Modeling Bottom Boundary Layer biogeochemistry changes forced by episodic anoxia

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Interaction between the seawater and the sediments plays an important role in the global biogeochemical cycling. The benthic fluxes of chemical elements affect directly the acidification characteristics (i.e. pH and carbonate saturation) and also determine the functionality of the benthic and pelagic ecosystems. In many regions redox state of the near bottom layer can oscillate in connection with supply of organic matter (OM), physical regime and coastal discharge influence. Climate Change affects oxygen depletion and leads to spreading of the bottom areas with permanent or temporal hypoxic and anoxic conditions. The goal of this work was to elaborate a model capable to describe the basic biogeochemical processes occurring at the sediment-water interface and apply it for analysis of changes occurring due to seasonal oscillations of redox conditions.

We use a 1-dimensional C-N-P-Si-O-S-Mn-Fe vertical transport-reaction Bottom RedOx Model (BROM) describing both the sediments and bottom boundary layers (BBL) coupled with biogeochemical block simulating changeable redox conditions, and the carbonate system processes block (Yakushev, Protsenko, 2014, submitted). In BROM we parameterize OM formation and decay, reduction and oxidation of species of nitrogen, sulfur, manganese, iron, and the transformation of phosphorus, silicate and carbon species. BROM includes a simplified ecological model with phytoplankton, heterotrophic organisms, aerobic autotrophic and heterotrophic bacteria, anaerobic autotrophic and heterotrophic bacteria as it was described in (Yakushev et al., 2007). Carbonate system equilibration is modeled using standard approaches, the components of total alkalinity significant in suboxic and anoxic conditions (i.e. forms of S, N, Mn, Fe) were taken into account. The model's domain includes the water column, the BBL and the upper layer of the sediments. To parameterize the water column turbulence we used results of simulation of turbulent mixing performed with GOTM (Bolding et al., 2001). In the limits of the BBL mixing was assumed to be constant. In the sediments molecular diffusion and bioirrigation/bioturbation were parameterized.

The model simulated basic features of the seasonality ecosystem functioning, i.e. growth of concentrations of phototrophic organisms in summer, production of excessive OM and summer development of heterotrophic organisms and heterotrophic bacteria. Hydrophysical block of the model reproduces intensive vertical mixing in winter and formation of a pycnocline in summer. The model shows a possibility of periodic replacement of oxic conditions with anoxic, that leads to changes in the distributions of the parameters and their fluxes. The seasonality in production and destruction of OM together with the mixing seasonality lead to a vertical displacement of the oxic/anoxic interface from the sediments in winter to the water in summer. This affects distribution of sulfur species, nutrients (N and P), redox metals (Mn and Fe) and carbonate system parameters. Bacteria play a significant role in the fate of OM due to chemosynthesis (autotrophs) and consumption of DOM (heterotrophs). Model can be used for analyzing and interpreting data on sediment-water exchange and estimating consequences of forcing (i.e. connected with eutophication, climate change, CCS leakages) as well as for boundary conditions parameterization for 3D models.

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Exploring a microbial ecosystem approach to modeling marine oxygen minimum zone biogeochemistry

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Though microbial respiration of organic matter in the deep ocean governs the biogeochemistry of low oxygen marine environments, it is not represented mechanistically in current global biogeochemical models. We seek approaches that are feasible for a global resolution, with the end goal of resolving the feedbacks between marine oxygen minimum zones and climate. We use a framework that represents microbial physiology as redox reactions from which microbial community structure emerges, based on the availability of the electron acceptor that maximizes fitness. The prototype model resolves the two dominant respiratory pathways in marine oxygen minimum zones- reduction of oxygen and nitrate- and associated microbial functional types. We use this biological model in combination with a two-dimensional ocean model to explore the organization, biogeochemistry, and ecology of oxygen minimum zones. Intensified upwelling and lateral transport conspire to produce an oxygen minimum at mid-depth, populated by the anaerobic denitrifiers. We will discuss how the extent of the oxygen minimum region is regulated by circulation and the feedbacks with microbial ecology.

Carbon isotopic compositions of particular matter in the hypoxic water in the East China Sea

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Particulate Organic Carbon (POC) and its stable carbon ($\delta^{13}C_{POC}$) isotopic ratio were determined for the samples collected from the Changjiang River and ECS during summer period in 2009. The $\delta^{13}C_{POC}$ values showed rather normal range from -25.9 ‰ to -18.5 ‰, with an average of -24.4 ‰. In combination with the horizontal gradient of seawater density, Suspended Particulate Matter (SPM), Chl-*a* and $\delta^{13}C_{POC}$ ratios indicated that the terrigenous material was dominated in the Changjiang River and its inner estuary, while plankton produced POC was the main source of organic matter in above or within the hypoxic water, suggesting that algal bloom is the main reason for the hypoxia water formation. It is noteworthy that a negative correlation between $\delta^{13}C_{POC}$ and the dissolved CO_2 concentration in surface waters from eastern area of salinity front was observed, which suggested the compound-specific carbon isotopic composition of sedimentary organic matter maybe a good proxy to reconstruct the paleo-pCO_2. However, this phenomenon reminds us more carefully to apply two-end member of $\delta^{13}C_{POC}$ value to calculating organic matter sources in the marginal sea.

Advances in hypoxic extent estimation through geostatistical modeling

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Hypoxia has been observed in many freshwater and coastal ecosystems globally over the last few decades. Robust estimates of its spatial extent are important for assessing its ecological impacts and guiding management decisions. Using in situ dissolved oxygen measurements, we have developed rigorous geostatistical approaches (i.e., geostatistical regression and conditional realizations) to produce accurate estimates of the two- or three-dimensional hypoxic region spatial extent and associated uncertainties in Lake Erie [Zhou et al., 2013], Chesapeake Bay [Zhou et al., 2014], and the Northern Gulf of Mexico [Obenour et al., 2013] over the last two to three decades. The basic geostatistical approach, accounting for spatial correlation, considers the specific character of each system by incorporating ancillary information (i.e., trend variables such as temperature, depth, and spatial position) to improve estimation accuracy and reduce estimation uncertainty. The purpose of the work to be presented here is to intercompare the unique nature of each of these three systems. To achieve this goal, we identify differences in spatial variability (i.e., variance and correlation length) of dissolved oxygen concentrations across these systems. We also make a cross-system comparison of how hypoxia in each system is explained by commonly available types of ancillary information. The three systems have different sampling network with various densities, therefore, we further explore the effect of sampling density on estimation uncertainty.

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High-resolution nitrate profiles measured by in situ ultraviolet spectrophotometer (ISUS) in hypoxia Changjiang Estuary and its implications

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During summer and autumn 2011, high-resolution nitrate profiles as well as dissolved oxygen were measured along several transects in East China Sea, to study the biogeochemical processes of nitrate in hypoxia area off Changjiang Estuary. Comparison analysis showed that nitrate values measured by ISUS and Skalar were close at high salinity (S>30psu) in summer, while the mismatch were found in fresher water, which might attribute to the UV spectra absorption of CDOM that induced the true nitrate value overrate. In autumn, there was a good correlation between the ISUS and Skalar nitrate concentration and the standard deviation of difference between two measurements was 1.5 μM. Nitrate distribution indicated in summer, it was determined by the share of Changjiang diluted water and the nitrate regeneration below the thermocline which was related to oxygen depletion (AOU). Besides, there was significant nitrate loss in subsurface water in mid-shelf, which was attributing to the invasion of poor-nutrients water. While in autumn, vertical mixing and invasion of Kuroshio water were the dominant factor controlling the nitrate and salinity distribution, the signal of diluted water was disappear. The nitrate change indicated that nitrate stock in the ECS shelf was largely depends on the interannual variability of Kuroshio water.

Feedback mechanisms between cyanobacterial blooms, transient hypoxia and benthic phosphorus regeneration in shallow coastal environments

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In hypereutrophic shallow coastal areas there is a strong link between algal blooms, pelagic respiration, water anoxia and P regeneration during periods of calm weather conditions. The latter act as a trigger for critical cyanobacteria blooms in shallow systems. We studied seasonal pelagic and benthic production and respiration rates and benthic P regeneration at two sites representing transitional and limnic areas of the Curonian lagoon (Baltic Sea). In addition, we also studied the spatial coverage of chlorophyll a concentrations by remote sensing. Combining pelagic and benthic oxygen community metabolism, we have assessed the risk of anoxia for the two sites and extrapolated these calculations spatially to assess the risk at the whole lagoon level.

Our data demonstrate that cyanobacterial blooms strongly inhibit light penetration, resulting in net heterotrophic conditions in which pelagic oxygen demand exceeds benthic oxygen demand by an order of magnitude. The combination of bloom conditions and reduced vertical mixing during calm periods, resulted in oxygen depletion of bottom waters and greater sediment nutrient release. The peak of reactive P regeneration (nearly 0.7 mmol m-2 d-1) coincided with oxygen depletion in the water column, and resulted in a marked drop of the inorganic N:P ratio (from >40 to <5, as molar).

Our results suggest a strong link between cyanobacterial blooms, pelagic respiration, hypoxia and P regeneration, which acts as a feedback in sustaining algal blooms through internal nutrient cycling. Meteorological data and satellite-derived maps of chlorophyll a were used to show that nearly 70% of the lagoon surface (approximately 1000 km^2) is prone to transient (night-time) hypoxia development when blooms coincide with low wind speed conditions.

Hypoxia in Eastern Boundary Upwelling Systems under modern and future climate

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The highly productive Eastern Boundary Upwelling Systems (EBUS) such as the California Current system (California CS) and the Canary Current system (Canary CS) occasionally experience low dissolved oxygen (DO) conditions because of the upwelling of deep oxygen -depleted water to the surface in addition to intense microbial respiration in the subsurface and on the continental shelf. Yet, ocean warming in combination with increasing upper ocean stratification are likely to lead to large-scale ocean de-oxygenation that further exacerbates coastal hypoxia in these regions. Not only is low DO detrimental to several fish species and benthic fauna whose growth and reproduction can be impaired by prolonged exposure to hypoxic conditions, but it also has strong implications for several key biogeochemical cycles. Additional concomitant changes in upwelling intensity and biological productivity further affect the local DO levels, thus adding to the complexity of the future evolution of hypoxia in EBUS. Here I (1) review the current scientific knowledge on the key processes that drive naturally occurring coastal hypoxia in EBUS, (2) explore the contrasting sensitivities of different EBUS to future climate change, (3) discuss the potential future evolution of hypoxia in the California CS and the Canary CS over the 21st century on the basis of recent regional model simulations and (4) identify the main knowledge gaps. A particular attention will be paid to timescales of variability and when the oxygen conditions in these two upwelling systems may move outside of their present-day variability envelopes.

Foraminiferal survival and community response to 10 months of experimentally induced anoxia

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Anoxia was successfully induced in four benthic chambers installed at 24-m depth on the Northern Adriatic seafloor from 9 days to 10 months. To accurately determine whether benthic foraminifera can survive experimentally induced prolonged anoxia, the CellTracker Green method was applied and calcareous and agglutinated foraminifera were analyzed.

Numerous individuals were found living at all sampling times and at all sampling depths (to 5 cm), supported by a Ribosomal RNA analysis that revealed that certain benthic foraminifera were active after 10 months of anoxia. The results show that benthic foraminifera can survive up to 10 months of anoxia with co-occurring hydrogen sulphides. Although no significant change in Shannon diversity and evenness was observed, the composition of the foraminiferal assemblages changed with time. This change is due to interspecific differences in tolerance with respect to anoxia and free sulphides. *Reophax nanus*, *Textularia agglutinans* and *Quinqueloculina stelligera* all showed a significant decrease with time, strongly suggesting they are sensitive to anoxia and sulphides. Conversely, *Eggerella scabra*, *Bulimina marginata*, *Lagenammina atlantica*, *Hopkinsina pacifica* and *Bolivina pseudoplicata* appeared to be more resistant to the experimental conditions. *Quinqueloculina seminula* was apparently sensitive to anoxia but showed a clear standing stock increase during the first month of the experiment, which we interpret as an opportunistic response to increasing organic matter availability due to the degradation of dead macrofaunal organisms.

None of the anoxia-sensitive species is able to accumulate intracellular nitrates. Nitrate accumulation could be shown for some tested specimens of the dominant anoxia-tolerant species *E. scabra* and *B. marginata*. However, tests on the denitrification capacity of these taxa yielded negative results, suggesting that their resistance to long-term anoxia is not due to their ability to denitrify.

Effects of hypoxia on the fish and crustacean fauna in the Gironde Estuary (France)

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The Water Framework Directive (WFD) requires the improvement of water quality in the EU and the assessment of the transitional waters ecological status considering the fish component of the ecosystem. In the WFD, the dissolved oxygen (DO) is considered as one of the physico-chemical quality elements that support the biology and have to be monitored. Estuaries are particularly essential to fish as refuge area, habitats for reproduction, nursery grounds and migration routes but they are impacted by multiple anthropogenic disturbances. Hypoxic threshold is largely characterized by a DO content of 2 mg L-1 whereas the median lethal concentration is about 2.45 mg L-1 for aquatic organisms. Since 2005, this parameter is monitored in the Gironde Estuary thanks to the continuous monitoring MAGEST network that has recorded several summer borderline hypoxic situations (DO close to 2 mg L-1) and a 7 days-long hypoxic event (DO $<$ 2.45 mg L-1) in July 2006 with a minimum measured value of 1.22 mg L-1. Biological responses to hypoxia depend on the period, intensity and extent of these events. Shads, Alosa fallax and Alosa alosa, and some shrimp developmental stages, are among the most sensitive species to hypoxia in the Gironde Estuary. A behavioral study was performed on shad juvenile and allowed to establish the DO threshold that could impact their downstream migration occurring from July to early October. Water temperatures in summer 2006 are the highest recorded in the period 2005-2012 with values higher than 28°C. Almost 43% of conditions (DO thresholds at 20°C and 25°C) are critical to shad juveniles during their migration period in 2006. More than 940 hours reached critical values including 460 hours that would result in the death of individuals. Although the fish taxa appear to be more sensitive towards hypoxia, the crustacean taxa show also a strong sensitivity in the early ontogenic stage and on eggs-bearing females. Because shrimp is a major component of the estuarine food web, this taxon appears as a promising indicator of ecosystem dysfunction.

Phosphorus limitation reduces hypoxia in the northern Gulf of Mexico: results from a physical-biogeochemical model

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In the northern Gulf of Mexico, excess dissolved inorganic nitrogen and phosphorus loads from the Mississippi-Atchafalaya River system promote high primary production and contribute to the seasonal development of hypoxic bottom waters on the Louisiana Shelf. While phytoplankton growth is considered to be typically nitrogen-limited in marine waters, phosphorus limitation has been observed in this region during peak river discharge in spring and early summer. Here we present a synthesis of recent investigations that quantitatively assessed, using a realistic physical-biogeochemical model, the effect of phosphorus limitation on primary production and hypoxia development in the Mississippi-Atchafalaya River plume. Our model simulations indicate that phosphorus limitation delays and displaces westward a portion of river-stimulated primary production and depositional fluxes, resulting in a redistribution of respiration processes toward the western Louisiana Shelf. Despite this redistribution, phosphorus limitation did not promote a westward expansion or relocation of hypoxia, as some had previously speculated. Rather, the onset of hypoxia was delayed and the size of the hypoxic zone reduced. In other words, P limitation diluted the effects of eutrophication on the Louisiana shelf. Simulations with altered nutrient river loads show that despite phosphorus limitation, the co-reduction of nitrogen and phosphorus remains the best strategy to reduce hypoxia. Yet, a 50% reduction in both nutrients was not sufficient to meet the Gulf Hypoxia action plan goal of a $5 \cdot 10^3$ km^2 hypoxic area in our model simulations. This result emphasizes the need for a drastic co-reduction of N and P loads from the Mississippi-Atchafalaya River system to significantly reduce hypoxia in this region.

Data mining and knowledge discovery based on dissolved oxygen concentrations recorded continuously: the Zenne river case study in Central Belgium

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The Zenne river in Belgium is a low discharge urban river (10 m³/s in average) crossing the city of Brussels over a distance of almost 20km with more than half of its Brussels reach culverted. Crossing Brussels, the river receives its main effluent discharge from the WWTP of Brussels North located just upstream of the outlet of the city border. The river is equipped with 3 YSI probes, one located upstream of Brussels city, the second at the outlet of the city and the third 8km downstream of the Brussels city border. They are measuring same diverse quality parameters such as dissolved oxygen (DO) and turbidity. All probes are providing continuous records with time frequencies equal to 2.5 minutes or 5 minutes. In this study, we will scrutinize all data together and interpret them in their spatial and temporal context in order to learn about the diversity of the dissolved oxygen processes and issues in such a particular urban river setting.

The analysis of DO long data series provided since 2011 downstream of Brussels city shows that the level of DO for that part of the river is dramatic for fish since DO concentrations daily average fall below 3 mg/L for 30.6% of the year in average (counted from 2011 to 2013). Most of the days where DO concentrations are so low are observed to occur in summer when temperatures of the river are sufficiently high (up to 17°C) and, in the same time, when the river discharge is low (3 folds the lowest river water level). Additionally, in spring and summer, photosynthesis is being limited in the Brussels river channel since it is culverted for the major part of the reach. All together, the warm conditions, the low discharge and the culverted configuration of the river lead, downstream of Brussels, to dramatic oxygen conditions for fish.

The major oxygen concentrations deteriorations occur during the crossing of the city. In average, we have evaluated that the diminishing of the DO concentration through the crossing of Brussels is 18% and can reach in summer the highest proportion of 65%. The effluents of the Brussels-North WWTP actually contribute to a significant increase of the oxygen level downstream of Brussels. From our hydrological analysis, it can be deduced that the Brussels discharges represent in average 50% of the river discharge flowing out of Brussels and that the oxygen concentration of the Brussels-North WWTP effluent is in average 7.6mg/L. Such oxygenated effluent discharges contribute to an average recovery of 60% of the Brussels impaired oxygen level and can reach in summer 200%.

Oxygen data monitored since 2011 downstream of Brussels also allow us to identify the main sources of intermittent oxygen depletion in the river. First of them are the combined sewer overflows (CSO) occurring regularly in the northern part of the urban agglomeration [*Le et al. 2013*]. Analyzing the oxygen data series reveals also non negligible pollution discharges (22 events on the year 2012) from urban effluent attributed to the WWTP of Brussels South. The pollution induced is most probably due to releases of poorly settled activated sludge flocs. Less frequent but also noticeable, quality and hydrometric parameters monitored upstream of the Brussels area show that oxygen depletion can be induced by the transfer of an upstream floodwave associated with fine-grained organic matter responsible of a river deposit-resuspension process affecting the river oxygen.

Continuous monitoring of oxygen can also lead to the evaluation of rate processes occurring in the river. By applying the Odum method on daily oxygen cycles monitored upstream of Brussels, the atmospheric reaeration coefficient and the respiration rate (as active in the hydro-system) can be deduced and are shown to be respectively $10 d^{-1}$ and $2.4 mgO_2/L.h$ in average in summer. Such knowledge is particularly valuable for the river quality modeling efforts.

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Time Series and Box Model Simulation of Nitrous Oxide (N_2O) and Methane (CH_4) at the Time Series Station Boknis Eck, SW Baltic Sea

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The southwestern Baltic Sea is subjected to extensive oxygen depletion, with major implications for biogeochemical cycling. The trend of further oxygen depletion in the bottom waters of the SW Baltic Sea is assumed to continue in the future due to the on-going temperature increase. The decreasing oxygen content in the bottom water may alter the emissions of climate relevant trace gases such as nitrous oxide (N_2O) and methane (CH_4), as oxygen significantly influences the production and consumption pathways of both gases. At the time series station Boknis Eck, which is located at the entrance of Eckernförde Bay (SW Baltic Sea), nitrous oxide and methane have been measured monthly since 2005 and 2006, respectively. In order to improve the understanding of relevant source and sink processes of these two gases in the southwestern Baltic Sea, a simple box model was developed for the Boknis Eck Time Series site. The time series of nitrous oxide and methane are presented together with the box model simulation of their concentrations in the mixed layer during the period 2005/2006-2012. Processes such as emission to the atmosphere, upward mixing and enhanced production after phytoplankton blooms are included in the model, based on the time series of temperature, salinity, and chlorophyll at Boknis Eck. Although uncertainties remain, the model approach enables a first quantitative estimation of the relevant source and sink processes for nitrous oxide and methane in a coastal environment with pronounced seasonal suboxia/anoxia such as found at Boknis Eck.

New monitoring method for persistent study of low oxygen zones in marine systems.

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Most countries with important ocean assets have significant interest in protecting and assuring the health of its various aquatic systems. While no one disputes the value of such attention, efficiently monitoring and understanding the evolution of these aquatic systems bring many challenges to countries and local communities alike.

This presentation will describe how autonomous sea-going robots can play an important role in monitoring aquatic ecosystems in coastal areas and off-shore regions of the World Ocean and provide the critical data that is needed for modelers, manager and decision makers. The Wave Glider, developed by Liquid Robotics, is an innovative wave propelled green technology that uniquely provides persistent monitoring in remote and vast spreads of ocean and water bodies. With its recently developed profiling capability, it provides a unique ability to bridge the sea-air interface and sample the water column from regions in the open ocean all the way back to shore where it can be used for sound analysis, management and decision making.

The Surface Profiler developed is a buoyancy controlled module capable of oscillating between the surface and depth of up to 40m. It can host large sensors and provides continuous power and communication, offering a sensor payload that can easily be configured and operate in shallow waters.

Moreover, this innovative autonomous platform can be deployed as single or small number of units where resources are scares, but can also easily be scaled up to fleet and networks of inter-connected assets for regional governance.

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Hypoxia as One of Multiple Stressors Influencing Benthic Community and Trophic Structure Across OMZ Margins

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Natural gradients offer one vehicle for understanding ecological consequences of changing ocean climates; often patterns across spatial gradients can help predict future trends in time. We use benthic data from cross-margin oxygen minimum zone (OMZ) transects to provide insight into the influence of low oxygen, high CO2, and temperature on sediment biota. Using benthic macrofaunal and environmental data from stations in the E. Pacific and Indian Oceans we apply regression partitioning methods to examine hydrographic effects associated with the OMZ on infaunal density and diversity. Random forest analysis of macrofauna from 24 benthic stations indicates that variation in animal diversity (H'), evenness (J') and density are best explained by temperature, with thresholds at 8-9oC; pO2 is of nearly equal importance for diversity and of secondary importance for evenness and density, with pCO2 relatively unimportant in these settings.

To test the hypotheses that hypoxia alters deep-sea macrofaunal trophic structure and trophic diversity within the OMZ, we assembled cross-margin feeding mode and stable isotope data for macrobenthos tissues (δ13C, δ15N). Community -level metrics that use isotope space as a proxy for trophic niche were generated to allow exploration of within- and between- species variation in use of food sources as a function of oxygenation. Measurements include total isotope space (SEA, SEAc, Convex Hull Area), food source diversity (δ13C range), trophic levels (δ15N range), species packing and functional redundancy (distance to centroid, distance to nearest neighbor, SEA overlap). Hypoxia, CO2 and T effects on trophic structure are predicted to be unimodal, with greatest trophic diversity (encompassing chemo-and photosynthetic food sources) at intermediate stress levels. To understand functional implications we compare trophic diversity with taxonomic diversity among and within margin systems. Further development of these approaches should allow their use for assessment of anthropogenic disturbance and climate-induced stress in the deep sea.

Impacts of Interannual Climate Variability and Extreme Weather Events on Plankton Productivity and Hypoxia in Chesapeake Bay

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Estuaries around the world have suffered from hypoxia, harmful algal blooms, and altered ecosystem productivity. These problems have primarily been attributed to anthropogenic nutrient enrichment, i.e., eutrophication. However, there is increasing evidence that climate variability has overwhelmed eutrophication in coastal ecosystems over the past 2 decades, particularly in developed countries. There is also evidence that extreme weather events can cause dramatic disruptions with long-term impacts. Using Chesapeake Bay as an example, I will describe recent modeling studies that are directed at understanding how interannual climate variability and storms affect plankton productivity and hypoxia. I will use a coupled hydrodynamic-biogeochemical model to diagnose physical and biogeochemical mechanisms driving interannual variability of plankton productivity and hypoxia in the estuary. Analysis of bottom water dissolved oxygen budget will be conducted to identify key physical and biogeochemical processes that regulate the interannual variations of hypoxic volume. For extreme weather, I describe research on two events: a windy storm (Hurricane Isabel) that caused destratification and restratification of the water column, leading to a fall phytoplankton bloom of unprecedented magnitude and the temporary relief of hypoxia; a wet storm (Tropical Storm Lee) that generated a large flood and extensive sediment plume with long-term implications for water quality and geology. These case studies demonstrate that changing climate and extreme weather events have become predominant drivers in the estuaries, requiring an increased focus in oceanographic research.

Nitric Oxide in the Oxygen Minimum Zone off Peru

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Nitric oxide (NO) is a short-lived intermediate in several processes of the oceanic nitrogen cycle, whereby denitrification is assumed to be the major pathway for NO in the ocean. Therefore, measurements of dissolved nitric oxide could be used to identify hot-spots of ongoing denitrification. Despite the fact that until today many laboratory studies about the role of nitric oxide in the nitrogen cycle have been performed, only a few depth profiles of dissolved nitric oxide from oceanic regions such as the eastern tropical North Pacific are available. One reason for this is the demanding analytical instrumentation necessary to detect the reactive and thus short-lived NO in seawater samples. To this end we set up a measurement system for dissolved NO which consists of a chemiluminescence analyzer connected with a stripping unit for discrete seawater samples. The first field test of this set up took place during a cruise near the coast of Peru in February 2013 (SFB 754 cruise M93). NO was measured at 40 stations in the oxygen minimum zone (OMZ) along 7 transects toward the coast. We found an accumulation of nitric oxide in oxygen depleted waters with the highest concentrations on the shelf and a decrease of nitric oxide concentrations towards the open ocean suggesting that denitrification rates on the shelf were higher than in the OMZ of the open ocean.

Relationships between water temperature, nutrients and dissolved oxygen in the northern Gulf of Aqaba, Red Sea

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Five years (1998, 2000–2003) of summer records of temperature, nutrients and dissolved oxygen concentrations in the upper 400 m of the water column of the northern Gulf of Aqaba were employed to produce a simple statistical model of the relationship between temperature versus nitrate, phosphate, silicate and dissolved oxygen concentrations. Temperature profiles in the upper 400 m during summer revealed a clear thermocline in the upper 200 m. This was reflected in nutrient and oxygen concentrations as nitrate, phosphate, and silicate increased from the surface to deep water while dissolved oxygen decreased. The best fit relationship between temperature versus nitrate and phosphate was inverse linear and the best fit correlation between temperature versus silicate and dissolved oxygen was fractional. The observed nutrient concentrations were shaped by a combination of the hydrodynamics and biological factors. Deep winter mixing and high nutrient concentrations dominate during winter. Shortly after the water stratifies in spring, the nutrients are drawn down by phytoplankton during the spring bloom and remain low throughout the rest of the year. The regression equations presented here will be useful in estimating nutrient concentrations from temperature records as long as the annual natural cycle is the main driver of nutrient concentrations and external inputs are insignificant. Deviations from these relationships in the future could provide insight into modifications in the nutrient concentrations probably resulting from new nutrient sources, such as anthropogenic inputs.

Hypoxia in macrophytodetritus accumulation: Species specific harpacticoid copepod adaptation?

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Mediterranean Posidonia oceanica seagrass meadows generate high primary production and support large biodiversity of associated fauna and flora. The majority of the foliar material falls on the unvegetated sea floor during the autumnal leaf senescence, fuelling the detrital food web. Whilst laying on the sea floor the freshly formed macrophytodetritus pile up into accumulations according to the local hydrodynamics and seafloor geomorphology.

In these litter accumulations, harpacticoid copepods (Crustacea, Copepoda) are the main meiofaunal players (metazoans in the size range of 38μm – 1mm) and show a high specific diversity. They are primarily grazers, but their high specific diversity suggests that they occupy also a large variety of trophic niches. This large morphological and trophic diversity can partly be promoted by the complexity of the phytodetritus in seagrass accumulations.

On the other hand, macrophytodetritus degradation and flux of reduced compounds from the sediments is responsible for oxygen consumption inside the accumulation of seagrass litter. Therefore, concentration of oxygen inside the accumulation is very variable and often under the concentration observed in the water column just above the litter. Frequently, oxygen levels reach very low values. The present study aims to link the oxygen variability inside the accumulation to the densities of the five most dominant harpacticoid copepods found living in the P. oceanica litter. Standardized samples were collected seasonally in two contrasting sites of the Calvi Bay (Corsica) during one year.

Our results showed no correlation between the oxygen concentrations and harpacticoid community diversity or their total abundances. The five most dominant species showed divergent results, but none had a clear correlation with the oxygen concentration. This contrasts with observation done for sediment meiofaunal community where most harpacticoid copepods are sensitive to oxygen level and where nematodes often dominate the community. This could be explained by their high mobility and the patchiness and variability of the oxygen concentrations present in the accumulations. Harpacticoid copepods, whilst being sensitive to hypoxia and anoxia developed a strategy to live in this fast oxygen changing environment.

To conclude, our results underline the importance of species-specific analysis of correlation data. Especially in complex and dynamic environments where a variety of potential trophic niches are present and species competition is very likely to occur. The overall abundance pattern and diversity of the copepod community showed no relation to the oxygen concentration while the most abundant copepod species did not responded to fluctuating oxygen concentrations.

Benthic diversity and consequences of hypoxia – introduction of alien polychaetes to the eastern Gulf of Finland enhances the resistance of ecosystem

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At the turn of the 21 century oxygen conditions were the main factor governed the ecosystem development in the eastern Gulf of Finland. The periodical hypoxic events in the sub-thermocline waters resulted in almost complete disappearance of bottom animals in the deep open areas. The decline of benthic biomass was one of the main reasons of fish resources decrease. Hypoxia leaded to phosphate release from bottom sediments stimulating cyanobacteria blooms and eutrophication. In 2008 the species-poor native benthic community was enriched with introduction of hypoxic-tolerant arctic polychaete Marenzelleria arctia. By 2009 this species became the dominant component of the soft-bottom macrozoobenthos. Polychaetes invasion caused the radical changes in the bottom communities, as well as, on the ecosystem level resulting in mitigation of ecological consequences of hypoxia despite of the extremely severe oxygen depletion recorded in 2010. Introduction of M. arctia radically accelerated the recovery successional processes after hypoxic events because it has planktonic larvae and is able to colonize quickly vacant bottoms. The biomass of macrozoobenthos increased drastically owing to mass development of M. arctia. This increase was especially evident in hypoxic areas which were inhabited practically by monoculture of this species. The invasion leaded to appearance of new functional group in benthic communities. These polychaetes dig the bottom deeper than native inhabitants of the Baltic Sea, essentially affecting the exchange processes at the water – bottom interface. Bioturbation and bioirrigation activity of M. arctia promotes oxygen penetration into sediments and formation of powerful oxidized layer, increasing the phosphorus retention in bottom sediments. As consequence of this, nitrogen/phosphorus ratio in water column enhanced and biomass of nitrogen-fixing colonial cyanobacteria declined drastically. Thus addition of new species as a result of biological invasion compensates for negative effects of hypoxia and leads to formation of new more resistant system.

Development of redox proxies based on benthic foraminifera and its application on the sediment record of upwelling regions: a SIMS and FT-ICP-OES approach

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Here we present a dataset of Mn/Ca, Fe/Ca, Cu/Ca, Mo/Ca and Mg/Ca measured on tests of the benthic foraminiferal species Eubuliminella exilis from the subtropical NE Atlantic, determined by secondary ion mass spectrometry (SIMS) and flow-through inductively coupled plasma atomic emission spectroscopy (FT-ICP-OES). The aim is to gain insight into the proxy potential of these elemental ratios in order to reconstruct redox conditions of the sea floor environment over time. The study area, site GeoB 7926 is located within the upwelling system off the coast of Mauritania, NW Africa. Previous studies from site GeoB 7926 demonstrate an indication of low oxygen conditions in the benthic environment during Heinrich Event 1 (18 – 15.5 ka BP) and the Younger Dryas (13.5 – 11.5 ka BP) (Filipsson et al. 2011; McKay et al. submitted) during times of high phyto-detritus input (Romero et al. 2008). These findings were derived from foraminiferal faunal evidence, whereby the low oxygen tolerant species E. exilis was dominant within the assemblage. Additionally, Mn/Al from bulk measurements correspond well (Gallego-Torres, in press) with the dominance of E. exilis. By analysing the trace elemental ratios in this particular species, we aim to develop a proxy of former oxygen conditions in the benthic environment, beneath a present-day intense coastal upwelling system. This method could assist in comparing the extent of anoxia of different localities and back in time; in this case, ca. 23 ka BP to the present. Furthermore, we aim to investigate whether changing redox conditions are recorded within foraminiferal tests during growth. New understanding of intra-test and temporal variability of redox sensitive elemental composition of foraminifera could serve as an analogue for impending climate and environmental change since hypoxic and anoxic coastal environments pose a threat to biota.

Modeling hypoxia in past and future climates of the Baltic Sea

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Using an ensemble of coupled physical-biogeochemical models driven with regionalized data from global climate simulations we are able to quantify the influence of changing climate upon oxygen conditions in one of the numerous coastal seas (the Baltic Sea) that suffers worldwide from eutrophication and from expanding hypoxic zones. The projected changes in future climate were compared with the variations in past climate to address the question how unique future environmental conditions may look like. For the past period 1850–2006, atmospheric, hydrological and nutrient drivers were reconstructed, based on historical measurements. For the future period 2007–2098, scenario simulations were driven by regional climate model data and forced by various future greenhouse gas emission and air- and riverborne nutrient load scenarios (ranging from a pessimistic 'business-as-usual' to the most optimistic case). We show that under the impact of warming climate hypoxic and anoxic areas will very likely increase or at best only slightly decrease (in case of optimistic nutrient load reductions) compared to present conditions, regardless of the used global model and climate scenario. The projected decreased oxygen concentrations are caused by (1) enlarged nutrient loads due to increased runoff, (2) reduced oxygen flux from the atmosphere to the ocean due to increased temperature, and (3) intensified internal nutrient cycling. In future climate a similar expansion of hypoxia as projected for the Baltic Sea can be expected also for other coastal oceans worldwide. Despite considerable shortcomings of state-of-the-art models, this study suggests that the future Baltic Sea ecosystem may unprecedentedly change compared to the past 150 yr. Further, we argue that a multi-model ensemble approach is mandatory to estimate uncertainties in projected hypoxia.

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Artificially induced migration of redox layers in Adriatic sediment: fate of some trace metals

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Long term experimental studies suggests that, under anoxic transient conditions, redox fronts within the sediment shift upwards causing sequencial rise and fall of benthic fluxes of reduced species (Mn(II), Fe(II) than S(-II)) [Balzer, 1982; Kristiansen et al., 2002]. In order to better understand such processes and their consequence to infaunal communities and trace metal recycling, benthic chambers were deployed on the seafloor of the Northern Adriatic and sampled after 9, 30 and 315 days of incubation. High resolution porewater profiles were sampled by DET probes and redox sensitive species were analysed (Alkalinity, Sulfate, Manganese, Iron, Arsenic, Antimony, Uranium, Molybdenum).

Results show that anoxia was reached after 7 days. Mn and Fe started diffusing towards the water column giving a rusty color to the seafloor. Infaunal species appeared at the surface. After 20 days (fig. 1), all macro-organisms were dead. Porewater chemistry showed expected redox shifts. However, bottom water chemistry followed a peculiar evolution: after 1 month, sulfide had a higher concentration in the overlying water than in the porewater leading to a diffusional flux into the sediment. The source of sulfide was attributed to the decomposition of dead macroorganisms laying on the seafloor. Our results suggest that the sulfide rise in the water column in coastal waters is strongly controlled by the biomass of benthic macrofauna and can be decoupled from sedimentary geochemical processes.

In this context trace metals showed different behaviors. For example Arsenic seems to be strongly correlated to Iron release into porewaters and overlying water while Antimony is released deeper down within the sediment and never crosses the sediment water interface.

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A novel way of life emerges from hypoxic sediments: microbial sulphur oxidation via long-distance electron transport

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Recently, an entirely novel type of microbial metabolism has been described from marine sediments, whereby filamentous bacteria are transporting electrons over centimeter-scale distances [Nielsen et al., 2010]. By establishing such electrical circuitry, these micro-organisms are able to exploit spatially segregated pools of electron acceptors and donors, equipping them with a competitive advantage. First observed in laboratory experiments, we show that this novel electrogenic form of sulfide oxidation also occurs naturally in the seafloor. We observed the geochemical fingerprint of electrogenic sulphide oxidation at three coastal sites in the North Sea area: a subtidal mud deposit, a salt marsh site and seasonal hypoxic basin. A detailed study at the seasonal hypoxic site (Marine Lake Grevelingen, The Netherlands) reveals that electrogenic sulphide oxidation strongly dominates the sediment geochemistry during winter months. In particular, the process ensures a deep oxidation of sulphide, which prevents the ventilation of free sulphide to the overlying water column during the anoxic summer months. In addition, the rapid development of the electrical biofilm in late autumn, engenders a rapid "detoxification" of the surface sediment, thus potentially promoting recolonization by infauna. Overall, our field observations suggest that electrogenic sulphide oxidation can strongly affect the water quality, biogeochemical cycling and ecosystem functioning in coastal systems with seasonal hypoxia.

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High-resolution modeling of the Eastern Tropical Pacific Oxygen Minimum Zone: Sensitivity to the tropical oceanic circulation

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The connection between the equatorial mean circulation and the oxygen minimum zone (OMZ) in the Eastern Tropical Pacific is investigated through sensitivity experiments with a high-resolution coupled physical-biogeochemical model. The model is first validated with observations to assess its performance in simulating a realistic vertical and horizontal oxygen distribution. Two sets of climatological open boundary conditions (OBCs, for the physical variables) which differ slightly on the intensity and vertical structure of the Equatorial Current System (ECS) are shown to lead to contrasted characteristics of the simulated OMZ by the regional model. Through a Lagrangian approach, the oxygen transport between the ECS and Peru-Chile Undercurrent is also evaluated, focussing on the main branches connecting both current systems. The experiments allow to demonstrate that the secondary Tsuchiya jet (secondary Southern Subsurface Countercurrent) is a key feature of the sensitivity of the OMZ to the equatorial circulation. We then study the differences in OMZ dynamics due to the different background conditions (both O2 concentration and mean circulation) between both simulations, based on an explicit O2 budget. The main results show that there is a significantly different balance between physical and biogeochemical processes within the energetic coastal current system between both simulations, illustrating the large sensitivity of the OMZ dynamics to the open boundary conditions.

Biogeochemistry of a large, meromictic tropical lake (Lake Kivu, East Africa): insights from a stable isotope study covering an annual cycle

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Lake Kivu (East Africa) is a large (2370 km^2) and deep (maximum depth of 485 m) meromictic lake. Its vertical structure consists of an oxic and nutrient-poor mixed layer down to 70 m maximum, and a permanently anoxic monimolimnion rich in dissolved gases (methane and carbon dioxide) and nutrients. Seasonal variation of the vertical position of the oxic-anoxic interface is driven by contrasting air humidity and wind speed regimes between rainy (October-May) and dry (June-September) seasons. The latter is characterized by a deepening of the oxic zone, and an increased input of dissolved gases and inorganic nutrients. The mean annual photic depth is 18 m, but water transparency slightly decreases during the dry season. In this study, we present a comprehensive data set covering a full annual cycle at a fortnightly resolution, which combine hydrochemical data, δ^{13}C and δ^{15}N measurements of particulate organic carbon and nitrogen (POC, PN) and zooplankton, δ^{13}C of dissolved organic and inorganic carbon (DOC, DIC), nutrients and gases (CH_4) concentrations, phytoplankton biomass and composition. In the euphotic zone, phytoplankton biomass was constant during the rainy season, but doubled during the dry season. In contrast, δ^{13}C-DIC increased linearly with time during the rainy season, deviating from the values expected at isotopic equilibrium with the atmosphere, then suddenly decreased in the dry season due to the vertical mixing with ^{13}C-depleted DIC. Results of mass-balance calculations indicate that the δ^{13}C-DIC increase reflects the net autotrophic status of the mixed layer. Irrespective of the season, the δ^{13}C-POC signatures were constant from the surface to the oxic-anoxic interface, then showed a local and abrupt excursion to values as low as -40 per mil, reflecting the incorporation of a ^{13}C-depleted source in the POC. While the large pool of DIC is the main carbon source for POC in surface waters, CH_4 contributes significantly to C fixation at the oxic-anoxic interface all year round. The δ^{13}C signature of the DOC pool shows very little variation in the mixolimnion and thus appears to be uncoupled from the POC pool, suggesting that old and refractory compounds constitute the major part of the DOC pool. Also the more labile and freshly produced DOC that reflects the δ^{13}C signature of the POC, is rapidly mineralized. Finally, we noticed a shift toward higher values in the δ^{15}N-PN during the dry season (from 0.5 per mil to 4.0 per mil) and δ^{15}N-PN was significantly related to the proportion of cyanobacteria in the euphotic zone. Hence the variation of δ^{15}N-PN in surface waters could either reflects a change in the dominant phytoplankton taxa or in the biogeochemical processes controlling the upward nitrate and ammonium fluxes. Zooplankton δ^{15}N signatures mirrored the seasonal changes in δ^{15}N-PN and were significantly correlated to phytoplankton biomass, highlighting their dependence on autochtonous sources of organic matter in this large lake.

Methanotrophy and chemoautotrophy within the redox gradient of a large and deep tropical lake (Lake Kivu, East Africa)

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Lake Kivu (East Africa) is a large (2370 km^2) and deep (maximum depth of 485 m) meromictic lake. Its vertical structure consists of an oxic and nutrient-poor mixed layer down to 70 m maximum, and a permanently anoxic monimolimnion rich in dissolved gases (methane and carbon dioxide) and inorganic nutrients. Seasonal variation of the vertical position of the oxic-anoxic interface is driven by contrasting precipitation and wind speed regimes between rainy (October-May) and dry (June-September) season, the latter being characterized by a deepening of the oxic zone, and an increased input of dissolved gases and inorganic nutrients. Our work aimed at quantifying methanotrophic and chemoautotrophic production within the redox gradient of Lake Kivu and identifying the micro-organisms involved in these processes using phospholipid-derived fatty acid markers and their carbon stable isotope composition. Our approach combined both natural stable isotope abundance analysis and ^{13}C-labelling (^{13}C-DIC ; ^{13}C-CH_4) experiments. Sampling was carried out at two stations in Lake Kivu during rainy (February 2012) and dry (September 2012) season conditions. Methanotrophic bacterial production rates were highly variable (from 0.1 to 7.0 μmol C L^{-1} d^{-1}), but maximum values were always observed at the oxic-anoxic interface when the CH_4:O_2 ratio varied between 0.1 and 10, suggesting that the majority of methane was oxidized aerobically. Furthermore, strong stable isotope labelling of monounsaturated C16 fatty acids indicate that active methane oxidizers were related to the group of type I aerobic methanotrophs (gammaproteobacteria). Despite the dominance of aerobic methane oxidation, significant methanotrophic bacterial production rates were found below the oxic-anoxic interface during the rainy season, indicating that at least a fraction of the upcoming methane may be oxidized anaerobically. This observation was further confirmed by the strong labelling at these depths of the 10Me16:0 fatty acid, biomarker for sulphate-reducing bacteria, the syntrophic partners of anaerobic methane-oxidizing archaea. The methanotrophic bacterial growth efficiency (MBGE) was variable (2-50%), and inversely related to methane concentration. Maximum chemoautotrophic bacterial production rates were recorded well below the oxycline, in sulfidic waters. However, during the rainy season, significant dark C fixation rates were measured near the oxic-anoxic interface, in a nitracline where sulphide was absent, suggesting that another energy source was involved. Incorporation of labelled carbon in the 16:1ω9c ; 16:1ω7c and 18:1ω7 fatty acids suggest that the active chemoautotrophic organisms belong to the phylum proteobacteria. Together, the vertically integrated methanotrophic and chemoautotrophic production rates were 31 mmol m^{-2} d^{-1} and 41 $mmol^{-2}$ d^{-1} during the rainy and dry season, respectively. These values are comparable to the net phytoplanktonic production rates in Lake Kivu ranging between 12 and 160 mmol m^{-2} d^{-1} (on average 52 mmol m^{-2} d^{-1}). Our results indicate that methanotrophs and chemoautotrophs contribute substantially to the carbon cycle in Lake Kivu.

Biogeochemistry of a large, meromictic tropical lake (Lake Kivu, East Africa): insights from a stable isotope study covering an annual cycle

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Nitrogen Cycling under marine variable oxygen and sulfidic conditions: Lessons from the Black Sea

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The Black Sea offers an excellent site to study the full spectrum of nitrogen transformations under oxic to suboxic to anoxic conditions. The strongly stratified water column has an oxic surface layer and sulfidic deep water. At the boundary there is a zone called the "suboxic zone" with essentially no oxygen or sulfide. The origin of the suboxic zone may be due to ventilation of oxygen into the upper sulfidic layer by the Bosporus Plume. We have studied several nitrogen transformations using an interdisciplinary approach that includes geochemical studies of nitrogen species concentrations and stable isotopes and microbial studies of DNA and mRNA. Many of the lessons learned from the Black Sea are probably applicable to open ocean low oxygen zones.

In the surface layer nitrogen is fixed into organic matter and nitrogen fixation is a source of fixed nitrogen. We documented this using experimental rate measurements, DNA and mRNA (*nifH*). The rate however is highly variable. As a result the $\delta^{15}N$ of both suspended and sinking particulate organic matter are often depleted relative to the normal values for plankton.

In the suboxic zone bacteria that mediate both anammox and denitrification are present. We also detected activity of both anammox and denitrifying mRNA (Scalindua-type *nirS* and conventional *nirS*) transcripts but with different spatial and temporal distributions. Scalindua-type *nirS* showed little variation, with 4 highly similar groups detected for all seasons but only in the lower part of the suboxic zone. Expressed types of conventional *nirS* were more variable and had a wider depth range than anammox. The evidence from both $\delta^{15}N$ on N_2 and the molecular data suggests that anammox is always occurring but that denitrification varies from year to year. The anammox bacteria are free-living while the denitrifying bacteria are more associated with aggregates of organic matter. We hypothesize that the relative importance of anammox versus denitrification depends on the flux of particulate organic matter from the euphotic zone. Our data suggest that ammonium produced from remineralization may be oxidized to nitrite and then denitrified inside the particles.

We also have found that nitrogen fixation potential (DNA) and activity (RNA) are present in the suboxic and sulfidic zones. DNA sequences were detected throughout the suboxic zone but mRNA copies of *nifH* were only found in the lower suboxic zone. mRNA was never found in the upper suboxic zone. These results confirm the single rate measurement of N_2-fixation in the suboxic zone by McCarthy et al (2007) and by our group.

Time series observations in the seasonally anoxic Tillari Reservoir, India

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The Tillari Dam (15.758°N, 74.09°E) is located near the foothills of the Western Ghats in the Indian state of Maharashtra. Time series observations in the Tillari Reservoir, carried out since March 2010, reveal significant inter-annual variations in the pattern of seasonal stratification with a resultant impact on H2S and CH4 production. Stratification during summer (March–June) leads to oxygen depletion in the hypolimnion. Vertical mixing during the southwest monsoon (June–September), when the region is subjected to strong winds and intense rainfall, and lateral advection of oxygen-rich waters from the upper reaches of the reservoir, cause reoxygenation of the hypolimnion. The oxygen concentration falls again after the monsoon, but does not get fully exhausted before winter convection results in the development of well-oxygenated conditions throughout the water column. We observed maximum concentrations of H2S (9 μM) and CH4 (156 μM), which also coincided with maximum chlorophyll a (6 mg m-3), in the summer of 2010. Anoxia was least severe in 2011 (H2S 1.3 μM, CH4 28 μM). Iron and manganese accumulate at micromolar levels during periods of anoxia, and the presence of H2S at shallow depths supports anoxygenic photosynthesis as indicated by the bacteriochlorophyll e pigments (from brown sulphur bacteria). The large inter-annual variability in anoxia intensity, presumably caused by subtle changes in meteorological conditions, reflects the sensitivity of tropical reservoirs that serve as a significant source of CH4 to future changes in climate and eutrophication.

Seasonal Anoxia in Indian Reservoirs

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India consumes 17 Megatons (MT) of synthetic nitrogen fertilizers, out of which less than 1 MT reaches the sea, presumably because of losses/accumulation in the terrestrial systems. We have undertaken the first ever systematic study of Indian reservoirs with an aim to understand the fate of anthropogenic nitrogen. So far we have covered 14 reservoirs located in various geographical regions of the country, and in different seasons. The water column in almost all reservoirs gets stratified in summer. Six of the reservoirs (Tillari, Anjunem, Selaulim, Nagarjuna Sagar, Srisailam and Ukai) were found to experience anoxic (sulphidic) conditions. The highest H2S concentration (80 μM) was observed in the Srisailam Reservoir which coincided with a high CH4 concentration of 186 μM. Suboxia was observed in five reservoirs (Supa, Markandeya, Koyna, Idukki and Sardar Sarovar), where loss of fixed nitrogen occurred to varying degrees, but H2S was not detected. Three reservoirs (Bhakra-Nangal, Rihand and Tungabhadra) experienced well-oxygenated conditions even during summer. The epilimnion had generally low concentration of nitrate ($<$2 μM), except in the case of Markandeya where it was 10 μM, even exceeding 100 μM during the southwest monsoon. Accordingly, the chlorophyll a concentration was also generally not very high ($<$ 6 mg m-3), although in the case of Nagarjuna Sagar and Srisailam reservoirs it exceeded 20 mg m-3. Ammonium accumulation was observed in many reservoirs, especially those experiencing sulfate reduction (maximum concentration of 70 μM in Srisailam Reservoir). Nitrous oxide levels were generally quite moderate, with the exception of a few high values (maximum 354 nM in Koyna Reservoir in June 2013). High dissolved levels of redox-senstive metals Fe (121 μM in Selaulim) and Mn (83.4 μM also in Selaulim) were also observed in the reservoirs which experienced sulphate reduction. Our results suggest that tropical reservoirs contribute significantly to cycles of key biogenic elements.

Benthic foraminifera can calcify under anoxia: Experimental evidences on three species

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Oxygen depletion is one of the most severe environmental stressors in marine ecosystems. It is predicted to increase in near future [e.g. Sarmiento et al., 1998; Keeling & Garcia, 2002] due to climate change, changes in circulation and enhanced eutrophication. Therefore, there is an urgent need to study past variability of dissolved oxygen concentrations in benthic ecosystems in response to climate change. Benthic foraminifera are among the most ubiquitous marine calcifying micro-organisms and among the most common used proxy carriers, as their fossilizing calcareous test registers the geochemistry of seawater. The identification of the geochemical microenvironments where calcification takes place is of prime importance for the interpretation of the proxies based on the geochemical composition of the foraminiferal shells. In this study we performed laboratory experiments to investigate the possibility for foraminifera to calcify under different redox conditions in the sediment, from normoxic to anoxic microenvironments. Our results show that for all three investigated species, calcification was not only possible under oxic and hypoxic, but also under anoxic conditions. This result demonstrates ongoing metabolic processes, suggesting the possibility that anaerobic metabolic pathways can be activated, potentially other ones than the only anaerobic metabolic pathway known today for some foraminiferal species, i.e. denitrification [Risgaard-Petersen et al., 2006]. Our observations of calcification under anoxic conditions open new possibilities for paleoceanographic reconstructions of intermittent short-term anoxia. The analysis of whole single specimens or of their successive chambers may provide essential information about short-term environmental variability and/or the causes of anoxia.

Time-series observations for hypoxia adjacent to the Changjiang estuary during summer

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Time-series data at 30-min intervals of near bottom (about 0.5m above seabed) temperature, salinity, oxygen and turbidity were obtained from some sites to study hypoxia during summer adjacent to the Changjiang estuary in recent years.

The data obtained from B3/C2/C4 sites in 2009 reveal the occurrence of episodic subsurface hypoxic events, but no occurrence at D3 where the observing period was shorter(3rd June-31st July). The fluctuating modes of oxygen concentration are obvious different in different sites, and show some interesting results. The time of the initial hypoxic event appearing is delayed from north to south, which it was in the middle of July at B3 and at the beginning of August at C2 and at the end of August. The reason maybe contributed to the trend of the Changjiang river diluted water during the period of June through September which flow in northeast in the beginning.

To study the mechanism of variability of oxygen concentration, the correlation among bottom oxygen concentration, intensity of thermocline and sea surface wind were analyzed. There is notable negative correlation between oxygen concentration and intensity of thermocline. When the velocity of wind is greater than 8m/s, it would weaken the thermocline obviously. For further study, the biochemical process , horizontal transport and tide should be considered.

Global patterns of deoxygenation deduced from observations and CMIP5 models

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A new observational estimate of global patterns of dissolved oxygen changes during the 50-year period 1960 to 2010 is compared against output of various CMIP5 models. While all models agree relatively well with the observed mean decline of dissolved oxygen, none of the models investigated shows a significantly positive correlation of simulated deoxygenation patterns with observations. A detailed analysis investigates uncertainties in the mapping algorithm and separates deficiencies in modelled regional oxygen trends into physical and biological contributions. Key areas of model-data misfits in deoxygenation are identified and we put forward hypotheses regarding the processes misrepresented in the models.

The oxic-anoxic interface in the northeastern Black Sea during anomalously cold winter of 2011/2012.

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Since 2011, the moored profiler Aqualog [*Ostrovskii and Zatsepin*, 2011] carries out automatic measurements in the northeastern Black Sea, the world's largest marine anoxic basin. The profiler is moored near 44°29.4′N, 37°58.4′ E at the isobaths of 265-270 m off the Bay of Gelendzhik. The profiler is equipped with the Idronaut 316 CTD probe complete with sensors for dissolved oxygen, ORP, and pH, as well as with the Nortek Aquadopp acoustic Doppler current meter. The profiler makes repeated round trips along the moored cable between the depths of 15 m and 200 m several times per day. Thanks to the regular descents into the hydrogen sulfide zone, the profiler avoids bio-fouling.

During two deployments in June - August 2011 and November 2011 - April 2012, the Aqualog profiler delivered the long-term time series of the multiparameter fine structure vertical profiles of the key characteristics of the sea oxic-anoxic interface. The data allowed us to study the temporal variability of the oxycline in relation to the horizontal advection and the thermohaline stratification. The Idronaut Redox Sensor data clearly showed that the boundary Eh = 0 coincides with the isopycnic surface of 16,1 kg/cubic meter. The temporal variations of these surfaces were coherent through the survey. The position of the oxic-anoxic boundary undergone huge variations, its depth fluctuated up to 40 m in amplitude caused by the short period daily time scale movements of the Black Sea Rim Current.

Interesting data were obtained about ventilation of the Black Sea at the second half of the winter 2011/2012. The sea cooling was due to the anomalously cold wind outbreaks and the penetration of the cold water from the north. The observations indicated the cooling of the Cold Intermediate Layer from about 8.4 degree C at the beginning of the winter to the values of about 6.5 degree C by mid April, which were lowest in recent years. The temperature of Cold Intermediate Layer dropped to 6.53 degree C at the depth of 87 m on April 14, 2012.

The significant correlation was found between the time series of the depth of the suboxic layer and the average acoustic backscatter amplitude at the depths of 70 to 170 m. The ensembles of the time series of these parameters from the beginning of November 2011 till the end of January 2012 were correlated as much as 0.69 ± 0.08 (CI 95%). The deepening of the suboxic zone was associated with the rising of the amount of the suspended matter.

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On climatic and anthropogenic forcing in the Black Sea biogeochemistry interannual changes

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The Black Sea is a unique, stratified, enclosed ocean basin of great importance. The water column provides a wealth of information concerning aerobic-anaerobic biogeochemistry, the responses of which can have links to anthropogenic and climatic forcing. Herein, we synthesize hydrophysical characteristics, dissolved oxygen (DO) and nutrient data (phosphate, dissolved inorganic nitrogen (DIN), and silica) for the period 1984-2010 received in the northeastern and western areas of the Sea. In the subsequent analysis we discuss the role of anthropogenic and climatic forcing in the context of the Black Sea oxic layer and oxic/anoxic interface characteristics.

During the last several decades the following changes in the affecting factors can be marked out:

• Climate change leaded to higher surface temperature, increased stratification and therefore there has been a decrease in winter mixing.

• Anthropogenic nutrient loads in the region have significantly decreased during the last 10-15 years compared to the period of progressive eutrophication (1970s and 1980s).

The biogeochemical regime of the Black Sea Proper oxygenated layer has notably changed since 1999:

• After 1999, DO concentration in the CIL decreased by 20% while the concentrations in the surface layer changed very little, therefore the CIL waters were not fully replenished during the winters of the last decade.

• Oxygen and nutrient dynamics in the middle pycnocline have been decoupled.

• Elevation of the hydrogen sulphide boundary by about 10-30 m has been observed.

• Nutrient concentrations in the upper layer decreased in line with the decrease in anthropogenic eutrophication.

Nowadays physical (climatic) forcing has become a dominant affecting factor of the Sea oxygen and nutrient regime:

• Warm periods (series of warm winters) lead to a decrease of oxygen in the CIL, an elevation of the hydrogen sulphide boundary and a decrease of nutrient in the surface layer.

• Cold periods (series of cold winters) lead to an increase of oxygen in the CIL, deepening of the hydrogen sulphide boundary and increase of nutrient in the surface layer.

Decadal and Interannual Variability of Oxycline along the Indian West Coast

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The Arabian Sea is home to one of the three major open-ocean Oxygen Minimum Zones (OMZ). Upwelling of low-oxygen, high-nutrient waters leads to the formation of the world's largest natural low-oxygen zone over the continental shelf off the Indian west coast during the post southwest monsoon. These oxygen deficiency events, also called anoxic events, are reported to have intensified at the turn of the 20th century, with a strong impact on biology and living resources, including a sharp decline in demersal fish catch, more frequent episodes of fish mortality and a shorter fishing season. The natural and anthropogenic forcings, the physical and biogeochemical factors that control the oxygen variability along the western Indian coastline however remain elusive. In the present study, we address this issue using an Indian Ocean regional configuration of NEMO/PISCES biogeochemical model. We show that the depth of oxycline along the western coast of India display considerable decadal fluctuations, along with interannual ones, with a shoaling from the late 70's until 2000 and a deepening since then. These variations agree qualitatively well with sparsely available oxygen measurements over the past 40 years. Our analysis indicates that these fluctuations are intimately tied to the decadal and interannual fluctuations of the thermocline depth, suggesting that the oxycline depth variations are mainly controlled by physical mechanisms, largely related to natural variability.

Long Term Variability of Hypoxia/Anoxia and Eutrophication in a semi-enclosed area of the Aegean Sea (East Mediterranean)

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Hypoxia, caused by a combination of eutrophication and hydrographic/climatic conditions, occurs frequently in the European seas. In Eastern Mediterranean Sea various aquatic environments with hypoxia occurrence can be identified, such as Ionian Sea lagoons and embayments and coastal marine environments of Aegean Sea. In these areas, strong stratification or stagnation result in low oxygen concentrations or even anoxia.

Elefis bay is a shallow (32m maximum depth), semi-enclosed marine area of the Eastern Mediterranean Sea, affected by important coastal pressures due to human activity. The anoxic layer in the Elefsis bay is a quasi-permanent feature that is developed every year between May and late October. The development of a strong temperature-driven pycnocline results in the isolation of the deeper part of the water column, leading to insufficient oxygen supply from either atmospheric or photosynthetic sources. As a consequence, the near-bottom layer of Elefsis bay remains periodically hypoxic and anoxic carrying the winter characteristics with lower temperatures and salinities and high amounts of silicate, phosphate and ammonium, while the availability of nutrients in the surface layer is reduced, resulting in limited primary production [Pavlidou et. al., 2013]. After mid fall, the water column is fully homogenized as densities increase rapidly throughout the water column.

In this work the temporal extent of hypoxia and its possible connection to eutrophication and climatic variability is investigated in order to understand the mechanisms which control the occurrence of hypoxia. Physicochemical and biological data from a 30-year monitoring were used to investigate the role of hypoxia in modulating responses of the Elefis bay ecosystem and the associated biogeochemical processes in relation to eutrophication and global climate change. A change in the intensity of the hypoxia/anoxia developed in the bay was observed during the last 10 years. After 2004, Dissolved Oxygen concentrations in the hypoxic layer bellow the pycnocline increased, whereas in the last few years a sign of a slow upgrade of the BAD eutrophication status of the bay was recorded. Additionally, an interesting signal of variability in the strength of the summer pycnocline appears which is qualitatively correlated with the evolution of interannual anoxic/suboxic conditions in Elefsis during the same period.

Incubation experiments in benthic chambers were utilized as a tool for direct measurement of the exchange rates of nutrients and dissolved oxygen consumption rates across the sediment-water interface. The experiments conducted during 2012 in two different seasons, winter and summer. In winter (February 2012), the bottom layer was oxygenated (oxygen in the bottom layer: 258 mmol/m^3) while in summer (September 2012) hypoxia occurred (oxygen in the bottom layer: 24 mmol/m^3).

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New insights for the oxygen dynamics in the Black Sea revealed by Argo floats measurements

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Since 2010 several autonomous profiling floats with oxygen sensors were deployed in the Black Sea in the frames of various international initiatives (Euro-Argo, BulArgo, Decosim). In the late 2013 two Bio Argo floats were deployed in the Black Sea in the frame of "E-AIMS: Euro-Argo Improvements for the GMES marine Service". Beside the traditionally CTD the floats are equipped with miniature optical sensors that offer unique opportunity to observe the biogeochemical processes in the Black Sea, which have been out of reach until recently [Claustre et al., 2010].

The Black Sea is known as the largest anoxic water body in the world and these new measurements contribute substantially to understand the oxygen distribution and relation to the biological production processes in the upper 200 m layer. The rich of oxygen surface water, oxycline and the oxic-anoxic interface (suboxic zone) are well observed [Stanev et al, 2013, Murray et al., 1989]. In the open sea the oxygen concentration is rather uniform in contrast to the coastal zone where the oxygen varies substantially in time and space. The two mechanisms for oxygenation of the deep anoxic water are well identified from the data. In the coastal zone dominated by the mesoscale variability, depending on the eddy intensity, due to the deepening of the pycnocline the interface between oxic-anoxic zone also deepens and could reach 150-200 m. The region near Bosporus Straits shows larger oxygen values around 200 m which undoubtedly indicates the influence of the Mediterranean water coming with the Bosporus plume [Konovalov, et al., 2003]. The Bosporus Straits intrusions fingerprints could be distinguished in the temperature and to less extend in the salinity profiles.

The new Bio Argo simultaneous measurements of DO and chl-a could contribute to better understand the occurrence of hypoxia events during the phytoplankton blooms and the relation to the physical properties of the ambient water.

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Microbial processes at the oxycline of humic lakes

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Humic lakes represent a poorly acknowledged environment where oxygen stratification plays a major role in determining the metabolism of the whole ecosystem. The driving force behind the elemental cycles and for example greenhouse gas (GHG) production in these lakes are microbes. Although the hotspot of the microbial production and consumption of GHGs in humic lakes is the transition zone between the anoxic and oxic layers, we know very little about the composition and function of these communities. Currently our perception of the microbe-mediated metabolic processes in these systems is based on surveys of certain targeted functional groups, such as Chlorobia, but the understanding of functioning at whole-community level is practically non-existing. To shed some light into the processes dominating these environments, we have conducted a first assessment on the metabolic capacities of the three different layers of humic lakes using shotgun sequencing. The results show that there is a clear difference in the functional beta-diversity between the layers. It could also be seen that while all layers have their characteristic gene pool, the microbial community at the oxycline harbors the richest pool of genes that appear to be layer-specific, i.e. only found from this part of the water column. The genes that were found only in the transition zone indicated, for example, capacity for sulfate transport through the membrane and for carbon monoxide oxidation. Still, we could also see substantial variation between lakes. Thus, the results suggest significant in-lake and inter-lake variation in microbial functioning and are stressing the importance of redox gradients for the elemental cycles of humic lakes.

Red tide and anoxia in a coastal embayment of the southern Benguela upwelling system

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Increasing events of anoxia are considered to have had a major impact on living resources of the nearshore of St Helena Bay in the southern Benguela upwelling system. Acquisition of high resolution time series of water column and bottom dissolved oxygen (DO) concentrations inform the dynamics of oxygen depletion in the Bay at several scales of variability. The bay is characterized by a seasonally persistent deep pool of cold, oxygen depleted water, while episodic anoxia is driven by the decay of red tide in warm inshore waters. Coastal wind forcing influences DO concentrations in the nearshore through its control of water column stratification and mixing, through inshore advection of the bottom pool of oxygen depleted water as determined by the upwelling-downwelling cycle, and through its influence on bay productivity and the development of red tides. A seasonal decline in bottom DO concentrations of ~1.2 ml l^{-1} occurs with a concurrent expansion of the bottom pool of oxygen depleted water. Upwelling of this water into the nearshore causes severe drops in DO concentration [<0.2 ml l^{-1}], particularly during end-of-season upwelling, resulting in a significant narrowing of the habitable zone. Episodic anoxia through the entire water column is caused by localized degradation of red tide within the confines of the shallow inshore environment. Bloom decay is attributed to the inaccessibility of subthermocline nutrients under persistent downwelling, and the high oxygen demand leading to anoxia results from the exceptional carbon load contributed by the red tide in a relatively small volume of water. The roles of micro-zooplankton grazing and virus-mediated cell lysis in episodic bloom termination are explored as plankton mortality processes. The onset of winter mixing ventilates the water column and a progressive deepening of the mixed layer during winter results in a widening of the habitable zone.

Seasonal and interannual variability of dissolved oxygen on the continental shelf of Concepción (36°S) over 2000-2008: physical versus biogeochemical factors.

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An oxygen minimum layer extends along most of the Chilean coast between about 100 m and 500 m depth. This layer has been related to the Equatorial Subsurface Water (ESSW) mass, which is transported poleward by the Peru-Chile Undercurrent along the continental shelf and slope. The ESSW is characterized by temperatures and salinities relatively high, low values of dissolved oxygen (DO), and high nutrient concentrations. This water mass is the main source of nutrient-rich water that reaches the euphotic zone during upwelling periods near the coast of central Chile. In this study, we use observations and model simulations to analyze the relationship between seasonal and interannual changes of the poleward transport of the Peru-Chile Undercurrent and changes in the intensity and extension of the oxygen minimum layer off the south-central Chilean. Simulations are based on the Regional Ocean Model system, coupled to a biochemical model (BioEBUS) at a 7km resolution. The model extends up to the ecuatorial region to take into account the equatorial connection through coastal trapped waves, but the focus of the study is on the central Chile region (29°-39°S). In situ data of temperature, salinity and DO, obtained from different cruises carried out in the study region (from 35.5° to 38°S) between 2004 and 2008, are used for model/data comparison and validation. The model outputs are further used to infer the main processes (physical versus biogeochemical) contributing to the seasonal and interannual changes in DO. Preliminary results indicate that DO variability can be interpreted, to a large extent, as resulting from seasonal variations in the PCU transport, although regional features (mesoscale activity and intraseasonal wind variability) can modulate this relationship.

Long-term observations of thermohaline stratification in north-eastern part of the Black Sea by using moored automatic mobile profiler Aqualog

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Variations of the hydrogen sulphide boundary depths linked to the density surfaces in the north-eastern part of the Black Sea near the Gelendzhik Bay are discussed. The research is based on long-term survey by moored automatic mobile profiler Aqualog [*Ostrovskii and Zatsepin*, 2011] at the station located about four nautical miles from the coast at the depth of 260 meters. Four moored profiler surveys separated by maintenance works of 3 days – 1 month were carried out from January 30 to December 12, 2013, with 257 days of observation in total. The profiling was conducted four times per day, between the depths of 15-34 meters and 220 meters. The observed parameters included temperature, salinity, horizontal current speed and direction.

It is well-known [*Rozanov*, 1995, *Murray et al.*, 1995, *Vinogradov and Nalbandov*, 1990] that the depths of certain features of hydrochemical profiles (for example, extremums) in the central and peripheral Black Sea are locked to the particular density surfaces, i.e. there are no significant horizontal gradients of chemical variables along the same density surface. Thus one can estimate variability of certain chemical features in the depth field, including hydrogen sulphide boundary position, or the onset point, by using only CTD data. As a conventional onset point of H_2S the density surface of σ_θ = 16.15 was used and its seasonal and short-term variability was examined. It was found that the depth of hydrogen sulphide boundary always changes, and such fluctuation can exceed 60 meters in three days. The diurnal amplitude can reach 30 meters. The lowest depth was reached in spring (211 meters on April 27). During warm season, the depth of the H_2S onset point tended to become shallower; the shallowest depth was observed in mid-autumn (117 meters on October 21). Thus the difference between the maximum and minimum depths of the hydrogen sulphide boundary reached 94 meters at the same location in one year. Fluctuations of the H_2S onset point correlated with the current velocity profiles depending on the dynamical processes.

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Expanding Oxygen Minimum Zones, Tropical Pelagic Predators, and Atlantic Fisheries That Exploit Them

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This paper links 50 years of ongoing ocean scale deoxygenation trends in the tropical Atlantic Ocean to changes in vertical habitat use of large pelagic predators, and the Atlantic fisheries that exploited them. Climate induced warming in this large ocean area (Oxygen Minimum Zones, OMZs) has compressed the volumes of surface mixed layer habitat by about 1 m y-1 over the last 5 decades, concentrating predators, preferred prey, and influencing Atlantic-wide fishing effort patterns into progressively shallower surface zones. This phenomenon increases the catchability of these predators and may contribute to overly optimistic abundance estimates derived from surface fishing gears. Overall, deoxygenation is estimated to have caused a 15% reduction in suitable habitat for tropical pelagic tunas and billfishes in the tropical Atlantic during this time period. To demonstrate ocean scale changes in available habitat we use Hydrobase 3 database to compute decadal matrices of OMZ size (volume and surface area), as well as the reciprocal decline in surface mixed layer from 1955 through 2004. Further, we tracked fishing effort and catch inside and outside of the Atlantic OMZ for 9 major ICCAT assessment species to examine potential compression impacts. We found that during the last decade analyzed (1995-2004), longline fishing effort has coalesced on-top of the Atlantic OMZ, while hooks from outside the OMZ have decreased by about the same proportion. During the initial decade (1955-1964), 3 longline fleets deployed about 500,000 hooks, while by the last decade (1995-2004) longline effort had expanded to 94 fleets and almost 4.2 billion hooks. We determined that at least 7 out of 9 major ICCAT stock assessment species examined here are severely impacted by the OMZ expansion and resulting loss of available habitat. We also point out some significant ecosystem interactions between predators and preferred prey that appear to fuel predator assemblages.in progressively shallow OMZ areas, including some predators that are not sensitive to low ambient DO levels. As deoxygenation is expected to continue during the current cycle of climate change and global warming, and has been observed in other oceans as well, this suggests it may have broad-scale impacts on the sustainability of pelagic fisheries and their management. In order to maintain sustainable fisheries for tropical pelagic fishes, we feel its incumbent upon the assessment community to incorporate hypoxia-based habitat compression impacts for species of concern (identified here) into the assessment process. One potential approach might be accomplished during the Catch-Per-Unit-Effort standardization process, by scaling catchability coefficients (by species and gear) using the progressive decadal decline in available surface mixed layer habitat (in volume) presented here.

Key words: hypoxia-based habitat compression, expanding oxygen minimum zones, pelagic predator management, catchability coefficients. CPUE standardization.

Effects of bioturbation in the oxygen regime of the sediment-water interface: modeling study.

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Nearby the sediment-water interface the rate of turbulent transport steadily decreases and finally tends to zero, then the most important role in exchange processes plays molecular mixing. Lower in sediment the effect of bioturbation become appreciable in the redox conditions changes. Using the 1-dimensional C-N-P-O-S-Mn-Fe vertical transport-reaction model Bottom Redox Layer Model, BROM [Yakushev, Protsenko] has been made an experiment assess the impact of bioturbation on the distribution of the model parameters. Model simulation of the seasonal bottom anoxia formation was taken as a background. In the experiment two scenarios were simulated: first scenario included only turbulent and molecular exchange, and in second scenario bioturbation effect was added. Experiment showed that in the presence of bioturbation the oxygen penetrates the upper 4-5 cm of sediment, while in the reverse situation the depth of oxygen penetration is first millimeters. Also seasonal changes in oxygen concentration are stronger with bioturbation. In presence of bioturbation, Mn (IV) forms a thicker layer that leads to disappearance of H2S in the top cm of sediment during winter-spring period. Beneath the maximum of Mn(IV) occurs a peak of Mn(III) followed then by a Mn(II) maximum and by MnS increase, that corresponds to the modern view of Mn species distributions in the sediments. In case of an absence of bioturbation, Mn(III) maximum is not observed. In presence of bioturbation Fe(III) is distributed similarly to Mn(IV), it extends on top 4-5 cm of sediment and layer of Fe(III) presence is thicker than in the first scenario. Maximum concentrations of Fe(II) are situated lower in this scenario and FeS concentratio

Multi-scale drivers of oxygen depletion in the North Sea: insights from glider observations

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Dissolved oxygen is an important ecosystem quality indicator for both the Marine Strategy Framework Directive and OSPAR. Two studies observed low dissolved oxygen in the bottom mixed layer of the central North Sea in 2007, 2010 and in historical data dating back to 1902, specifically in regions characterised by low advection, high stratification, elevated organic matter production from the spring bloom and a deep chlorophyll maximum.

We deployed a Seaglider in a region of known low oxygen during August 2011 to investigate the processes regulating supply and consumption of dissolved oxygen below the pycnocline. The glider provided extremely high resolution observations (one profile every 16 min, 0.2 Hz) during a three day deployment of cross-thermocline biological, chemical and physical processes. The Seaglider identified cross-pycnocline mixing features responsible for re-oxygenation of the bottom mixed layer not currently resolved by models of the North Sea. Using the data, we were also able to constrain the relative importance of different sources of organic matter leading to oxygen consumption and determine a budget of dissolved oxygen supply and demand within the bottom mixed layer. Observations of organic matter fluxes also led to preliminary estimates of carbon export to the bottom mixed layer. The Seaglider proved to be an excellent tool for monitoring shelf sea processes despite challenges to glider flight posed by high tidal velocities, shallow bathymetry, and very strong density gradients (8 σ over 3 m). These data highlight the necessity of resolving these fine scale features within models of the North Sea to adequately determine predict the importance of seasonal oxygen depletion within the central North Sea under changing climates.

Interannual to interdecadal variations of the macrobenthic biomass from the Peruvian continental shelf associated to changes in bottom water oxygenation (1976 – 2009)

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The oxygen minimum zone (OMZ) off the Peruvian coast exhibits a spatial distribution that varies with latitude, depth and distance to the coast. The spatial variability in oxygen content imposes latitudinal and bathymetric patterns of the benthic communities. This study analyzes the inter-annual and inter-decadal variations of bottom water oxygenation and benthic macrofaunal biomass on the continental shelf (04° and 14° S), taking into account the latitudinal and bathymetric patterns. Particularly, we examined whether oxygen and biomass of macrobenthos varied between two interdecadal periods (1976 – 1991 and 1994 – 2009), under differing signatures of the PDO and anchovy biomass and meridional distribution. To do this, we analyzed historical databases of 31 hydroacoustic surveys and 03 monitoring platforms, using ANOVA and ANCOVA linear models.

Our results confirm that oxygen availability is the main factor controlling the dynamics of benthic macrofauna south of 10° S, while food availability seems to be more important in the north. Therefore, interannual variation of biomass in south and central areas respond positively to sea floor oxygenation, while in the north interannual fluctuations respond differently. In addition our results indicate that the two interdecadal periods exhibited differences in bottom water oxygentation that varied with latitude (increasing north of 09°S), while the nucleus of macrobenthic biomass was displaced from ~ 5 - 7 ° S, during 1976 – 1991, to ~ 6 - 8 ° S during 1994 – 2009. The latter observation is thus at least partly explained by the amelioration of oxygen concentrations north of 09°S, but also to the reported increased productivity south of 06 ° S, and particularly to the possible increase in the vertical carbon flux associated to the northward shift in the gravitational center of the anchovy population and pellet' sedimentation.

In conclusion our observations suggest that changes in the global and spatial variation of the anchovy population, along with oceanographic conditions associated with upwelling and oxygenation, generate significant impacts on the carbon budget and the dynamics of benthic communities associated with the coastal upwelling ecosystem.

Deoxygenation in a global change context – coastal conditions

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Deoxygenation in the coastal ocean is driven primarily by eutrophication, the increased rate in primary production and the accumulation of the resulting carbon. This process is usually a trajectory of increased nitrogen or phosphorus loads or both in a naturally stratified water column (thermal, saline, or both). Some deoxygenation is driven by excess organic inputs but is mitigated more directly than the nonpoint pollution that leads to coastal hypoxia. Many of the same processes are at work in coastal deoxygenation as in the open ocean, but the more incipient global change is aggravated by human activities in the watersheds draining to the hypoxic zones. Human activities, based on expected human population growth and the necessary production of food and fiber, will lead to additional excess nitrogen and phosphorus coming from the land. In some, many, cases, the hydrologic cycle is expected to generate more precipitation and river runoff, which would lead to stronger water column stratification offshore and a worsening of the low oxygen conditions. On the other hand, global change may lead to desertification and reduction in river flow. Humans will also alter the distribution of water in rivers for human use and agriculture, thus removing some of the nutrients from delivery to the coast but rather into inland waters.

Climate change that results in increased water temperatures will increase metabolic processes, rates of photosynthesis and rates of respiration, within the context of other limiting factors, and thus flux of increased carbon to the lower water column of a stratified coastal system and lead to worsening hypoxia. Increased water temperatures will also intensify stratification and reduce the solubility of oxygen, both of which would lead to worsening oxygen conditions. On the other hand increased air and water temperatures may influence coastal currents and the frequency and intensity of storms. Coastal currents that move closer to shore may bring deeper, deoxygenated waters into coastal areas. Storms may destratify the water column and temporarily alleviate hypoxia until stratification is redeveloped.

In total, the increase in human population and related effects and warming air and water temperatures will most likely aggravate coastal hypoxia and lead to more and worsening deoxygenation of coastal waters.

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Combining sediment and water column investigations to study the processes generating hypoxia in the Pearl River Estuary (China)

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Hypoxia in river estuaries and adjacent coastal zones is one of the important threats for ecosystems which sustain large population in the coastal area (Diaz and Rosenberg, 2008; Rabouille et al., 2008). The Pearl River Estuary has been described as a low oxygen environment: it is hypoxic (even anoxic) in its upstream part (Dai et al., 2006) and displays low oxygen areas in its marine part (Yin et al., 2004). It drains one of the most populated area of the planet encompassing the cities of Guangzhou (Canton), Shenzhen and Hong Kong, a total of over 50 Million inhabitants in 2005. A recent investigation of the processes responsible of hypoxia in this estuary was undertaken under the auspices of a French-Chinese exchange programme (Partenariat Hubert Curien, Cai Yuan Pei programme). The originality of the approach is the coupling between water column and sediment compartments. Water column sampling and sediment cores collection were performed at similar stations along the estuary from upstream near the city of Guangzhou to downstream near the coastal South China Sea. Oxygen demand from the water column was investigated using bulk water incubation whereas sediment diffusive oxygen demand was calculated from core oxygen microprofiles. Dissolved and particulate carbon and nitrogen compositionwere also investigated in the sediment and water column to collect information on the relative role of nitrification versus organic carbon mineralization in oxygen consumption in the Pearl River Estuary, as previously underlined by Dai et al. (2006). A comparison of the respective role of the sediment and water column in causing/maintaining hypoxia is investigated through the calculation of mass balances.

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Improving Spatial and Temporal Variability of Hypoxia Regions in Chesapeake Bay with HF Radar Assimilation

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An operational system for the forecasting and monitoring of coastal and marine conditions needs to identify shortcomings and advantages of sensors and models in order to produce a forecast that is adequate for operational purposes. A way of mediating among shortcomings of both models and sensors and leveraging advantages of those is by employing data assimilation. Traditionally, data assimilation in coastal and marine applications has been mainly applied to hydrodynamic studies, with very little investigation and validation in biogeochemical studies.

In this work a scheme for the assimilation of ocean surface current measurements into a numerical ocean model based on data from High Frequency radar (HFR) systems is deployed. The scheme is employed for the forecast and hindcast of the surface and volumetric circulation of water in Chesapeake Bay, on the East Coast of the United States. The scheme is the combination of supplementary forcing on the surface and of Ekman layer projection of the correction in depth. Optimal interpolation through BLUE (Best Linear Unbiased Estimator) of the model predicted velocity and HFR observations is computed in order to derive a supplementary forcing applied at the surface boundary. In depth the assimilation is propagated using an additional Ekman pumping (vertical velocity) based on the correction achieved by BLUE. Observations for the scheme are given by an HFR network (part of MARACOOS, the Mid-Atlantic Regional Association Coastal Ocean Observing System, http://maracoos.org/) deployed within the lower Chesapeake Bay study site, providing real-time synoptic measurements of surface currents in the zonal and meridional direction at hourly intervals.

The scheme is then applied to the study of spatial extent and temporal variability of the hypoxia region within the main channel of Chesapeake Bay. The time period for the analysis is a 30 day window centered during the fall of 2012 (when the wind accelerates the vertical and lateral mixing oxygenating the bottom water [Goodrich, 1987]), comparing the skills scores of the forecast of the assimilation scheme within 24, 48 and 72 hours periods with the Oxygen data collected from the Chesapeake Bay Program (CBP).

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Has low oxygen condition an impact on nutrients dynamics and macrofauna in a coastal macrophytodetritus accumulation?

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Posidonia oceanica is an endemic Mediterranean highly productive seagrass. Depending on the ability of the primary consumers to digest it alive, a generally important part of its foliar primary production falls in autumn, to decay inside the meadow or to be exported to sand patches to form "exported litter accumulations". These accumulations are highly dynamic depending on hydrodynamics and seafloor geomorphology. Literature says that low O2 conditions might occur inside litter accumulations, but the annual oxygen dynamics or its impact on the litter-associated macrofauna has never been measured. We focused on 2 exported litter accumulations in Calvi Bay (Corsica), during 2 years for a total of 8 seasons. For each season, we collected water samples (n=6) from 3 different strata: Water Column (WC), Water Just Above the litter (WJA) and Water Inside the litter (WI). Oxygen was measured for each replicate using a Winkler-based automated routine for oxygen concentration measurements on micro-volumes. At the same time, nutrients concentrations (PO4, NH4, and NO2+NO3) were measured in WC, WJA and WI, but also in the Interstitial Water (IW) using a spectrophotometric continuous flow analyzer (adapted for low nutrients level in an oligotrophic environment). In parallel, macrofaunal (size $>500\mu$m) samples (n=3-6) were also collected, counted and identified to the specific level.

Our results show significant differences between O2 concentrations/saturation from WI and the two other strata. Significant differences were detected between seasons, sites and years for WI which is the only stratum where really low O2 conditions can be observed. Significant differences were also detected between seasons for both WC and WJA but no differences between sites and years. On the other hand no significant differences were detected between WC and WJA. A similar observation was made for the nutrients at the annual, seasonal and spatial level. Moreover differences are also observed between the nutrients themselves. Our data shows no correlation between WI O2 concentrations and saturation, and global macrofauna abundance or biodiversity. Results are more contrasting at an individual specific level for the 4 most dominant species. For two amphipod species, Gammarella fucicola (55% of the global abundance) and Gammarus aequicauda, no significant correlations were detected between their abundance and O2. For the leptostracan species, Nebalia strausi, a significant negative correlation with O2 concentration was detected. For the last amphipod species, Melita hergensis, a significant positive correlation was observed. Our analyses also show significant correlations between WI O2 concentration/saturation, and WI / IW nutrients concentration.

To conclude, this work shows that WI is a very particular and dynamic environment considering O2 concentration and saturation. Low O2 conditions can be observed in WI but never in WC or WJA showing that internal processes and relations with the sediment determine the O2 dynamics in WI and showing a potential "barrier" effect between WI and WC. Moreover O2 dynamics and its consequences may play a role in the nutrients dynamics and cycles. It is clear that faunal responses to low O2 conditions are not identifiable at a global community level. At a specific level, we show a more complex situation: some species do not seem to be impacted by low O2 conditions, but some present a significant positive, or a significant negative response. This shows the existence and complexity of species-dependent low O2 tolerance/adaptation, and the importance of a specific level data analyses to detect responses of dominant litter associated macro- invertebrates to O2 concentration and saturation variations.

Oxygen, respiration and photosynthesis in the OMZ

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High-resolution measurements in the OMZs of the Pacific Ocean, the Indian Ocean, and the Bay of Bengal have shown that the OMZ cores are usually anoxic, i.e., below O2 detection limits varying from 2-50 nM. In some instances intrusions of oxic water (which could have concentrations at the 100 nM level) could be detected deep into the otherwise anoxic core. In most cases where a deep secondary chlorophyll maximum consisting of Prochlorococcus was found the high-chlorophyll layer was anoxic, but we also observed chlorophyll maxima with concentrations of O2 $>$ 1 uM. Respiration rates were determined by bottle incubations, and in the layers close to the upper oxic-anoxic interface the rates varied from 2-20 nM h-1 with some higher rates at coastal stations. Rates were usually higher in secondary chlorophyll maxima than in the adjacent layers. Rates of photosynthesis in the secondary chlorophyll maxima were determined by oxygen formation during bottle incubations at in situ light intensities and spectral composition. The starting O2 concentrations in these bottles were adjusted to about 200 nM before the incubations. Maximum rates of photosynthesis were usually lower than the rates of respiration in the same layer and the rates of photosynthesis were thus determined as the difference in net oxygen consumption in bottles with and without illumination. Our bottle incubations indicated that incubations exceeding 16-24 h should be avoided as rates of respiration increased dramatically by longer incubations. Longer incubations were possible at low temperatures, probably due to the slower growth rates of bacteria. Addition of amino acids to the water had little effect on the respiration rates by incubations of less than 16 h, and low levels of contamination of the ocean water by sampling may thus not cause severe artifacts by measurement of respiration rates, including rates of denitrification. Most of the low-oxygen measurements were made with electrochemical STOX sensors, but very sensitive optodes are now becoming available, and we have applied a type with an optimal range from 1-1000 nM.

Anaerobic methane oxidation in two tropical freshwater systems

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Lake Kivu is one of the East African Great Lakes. It is located at the border between Rwanda and the Democratic Republic of the Congo. It is a deep meromictic lake characterized by huge amounts of methane (CH_4) (60 km^3 at 0°C and 1 atm) dissolved in its deep waters. Two thirds of the CH_4 originates from anoxic bacterial reduction of dissolved carbon dioxide and one third from anaerobic degradation of settling organic material. CH_4 then diffuses slowly from the monimolimnion to surface waters where many is oxidised by methanotrophic microorganisms. In Lake Kivu, this biological oxidation of CH_4 could occur with different final electron acceptors: oxygen (aerobic oxidation) but also nitrate (NO_3^-), nitrite, sulfate (SO_4^{2-}), iron (Fe) or manganese (Mn) in anaerobic conditions. If the anaerobic oxidation of CH_4 (AOM) is generally coupled to SO_4^{2-} reduction in marine waters, electron acceptors of the AOM were rarely investigated in freshwater systems. Five field campaigns were conducted from 2011 to 2013 during periods with contrasted ventilations of the upper water column. The dry season is characterized by a deeper mixing of surface waters ended by a steep gradient of physico-chemical conditions at the redox interface, while during the rainy season the mixed layer is shallower and ended at its deeper part by a NO_3^- accumulation zone. Sampling was conducted in the main basin of Lake Kivu but also in a particular sub-basin located northeast of the lake, the Kabuno Bay. Both systems are meromictic but differ in terms of morphometry and geochemistry with a shallower permanent chemocline and higher concentrations of CH_4, Fe and Mn in the anoxic waters in Kabuno Bay compared to the main lake. Samples were collected for the measurements of CH_4 concentrations and the various potential electron acceptors of the AOM. CH_4 oxidation rates were measured along vertical profiles at 5 m and 0.5 m depth intervals respectively in the main basin and Kabuno bay water columns. Results indicate high rates of AOM in both main basin (up to 7 µmol L^{-1} d^{-1}) and Kabuno bay (up to 16 µmol L^{-1} d^{-1}). In the main basin, we observed a co-occurrence of the AOM and the SO_4^{2-} reduction in the dry season. During the rainy season, higher oxidation rates occurred in the NO_3^- accumulation zone, which is in favour of a coupling between AOM and NO_3^- reduction. In Kabuno Bay, the higher AOM rates were observed at depths with highest particulate Fe concentrations. Our results suggest that AOM coupled with SO_4^{2-}reduction may occur during the dry season in the main basin, whereas this oxidation could be coupled with NO_3^- reduction during the rainy season. In Kabuno Bay, the co-occurrence of the Fe [III] peak with high AOM suggests a coupling between the AOM and Fe reduction.

Effects of coastal hypoxia on pelagic zooplankton spatial ecology.

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The effects of hypoxic bottom waters on pelagic zooplankton, which can alter their vertical positions in the water column, are variable. Depending on the severity of hypoxia, physical conditions and physiological tolerances of the species present, zooplankton may use hypoxic bottom waters as a refuge from predation or avoid hypoxic bottom waters and aggregate at oxyclines, potentially forming chow lines for their predators. Hypoxia can reduce or eliminate lower temperature thermal refuges for organisms, increasing energy demand, respiration and possibly reducing overall fitness. In coastal systems with differential flow at depth, avoidance of low oxygen bottom waters can influence zooplankton population residence time by impacting emigration and immigration. Hypoxic conditions can also result in species and size changes in zooplankton communities, which will influence the food resources available to their fish predators. We will review these hypoxia-induced effects on zooplankton using data collected in two different coastal systems in the United States experiencing seasonal hypoxia, the Chesapeake Bay and the Gulf of Mexico.

Early stages of dominant pelagic copepods at Humboldt Current System: effects of hypoxia over physiological responses

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We studied the effect of the hypoxia over physiological rates of early stages and egg viability of copepods to understand potential responses of the expansion and intensification of the Oxygen Minimum Zone (OMZ) in the eastern boundary upwelling system of the Humboldt Current. The Hatching Success (HS) and naupliar development rate (NDR) were experimentally studied on two dominant copepods off northern Chile (23°S; 70°W). Ovigerous females of *Calanus chilensis* and *Acartia tonsa* were collected to obtain eggs and naupliar stages under hypoxia (~0.4 - 0.8 ml L^{-1}) and oxygenated (~4 - 5 ml L^{-1}) conditions at constant temperature of 14ºC. The females were individually incubated to estimate HS and by groups to collect and incubate eggs, to obtain naupliar stages and ND estimates. The HS of the copepods species were negatively affected by hypoxia in contrast with oxygenated conditions, showing a decrease of 50% and 80% of hatching eggs in *C. chilensis* and *A. tonsa*, respectively. Naupliar stages were followed until stage NIII, showing that the NDR at hypoxia was slower than in oxygenated waters. Preliminary results suggest that the egg and nauplii viability and the reduction of early stages development time under low oxygen concentrations could determine the copepods population dynamic and consequently the structure and productivity of upwelling ecosystems.

Multidecadal to centennial scale changes in OMZ intensity, marine productivity and anchovy biomass in the Peruvian Upwelling Ecosystem during the last two millennia.

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The Peruvian Upwelling Ecosystem (PUE) sustains high biological productivity and one of the world's largest fisheries due to the upwelling of nutrient-rich waters from the subsurface oxygen minimum zone (OMZ). In the PUE, OMZ intensity, marine productivity, and anchovy biomass show strong interannual to centennial-scale variations. Currently, OMZ intensity and the alongshore wind stress, driven by the South Pacific anticyclone (SPA), are experiencing strong changes due to global warming. The consequences of these changes on marine productivity and anchovy biomass remain largely unknown. In order to reveal the mechanisms that control OMZ intensity and marine productivity in the PUE at centennial timescales, we used a multi-proxy approach including paleontological, organic and inorganic proxies in finely laminated sediments retrieved off Pisco (~14 °S), Peru, and compared them with other relevant paleoclimatic reconstructions. According to our analyses and interpretations, OMZ intensity, marine productivity and anchovy biomass show a strong link with total solar irradiance and northern hemisphere (NH) climate. During periods of NH warmer climate (i.e. Medieval Climate Anomaly) and during the last 100 years, the PUE exhibited a La Niña-like mean state characterized by an intense OMZ, high marine productivity and anchovy biomass. By contrast, during NH cool periods (i.e. Dark Ages Cold Period and the Little Ice Age), the PUE exhibited an El Niño-like mean state, characterized by a weak OMZ, low marine productivity and low anchovy biomass. Comparing our results with other relevant paleoclimatic reconstructions revealed that changes in the strength of the Walker circulation and the expansion/contraction of the SPA controlled productivity and subsurface oxygenation in the PUE during the last two millennia. The observed changes in productivity and oxygenation in the PUE are concordant with the "ocean thermostat mechanism" proposed by Clement et al. (1996), suggesting that stronger solar irradiance produces a shallower thermocline in the eastern Pacific induced by a stronger Walker circulation. Moreover, during the Medieval Climate Anomaly, the SPA expansion/contraction had more influence over the PUE than the Walker circulation changes. This indicates that the current SPA expansion observed during the last decades may likely lead to increased productivity in the PUE.

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Methane in three contrasting large lakes: Kivu, Tanganyika, and Baikal.

SCHMID MARTIN

Surface Waters – Research and Management, Eawag: Swiss Federal Institute of Aquatic Science and Technology

This presentation summarizes what we have learnt from several studies about the effects of physical transport processes and the resulting vertical distributions of oxygen concentrations on methane cycling in three contrasting permanently stratified, deep and large lakes.

Lakes Tanganyika and Baikal share some surprisingly similar physical properties besides their similar sizes, depths and shapes, even though they are located at extremely different climatic conditions. In both lakes, the deepwater is only very weakly stratified. As a consequence, turbulent diffusivity in the deepwater is intense and gradients of dissolved substances are weak. In Lake Baikal, advective deepwater renewal by plumes of surface water that plunge down to the bottom of the lake are an important process, and it seems probable that this is also the case in Lake Tanganyika, even though based on different physical forcing. However, while in Lake Baikal, the total vertical exchange is sufficient to supply more than enough oxygen to the deepwater to compensate for the oxygen consumption by mineralization, this is not the case in Lake Tanganyika, where the deepwater remains permanently anoxic. As a consequence, the deepwater of Lake Baikal is actually a sink for methane diffusing downwards from the surface layer [*Schmid et al.,* 2007], while that in Lake Tanganyika is a source of methane diffusing upwards towards the surface layer. Near the oxic-anoxic interface it is oxidized to a similar extent by both anerobic and aerobic methane oxidation, and only a small fraction can escape to the atmosphere [*Durisch-Kaiser et al.*, 2011].

In Lake Kivu, a very strong density stratification is imposed by inflows of saline hydrothermal sources to the deepest reaches and discharges of fresher groundwater at mid-depths. This strong stratification limits the exchange of dissolved substances out of the deepwater of the lake and allowed methane to accumulate in the permanently stratified anoxic deepwater over many centuries. The methane is transported from the deepwater towards the surface by a slow advective upwards transport. Most of the methane is oxidized by aerobic methane oxidation, while the role of anaerobic oxidation is limited by the availability of sulphate [*Pasche et al*., 2011].

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Investigating dissolved oxygen in the Gironde estuary based on continuous in situ monitoring: merits and drawback

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With its 625 km2, the Gironde fluvial-estuarine system of southwest France is one of the largest European estuaries in terms of surface area (625 km2) and annual mean discharges (1000 m3 s-1). The Gironde is marked by a pronounced turbidity maximum zone (TMZ) with suspended particulate matter concentration in surface waters $>$ 1 g L-1. The upper estuary branches into two rivers, the Garonne and Dordogne Rivers. The tidal Garonne, comprising 65% of the freshwater input, had already presented episodic low dissolved oxygen (DO) content close to Bordeaux, a large urban area (715,000 inhabitants), in particular during severe droughts of 1962, 1976, 1989 and 2006. Increasing frequency and duration of such events could be problematic for instance for downstream migration of juvenile fish, such as shads or sturgeon. The trends in increasing temperature and decreasing summer river discharges is expected to promote the establishment of seasonal hypoxia in the fluvial section of the Gironde Estuary close to Bordeaux in the next decades. Assessing the impact of climatic and anthropic pressures on such a large, hyper-turbid fluvio-estuarine system is complex, because it is contextual with several natural processes acting over a wide range of temporal and spatial scales. A prerequisite to predict the evolution of DO in waters of the Gironde estuary is to understand the factors controlling its concentration and saturation. Since 2004, a real-time high frequency monitoring system (MAGEST network) records temperature, salinity, turbidity and dissolved oxygen to establish a reference database. Here we will present the 10-year time series of DO in the Gironde estuary, to discuss the merits and drawbacks of continuous monitoring. It reduces uncertainties in DO concentrations from tidal to inter-annual timescales and shows reliable inter-annual variability in relation with the local hydrology and climatology. However we will demonstrate that interpretations from fixed stations must also be considered with special care, and specific sampling, like longitudinal survey, are indispensable to a complete interpretation.

Context between phytoplankton development in the river and hypoxia in the Elbe estuary (Germany)

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In summer, the freshwater region of the mesotidal Elbe estuary is loaded by high inputs of algal biomass from the highly productive river. In the Hamburg Harbour area (km 610 – 630), a strong decline of algal biomass can be observed. In parallel, a strong depletion of oxygen lowers the ecological state of the Elbe estuary dramatically. Based on a 1-d water quality modelling approach, the longitudinal development of phytoplankton and the oxygen budget of the Elbe river and its estuary (km 0 to km 727) are simulated. We show the importance of large scale (catchment) modelling and focus on growth and decay of phytoplankton as a main driver for the oxygen deficit in the Elbe estuary.

Sediment oxygen uptake in Lake Geneva

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Between 1960 and 1980, the trophic state of Lake Geneva (situated between France and Switzerland) has changed from oligotrophic to eutrophic. Since then, the areal hypolimnetic oxygen demand of 1.31 gm^{-2} d^{-1} is now the highest measured in Switzerland and low oxygen contents of less than 4 mg l^{-1} regularly occur in the deepest parts (300m deep). Oxygen depletion is to a large amount driven by sediment oxygen uptake (SOU). In a large and complex lake like Lake Geneva, SOU can vary significantly temporally and spatially and is strongly dependent on the diffusive boundary layer (DBL) thickness which in turn varies with bottom boundary layer (BBL) currents.

In this study, an automated microprofiling system (MiniProfiler MP 8, Unisense) is used to measure oxygen concentration at the sediment-water-interface in sub-millimeter resolution. An attached oxygen optode (Aanderaa) enables in-situ calibration of the oxygen sensors. Here we present the first series of microprofile measurements in Lake Geneva at locations situated in varying depths. On the basis of the microprofiles, SOU and DBL thickness is calculated. Parallel measurements with a 2 MHz uplooking ADCP (Aquadopp HR, Nortek) in close proximity provide information about the BBL currents at the measurement site. The results give a first insight into the spatial variability of SOU in a large lake and the dependency of DBL thickness on BBL currents which was already observed in smaller lakes [*Lorke et al.,* 2003, *Bryant et al.* 2010] and coastal areas [*Wang et al.* 2013].

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Efficient sulfide detoxification in seasonally hypoxic sediments by competing S-oxidizing bacteria

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The occurrence of hypoxia in coastal systems can lead to strong accumulation of free H_2S in surface sediments, and upon transfer to the water column, this may have toxic effects for the resident fauna. In the seasonally hypoxic Marine Lake Grevelingen (The Netherlands), we observed that sulfide is efficiently removed by two different groups of sulfur oxidizing bacteria: long filamentous *Desulfobulbus*-like bacteria (DSB) and the large, motile *Beggiatoa*. Both groups use a very different strategy for harvesting sulfide in deeper sediment layers: DSB are capable of centimeter-scale electron transport [*Nielsen et al.*, 2010], while *Beggiatoa* use motility and intracellular nitrate storage. The co-occurrence of these two microbial groups is remarkable, as they are competing for the same geochemical niche. To elucidate the nature and the effects of this microbial competition we performed monthly sampling campaigns over 2012, with a detailed investigation of water column and sediment geochemistry. Microsensor profiling (O_2, pH and H_2S) revealed which microbial sulfide oxidation pathway was dominant at any given time, while FISH tagging (DSB) and microscopic counting (*Beggiatoa*) was used to quantify the abundance of the two bacteria. Our results show that both modes of microbial sulfide oxidation follow a seasonal succession, where *Beggiatoa* are dominant in autumn after summer hypoxia, while DSB become dominant throughout late winter and spring. The deep removal of sulfide by both DSB and *Beggiatoa* prevents the escape of free H_2S to the bottom water during summer hypoxia, and rapidly detoxifies the sediment in autumn, which may facilitate the recolonization by fauna. Hence, these S-oxidizing bacteria seem to play a crucial role during the recovery phase from hypoxia.

MODERN STATE OF THE CASPIAN OXYGEN MINIMUM ZONE

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Hypoxia development in the important fishery areas is an actual scientific problem. Long-term monitoring data on hydrochemical conditions in the deep-water basins of the Caspian Sea were collected by Russian scientists. This data shows the deep-water ventilation weakening, the development of hypoxia below the photic layer, and the hydrogen sulphide contamination of the bottom layers. Study of the Caspian Sea level variations in conjunction with hydrochemical parameters suggests that during the periods of low level (1970-1977) convective ventilation occurs throughout the water column in both deep-water basins. Oxygen concentration increases at the bottom, and the photic zone is supplied with nutrients. The existing environmental state is characterized by a high level position and stable stratification of the water column, creating conditions for the removal of nutrients from the upper layer and their accumulation in the bottom waters. The intensifying oxidation of the organic matter leads to the depletion of oxygen in the water column and the hydrogen sulfide layer formation. Our results of hydrochemical studies in the Caspian Sea in 2012-2013 allow us to draw an analogy between the current state of the ecosystem and the situation observed in 1930s, when the hydrogen sulfide in the bottom layers was also present during the high level period. Phosphate concentration in 1934 equalled to 1.7 mkM for the Middle Basin and 2.7 mkM for the South Caspian Basin; silica - 130 mkM and 100 mkM, respectively [Bruyevich, 1937]. In 2012-2013 phosphate and silicon contents in the bottom layers of the Middle Caspian Basin increased 1.5 times in comparison to 1934 as a result of the anthropogenic influence on the Volga basin. The Southern Caspian Basin condition repeated the state of the year 1934 more closely, with the hydrogen sulfide concentration of 0.1-0.3 ml/l in deep and bottom waters. Dissolved oxygen concentration in the Middle Caspian Basin in 2013 decreased rapidly with depth to less than 0.75 ml/l at 400 m. The level of 630 m was marked by the appearance of hydrogen sulfide, with its concentration increasing to 0.36 ml/l to the bottom. On the depth of 500 meters in South Caspian Basin, the dissolved oxygen concentration was 0.66 ml/l, and hydrogen sulfide appeared at the depth of 800 m. The concentration of hydrogen sulfide in the bottom layer (990 m) was 0.32 ml/l. Low oxygen content leads to the formation of the explicit intermediate nitrate maximum (13.0-13.2 mkM) at the depths of 300-400 m. In the presence of hydrogen sulfide the processes of nitrate-reduction and autotrophic denitrification cause a decrease in nitrate concentrations to near zero, and a sharp increase in the content of ammonium to 4.0 mkM. Unlike the coastal upwelling oxygen minimum zones, there is no nitrite maximum noted in deep waters of the Caspian Sea. It is a result of different contributions of nitrification, denitrification, nitrate reduction and anammox in the vertical distribution of mineral forms of nitrogen in dependence on the oxygen content, total nitrogen amount and dynamic conditions. In the isolated water basin, the observed interannual variations in the concentrations of mineral forms of nitrogen were rather a consequence of changes in the ratio of its various forms, than of the total nitrogen stock. As a result of the research we were able to identify a significant similarity of states of the Caspian ecosystem in 1930s and 2010s. However, the artificial regulation of the Volga river, the emergence of invasive species, such as Pseudosolenia calcar-avis and Mnemiopsis leidyi, and increasing pollution by industrial and domestic effluents have a significant impact on the redistribution of nutrients, disrupting natural cyclic variability of hydrochemical characteristics of the Caspian Sea.

Creaction of an enabling environment and icrease the quality of life- priorities of the "Green Economy"

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The Republic of Kazakhstan, being a full participant in the global development process, has taken on the commitment to the objectives set out in Agenda for the XXI century, Declaration of Millennium Summit and the World Summits on Sustainable Development. In the decisions of the summits were defined the aims to develop ways of stabilization of the environmental situation as factors ensuring improvement of the quality of life and improving the health of population. The vast territories of the Aral Sea region are a zone of ecological disaster. Intensive desertification and sustainable irreversible degradation of the environment, led to the deterioration of the socio-economic living conditions and growth morbidity. Analysis of cause-effect relationships growth in the number of diseases and environmental degradation showed that the population living in the Aral Sea region, an increase in the basic socially significant, including chronic diseases amid increasing natural and anthropogenic environmental risk factors. Mapping of the Aral Sea region using GIS technologies in environmental levels of pollutants shows a significant excess of the maximum allowable limits ions of heavy metals, biogenic and organic matter in aquatic and terrestrial ecosystems. Practical implementation of the application of GIS technology has allowed to determine the extent of land degradation, transformation of landscapes, the degree of loss of resource potential, the area of distribution of environmentally toxic substances in the environment. Based on developed us ecological mapping (a series of digital maps) are defined territory spread of malignant neoplasms and other socially significant diseases ((by area) frequency and dynamics congenital malformations under influence of environmental factors. Our developed an algorithm environmental screening state of health of mother and child, as well as the degree of tension of medical-ecological situations using international evaluation criteria on indicators environmental contamination and changes in health: satisfactory; relatively strained; significantly strained, critical and catastrophic. This integrated approach allows making managerial decisions on the improvement of the environmental situation, the improvement of population and economic development in specific territories at the level of individuals, the Executive bodies, and business structures. For example, digital maps of the epidemiological status, pollution eco-toxicants and the availability of data on specific diseases allow you to develop safe tourist routes. Gives the opportunity to the local Executive bodies to work out the optimal scheme of the tolerance limits withdrawal of resources, identify the reserve areas for the production of high-quality agricultural products (crops, animal husbandry); health agencies to develop a scheme to reduce the risk of epidemics, prevention and improvement of the population. For business structures to organize the production and processing of food, pharmaceutical and other products in a manner consistent with the sanitary and technical requirements. We have taken measures to restore the natural potential of the Aral and improve public health in the framework of the Strategy "Kazakhstan-2050". The main priority directions of strategic programs are to ensure the access of the population to quality drinking water, through the sanitary and-technical equipping of settlements; provision of qualitative purification of drinking water; improve the culture of consumption; improvement of the quality of the food. The development of the economic infrastructure and the provision of employment growth, health, and the implementation of effective prevention and wellness programs that increase the level of medical-ecological security of the population; improvement of the epidemiological situation.

Stabilization of the environmental siruation- the basis of development of the ”Green Economy” in the Aral sea region

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Kazakhstan Aral Sea region is a region of the ecological crisis, which resulted in drying of the Aral Sea in regulation of the rivers flow in the Aral Sea basin and the emergence of the devastated ecosystems on the dry bottom of the Aral Sea. Just over 40 years, the Aral Sea has lost 90% of its water supplies because of the large-scale irrigation of the fields. The region is located in the zone of deserts, combines features of the Northern and the Southern deserts of Sugar Gobi desert region. Thanks to the variety of ecological conditions in the Aral Sea basin and the alluvial plains of the Syrdarya Delta, there are marked variations meadows, riparian forests, halophilic and psammophilic plant communities. All this creates a significant diversity of natural ecological systems, defines and clearly-expressed complexity of vegetation and ecosystems. Desertification of the Aral Sea region was caused by a fence of water from rivers; discharge of collector-drainage waters into the river; the second time-initiated by changes in natural systems as a result of water intake; discharge of collector-drainage water in closed depressions. One of the factors of desertification is the leaking of the filterable waters from irrigated territories and the collector-drainage network; additional drainage of the territories after the termination of their irrigation; irrigation and flooding; secondary-initiated changes of natural systems as a result of irrigation. The most powerful transformation of soils and vegetation is observed during the reboot of pastures; secondary changes of the natural systems upon nomadic animal industries, tracing linear structures; direct impacts of offshore drilling installations on the soil and vegetative cover; as well as in destruction of the arboreal-shrub vegetation. For the development of an effective system of stabilization of the ecological situation in the region we offer the use the main provisions of ecological zoning concept. Strategy zoning of natural-anthropogenic environment should be considered as the first step of the administrative management and control of the environment, including the development of sustainable management and development of territories. The ecosystem approach and the greening of socio-economic spheres lie in the basis of a system of sustainable management. The basis for the analysis of the extent and causes of the transformation of the development schemes for sustainable management of natural potential of the territories are developed by us desertification maps and maps of zones of ecological risk. For practical implementation of the stabilization of the ecological situation in the region, we have developed the principles of creating GIS ecological and economic development Aral region, taking into account the admissible norms extraction of natural resources, measures to stabilize the environmental situation and the improvement of the population.

Creaction of an enabling environment and icrease the quality of life- priorities of the "Green Economy"

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Functional traits of the nematofauna from the Indian western continental margin in relation to habitat heterogeneity.

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Abstract

Conservation and management of the Earth's ecosystem requires knowledge of biodiversity and its role in ecosystem functioning. Since ecosystem functioning is complex, the use of biological traits for this purpose has been successfully tested in many regions. However, very few studies have used the functional trait approach in relation to extreme marine environments such as the Oxygen Minimum Zones (OMZ). Therefore we use the functional trait of nematofauna to understand the ecosystem functioning along the western Indian margin, which is known to have the strongest OMZs. The aim was to study what environmental drivers were responsible for changes in the taxonomical and functional community structure of nematofauna along a bathymetric gradient crossing the OMZ from the shelf to the deep basin. A single transect, perpendicular to the coast at 14° N latitude was sampled from 34-2546 m depth for biological and environmental variables during August 2007. Nematodes were identified to species level and classified them according to different biological/functional traits which are known to relate to important ecological functions includes buccal morphology, tail shape, body size, body shape, and life history. A total of 118 nematode species belonging to 24 families were identified along the transect. Nematode abundance reduced decreased from the shelf to basin. The nematode species were characteristic for each habitat. The multivariate analysis clearly shows that that habitat heterogeneity contributes significantly to nematode diversity. Our results indicated that not all nematode species can tolerate oxygen minima. Therefore hypoxia has certain differential effects on nematode diversity and the specific functional biological traits are more adapted in tolerating this hypoxia.

Key words: Oxygen Minimum ZonesOMZ, Nematoda, functional diversity, deep sea, Arabian Sea, Indian Margin.

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Sediments as recorders of spatial and temporal variability in Baltic Sea hypoxia

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Low-oxygen conditions are becoming increasingly common in coastal waters worldwide [*Diaz and Rosenberg, 2008*]. This increase is at least partly related to anthropogenic inputs of nutrients from land that fuel algal blooms and create an oxygen demand in bottom waters that outpaces supply. In many coastal systems, direct measurements of oxygen concentrations are limited or not available. Sediments act as recorders of conditions in the water column, however, and can be used to reconstruct past periods of low oxygen. Sediment molybdenum (Mo), is a simple yet powerful proxy for bottom-water redox conditions because of its enrichment in sediments overlain by waters that are anoxic and sulfidic. Low oxygen conditions also lead to major changes in the dynamics of manganese (Mn), iron (Fe) [*Lyons and Severmann, 2006]*.

Here, I will discuss how the spatial and temporal variability in Baltic Sea hypoxia can be reconstructed from sediment records of Mo, Mn and Fe. For example, Mo/Al records for the deep basins show multicentennial oscillations during past periods of hypoxia during the Holocene, suggesting rapid alternations between hypoxic and relatively oxic conditions [*Jilbert and Slomp, 2013a*]. These alternations in redox conditions also can lead to major changes in Mn sequestration, with extended periods of euxinia leading to a reduction in Mn carbonate formation. Manganese is then present at low concentrations in association with Fe-sulfides [*Lenz et al., 2014*). Finally, I discuss the strong variations in Fe shuttling that occur in the Baltic Sea linked to widespread changes in bottom water redox conditions and the potential feedbacks on nutrient availability [*Jilbert and Slomp, 2013b*].

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Heterocyst glycolipids as tracers of cyanobacterial blooms in the Baltic Sea. A proxy to reconstruct a possible trigger of anoxic events.

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The Baltic Sea represents one of the major existing brackish bodies of water, hosting an expanding dead zone. A combination of climate and human forcing together with the peculiar structure of the basin seems to be responsible for the present spreading of hypoxic areas [*Kabel et al.*, 2012; *Zillén et al.*, 2008]. The Baltic Sea has a shallow seafloor and maintains weak water exchange with the more oxygenated North Sea. Severe density stratification of the water column, due to freshwater inputs from the surrounding river systems, makes the water below the pycnocline often hypoxic [*Kabel et al.*, 2012]. The spatial extent of the hypoxia has substantially increased in the last century after anthropogenic overload of nutrients into the system and eutrophication, with consequent feedbacks such as higher primary production, intensification of cyanobacterial summer blooms and enhanced oxygen consumption in the deep basin [*Kabel et al.*, 2012; *Zillén et al.*, 2008]. A strong correlation between temperature increase and the recent spreading of anoxia in the Baltic Sea has been established [*Kabel et al.*, 2012]. Moreover summer sea surface temperature (SST) has been postulated as one of the main factors promoting massive cyanobacteria blooms and the consequent increased consumption of oxygen in the bottom waters of the basin [*Kabel et al.*, 2012]. Hypoxic events have been recurring in the Baltic Sea since the Holocene over the past 10,000 years. However such events and their possible triggers are poorly understood [*Zillén et al.*, 2008]. The coinciding increases in SST and cyanobacteria blooms have been proposed as a significant support to the recurrence of anoxic events. Heterocyst glycolipids (HGs) are membrane lipids specifically produced by heterocystous nitrogen-fixing cyanobacteria to avoid oxygen diffusion into the compartment were N2-fixation occurs and the O2-sensitive enzymes involved are located. HGs have proved to be highly specific biomarkers to trace cyanobacterial presence and nitrogen fixation back to the Pleistocene in the eastern Mediterranean [*Bauersachs et al.*, 2010]. In this study we apply these biomarkers to investigate the co-occurrence of cyanobacteria blooms with past hypoxic events in the Baltic Sea, over a period spanning from 10,000 years ago to 600 years ago. A gravity core recovered in the Gotland Basin will be analyzed at high resolution for HGs, specific biomarkers for cyanobacteria, and this record will be compared with summer SST as determined by the TEX86 palaeothermometer. Our investigation provides a possible new approach to trace past anoxia events.

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The Black Sea biogeochemistry: focus on temporal and spatial variability of oxygen

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The temporal and spatial variability of the upper ocean hydrochemistry in the Black Sea down to its suboxic zone was analyzed using data originating from historical observations, profiling floats with oxygen sensors and numerical simulations carried out with a coupled three-dimensional circulation-biogeochemical model including 24 biochemical state variables. The validation of the numerical model against observations demonstrated that it replicated in a realistic way the statistics seen in the observations. The suboxic zone shoaled in the central area and deepened in the coastal area, which was very well pronounced in winter. Its depth varied with time in concert with the variability of the physical system. Two different regimes of ventilation of the pycnocline were clearly identified: gyre-dominated regime in winter and eddy dominated regime in summer. These contrasting regimes were characterized by very different pathways of oxygen intrusions along the isopycnals. The contribution of the three-dimensional modeling to the understanding of the Black Sea hydro-chemistry, and in particular the coast-to-open-sea diapycnal mixing was also demonstrated.

Global oxygen changes and oxygen variability in the eastern Pacific off Peru

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Numerical model runs predict decreasing ocean oxygen with increasing CO_2 emission scenarios. Oxygen measurements are generally sparse in the ocean, nonetheless at some key locations longer-term oxygen time series exist and trends for the global ocean can be estimated. In many regions especially the tropical oceans oxygen has decreased during the last 50 years, however especially in the subtropical ocean regions with increasing oxygen values exist. Typical oxygen trends range from -0.5 to +0.4 μmol kg^{-1} yr^{-1} in the upper ocean for the last few decades, with a global mean oxygen trend of -0.066 μmol $kg^{-1}yr^{-1}$ between 50°S and 50°N at 300 dbar for the period 1960 to 2010 [Stramma et al., 2012]. In a measurement to model comparison for the last 50 years the model reproduce the overall sign and to some extent magnitude of observed ocean deoxygenation, though with a mismatch in regional pattern. Further analysis of the processes that can explain the discrepancies between observed and modeled oxygen trends is required to better understand the climate sensitivity of oceanic oxygen fields and predict potential oxygen changes in the future. Further expansion of low oxygen regions in conjunction with overfishing may threaten the sustainability of pelagic fisheries and accelerate shifts in animal distributions and changes in ecosystem structure.

In the eastern Pacific Ocean multidecadal variability (Pacific Decadal Oscillation) and also El Nino phases have a strong influence on long-term oxygen trends [e.g. Czeschel et al., 2012]. Historical data combined with new hydrographic measurements from two ship expeditions in the eastern tropical Pacific in 2009 and 2012 as well as oxygen sensor data from floats allow an enhanced view at the circulation, oxygen variability and trends in the oxygen minimum zone off Peru. Oxygen differences derived by comparison of ship sections show large variability in some locations. This local variability from eddies, seasonal and longer-term variability obscure trends in oceanic dissolved oxygen. Caution in interpretation of the data is necessary.

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Oxygen of nanomolar concentration is not found in the Black Sea

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Recent studies of the redox zone were conducted in the northeastern part of the Black Sea of using two types of sensors O_2: electrochemical mebranefree (MFS) and optical luminescence (optod) domestic design. Each of them has its advantages and disadvantages . The first one was used at the Black Sea since 1999, and with its help was first obtained true, i.e. later confirmed by other measurements distribution of O_2 between oxicline and H_2S zone. Due to the absence of the membrane it has virtually zero time-lag and can resolve the fine structure of the distribution of O_2 of up to 10-15 cm. Sensor disadvantages : 1) the inability to calibrate it in the laboratory due to the strong dependence of the sensor readings on the speed, and 2) the absence of long-term (days) stability readings due to environmental influences. Therefore, it is desirable to use the sensor in a mode of constant speed in water with sampling probes for analysis by Winkler, or parallel using such sensor as optod. Advantages of optod is unique selectivity for oxygen, and the ability to calibrate the sensor in a gaseous medium without the Winkler method. The main disadvantage is the relatively large time-lag (5-6 sec.) Correction for time-lag was made according to our formula, taking into account the 21 consecutive frames.

Measurements have shown full identity readings of both sensors. Thereby received confirmation earlier findings and conclusions of the MFS data the structure of redox zone. They are as follows. Before the introduction of MFS scientists had two concepts : 1) direct interaction of O_2 and H2S in a layer of their joint existence [*Sorokin, 1982*], 2) notion of suboxic layer and no notable overlap O_2 and H_2S [Murray at al., 1989]. The first measurements with MFS [*Stunzhas, 2000*] showed that both of them are poor : the first is just wrong, the second is too general and uninformative . For the Black Sea more correct and valuable is the concept of suboxidative and subreduced zones ranging between oxycline and H2S zone. In the first O_2 present in a concentration up to 10 µM, but almost not used for oxidation of organic matter. In the second both concentrations of H2S and O2 are very low, and the main role play the compounds of Mn (oxidized and reduced). The upper limit of the possible presence of O2 was initially estimated at 2 µM, later on as 1 µM [*Stunzhas, Yakushev, 2006*]. Analogic result of O_2 distribution was also obtained in [*Glazer at al., 2006*] with the sensitivity 3 µM. Now with hypersensitivity optod it was shown that in subreduced zone oxygen concentration is less than 20 nM. This applies to cases of calm hydrological situation. When, for some reasons, a volume of water containing appreciable concentrations of O_2 penetrates in water containing H2S, very quickly (probably within a few hours) there is mutual destruction and H_2S, and O_2, so that there is interleaved layers: O_2, H_2S, O_2 and again H_2S. Such cases occur regularly in the area of the Bosphorus, and are very rare in the northeastern part of the Black. Sign of this is the emergence of 3 narrow maxima turbidity caused by reaction of Mn and O_2 [*Stunzhas, 2000*].

Thus in the Black Sea reduced compounds (Mn^{+2}, ammonia, etc.) represent an effective scavenger of O_2 so that it is completely consumed, consequently there is no conditions for resistant layers with nanomolar concentration of O_2.

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Sediment phosphorus dynamics in a marine coastal lake: Response to seasonal variations in bottom water redox conditions

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Increased availability of phosphorus (P) drives the development and sustainment of hypoxia, a phenomenon that is progressively enhanced in coastal marine systems, yet there is a limited understanding of controls on the recycling and burial of P in these settings. Monthly water column and pore water profiles of oxygen and sulphide for 2012 at a seasonally-anoxic site in marine Lake Grevelingen, show a short (1 month) but intense period of bottom water anoxia in the system. Strong seasonality in pore water dissolved ferrous iron (Fe2+) and phosphate is seen. In spring, when bottom waters were oxic, pore water data indicate dissolution of iron sulphides and calcium carbonate from activity of filamentous cable bacteria. Consequently there is a strong release of Fe2+ to the pore water without an associated release of dissolved phosphate. Concurrently, most released phosphate remains in the sediment. Upon the onset of anoxia, phosphate release from the sediment is enhanced, both in absolute terms, when compared to the prior oxic period and relative to dissolved inorganic carbon and ammonium. With the return of oxic conditions, Beggiatoa establish at the sediment-water interface and the benthic flux of phosphate is again reduced. Sediment P analyses indicate most P in the sediment is present in the form of organic- and iron (Fe)-bound P, even at depths where sulphide is present at high concentrations throughout the year.

Multi parameters observatories and their contribution to a better knowledge of the ocean

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This poster will give some examples on how multi-parameter platforms are used in different applications ranging from surface water measurements with compact ship mounted systems to shallow coastal on-line observatories for fjord and coral reef studies and down to measuring in deep Antarctic waters. Parameters that will be discussed include: Oxygen, CO2, Currents, Conductivity/Salinity, Temperature, Pressure, Chlorophyll A and Turbidity.

Improve your oxygen optode measurements - user examples, practical handling and calibrations

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The introduction of oxygen optodes more than 10 years ago created new possibilities in understanding oxygen dynamics in oceans and lakes. The intention of this presentation is to share some of the acquired experiences using these sensors. The technology and how it has evolved will be briefly described. A wide range of scientifically oriented applications will be presented. Methods on how to enhance the oxygen data quality will be suggested including practical handling, simple field adjustments and advanced multipoint calibrations. An introduction to pCO2 and pH measurements using prototype optodes will also be done.

QUANTIFYING BIOLOGICAL AN PHYSICAL CONTROLS ON DISSOLVED OXYGEN IN CHESAPEAKE BAY USING A COUPLED HYDRODYNAMIC-BIOGEOCHEMICAL MODEL

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Dissolved oxygen concentrations in Chesapeake Bay are influenced by external climatic, hydrologic, and anthropogenic forcing, as well as internal biogeochemical interactions. Because observations are often inadequate to understand interactions among these varied and complex biological and physical processes over multiple time and space scales, numerical models are needed to simulate these processes towards understanding their effects on dissolved oxygen. Recent modeling efforts have highlighted many of the important physical processes controlling dissolved oxygen in Chesapeake Bay, but fewer have investigated interactions with biogeochemical controls. Thus, a water-column and sediment biogeochemical model (RCA-SFM) with state variables representing inorganic and organic forms of carbon, nitrogen, phosphorus, and silica, as well as algal biomass and dissolved oxygen was coupled to an implementation of ROMS in Chesapeake Bay. We report the results of multi-year model simulations that reveal how oxygen concentrations are regulated by (1) altered external loading of nitrogen and phosphorus, (2) the seasonal timing and spatial distribution of phytoplankton production, and (3) the balance between physical replenishment and biogeochemical oxygen uptake.

Two-dimensional distribution of living benthic foraminifera in an anoxic estuarine mudflat (Loire River)

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Most benthic foraminifera inhabit the sediment-water interface, taking advantage of oxygen and fresh organic matter availability. Some centimeters below, anoxia may cause inhospitable conditions. Those anoxic horizons, rich in dissolved iron, may still host live specimens of species considered aerobic. The survival strategies of those species and the way they reach deep layers are until now poorly understood, especially in bioturbated tidal environments such as the Brillantes Mudflat in the Loire Estuary. Based on a two dimensional approach this study analyzes the relationship between geochemistry and foraminifera distribution at scales of millimeters to centimeters.

As first step, the vertical distribution of benthic foraminifera in relation to dissolved oxygen penetration was described. Replicate cores were sampled and split in 2 mm slices. Living foraminifera were determined by cell tracker green incubation. O_2 profiles were measured with a 50-µm tip Clark electrode. As second step, lateral heterogeneity was assessed with two planar gel probes and the sediment facing them. The sediment was cut into 1-ccm pieces, living foraminifera were identified and counted, and organic carbon and metallic oxides analyzed.

The first results on vertical distribution of foraminifera show a decrease of one dominant species *Ammonia tepida* from 250 ind/10cm^3 at the sediment-water interface, to a stationary state around 40 ind/10cm^3 between 0.6 cm and 5 cm depth. The second experiment shows a significant heterogeneity at the centimeter scale of both foraminifera and solid and dissolved phases. It is hypothesised that organic matter controls both foraminifera and bacteria-mediated iron reduction which implies a correlation between organic carbon, foraminifera density, and iron reduction rate. Our results show no clear correlation between dissolved iron and foraminifera distribution, which suggests that at least one of our hypotheses needs to be revisited.

Oxygen time series at the Scotian Shelf, NW Atlantic Ocean

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An oxygen time series has been established in the late 90s at a monitoring station (HL2) on the Scotian Shelf as part of the Atlantic Zone Monitoring Program (AZMP) of Fisheries and Oceans Canada (DFO) Dissolved oxygen and related hydrochemical properties of the water column have been determined in approximately monthly intervals at HL2, which is approximately 30km offshore. The duration of the spring bloom is variable over the range of weeks, and the mixed layer depth at the time of the bloom varies between 20-30m and deeper than 100m water depth. We analyze this time series with respect to timing and accentuation of the bloom and post bloom biological activity, and with respect to the physical and chemical controls affecting those.

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Influence of atmospheric circulation on the Namibian upwelling system and the oxygen minimum zone

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The Namibian upwelling region is one of the four Eastern Boundary Upwelling Ecosystems and among the most productive areas in the World Ocean. Here, upwelling indices have been defined in three ways. First, by performing EOF analyses of Sea Surface Temperature (SST) observations HadlSST1 and high resolution ocean model simulations (MPI-OM (STORM) and MOM4), driven by meteorological reanalysis. Second, water vertical velocity of STORM and MOM4. Third, the area between the 13°C isotherm and the coastline was used to indicate the intensity of the upwelling. Correlations with observed atmospheric variables (NCEP reanalysis) over the whole southern Atlantic show which conditions favour upwelling: higher than normal South Atlantic anticyclone, strong and southerly wind/wind stress and pressure and air temperature contrast between ocean and land. Separating the coastal area off southern Africa at Lüderitz (28°S) depicts the differences between the northern and southern Benguela upwelling region. Northern Benguela is characterised by a negative trend in upwelling over the last 60 year, Southern Benguela by a positive one. Furthermore, Northern Benguela upwelling seems to be influenced strongly by the conditions described above while the wind field correlated with the upwelling south of 28°S do not show stronger southerly winds. Additionally, the southern upwelling index of MOM4 is not reflected properly in the corresponding SST field. A reason for this could be an overlaying signal, possibly the advection of warm air from the Indian or the central Atlantic Ocean. The sea level pressure (SLP) gradient between land and ocean of NCEP reanalysis provide a opposite trend to the one postulated by Bakun ([1]). We did not find an indication for a stronger pressure contrast between land and ocean. Correlations with indices of El Niño Southern Oscillation (ENSO), the Antarctic Oscillation (AAO) and an index of the tropical Atlantic SST variability, display a significant relationship between the summer upwelling and ENSO. The SST-based index is also significantly correlated with the tropical Atlantic. In contrast, the upwelling indices of the vertical velocities show significant correlations with the AAO. None of these correlations is strong enough to claim a detection of a main driver of upwelling. Spectral analysis of the vertical velocity index (STORM) shows especially in summer a clear peak at timescales of 5 years. The longer series of HadlSST1 additionally displays decadal variability.

The oxygen minimum zone in the Benguela region has an important impact on the ecosystem and local fisheries. The content of South Atlantic Central Water (SACW) on the shelf drives the intensity and extension of the oxygen minimum zone. Therefore, the water masses with the STORM and MOM4 simulations have been analysed. The STORM simulation does not contain biogeochemistry and the MOM4 simulation is too short. Thus, the analysis of the water masses, their origin and pathways through the South Atlantic will be analysed with a longer MOM simulation and the MPI run of the Climate Model Intercomparison project 5.

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Seasonal Hypoxia of Amurskiy Bay in the Japan Sea

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Based on detailed hydrological and hydrochemical surveys carried out in since 2007 to 2013, Amursky Bay in the north west quadrant of the Japan Sea was found to experience seasonal hypoxia. The primary process of hypoxia formation is a microbiological degradation of the "excess" amount of diatoms under rather low photosynthetic active radiation in bottom layer and weak water dynamics in summer. The microbiological decay of dead diatoms under light deficient conditions intensively consumes dissolved oxygen and produces phosphates, ammonium, silicates, and dissolved inorganic carbon. Existence of a phytoplankton "excess" is caused by phytoplankton bloom resulting from nutrient pulses into Amurskiy Bay. There are two main sources of these nutrients: the waste waters of Vladivostok city and discharge from Razdolnaya River. The river delivers more than two times the amount of nutrients than the waste waters of Vladivostok. It is suggested that the phytoplankton "excess" might be caused by an enhanced supply of nutrients delivered into the surface layer resulting from the increased discharge of the river on a short time scale. Our data suggest that hypoxia is seasonal, with a peak at the end of summer. Water quality monitor (WQM) was deployed at one meter from the bottom of Amurskiy Bay in the hypoxia area. During more than three months WQM provides measurements of conductivity, temperature, pressure and dissolved oxygen each four hour. Obtained data and suggested model permit to estimate average rates of the biochemical oxygen demand and hypoxia formation as 10 and 8 umol/(kg day), accordingly. Our observations documented that hypoxia exist during 93 days. The upwelling of the Japan Sea water in the beginning of the fall season and its advection across the shelf is the primary process by which the hypoxia is destroyed. During the winter, strong vertical mixing due to termohaline convection makes the water column uniform and brings more oxygen into the water along with high primary production under the ice. Thus, during the winter season, the ecosystem of Amursky Bay recovers completely [*Tishchenko et al*., 2013; *Tishchenko*, 2013].

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Modeling Coastal Hypoxia: Lessons Learned and Perspectives for the Future

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Hypoxia (< 2 mg O_2 l^{-1}) in coastal bottom waters has received a significant amount of scientific and policy attention because of rapidly expanding coastal hypoxic zones, different real or perceived ecosystem impacts of hypoxia, and the need to understand the implications of various hypoxia management strategies. Different hypoxia modeling approaches have been increasingly used to complement more traditional observational and experimental studies. Modeling is often necessary because direct observations are severely limited due to the high temporal and spatial variability in hypoxia and the large spatial scales over which hypoxia develops. By relying on real-time, high-frequency observations modeling has profoundly influenced hypoxia monitoring and the ways how environmental data are archived and distributed. We present an overview of hypoxia models of differing complexities that were developed for the Gulf of Mexico hypoxic zone and discuss the lessons learned, future perspectives, and some fundamental problems remaining in hypoxia modeling.

A number of modeling approaches have been used to simulate the severity and areal extent of hypoxia in the northern Gulf of Mexico, and to predict the consequences of management actions ranging from simple statistical models to three-dimensional (3-D), fully coupled hydrodynamic-water quality models. Relatively simple regression models were developed to explain the relationship between variation in the hypoxic zone size in the northern Gulf of Mexico and various forcing functions, such as riverine nutrient loading and wind. The trajectory of improvements in these models has included 2-3 month forecasts for the midsummer extent of hypoxia that were surprisingly accurate ($R^2 \sim 0.8$) given the simplicity of model formulations. Simple simulation box and 1-D models were also developed to explain oxygen dynamics at a single station within the core of the hypoxic zone, or downstream from the Mississippi and Atchafalaya Rivers along the Louisiana-Texas shelf. On the opposite side of the modeling spectrum, several high-resolution 3-D hydrodynamic-water quality models were develop to study the dynamics of hypoxia over the entire inner Louisiana-upper Texas shelf. These models involve different hydrodynamics (e.g., FVCOM, ROMS, IASNFS) and water-quality models (e.g., WASP, NPZD, EPACOM, GoMDOM), thus allowing for model inter-comparison and ensemble forecasting.

Collectively, all models give an unambiguous result that reducing riverine nutrient loading by more than 50% will be necessary to meet the Gulf Hypoxia Action Plan goal of < 5,000 km^2. But, how can this goal be achieved? A new generation of landscape scale models is evaluating different scenarios that can achieve various levels of water quality improvements in the massive Mississippi River watershed. The model results suggest that a non-targeted adoption of the most aggressive conservation scenario can reduce the hypoxic zone to less than 3,000 km^2 at a cost of $5.6 billion annually. By targeting cropland conservation practice investments to the most cost-effective watersheds, the achievement of the Action Plan goal would cost $2.7 billion annually.

Multi-patches distribution of summer hypoxia waters and autumn dissolved oxygen depletion waters off the Changjiang Estuary

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Hypoxia zone at the Changjiang estuary is one of the largest coastal hypoxia zones in the world. Several comprehensive cruises carried out in order to understand the developing of hypoxia waters in summer between 2006 and 2009. The highlights of our results were that we found two patches of dissolved oxygen depletion bottom waters in autumn 2006, one of which was the remain of the previously summer hypoxia waters, and the other one was newly formed in autumn. There was also different formation mechanism for the multi-patches distribution of summer hypoxia, the Changjiang diluted water, stratification, upwelling water and near front bloom were the main reasons for the hypoxia developing. A three end-member (Changjiang River Plume (CRP), Outer-shelf Surface Water (OSW) and Outer-shelf Deep Water (ODW)) mixing model based on quasi-conservative temperature and salinity was adopted to identify the relative contribution of water column algal bloom to the bottom hypoxic water in summer 2009.

Zooplankton ecology in oceanic oxygen minimum zones: Structure, trophic webs, and global change

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Oxygen minimum zones (OMZs) are among the most extreme oceanic habitats, with oxygen concentration in their core depths near the limits of aerobic life. Yet in the surface waters just above those depths are large animal populations, including important fisheries resources. OMZs are expected to expand in geographic and vertical extent with increased global warming, with many potential biological and economic consequences.

Through my previous participation in the Joint Global Ocean Flux Study (JGOFS) Arabian Sea Program, and over two decades working in the Eastern Tropical North Pacific (ETNP), we have helped elucidate broad principles structuring zooplankton distributions in these extremely hypoxic environments. It has been known for many years that resident zooplankton biomass and abundance in the OMZ core (depth zone of lowest oxygen) are much reduced compared to more oxygenated regions, although substantial diel vertical migration occurs several hundred meters into very hypoxic water. What is not as well appreciated is that both the upper and lower oxyclines (oxygen gradients) at the upper and lower OMZ core boundaries are locations of strong zooplankton and fish layering. The layer associated with the upper boundary of the oceanic OMZ (within the upper 100 m), with its strong oxygen and temperature gradients, has been well documented. However, another less well known zooplankton and fish layer exists at the lower oxycline of the OMZ at mesopelagic depths (600-800 m). This represents an order of magnitude increase in zooplankton biomass over a small depth interval and occurs at a very precise and very low oxygen concentration. The animals in this layer (copepods, fish, shrimp) are important in the processing of sinking material as part of the biological pump and also in food webs of the deeper ocean. The lower oxycline zooplankton layer also contributes to benthic-pelagic coupling on continental slopes and seamounts, serving as a potential food source for benthic animals where the OMZ intersects the sea floor.

A spatial comparison between locations with different OMZ thickness in the ETNP suggested that the oxycline layers would track oxygen concentration and shift depth as a result of future OMZ expansion, potentially altering zooplankton distributions and trophic interactions (Wishner et al., 2013). For example, as the upper oxycline boundary moves vertically over short or longterm time intervals, zooplankton and fish layers will change depth also. These layers are the prey of larger commercial fish, and the behavior of those fish may be affected. At the lower oxycline, zooplankton layers may be forced deeper below an expanded OMZ, with potential impacts on vertical fluxes and both pelagic and benthic food webs and life history strategies. This talk will highlight comparative features of the Arabian Sea and ETNP zooplankton OMZ communities and suggest how scientists and policymakers might evaluate and plan for possible longterm consequences of changing OMZ ecosystems.

Influence of wind and river discharge to the hypoxia in a shallow bay

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An existing calibrated eutrophication model, as described in Xia et al. [2011a], was used to simulate the bottom hypoxia of Perdido Bay in response to the changing local wind forcing and river discharge variation. The response of nutrient dynamics and algae distribution to these physical forcing was also given a discussion to fully understand the hypoxia dynamics.

Based on the calibrated simulation, it was found that surface nutrients peaked in the upper bay and the nutrient gradient was reverse with the increasing of salinity; the algae concentration above 0.5 mg C/L was represented by a long band; bottom hypoxic waters were transported eastward and northward, which was consistent with the predominant wind force during July 1994.

Compared to no wind case, southerly (onshore) and westerly upwelling favorably winds with 3 m/s or less inhibits the nutrient transport, and easterly downwelling favorably winds and northerly (offshore) winds favor the nutrient transport. High algae zones stretched to the lower bay and the coastal ocean under the offshore and downwelling winds, while onshore and upwelling winds push these high algae area back to the upper and middle bay. Onshore and upwelling winds are most effective at inducing significantly broader and thicker hypoxic/anoxic conditions than that of offshore and downwelling winds. The increasing wind speed could limit the nutrient-rich freshwater to the upper bay and have a similar effect to the algae distribution; a 5m/s southerly wind or above was sufficient make nutrients vertical distribution very uniform and could significantly reduce areal coverage of hypoxia/anoxia.

Increasing river discharge drove the nutrient distribution, high algae waters down to bay mouth. The freshwater could reach bottom under a high volume river discharge (100 cms or m3/s) and then the severity of anoxia and hypoxia were reduced, while the increasing river discharge has little effect to the bottom hypoxia and nutrient variation at the deep-water part.

Using a calibrated 3-d model, this work demonstrated the importance of physical forcing to the hypoxia and nutrient dynamics at this bay and similar waterbody elsewhere.

Key Words: Perdido Bay, nutrient transport, algae, hypoxia, wind, river discharge

Modeling Bottom Boundary Layer biogeochemistry changes forced by episodic anoxia

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Interaction between the seawater and the sediments plays an important role in the global biogeochemical cycling. The benthic fluxes of chemical elements affect directly the acidification characteristics (i.e. pH and carbonate saturation) and also determine the functionality of the benthic and pelagic ecosystems. In many regions redox state of the near bottom layer can oscillate in connection with supply of organic matter (OM), physical regime and coastal discharge influence. Climate Change affects oxygen depletion and leads to spreading of the bottom areas with permanent or temporal hypoxic and anoxic conditions. The goal of this work was to elaborate a model capable to describe the basic biogeochemical processes occurring at the sediment-water interface and apply it for analysis of changes occurring due to seasonal oscillations of redox conditions.

We use a 1-dimensional C-N-P-Si-O-S-Mn-Fe vertical transport-reaction Bottom RedOx Model (BROM) describing both the sediments and bottom boundary layers (BBL) coupled with biogeochemical block simulating changeable redox conditions, and the carbonate system processes block (Yakushev, Protsenko, 2014, submitted). In BROM we parameterize OM formation and decay, reduction and oxidation of species of nitrogen, sulfur, manganese, iron, and the transformation of phosphorus, silicate and carbon species. BROM includes a simplified ecological model with phytoplankton, heterotrophic organisms, aerobic autotrophic and heterotrophic bacteria, anaerobic autotrophic and heterotrophic bacteria as it was described in (Yakushev et al., 2007). Carbonate system equilibration is modeled using standard approaches, the components of total alkalinity significant in suboxic and anoxic conditions (i.e. forms of S, N, Mn, Fe) were taken into account. The model's domain includes the water column, the BBL and the upper layer of the sediments. To parameterize the water column turbulence we used results of simulation of turbulent mixing performed with GOTM (Bolding et al., 2001). In the limits of the BBL mixing was assumed to be constant. In the sediments molecular diffusion and bioirrigation/bioturbation were parameterized.

The model simulated basic features of the seasonality ecosystem functioning, i.e. growth of concentrations of phototrophic organisms in summer, production of excessive OM and summer development of heterotrophic organisms and heterotrophic bacteria. Hydrophysical block of the model reproduces intensive vertical mixing in winter and formation of a pycnocline in summer. The model shows a possibility of periodic replacement of oxic conditions with anoxic, that leads to changes in the distributions of the parameters and their fluxes. The seasonality in production and destruction of OM together with the mixing seasonality lead to a vertical displacement of the oxic/anoxic interface from the sediments in winter to the water in summer. This affects distribution of sulfur species, nutrients (N and P), redox metals (Mn and Fe) and carbonate system parameters. Bacteria play a significant role in the fate of OM due to chemosynthesis (autotrophs) and consumption of DOM (heterotrophs). Model can be used for analyzing and interpreting data on sediment-water exchange and estimating consequences of forcing (i.e. connected with eutophication, climate change, CCS leakages) as well as for boundary conditions parameterization for 3D models.

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On definitions of redox conditions using biochemical thresholds

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The redox conditions of natural waters are an important element of water quality legislation, e.g. in the Water Framework Directive (European Commission, 2000). There are several terms that are in use to describe the changes in redox condition, connected with the oxygen depletion i.e. oxic, oxygen deficient, hypoxic, suboxic, anoxic. These terms reflect the associated processes and usually are formally characterized by a content of dissolved oxygen (DO), the quintessential oxidizer. The boundaries in terms of oxygen concentrations are rather arbitrary and therefore there are several problems to the currently used definitions. Biochemical thresholds provide less arbitrary boundaries (Yakushev, Newton, 2013). Normoxic or oxic conditions correspond to high concentrations of oxygen (greater than 80% saturation). The term "oxygen-deficient" is used for a wide range of low oxygen concentrations, from below 3 ppm (or 80% saturation) and characterize waters that certain organisms avoid (Renaud, 1986). Boundary between oxic and hypoxic conditions corresponds to the threshold of tolerance, stress responses and morbidity of pelagic and benthic animals that is usually in the range of 1-4 mg O2 L-1 (e.g. Diaz 2001, Vaquer-Sunyer and Duarte 2008). A formal boundary is set at 2 mg O2 L-1 (63 µM O2 , i.e. (CENR, 2000)) or 2 ml O2 L-1 (89 µM O2 , i.e. (Diaz and Rozenberg, 2008). The boundary between hypoxic and suboxic conditions is also arbitrary and there has been opposition to the use of the term "suboxic" once oxygen might not be longer present (Canfield and Thamdrup, 2009). However, we need a term that corresponds to the biochemical threshold after which the dominant electron acceptors are oxidized ions of N (Nitrate, Nitrite) or oxidized species of metals (Mn(IV), Fe(III)), whereas DO becomes an auxiliary oxidant. In the Black Sea for example, the reported suboxic values range from 4.5 μM O2 (Lam et al. 2007) to 15 μM O2 (Zubkov et al. 1992). A formal value of 10 μM proposed by Murray (1991) is more often used, but we suppose that the boundary of 15 μM is better since it corresponds to the point where DO vertical gradient abruptly decreases and becomes equal to that of nitrate (Yakushev et al., 2006). The suboxic layer maybe further divided into "suboxidized" layer, where DO is present, and "subreduced" layer, where DO is absent, Stunzhas (2005).. The subreduced layer, where there is no longer any DO but H2S is not yet present, should correspond to the conditions necessary for the onset of processes such as anammox (Kuypers et al., 2003) or formation of Mn(III) (Trouwborst et al., 2006), that are inhibited by both oxygen and hydrogen sulphide. Once the oxidized species of nitrogen, manganese or iron and DO are completely depleted, OM microbial decomposition uses sulphate as the next electron acceptor for oxidation. This is the appropriate threshold for the term anoxic.

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