Oxygen depletion events in the European Seas: observations and modelling

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Plan

- Some examples
- Redox layer structure and related definitions
- Modeling
Oxygen depletion zones form when there is an imbalance between the supply of organic matter (OM) and the supply of dissolved oxygen (DO) for its decomposition.

The occurrence of oxygen-depleted and anoxic water depends on the combined influence of eutrophication (organic matter and nutrient loads) and hydrodynamics (intensity of mixing and water renewal).

Common feature in numerous areas in coastal and marginal seas.
Black Sea

Anoxic conditions in the water column
Anoxic conditions in the water column
Oslofjord

Stasjoner i fjorden

den 15-4-2008
Oxygen equivalent (ml/l) in Inner Oslofjord, Bunnefjord basin (Station Ep1), 1973-2011
The Sea of Azov, July 2001

Catastrophic anoxia in 1937, 1946, 1987
Oxygen depletion vs. ventilation

- Permanent anoxic (Black Sea)
- Dominant anoxic (Fjords, Gotland Deep)
- Seasonally anoxic (Elefsis Bay)
- Sporadic anoxic (Sea of Azov)

Coastal oxygen depleted spots are characterized by:

Intensive inetrannual variability caused by:
1. Climatic «physical» forcing (restricted mixing due to warmer winters and increased precipitation)
2. Nutrient supply («anthropogenic» eutrophication)

«Physical» forcing dominates.
Redox interfaces structure

Black Sea

Turbidity layer
Common features of different Seas redox layer structure are formed with the similar mechanism.
Redox conditions

(O₂ ~ 75 µM)

(Oxic mineralization of OM)

(O₂ ~ 0 µM)

(H₂S > 0 µM)

(Mn(III) ~ 15 µM)

(Sulfate reduction)

(H₂S ~ 0 µM)

(O₂ ~ 0 µM)

(Oxic mineralization of OM)

(Mn(II) ~ 0 µM)

(Denitrification, mineralization of OM with Me)

(Mn(III) ~ 0 µM)

(Sulfate reduction)

(Mn(II) ~ 0 µM)

(NH₄ ~ 0 µM)

(Yakushev, Newton, 2012)
Redox conditions

OXIC
$O_2 \approx 75 \mu M$

HYPOXIC
$O_2 \approx 15 \mu M$

SUBOXIC
$O_2 \approx 0 \mu M$

ANOXIC
$H_2S > 0 \mu M$

Oxic mineralization of OM

HYPOXIC mineralization of OM

SUBOXIC

Denitrification,

Mineralization of OM with Me

Sulfatereduction

(Yakushev, Newton, 2012)
<table>
<thead>
<tr>
<th>Oxygen conditions</th>
<th>Oxic</th>
<th>Hypoxic</th>
<th>Suboxic</th>
<th>Anoxic</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO concentration</td>
<td>&gt;75 μM</td>
<td>15-75 μM</td>
<td>0-15 μM</td>
<td>0 μM</td>
</tr>
<tr>
<td>H₂S concentration</td>
<td></td>
<td></td>
<td></td>
<td>&gt;0 μM</td>
</tr>
</tbody>
</table>

- **Oxic** conditions:
  - Oxic mineralization of OM
  - Nitrification

- **Hypoxic** conditions:
  - Oxidation with DO of reduced species of S, Mn, Fe, C, N
  - Denitrification
  - Mineralization of OM with metals
  - Anammox
  - Accumulation of Mn(III)
  - Reduction of oxidized species of S, Mn, Fe, C
  - Sulphate reduction
  - Methanogenesis
  - Increased mortality
  - Synthesis of OM

- **Suboxic** conditions (suboxidized, subreduced):
  - Oxidation with DO of reduced species of S, Mn, Fe, C, N
  - Denitrification
  - Mineralization of OM with metals
  - Anammox
  - Accumulation of Mn(III)
  - Reduction of oxidized species of S, Mn, Fe, C
  - Sulphate reduction
  - Methanogenesis
  - Increased mortality
  - Synthesis of OM

- **Anoxic** conditions:
  - Sulphate reduction
  - Methanogenesis
  - Increased mortality
  - Synthesis of OM
Requirements for model of O2-def. and anoxic conditions

Several elements

Parameterization of processes:

- Mineralization of OM (oxic, nitrate reduction, sulfate reduction)
- Reactions between oxidized and reduced chemical species
- “Ecological model” +Chemosynthesis

Tasks to be solved:

- Analysis of the field and experimental data
- Reaction on forcing (Forecast)
Goal:

to study the process of formation of anoxic \((O_2=0)\) conditions

\[ Am = K_{Am} [\text{Norg}] \]  
– ammonification

\[ Nf1 = K_{Nf1} [\text{NH}_4] f_{Nf}(O_2) \]  
– nitrification 1

\[ Nf2 = K_{Nf2} [\text{NO}_2] f_{Nf}(O_2) \]  
– nitrification 2

\[ Nr1 = K_{Nr1} [\text{NO}_3] f_{Nr}(O_2) \]  
– nitratereduction 1

\[ Nr2 = K_{Nr2} [\text{NO}_2] f_{Nr}(O_2) \]  
– nitratereduction 2

\[ Dn = K_{Dn} [\text{NO}_2] f_{Dn}(O_2) \]  
– denitrification

Sources:

\[ R_{\text{Norg}} = -Am \]

\[ R_{\text{NH4}} = Am - Nf1 + Nr2 \]

\[ R_{\text{NO2}} = Nf1 - Nf2 + Nr1 \]

\[ R_{\text{NO3}} = Nf2 - Nr1 - Dn \]

\[ R_{O2} = -m_{12} Am - m_{10} Nf1 - m_{11} Nf2 + m_{21} Nr1 + m_{21} Nr2 \]
Calculations

- Anoxic conditions due to OM flux and restricted aeration of deep waters.

Observations

- Necessity of parameterization of cycles of several elements

(Yakushev, 1992)
ROLM biogeochemical model

Phy

Zoo

PON

DON

Bacteria

Ox.Aut
Anox.Aut
Ox.Het
Anox.Het

NO$_3$

NO$_2$

NH$_4$

O$_2$

SO$_4$

S$_2$O$_3$

S$^0$

H$_2$S

N$_2$
Application of the model: vertical structure (analysis)

\[ \text{Mn(II)} \rightarrow \text{O}_2 \rightarrow \text{Mn(III)+Mn(IV)} \rightarrow \text{H}_2\text{S} \]

- \( \text{O}_2 \) 250-400 \( \mu \text{M} \)
  4-5 \( \mu \text{M m}^{-1} \)
- \( \text{Mn(II)} \) 25 \( \mu \text{M} \)
  3-4 \( \mu \text{M m}^{-1} \)
- \( \text{Mn(III)+Mn(IV)} \) 0.1-1.5 \( \mu \text{M} \)
- \( \text{H}_2\text{S} \) 300 \( \mu \text{M} \)
  3-4 \( \mu \text{M m}^{-1} \)
Application of the model: vertical structure (analysis)

**O₂**
- 250-400 μM
- 4-5 μM m⁻¹

**Mn(II)**
- 25 μM
- 3-4 μM m⁻¹

**Mn(III)+Mn(IV)**
- 300 μM
- 3-4 μM m⁻¹

**H₂S**
- 0.1-1.5 μM

**Application of the model:**
- Fe(III), Fe(II), Mn-part, Mn-bou, Mn-diss, O₂, H₂S
Central Black Sea, 2009

Coastal Black Sea, 2006

**Application of the model: vertical structure (analysis)**

- **O$_2$**: 250-400 μM, 4-5 μM m$^{-1}$
- **Mn(II)**: 25 μM, 3-4 μM m$^{-1}$
- **Mn(III)+Mn(IV)**: 300 μM, 3-4 μM m$^{-1}$
- **H$_2$S**: 0.1-1.5 μM

**Central Black Sea, 2009**

**Coastal Black Sea, 2006**
Application of the model: reaction on forcing (forecast)

Modeling of the flushing events in the Gotland Deep

- T,S, weather conditions
- ROLM
- Parameterized biogeochemical properties of the intrusions

GOTM

- T,S, light
- Turbulence, sinking

Integration

Biogeochemical changes

ROLM

GETM (General Estuarian Transport Model),
http://www.bolding-burchard.com/html(GETM.htm)
Observations in 1992-1993 (DB "ODIN"): T, O₂, H₂S, S, PO₄
Parameterization of intrusions:

\[ Q_{c_i}^{\text{Inf}} = \tau_{\text{Inf}}^{-1} (C_{\text{Inf},i} - C_i)\text{Inf}(t,h) \]

\[ \tau_{\text{Inf}}^{-1} = 6000 \text{ s}, \text{ is the relaxation time scale} \]

\[ \text{Inf}(t,h) = \sin \left( \frac{t_i - t_{\text{start}}}{t_{\text{end}} - t_{\text{start}}} \pi \right) \sin \left( \frac{h_i - h_{\text{start}}}{h_{\text{end}} - h_{\text{start}}} \pi \right) \] is the dependence on \( t \) and \( h \)
Intensive Mn precipitation during the inflow (Pollehne, p.c. 2007)

Formation of the Mn-rich sediment layers after the inflows (Heiser et al., 2001)

Denitrification/anammox change in 1 year after an inflow (Hannig et al., 2007)

> 2 years required for the reestablishment of the stable redox interface structure (100 m thick with $K_z \sim 10^{-5} \text{ m}^2\text{s}^{-1}$)
Conclusions:

- Models are oversimplifications of real system, sometimes overemphasizing particular characteristics, as in a caricature. Nevertheless, modelling seems to be appropriate for use as a diagnostic tool. Models can be used to test the hypothesis of which processes are responsible for the observed distributions.

- Periods of oxygenated inflows are characterized by sudden increase of particulate Mn(IV) and vanishing of the total Mn from the water column.

- Periods of reestablishing of the anoxic conditions are characterized by inbalanced redox structure with absence of Mn(IV) maximum between $O_2$ and $H_2S$.

- Application of the models (2D, 3D) can be useful for analyzing and prediction of the reactions of the oxygen-deficient and anoxic systems on the possible changes of climatic (mixing events) and anthropogenic factors (eutrophication).
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