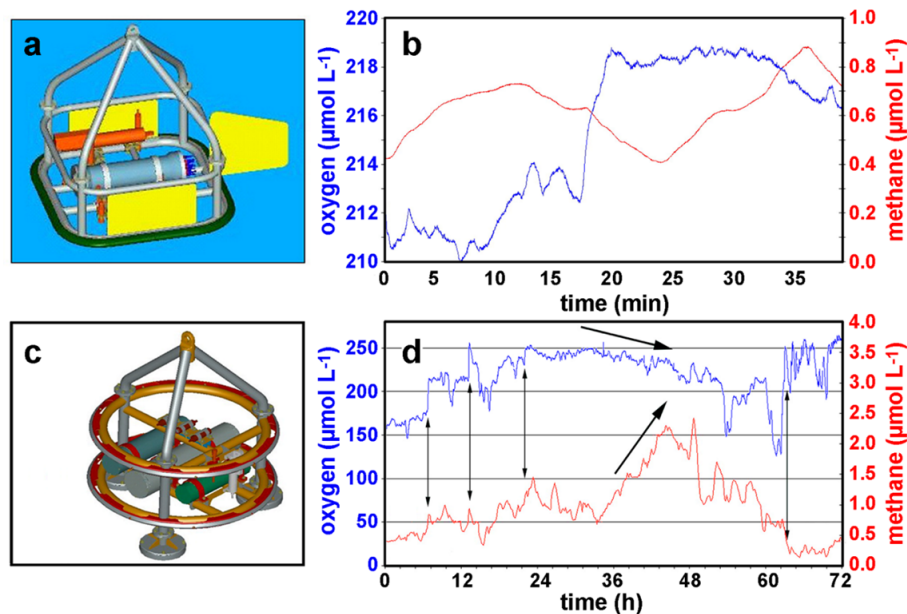
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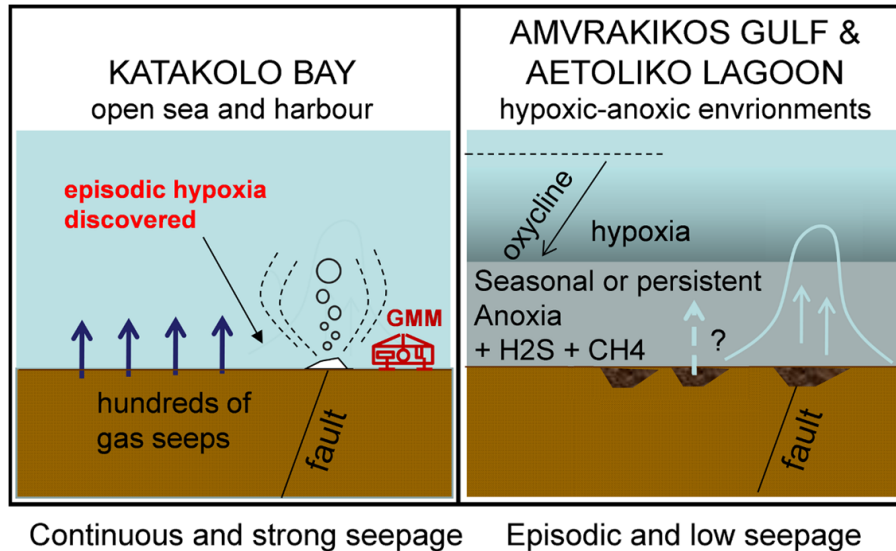
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**Fig. 11.** Left panels: MEDUSA system (a) and GMM benthic observatory (c) used for spatial survey and temporal monitoring in Katakolo Bay, respectively. Right panels: exemplary recordings showing the inverse relationship between  $\text{O}_2$  and  $\text{CH}_4$ : oxygen depletion due to methane increase over submarine bubbles seep recorded by MEDUSA towing system (b) and short and long-term changes of oxygen accompanied by inverse changes of methane recorded over a period of 3 days in a submarine seep by the GMM (d).

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**Fig. 12.** Simplified graphical representation of the hypoxia/anoxia drivers in Katakolo Bay (left panel) and Amvrakikos Gulf and Aetoliko Lagoon (right panel). “GMM” indicates the benthic observatory used for time-series monitoring of dissolved gases, see text for explanation).

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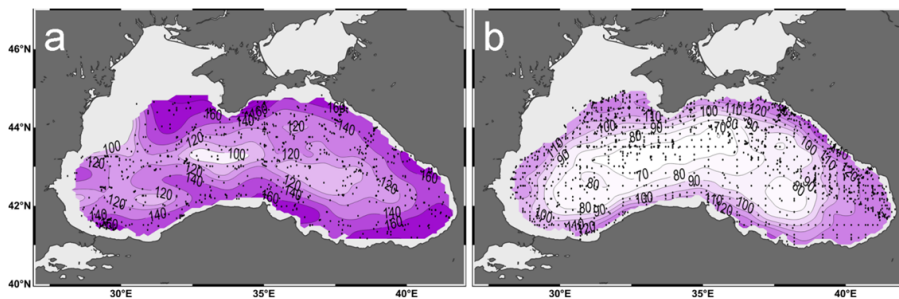


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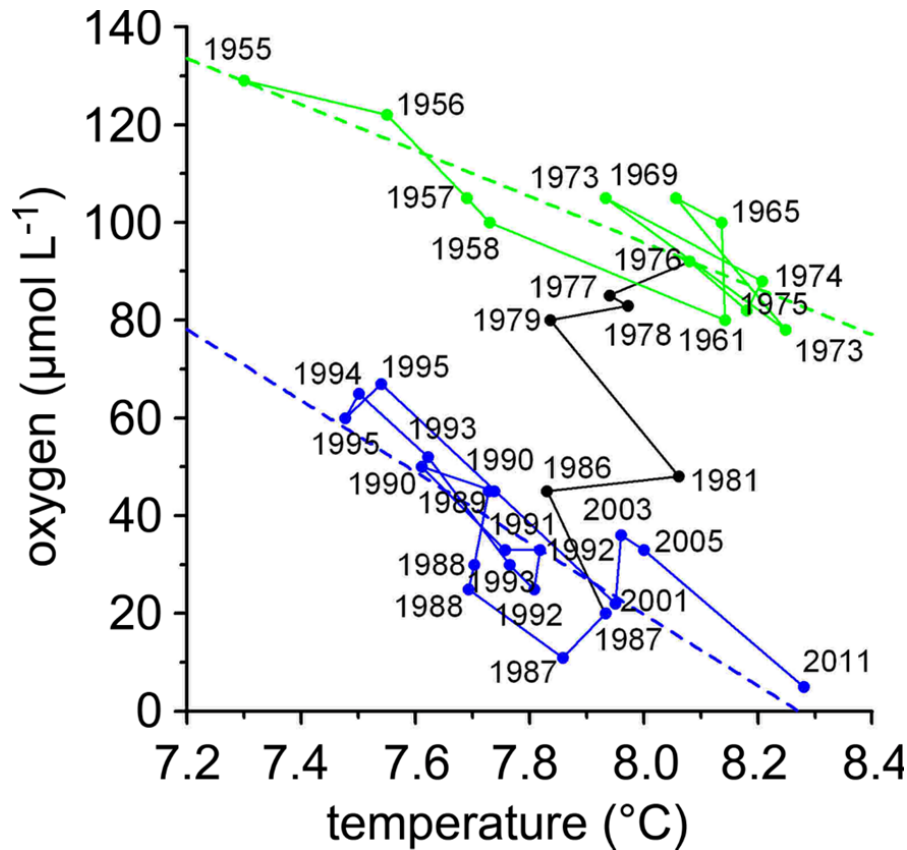
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**Fig. 13.** The mean depth of the upper boundary of the suboxic zone (UBSOZ) in the Black Sea for the period of 1955–1976 (a) and 1987–2011 (b).

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**Fig. 14.** Relationship between basin-averaged oxygen concentration and water temperature in the main pycnocline of the Black Sea ( $\sigma\text{-}t = 15.4$ ) from 1955–2011. Individual points represent the mean values of oxygen concentration for individual cruises; thus they are available for only years when cruises were performed.

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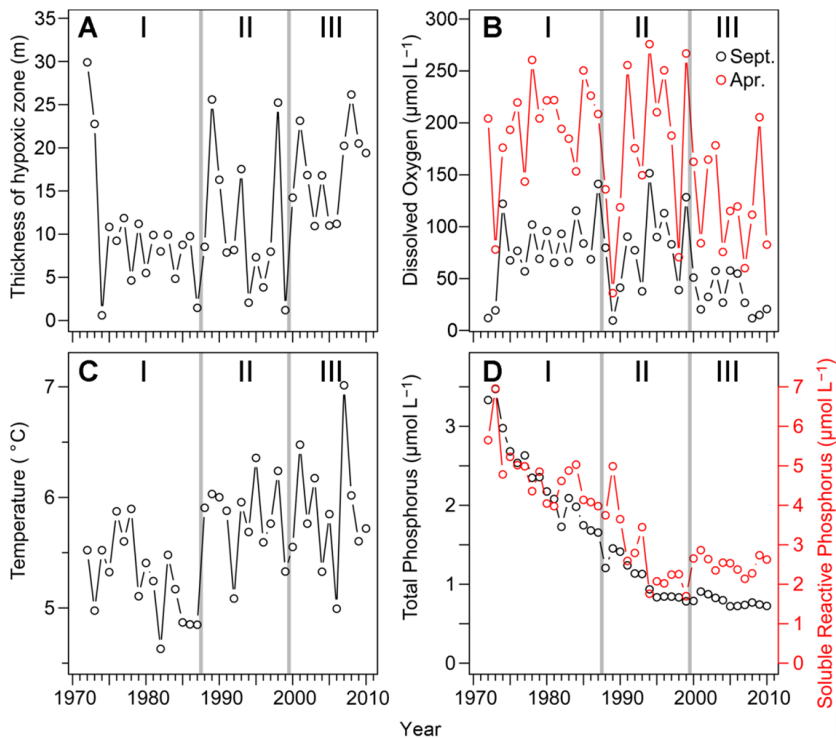
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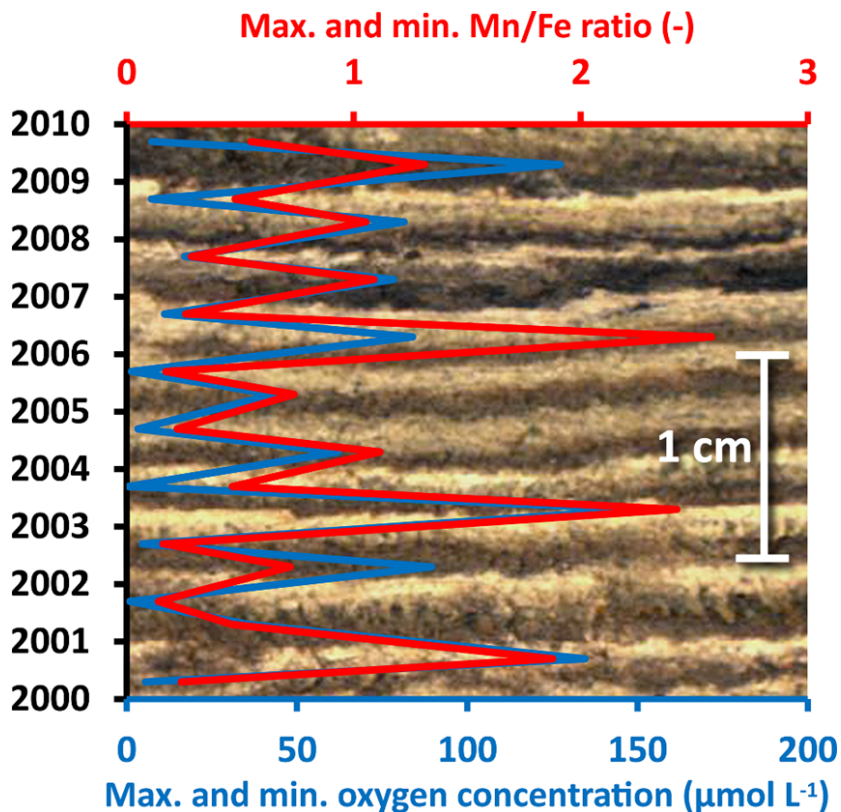
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**Fig. 15.** The Lake of Zurich data set (1972–2010). **(A)** Thickness of the hypoxic zone (oxygen concentrations  $< 62.5 \mu\text{mol L}^{-1} / < 2 \text{mg L}^{-1}$ ) in September. **(B)** Mean volume-weighted deep-water (120–136 m) oxygen concentration in September (black) and in the previous April (red). **(C)** Mean volume-weighted temperature of the uppermost 20 m of the lake from December to April. **(D)** Mean annual volume-weighted concentration of total phosphorus (black) in the entire lake (0–136 m) and of soluble reactive phosphorus (red) in the deep water (120–136 m). For further information see North et al. (2013a, b).



**Fig. 16.** Detail of the laminated sediment core from the Lake of Zurich covering the period 2000–2010. The profiles show seasonal changes of the Mn/Fe ratio (based on maximum and minimum XRF counts in the respective layers of the core, red line) and bottom-water oxygen concentrations at 135 m water depth (maxima and minima of three month running mean of monitoring data, blue line).

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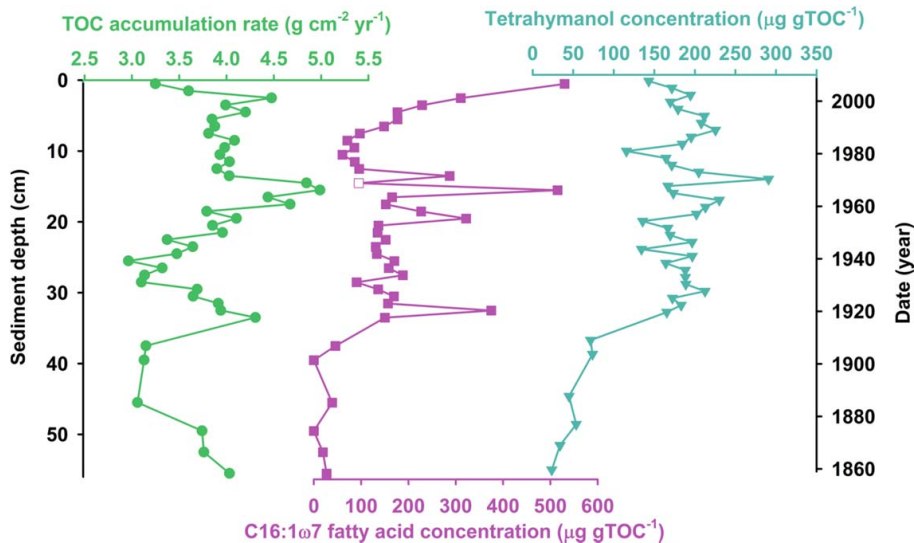
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**Fig. 17.** Profiles of TOC accumulation rate, C<sub>16:1ω7</sub> fatty acid and tetrahymanol concentrations in Rotsee as a function of sediment depth (cm) and age (yr AD).

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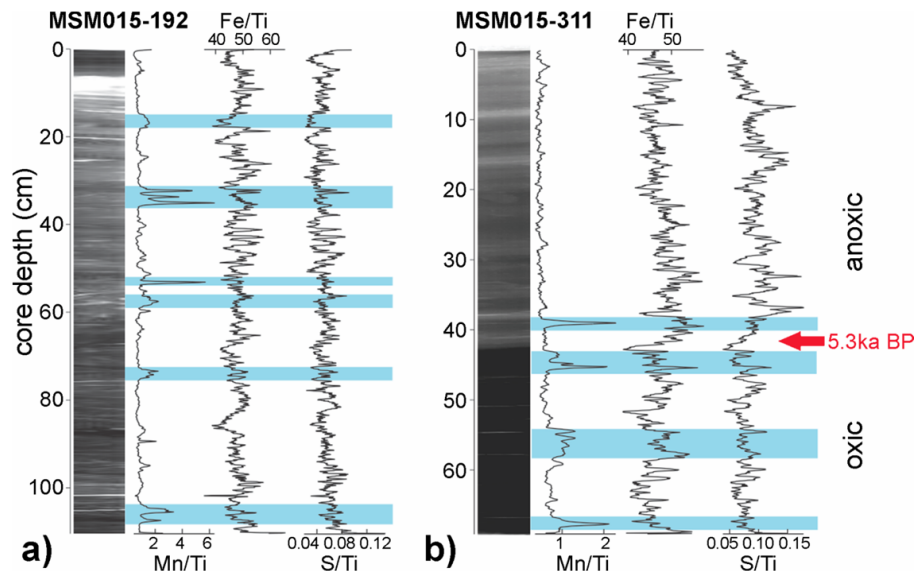
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**Fig. 18.** X-ray radiographic images and XRF element/Ti profiles of cores located at 307 m water depth below the present oxic/anoxic interface (see Fig. 1 for location). Mediterranean Water ventilation effect is indicated by Mn fluctuations (blue faded) not associated with Fe and S throughout the core length; **(a)** core MSM015-192 located at eastern part of the area, ( $41^{\circ}30.143' \text{ N}$ ,  $29^{\circ}16.340' \text{ E}$ ). **(b)** Core MSM015-311 located at western part of the area ( $41^{\circ}34.784' \text{ N}$ ,  $29^{\circ}03.46' \text{ E}$ ). The X-ray radiographic image shows an abrupt change in density at 42 cm dated as 5.3 ka BP.

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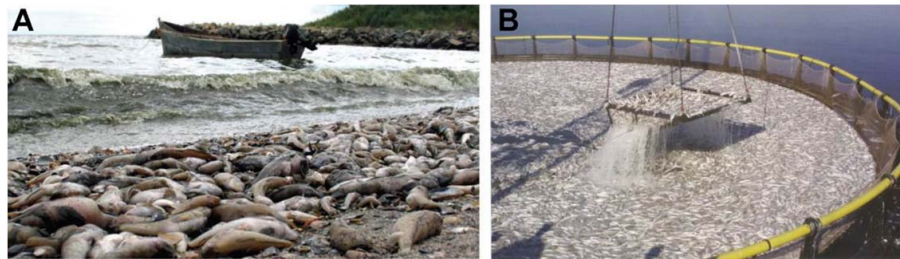


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**Fig. 19.** (A) Mass mortality of benthic fauna in July 2010 in a semi-enclosed bay on Constanta beach (Photo: Adrian Teaca). (B) Dead fish floating in a cage after a massive fish kill in fish farms at Amvrakikos Gulf (February 2008).

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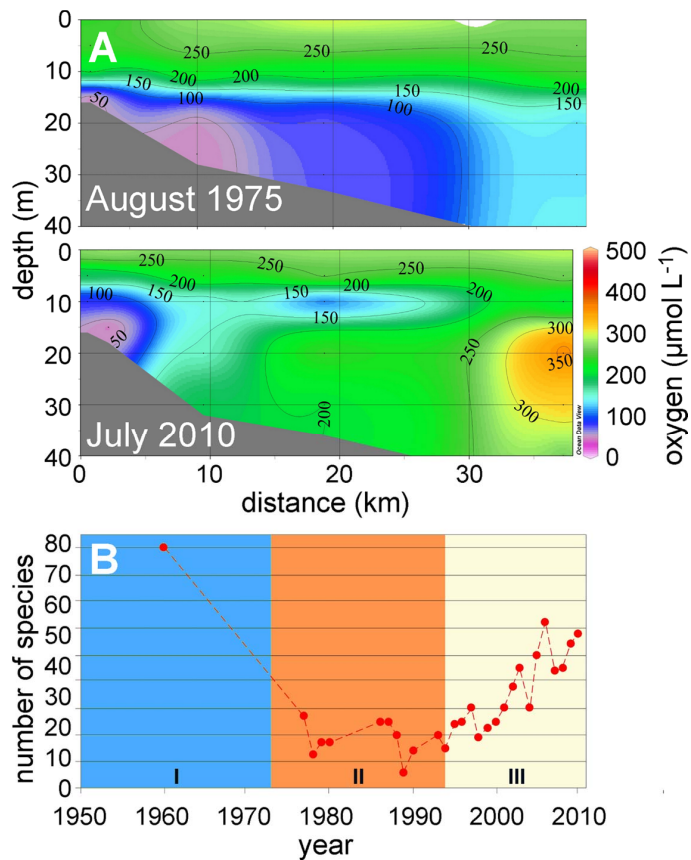
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**Fig. 20. (A)** Distribution of O<sub>2</sub> [μmol L<sup>-1</sup>] concentration in Romanian coastal waters (transect East-Constanta) in August 1975 and July 2010. **(B)** Temporal changes in the species diversity of the total macrobenthic community in the Romanian pre-Danubian sector (Period: 0 – pristine, I – eutrophication, II – ecological crisis, III – present).

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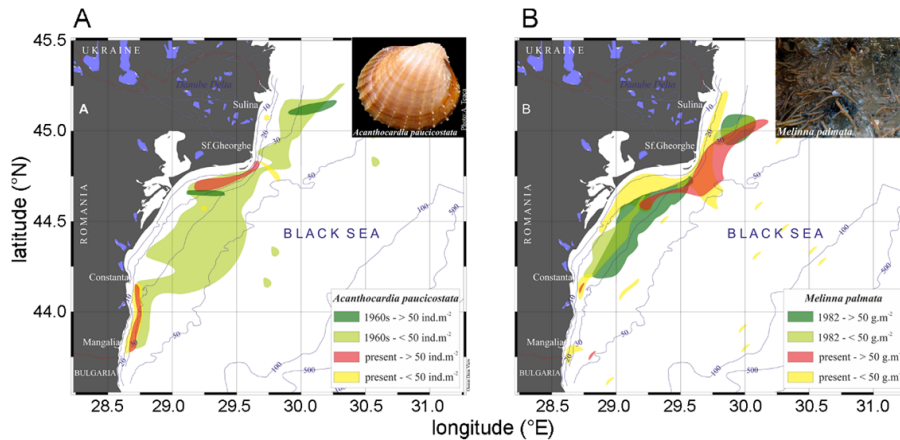
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**Fig. 21.** The density distribution of the bivalve *Acanthocardia paucicostata* in the 1960s and after 2000 (A) and the biomass distribution of the polychaete *Melinna palmata* in the 1980s and after 2000 (B) along the Romanian Black Sea coast. Bivalves are the losers and polychaetes are the winners in a situation of increasing eutrophication and hypoxia.

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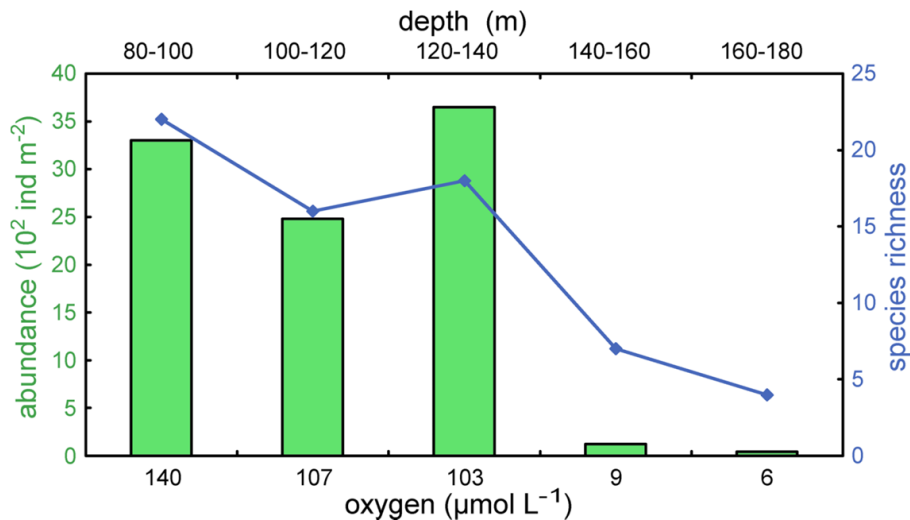
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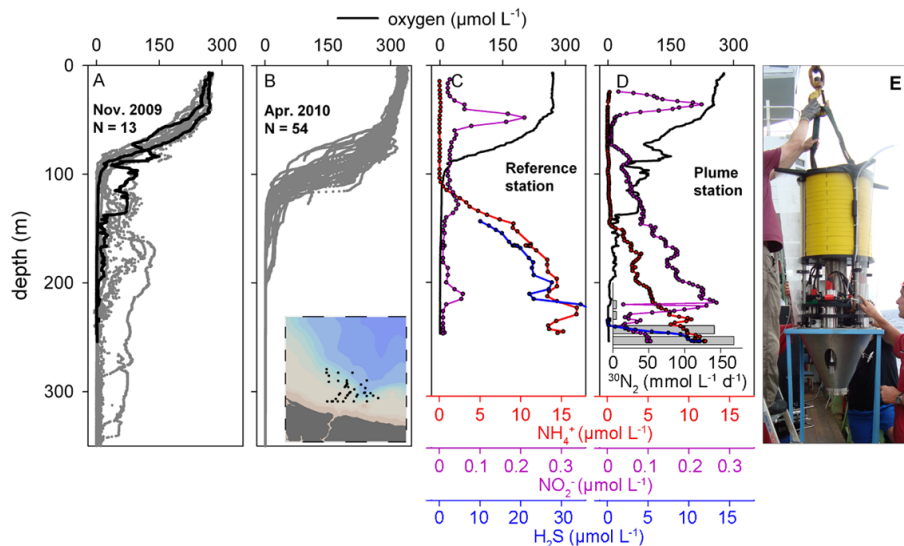


**Fig. 22.** Dependence of the abundance and species richness of the benthos in the Bosphorus area on water depth and on the dissolved-oxygen concentration measured just above the sediment.

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**Fig. 23.** (A and B) Oxygen concentration profiles measured in November 2009 and April 2010 in the Bosphorus outlet area (see inset map). The black curves show the examples illustrated in panels (C) and (D). (C and D) Vertical distributions of oxygen, ammonium, nitrite, and sulfide at a reference station and a plume site affected by waters of Mediterranean origin. For the plume station,  $\text{N}_2$  production rates at the depth at which sulfide first occurs are provided (grey bars). (E) The free-falling pump CTD just before deployment. The sensors for temperature, salinity, and oxygen, and the inlet of the pump, protrude out of the downward-facing cone. The yellow-painted syntactic foam provides buoyancy to the upper part of the pump CTD. In free-falling mode the pump CTD descends slowly along a wire that runs through the center of the instrument.

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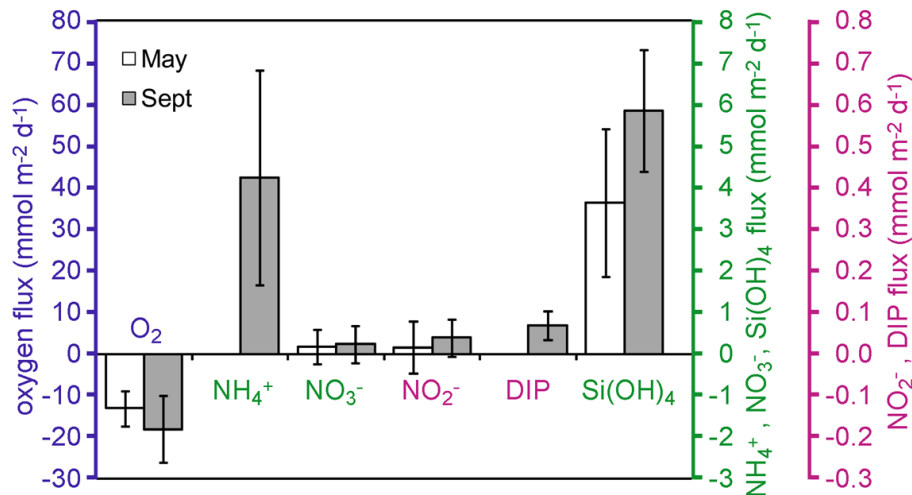
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**Fig. 24.** Mean values of in situ and ex situ benthic total oxygen utilization ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) and benthic nutrient fluxes in May 2010 ( $n = 6$ ) and September 2010 ( $n = 7$ ) measured at the site of the RCM mooring at Portita on the north-western Black Sea shelf. Error bars represent the standard deviation of the flux measurements from the calculated mean value. Ammonia and phosphate fluxes in May were below their respective detection limits.

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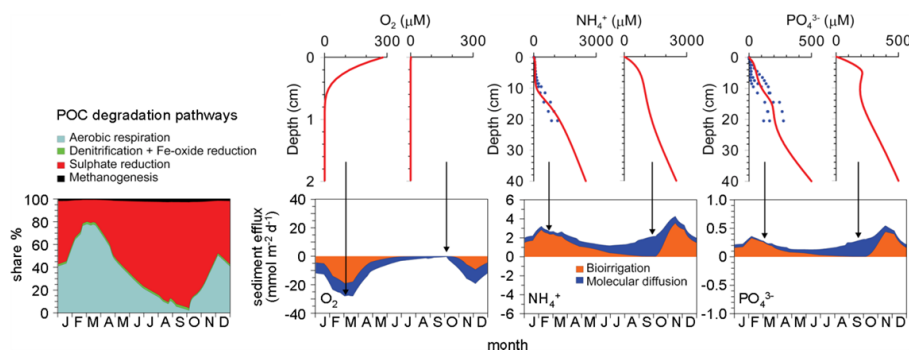
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**Fig. 25.** Left-hand panel: model results showing the daily fraction of organic carbon mineralized by each degradation pathway. Upper right-hand panels: representative depth concentration profiles of  $O_2$ ,  $NH_4^+$ , and  $PO_4^{3-}$  during winter (high bioirrigation) and during hypoxia (low/zero bioirrigation) with measured winter concentrations from Boknis Eck (blue symbols). Lower right-hand panels: solute fluxes across the sediment–water interface ( $mmol\ m^{-2}\ d^{-1}$ ) by molecular diffusion and bioirrigation (negative values represent fluxes from the water column to the sediment). Figure modified from Dale et al. (2013).

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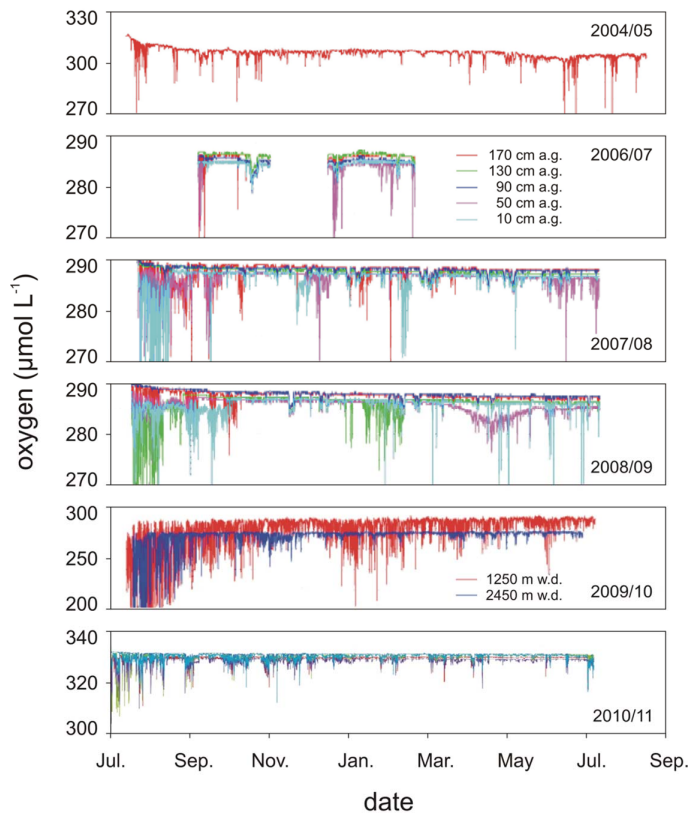
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**Fig. 26.** Oxygen time-series records obtained using optical oxygen sensors (“optodes”; types 3830 and 4330, AADI, Bergen, Norway) from single-sensor and multi-sensor instruments deployed at the HAUSGARTEN observatory between July 2004 and July 2011 (a.g.: height of sensors above ground; w.d.: station water depth).

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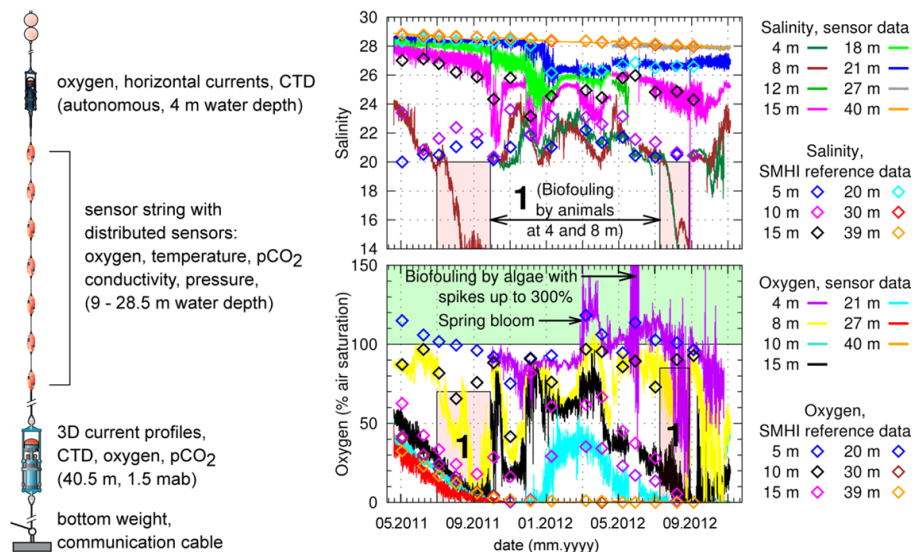
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**Fig. 27.** Left-hand panel: schematic diagram of the cabled observatory at Koljoe Fjord. More than 30 sensors for measuring temperature, salinity, water level, turbidity, oxygen, and currents, including 3-D current profiles and backscatter from particles in the water column, are connected to data loggers (Seaguard and RDCP, AADI, Bergen, Norway). An offline self-logging shallow system (not shown) used for monitoring conductivity, temperature, and oxygen at 4 m depth was updated with sensors for pH, CO<sub>2</sub>, DOM, Chl *a* fluorescence, and horizontal current in October 2012. Right-hand panel: salinity and oxygen time-series (measurement interval = 0.5 h), and SMHI monthly reference data. The strongest biofouling occurred during the summer months on sensors deployed at depths of 4 and 8 m in warm oxygenated surface water (colonization by sessile fauna, mostly tunicates and mussels). Biofouling resulted in much lower readings for salinity and oxygen as compared to the reference data, until the observatory had been recovered and cleaned. Gaps in the data are a result of down-time because of instrument repair. More detailed information is available at <http://mkononets.dyndns-home.com:8080/>.

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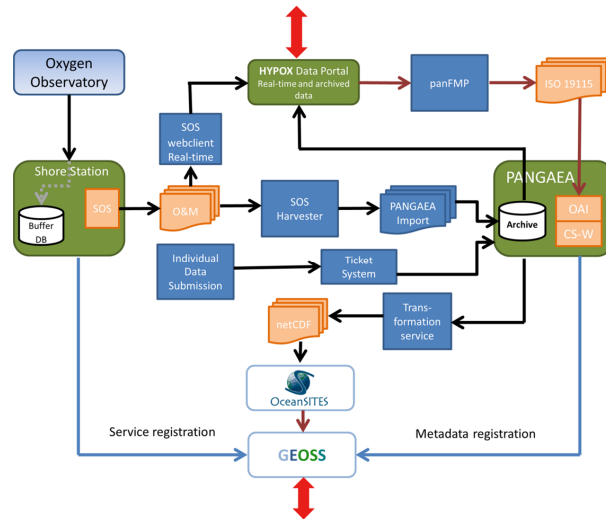
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**Fig. 28.** Integration of the data flow from HYPOX sites to the central data archive Pangaea, and the link to other programs. The green boxes represent data buffers and permanent data archives, the blue boxes indicate processes involved in data flow and data transformation, and the reddish boxes represent to the standards involved. Black arrows signify the flow of data and metadata from the cabled observatories in Koljoe Fjord and Loch Etive as well as from individual data sets submitted by HYPOX members. The HYPOX data portal is linked directly to the data archive and additionally receives data from the observatories in near real-time to allow immediate access to the most recent measurements. After transformation to netCDF format, the data are supplied via OceanSITES to GEOSS. The blue arrows represent additional services supplied to GEOSS by HYPOX, namely the provision of metadata and a georeferenced news feed, as well as the direct provision of data from cabled observatories. Interactive user access to data and metadata is possible via GEOSS and the HYPOX portal (red arrows), as well as through additional distributed web portals serving the specific needs of experts. See text for details and an explanation of the abbreviations used.

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