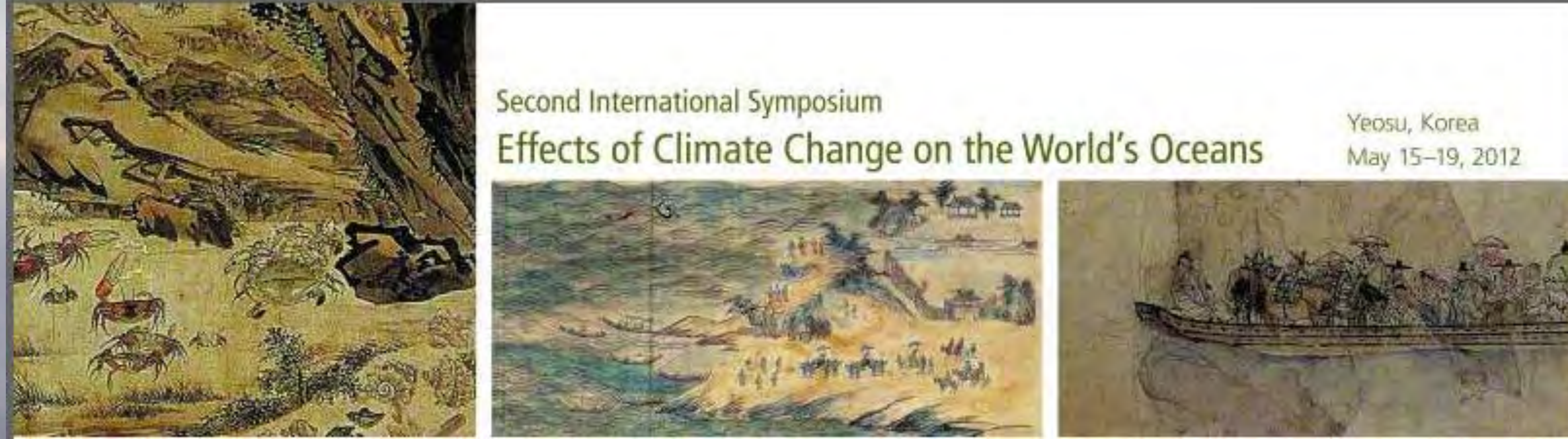


Oxygen depletion events in the European Seas: observations and modelling

Yakushev E.V.

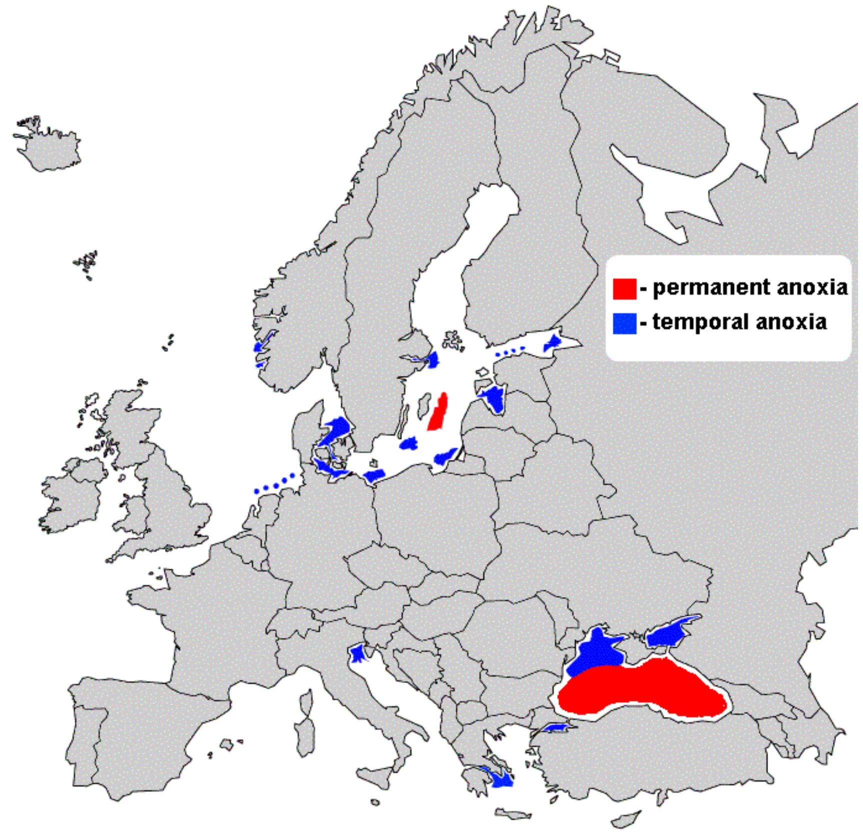
Norwegian Institute for Water Research, Oslo, Norway
Shirshov Institute of Oceanology RAS Southern Branch, Gelendzhik, Russia

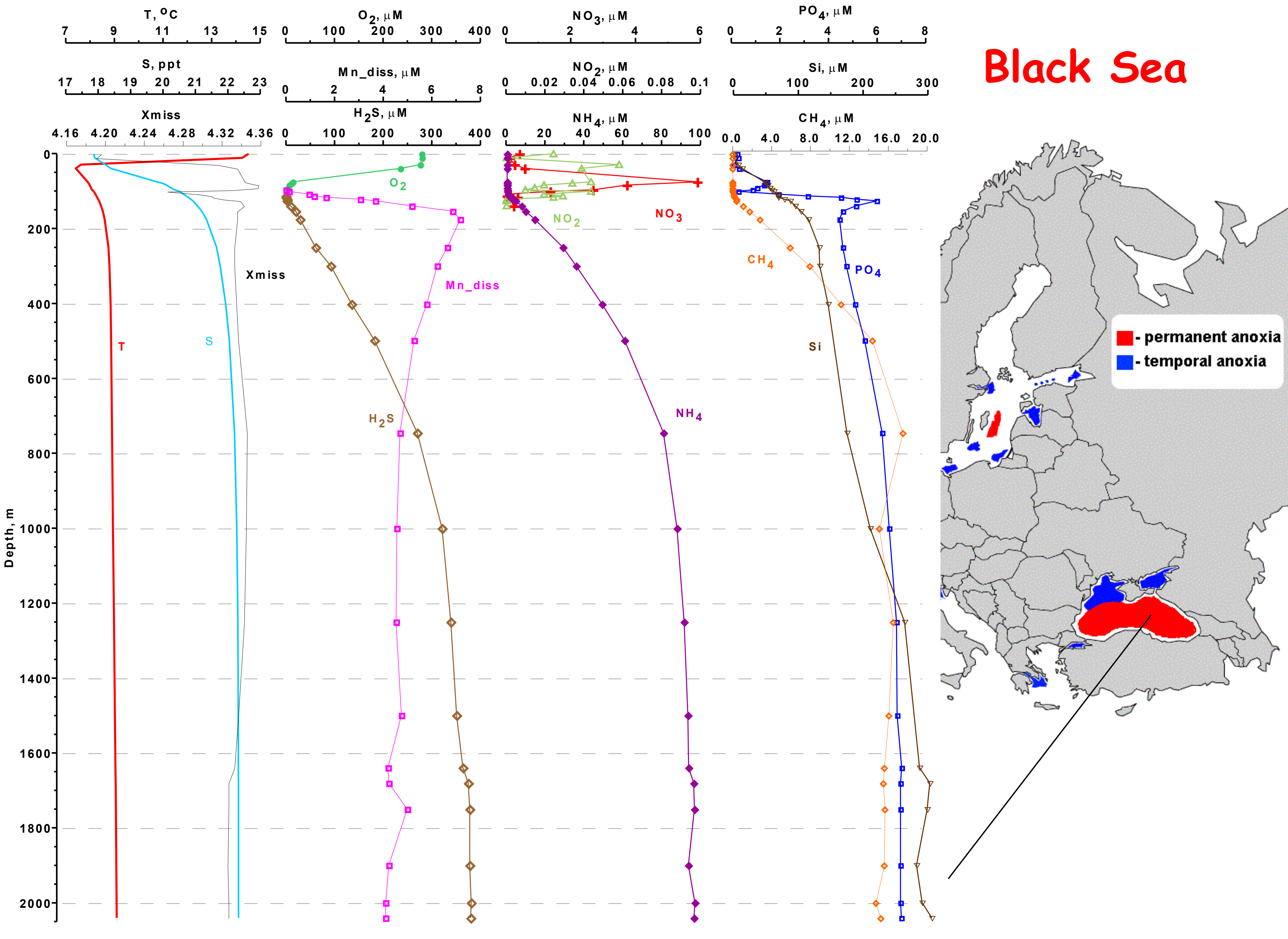
Plan

- Some examples
- Redox layer structure and related definitions
- Modeling

Oxygen depletion

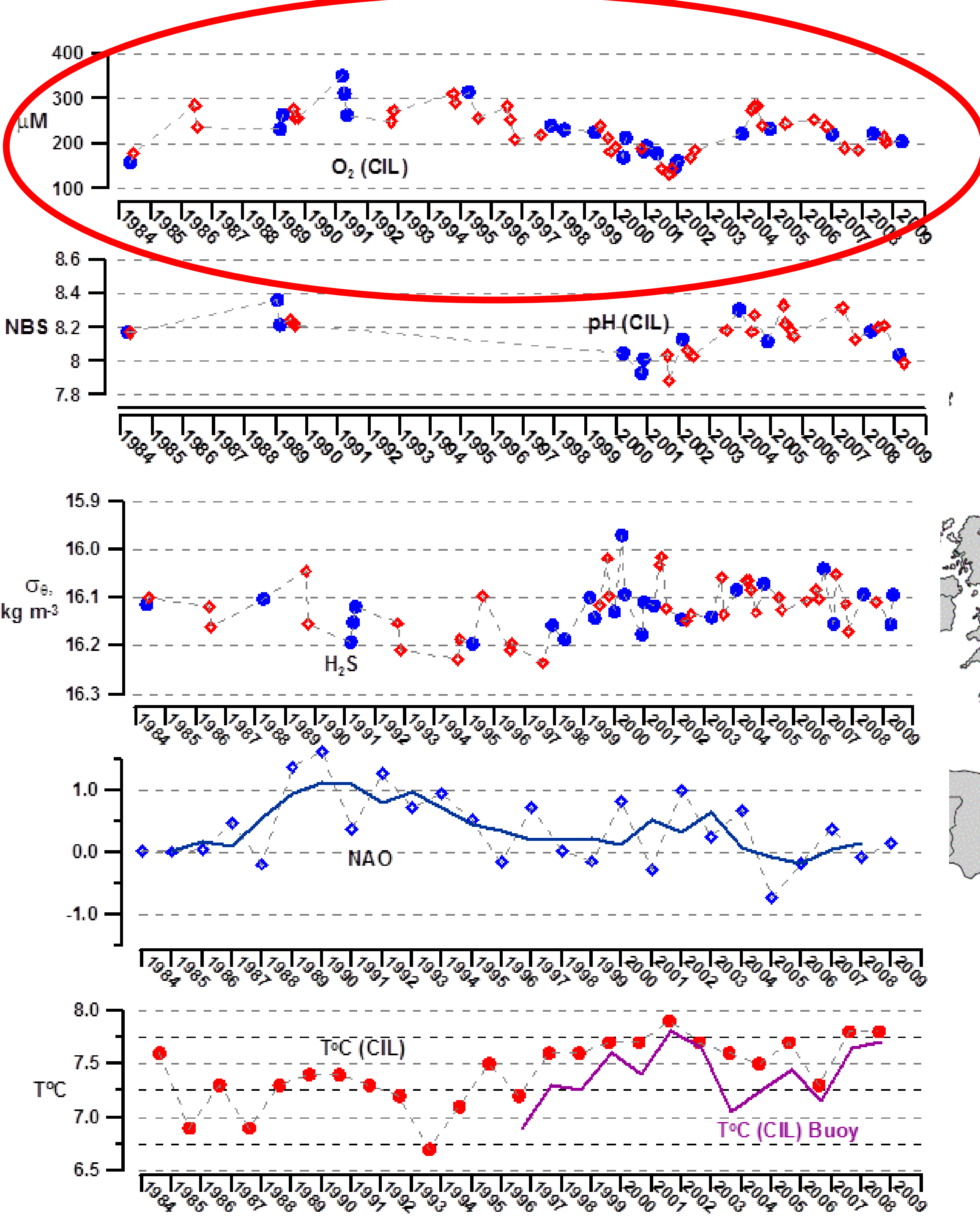
- Oxygen depletion zones form when there is an imbalance between the supply of organic matter (OM) and the supply of dissolved oxygen (DO) for its decomposition
- The occurrence of oxygen-depleted and anoxic water depends on the combined influence of eutrophication (organic matter and nutrient loads) and hydrodynamics (intensity of mixing and water renewal).
- Common feature in numerous areas in coastal and marginal seas



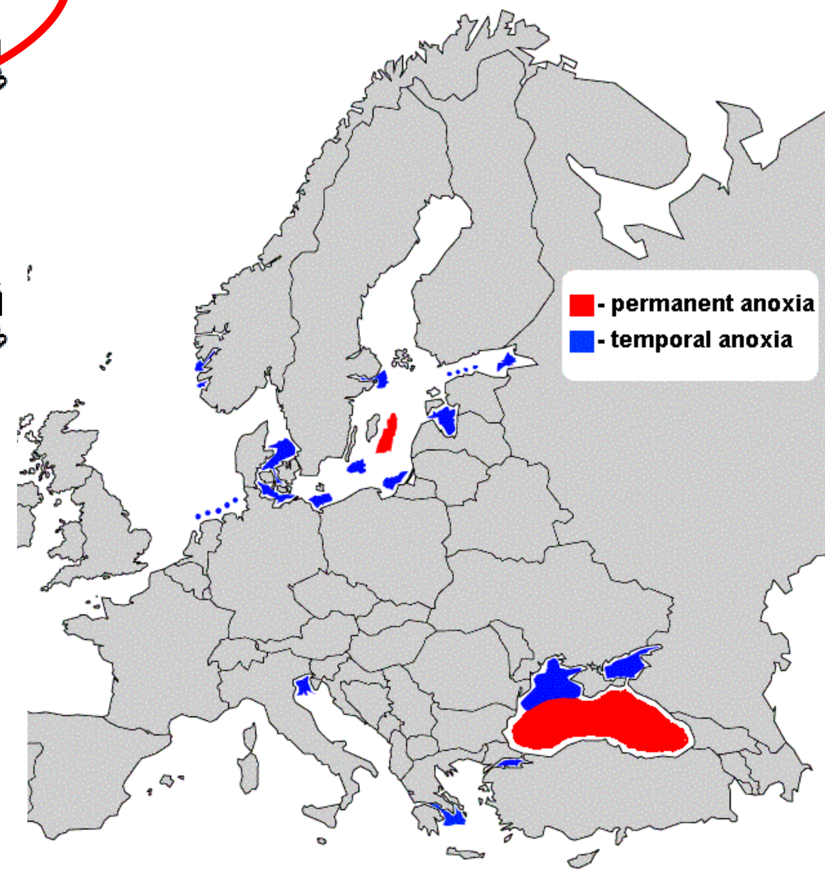


R/V "Akvanavt", st # 231, Lat: 42.951, Lon: 39.114, 03.12.2000

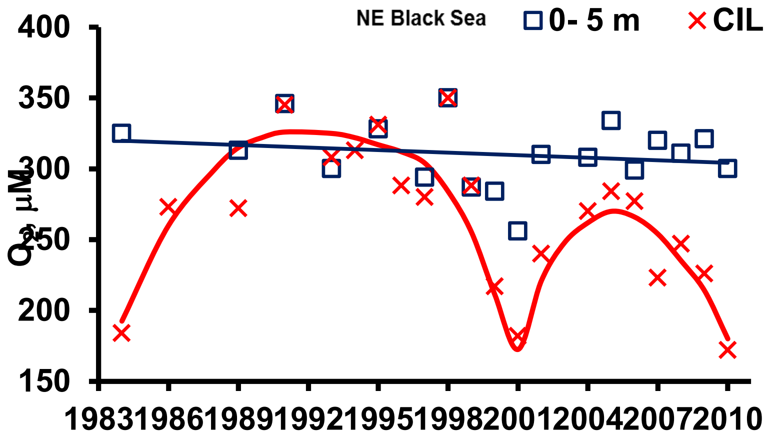
Black Sea

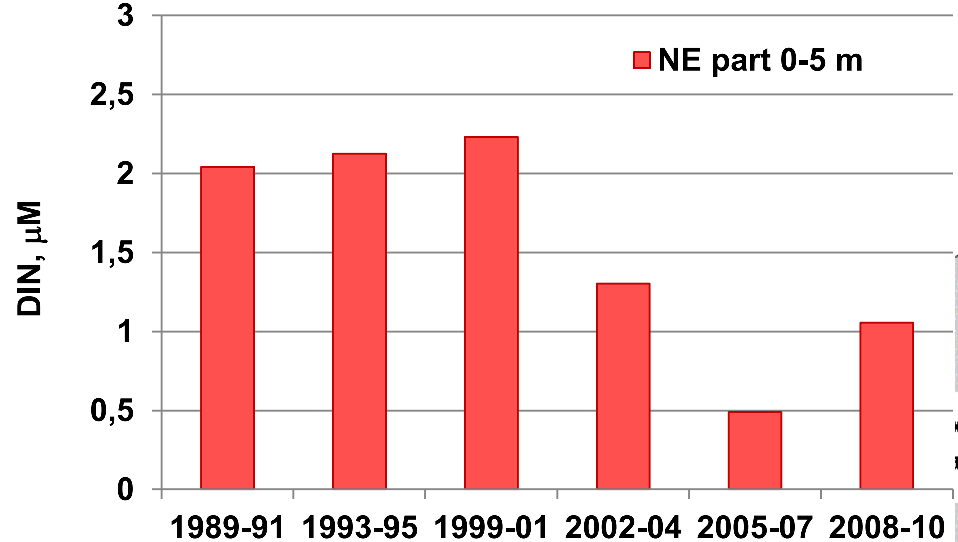


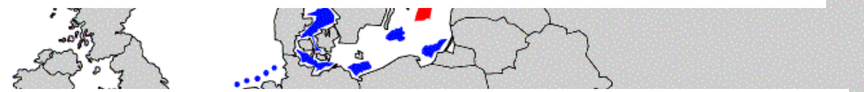
400
300
µM
200
100
O₂ (CIL)
8.6
8.4
NBS 8.2
8
7.8
pH (CIL)
15.9
16.0
σθ, kg m-3
16.1
16.2
16.3
H₂S
1.0
0.0
-1.0
NAO
8.0
7.5
T°C
7.0
6.5
T°C (CIL)
T°C (CIL) Buoy
1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009

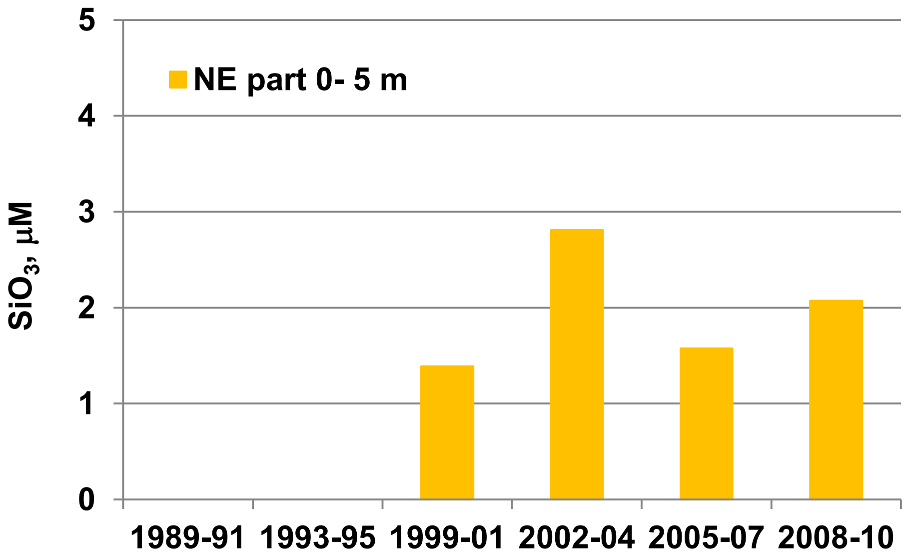


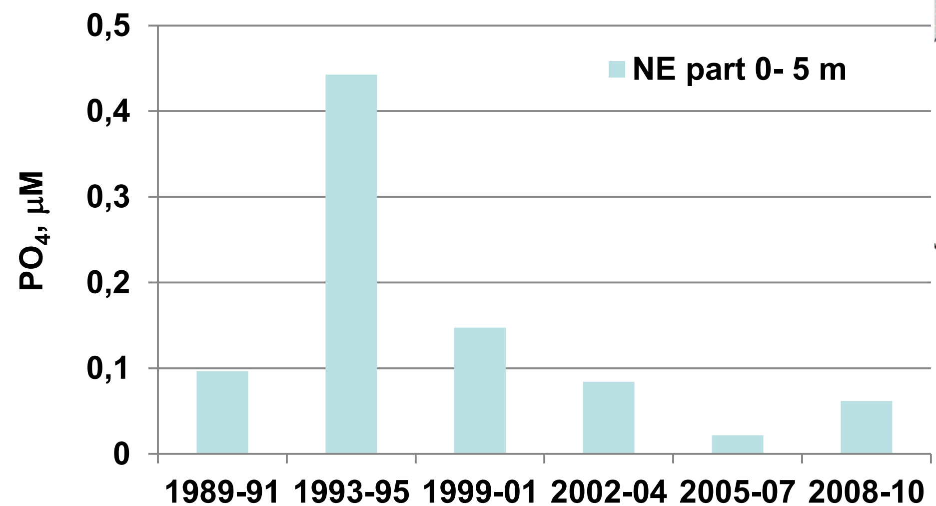
- permanent anoxia
- temporal anoxia


NE Black Sea
0- 5 m
CIL
O_2, µM
400
350
300
250
200
150
1983 1986 1989 1992 1995 1998 2001 2004 2007 2010

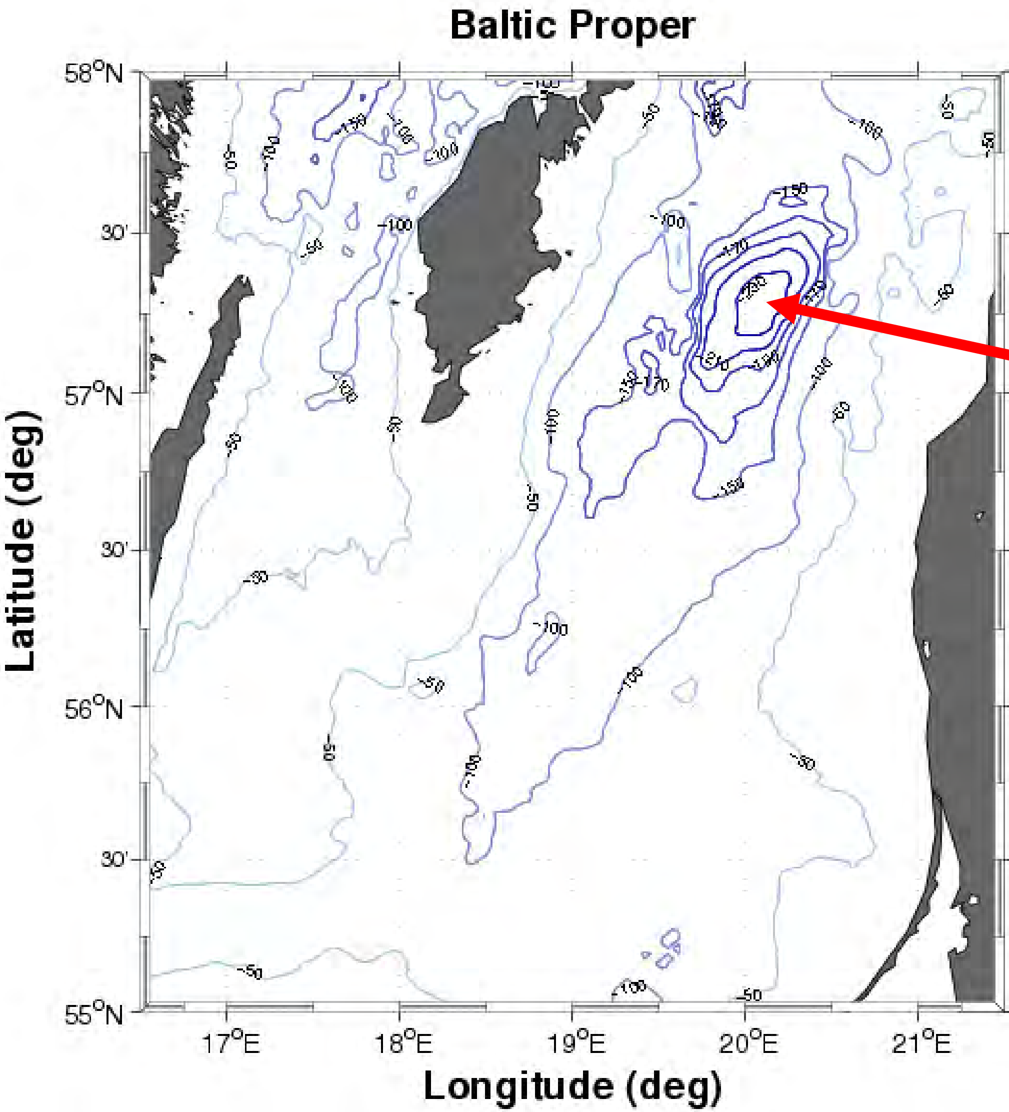

NE part 0-5 m
DIN, µM
3
2,5
2
1,5
1
0,5
0
1989-91 1993-95 1999-01 2002-04 2005-07 2008-10

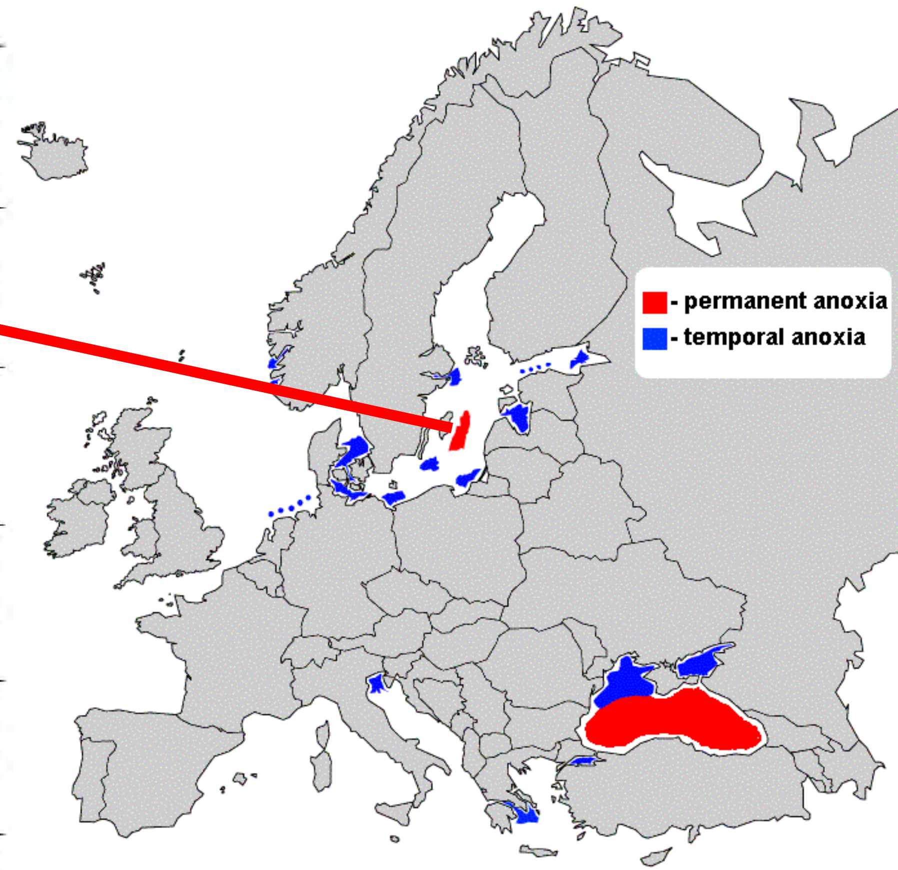



NE part 0- 5 m
SiO_3, µM
5
4
3
2
1
0
1989-91 1993-95 1999-01 2002-04 2005-07 2008-10

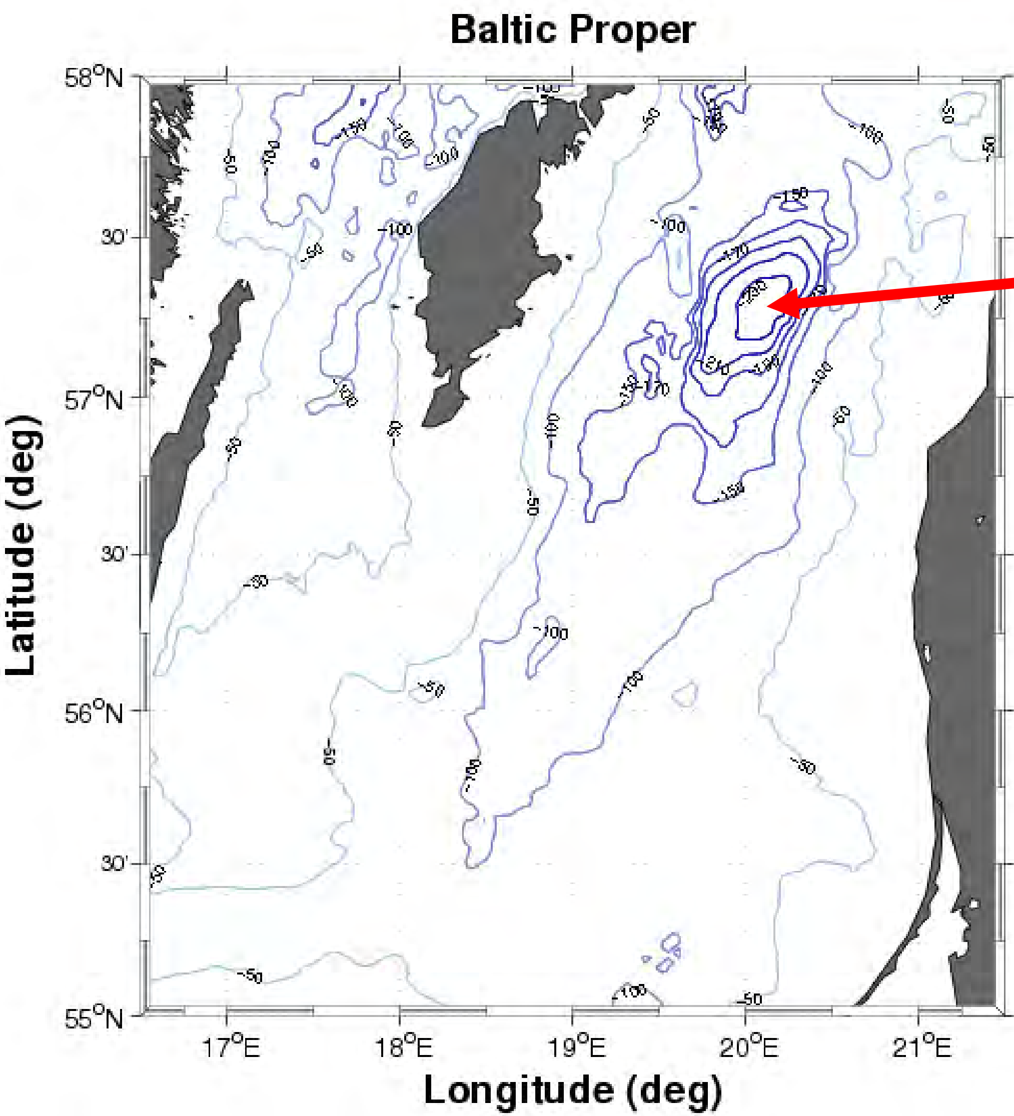

NE part 0- 5 m
PO_4, µM
0,5
0,4
0,3
0,2
0,1
0
1989-91 1993-95 1999-01 2002-04 2005-07 2008-10

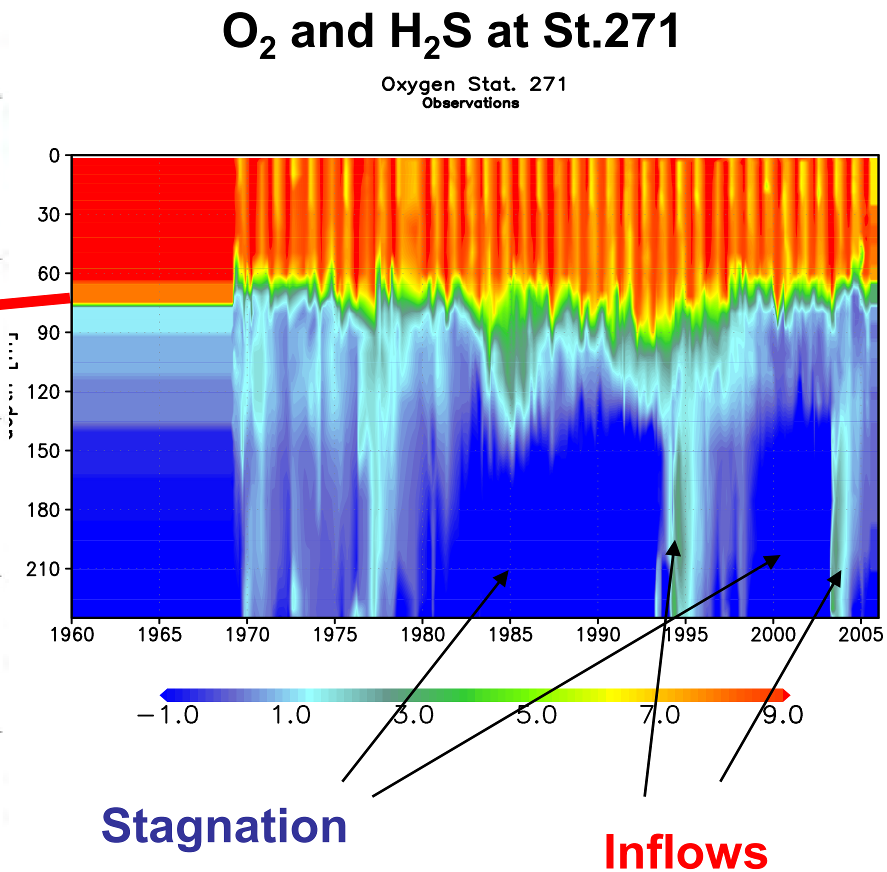
Anoxic conditions in the water column



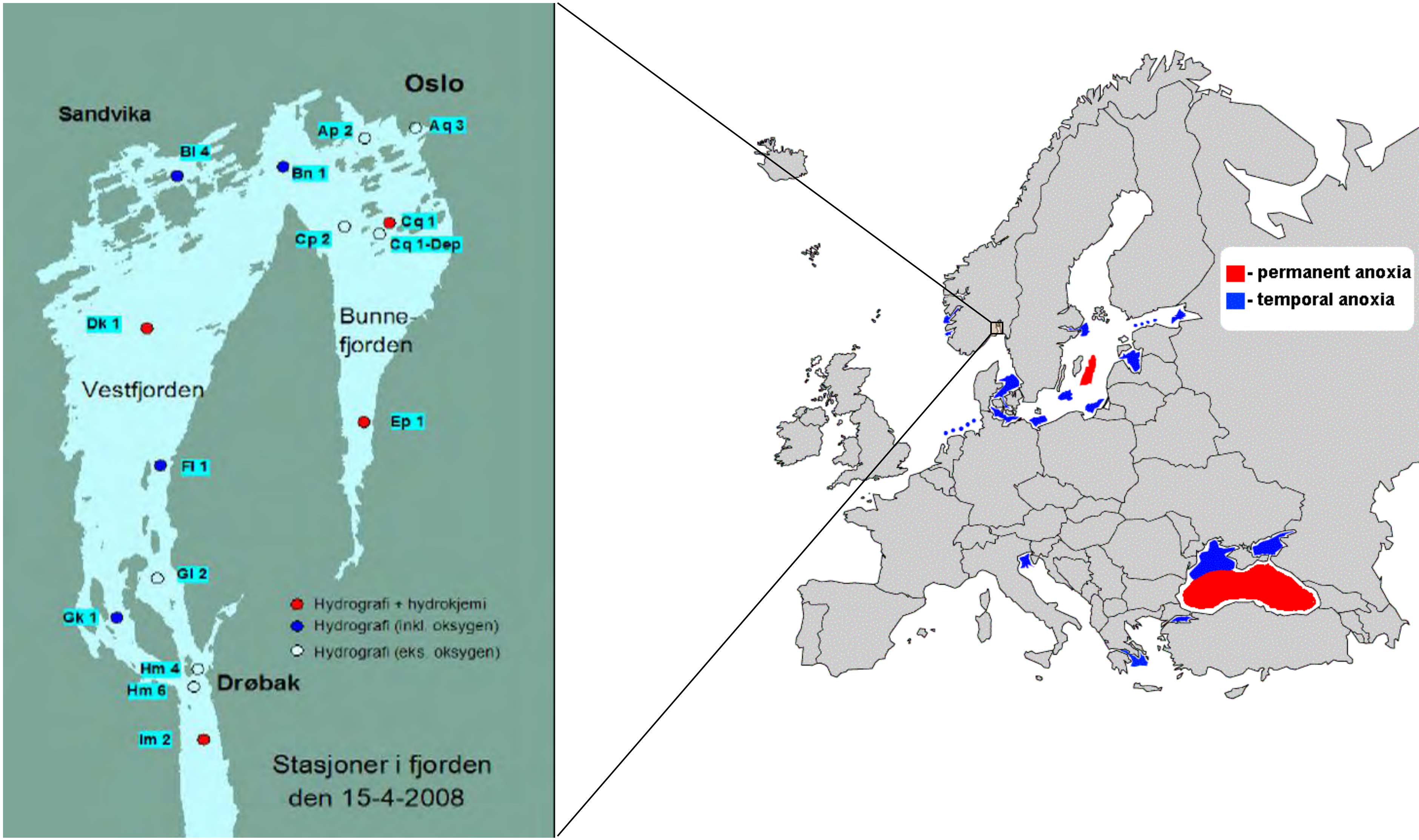


Gotland Deep

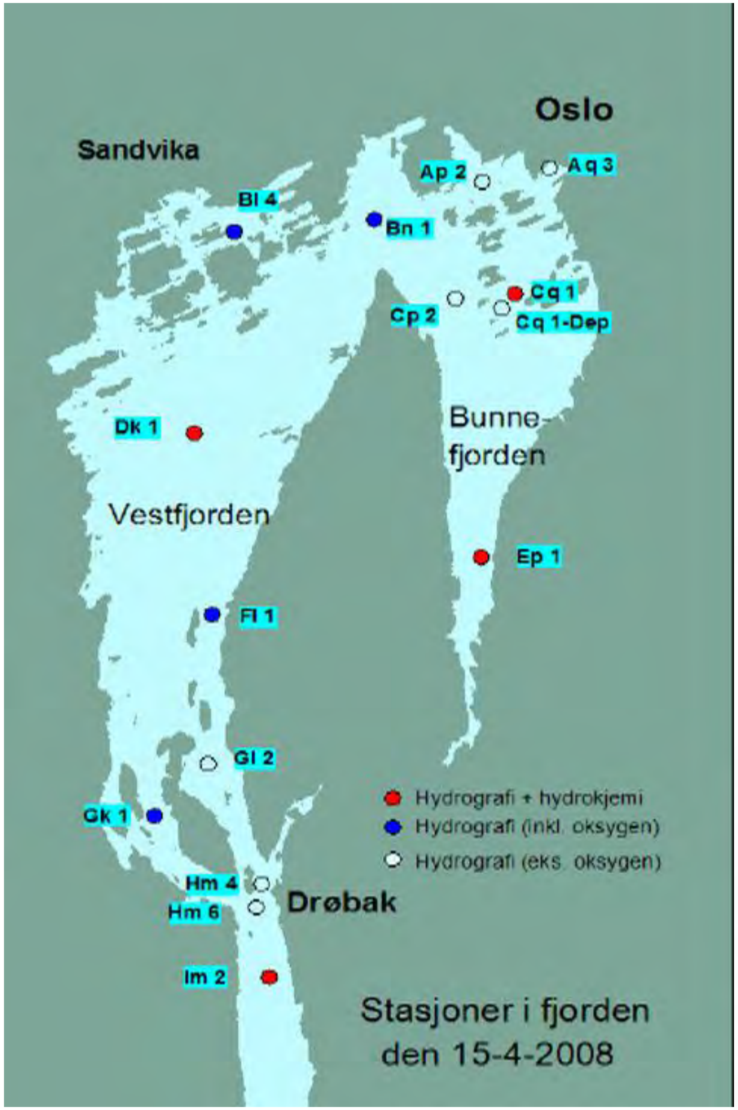




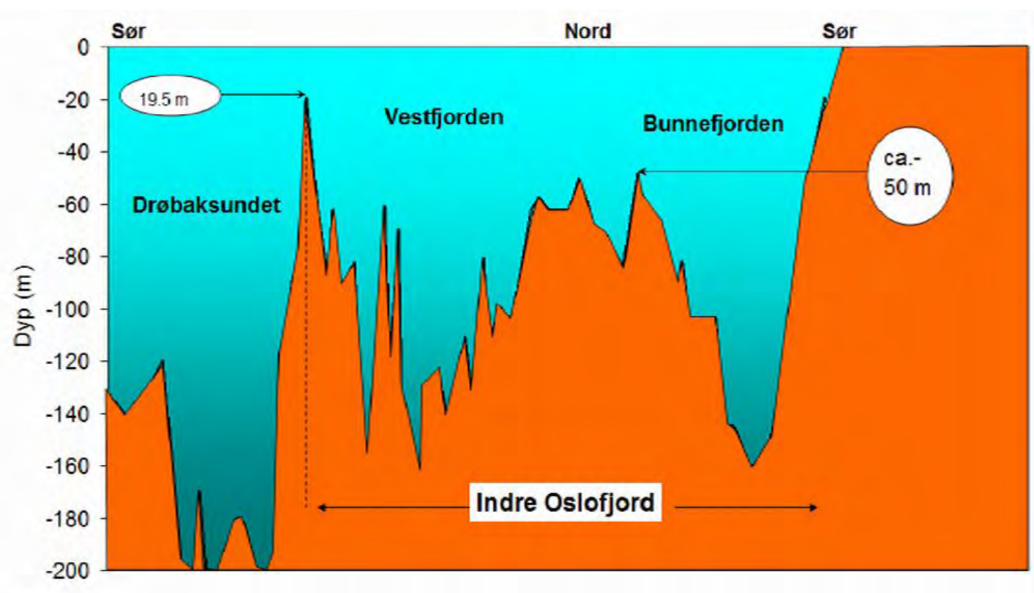
Anoxic conditions in the water column



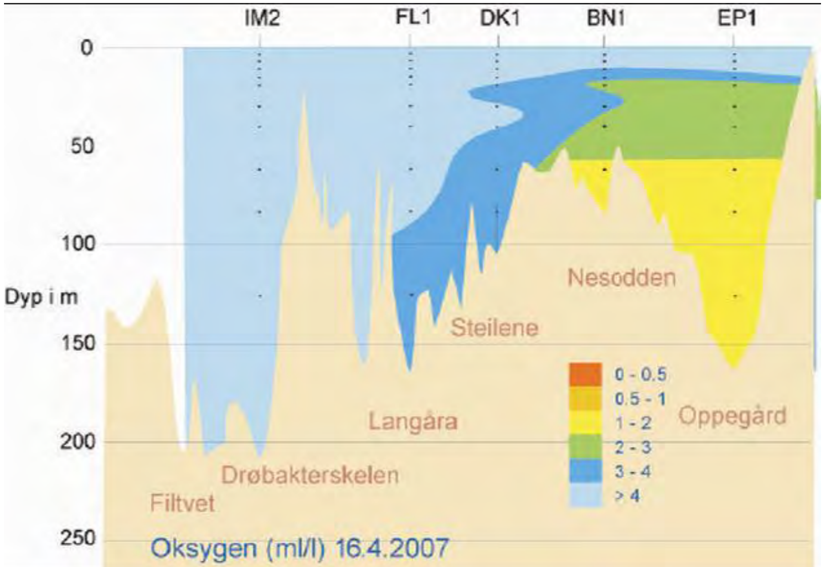
Oslofjord

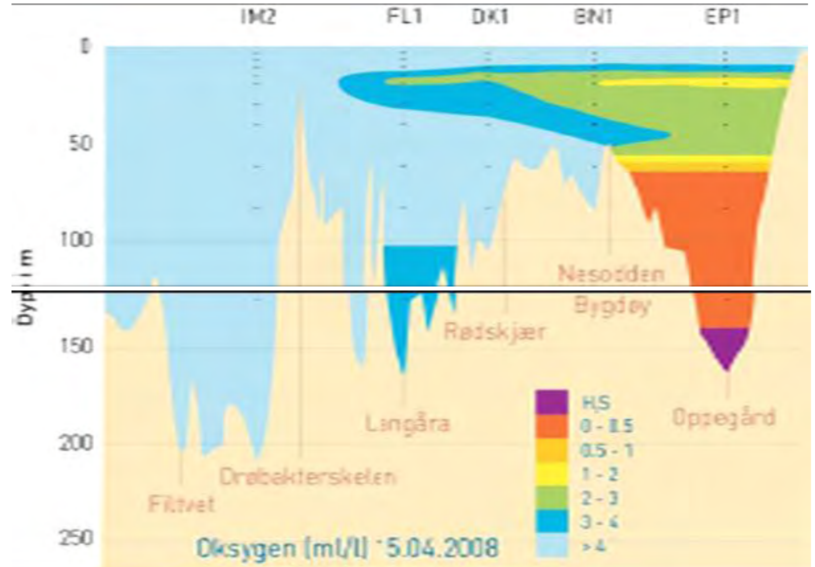


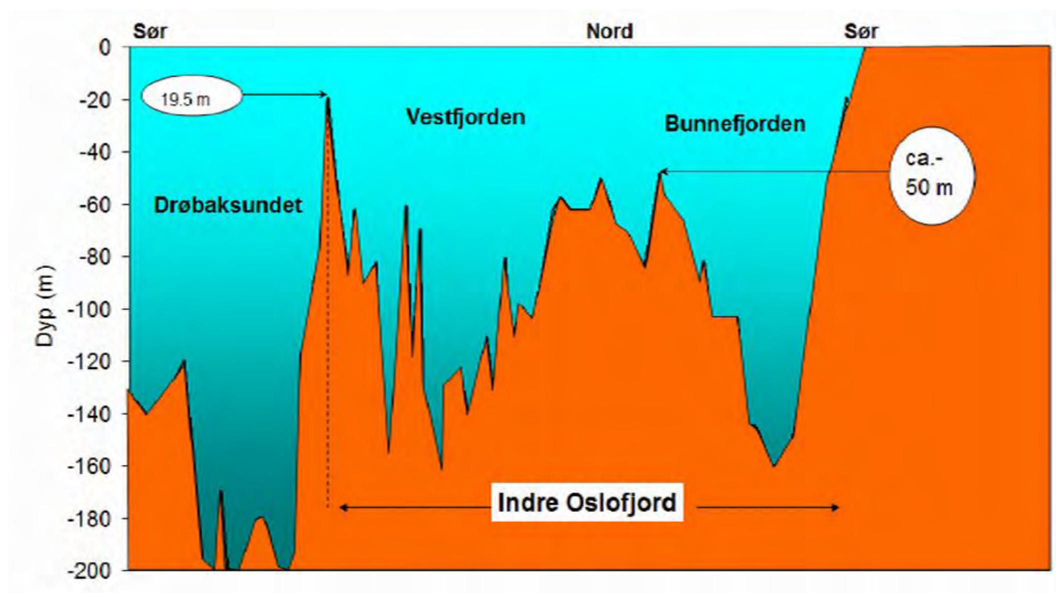
Oslo
Sandvika
Ap 2
Aq 3
Bl 4
Bn 1
Cq 1
Cp 2
Cq 1-Dep
Dk 1
Bunne-
fjorden
Vestfjorden
Ep 1
Fl 1
Gl 2
Gk 1
Hm 4
Hm 6
Drøbak
Im 2
Hydrografi + hydrokjemi
Hydrografi (inkl. oksygen)
Hydrografi (eks. oksygen)
Stasjoner i fjorden
den 15-4-2008

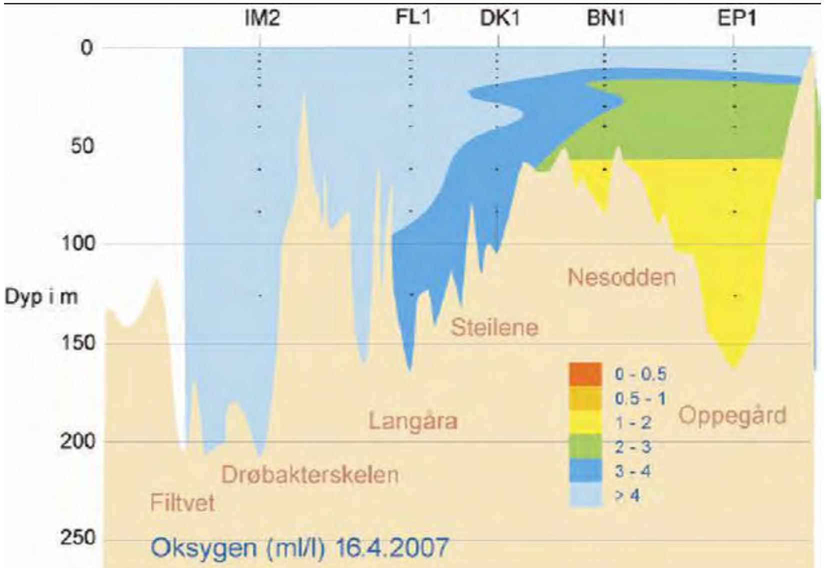


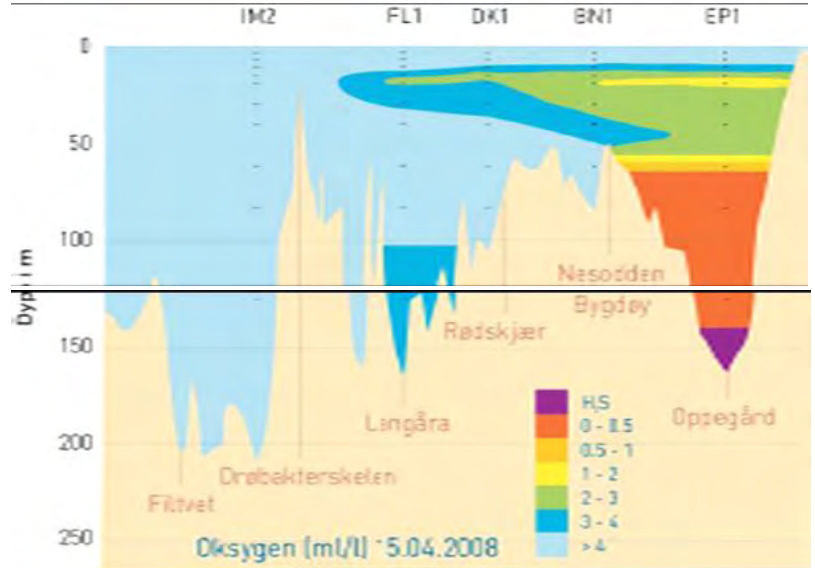
Sør
Nord
Sør
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Dyp (m)
19.5 m
Vestfjorden
Bunnefjorden
ca.-
50 m
Drøbaksundet
Indre Oslofjord


IM2
FL1
DK1
BN1
EP1
0
50
100
150
200
250
Dyp i m
Nesodden
Steilene
Langåra
Oppegård
Drøbakterskelen
Filtvet
0 - 0.5
0.5 - 1
1 - 2
2 - 3
3 - 4
> 4
Oksygen (ml/l) 16.4.2007

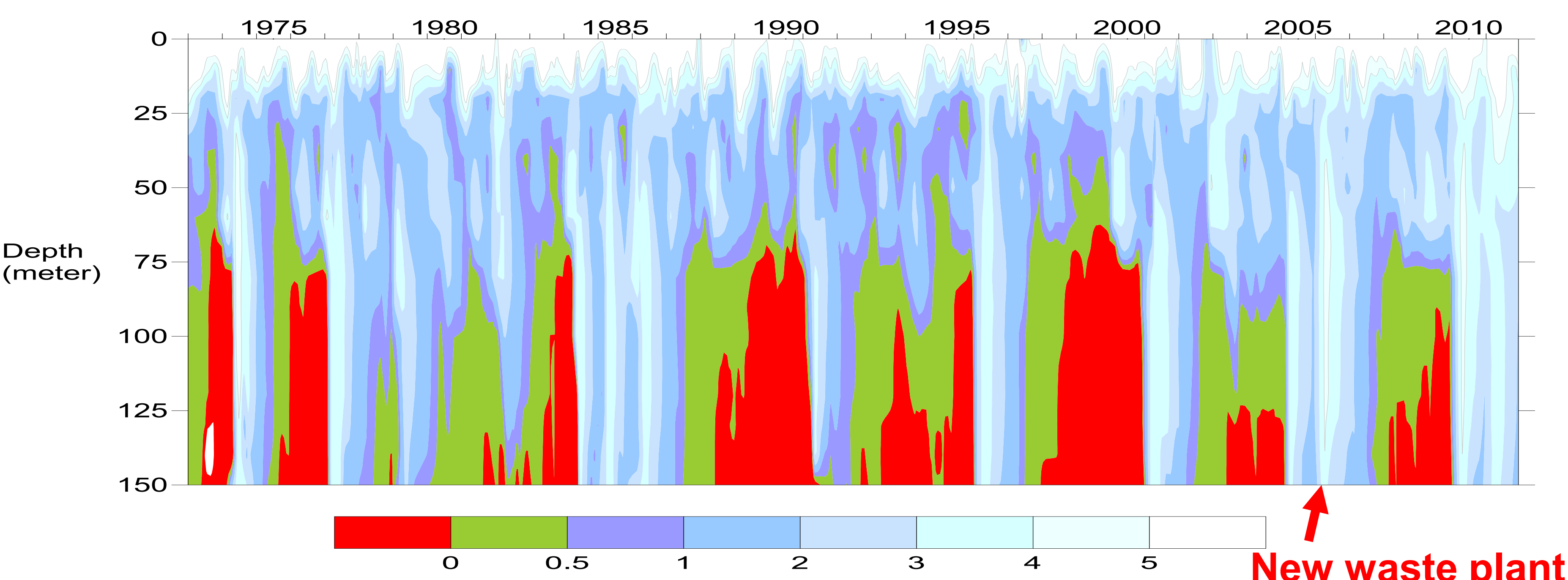

IM2
FL1
DK1
BN1
EP1
0
50
100
150
200
250
Dyp i m
Nesodden
Bygdøy
Rødskjær
Langåra
Oppegård
Drøbakterskelen
Filtvet
H_2S
0 - 0.5
0.5 - 1
1 - 2
2 - 3
3 - 4
> 4
Oksygen (ml/l) 15.04.2008


Sør
Nord
Sør
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Dyp (m)
19.5 m
Vestfjorden
Bunnefjorden
ca.-
50 m
Drøbaksundet
Indre Oslofjord

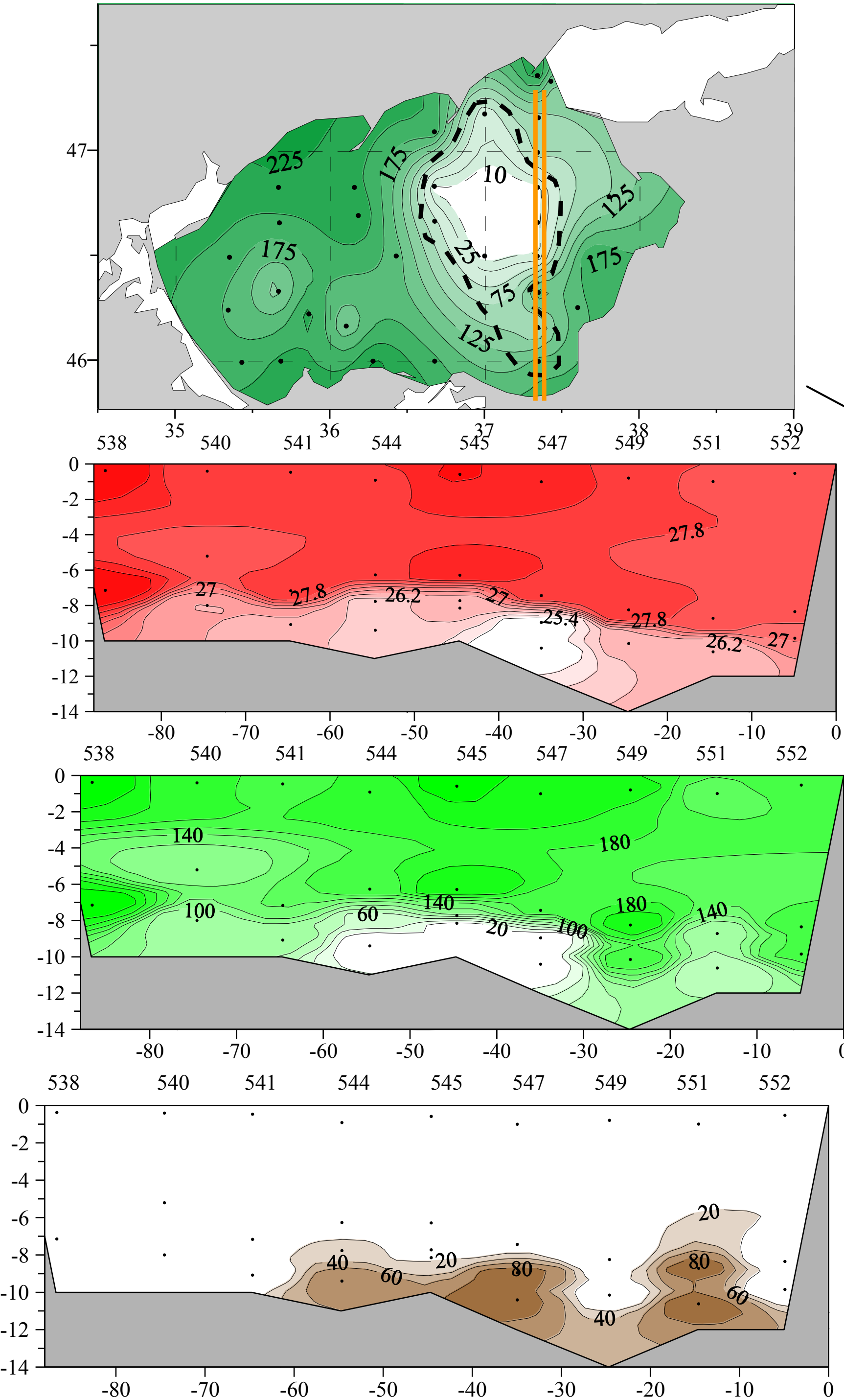




Oxygen equivalent (ml/l) in Inner Oslofjord, Bunnefjord basin (Station Ep1), 1973-2011



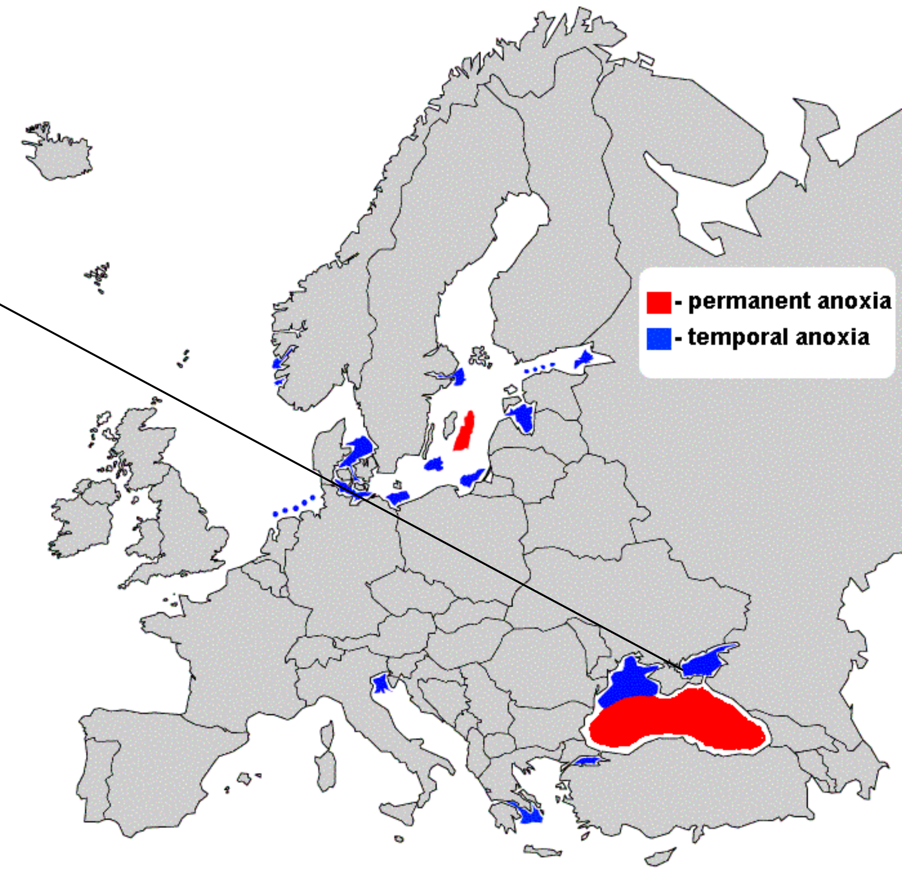
The Sea of Azov, July 2001



T

O_2

H_2S



Catastrophic anoxia in 1937, 1946, 1987

Oxygen depletion vs. ventilation

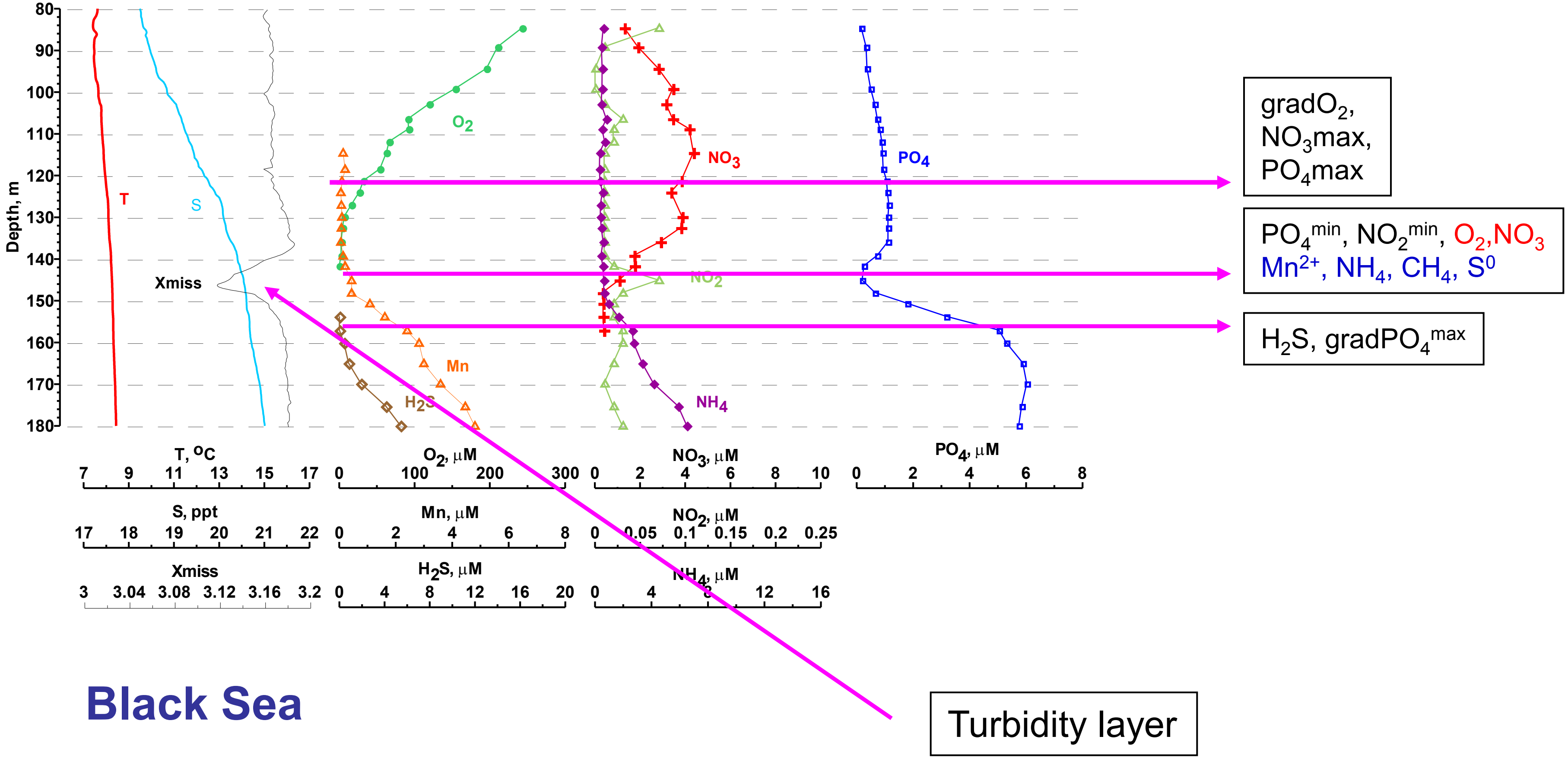
- Permanent anoxic (Black Sea)
- Dominant anoxic (Fjords, Gotland Deep)
- Seasonally anoxic (Elefsis Bay)
- Sporadic anoxic (Sea of Azov)

Coastal oxygen depleted spots are characterized by
Intensive inetrannual variability caused by:

1. Climatic «physical» forcing (restricted mixing due to warmer winters and increased precipitaion)
2. Nutrient supply («anthropogenic» eutrophication)

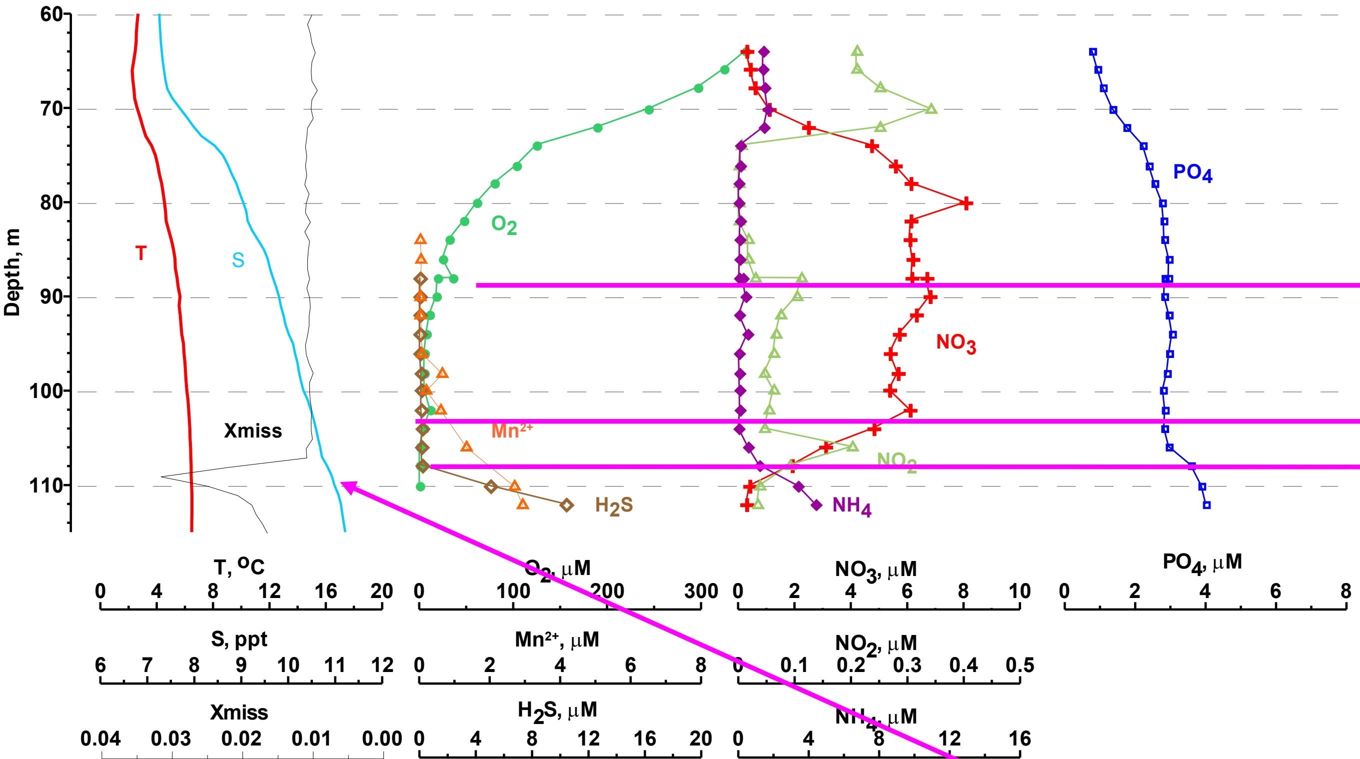
«Physical» forcing dominates.

Redox interfaces structure



Black Sea

Redox interfaces structure



$gradO_2$, NO_3max, PO_4max

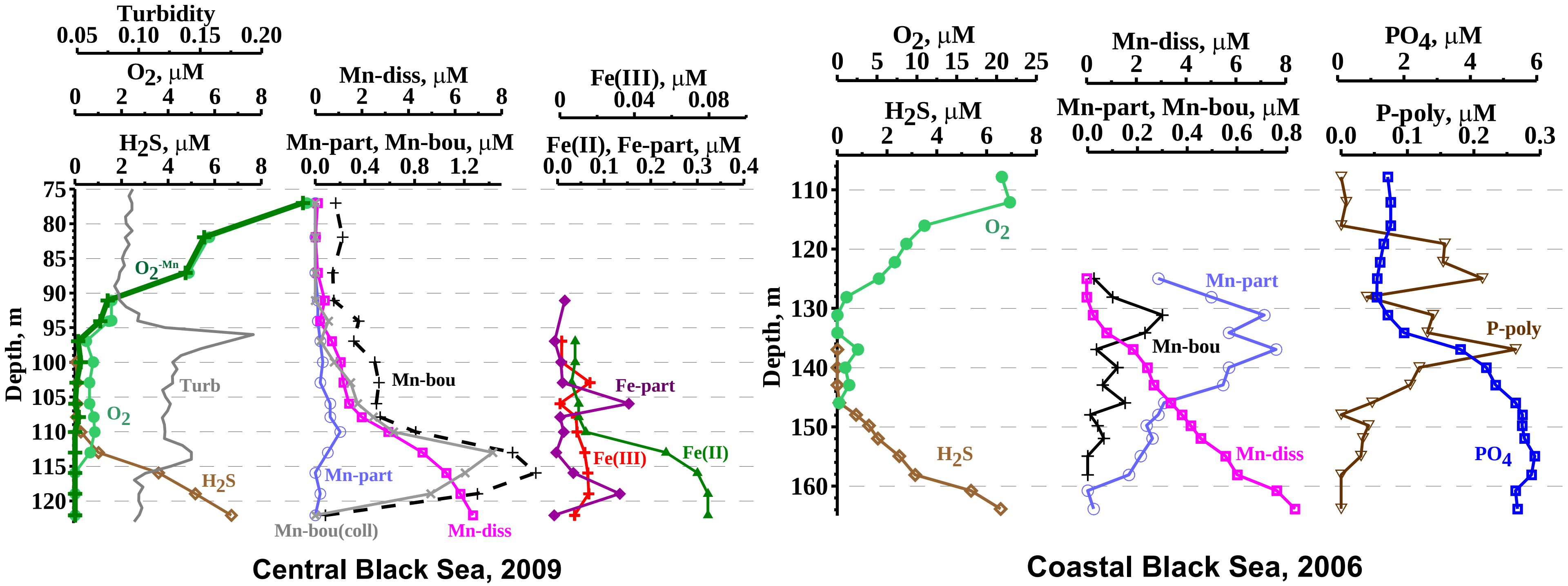
PO_4^{min}, NO_2^{min}, O_2, NO_3 Mn^{2+}, NH_4, S^0

H_2S, $gradPO_4^{max}$

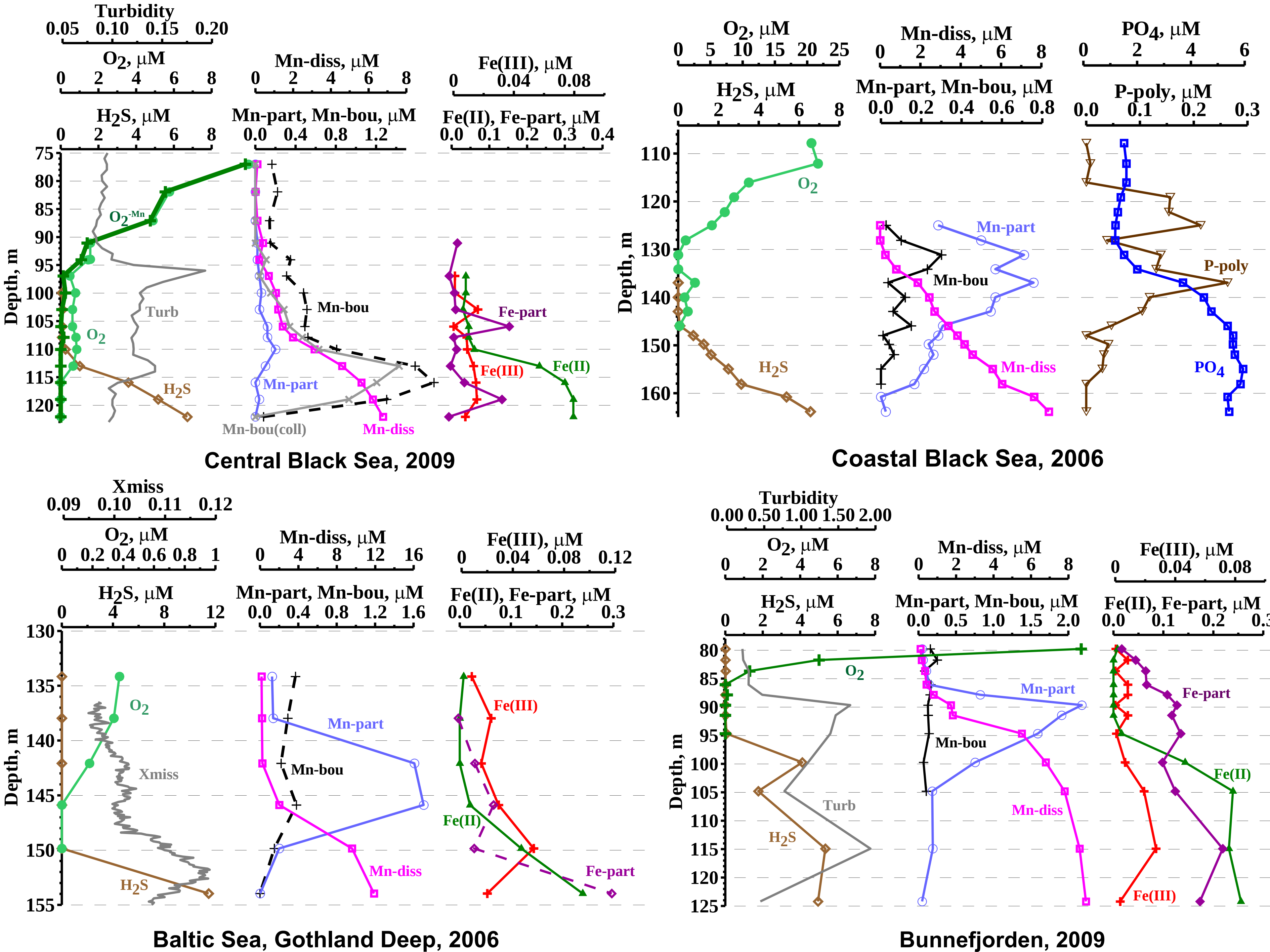
Turbidity layer

Gotland Deep (Baltic Sea)

Common features of different Seas redox layer structure are formed with the similar mechanism

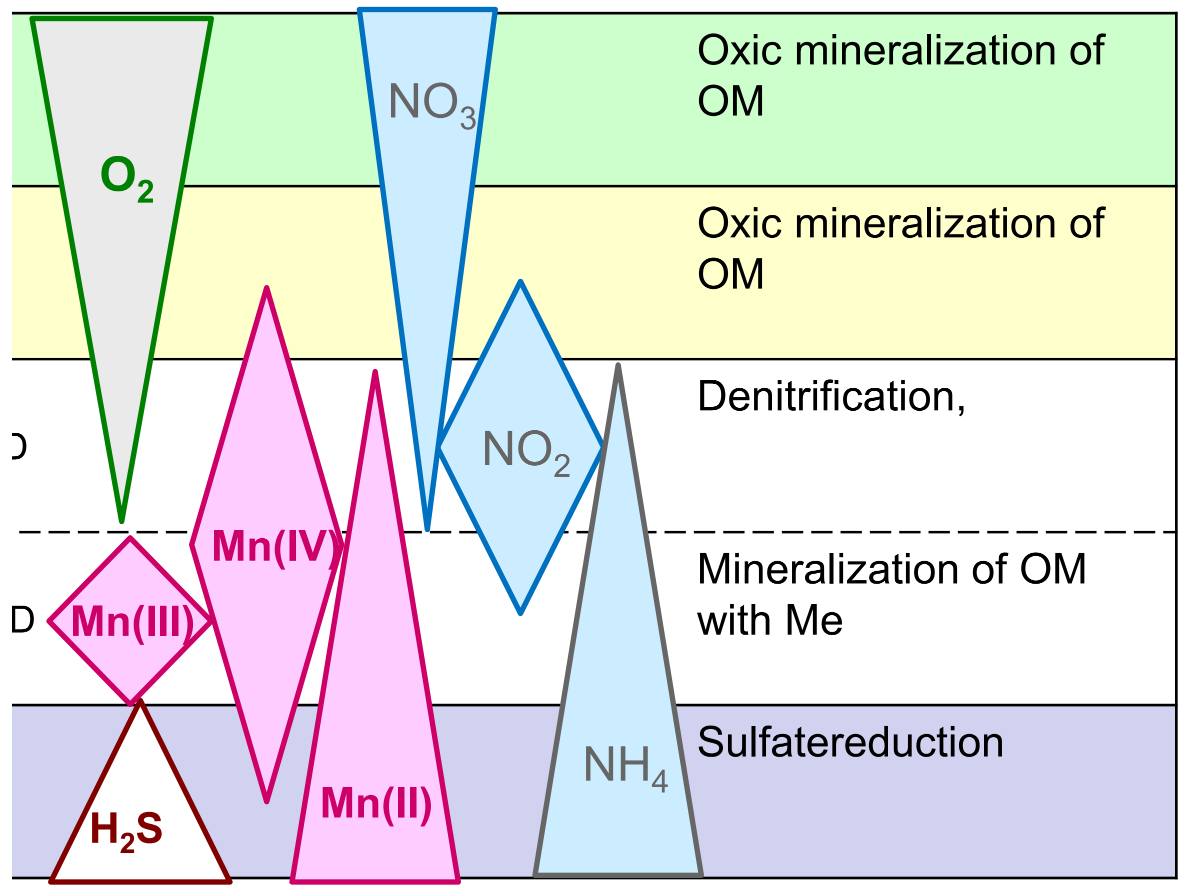


Turbidity
0.05 0.10 0.15 0.20
O2, μM
H2S, μM
Mn-diss, μM
Mn-part, Mn-bou, μM
Fe(III), μM
Fe(II), Fe-part, μM
Depth, m
O2-Mn
O2
Turb
H2S
Mn-bou
Mn-part
Mn-bou(coll)
Mn-diss
Fe-part
Fe(III)
Fe(II)
Central Black Sea, 2009
PO4, μM
P-poly, μM
P-poly
PO4
Coastal Black Sea, 2006



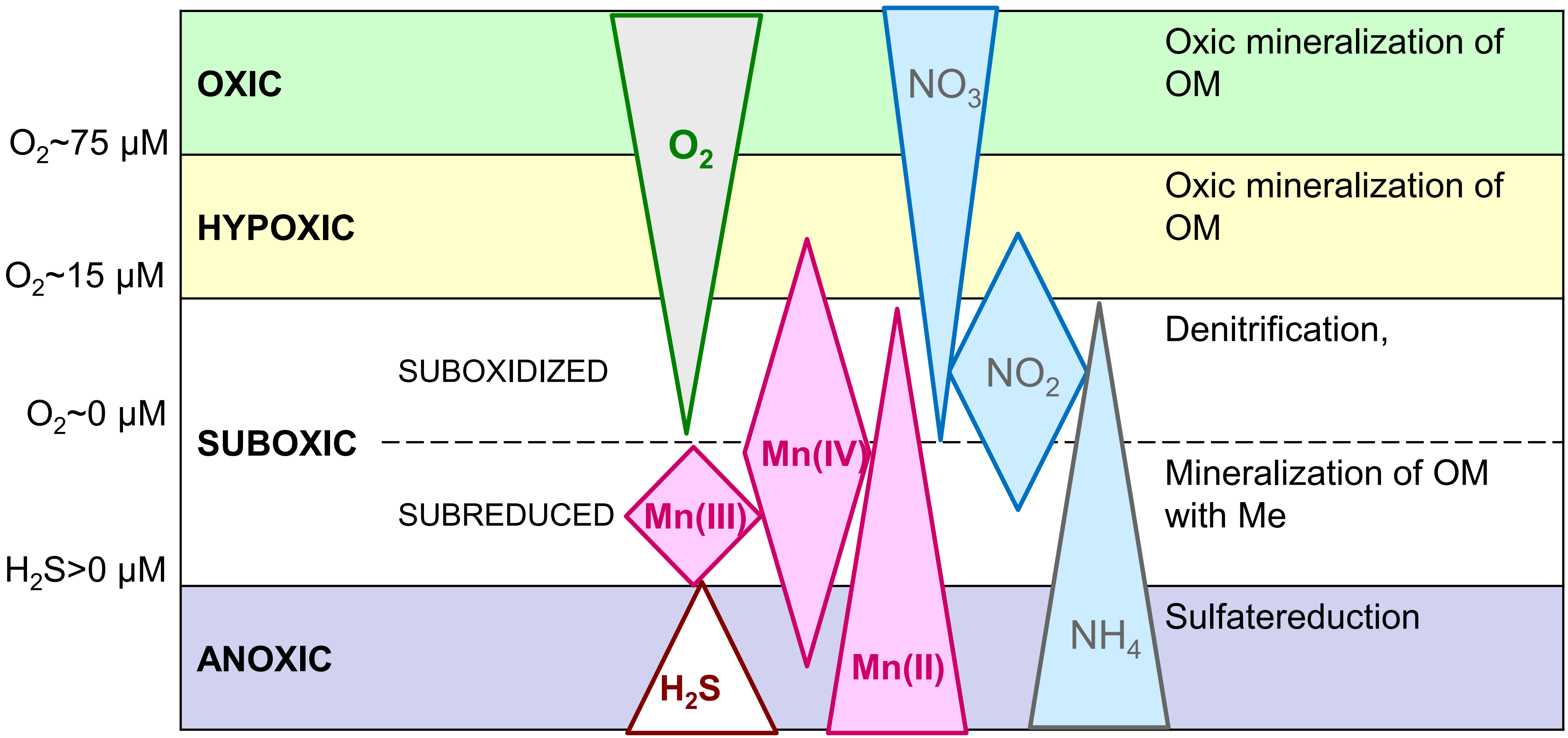
Turbidity
O2, µM
H2S, µM
Mn-diss, µM
Mn-part, Mn-bou, µM
Fe(III), µM
Fe(II), Fe-part, µM
Depth, m
O2-Mn
Turb
O2
H2S
Mn-bou
Mn-part
Mn-bou(coll)
Mn-diss
Fe-part
Fe(III)
Fe(II)
Central Black Sea, 2009
PO4, µM
P-poly, µM
P-poly
PO4
Coastal Black Sea, 2006
Xmiss
Baltic Sea, Gothland Deep, 2006
Bunnefjorden, 2009

Redox conditions



(Yakushev, Newton, 2012)

Redox conditions



(Yakushev, Newton, 2012)

Redox conditions

Oxygen conditions	Oxic	Hypoxic	Suboxic: suboxidized	Suboxic: subreduced	Anoxic
DO concentration	>75 μM	15- 75 μM	0-15 μM	0 μM	
H_2S concentration					>0 μM
• oxic mineralization of OM • Nitrification	+	+			
• 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	+	+	+	+	+

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

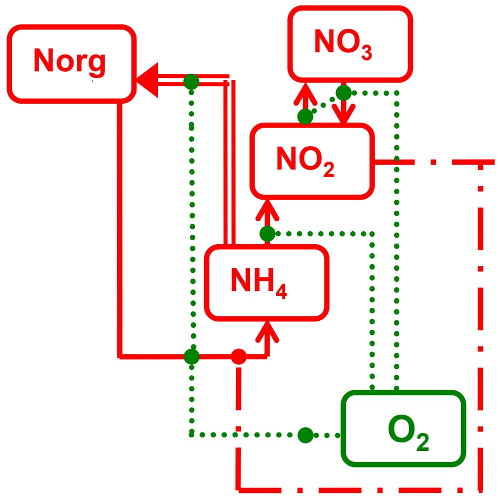
“Ecological model” +Chemosynthesis

Tasks to be solved :

Analysis of the field and experimental data

Reaction on forcing (Forecast)

N+O model



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

$Am = K_{Am}$ [Norg] – ammonification
$Nf1 = K_{Nf1}$ $[NH_4]$ $f_{Nf}(O_2)$ – nitrification 1
$Nf2 = K_{Nf2}$ $[NO_2]$ $f_{Nf}(O_2)$ – nitrification 2
$Nr1 = K_{Nr1}$ $[NO_3]$ $f_{Nr}(O_2)$ – nitratereduction 1
$Nr2 = K_{Nr2}$ $[NO_2]$ $f_{Nr}(O_2)$ – nitratereduction 2
$Dn = K_{Dn}$ $[NO_2]$ $f_{Dn}(O_2)$ – denitrification

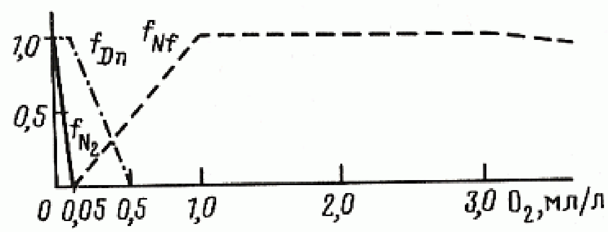


Рис. 2

Dependence of rates of processes on O_2

Sources:

$R_{Norg} = -Am$
$R_{NH4} = Am - Nf1 + Nr2$
$R_{NO2} = Nf1 - Nf2 + Nr1$
$R_{NO3} = Nf2 - Nr1 – Dn$
$R_{O2} = -m_{12}\,Am - m_{10}\,Nf1 –$
$-m_{11}\,Nf2 + m_{21}\,Nr1 + m_{21}Nr2$

N+O model

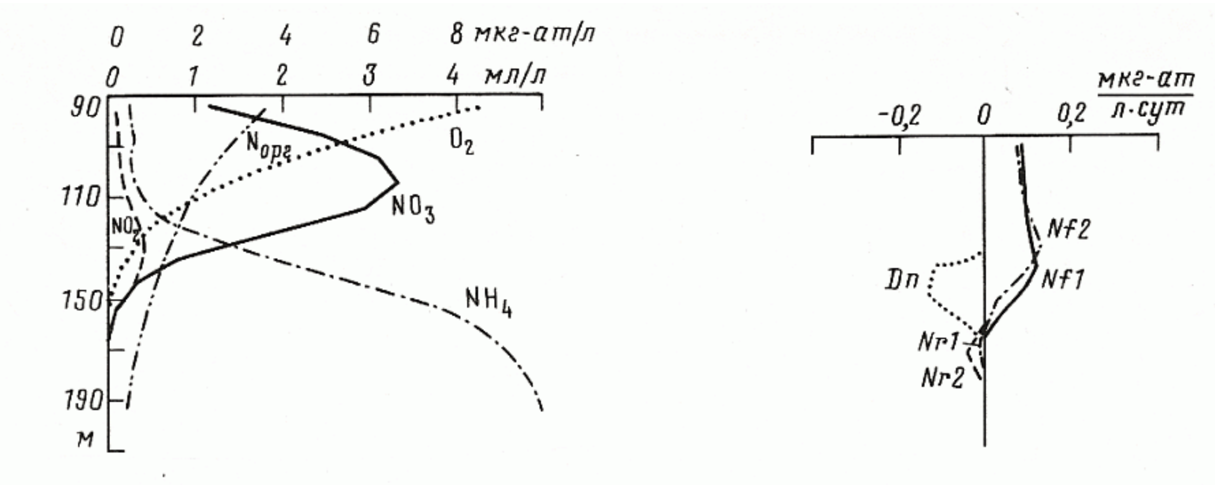


Рис. 3

Calculations

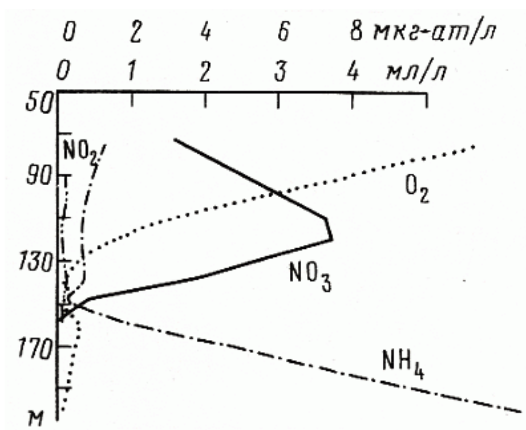


Рис. 4

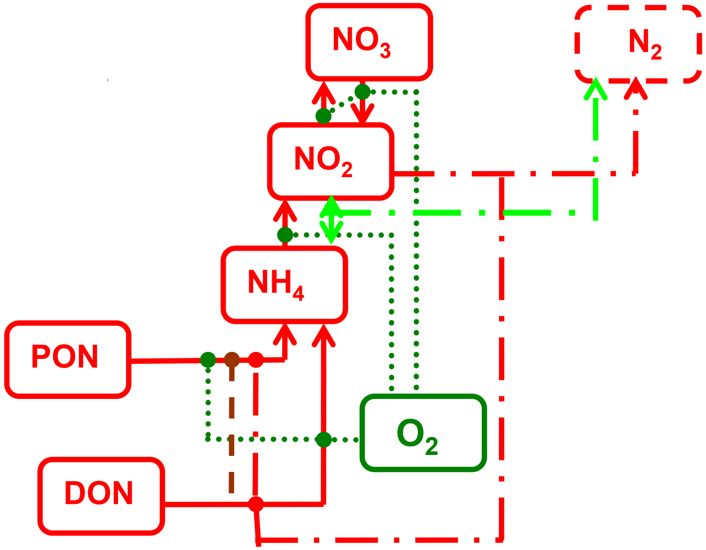
Observations

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

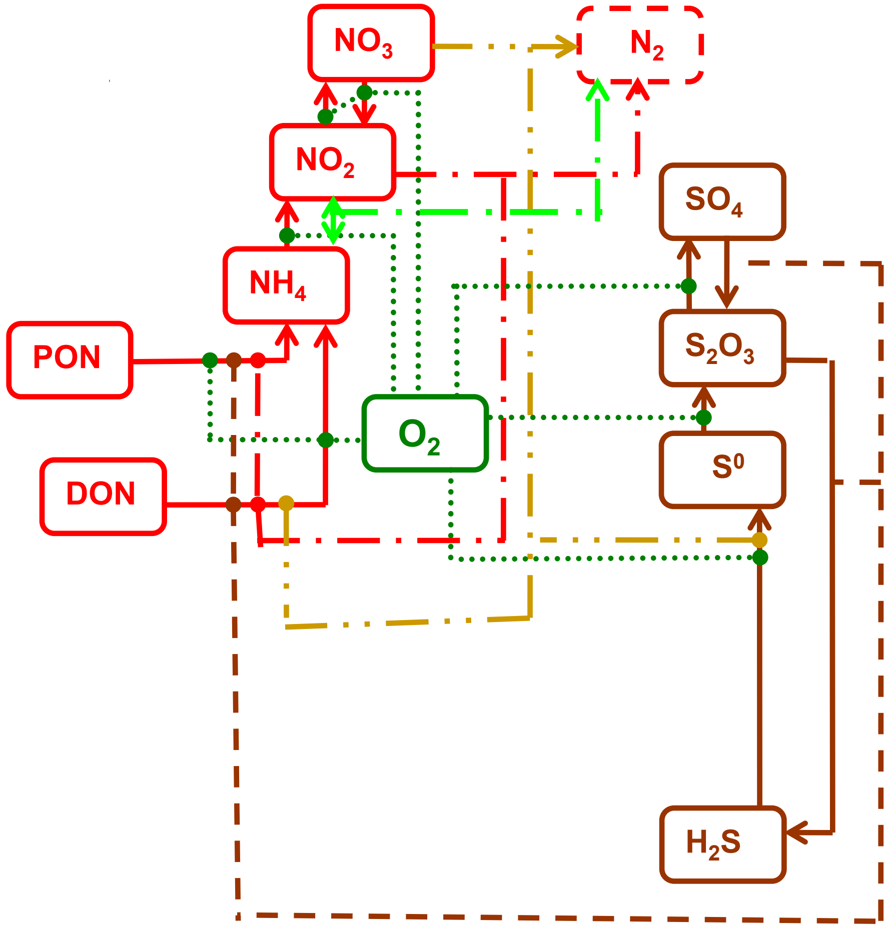
Necessity of parameterization of cycles of several elements

(Yakushev, 1992)

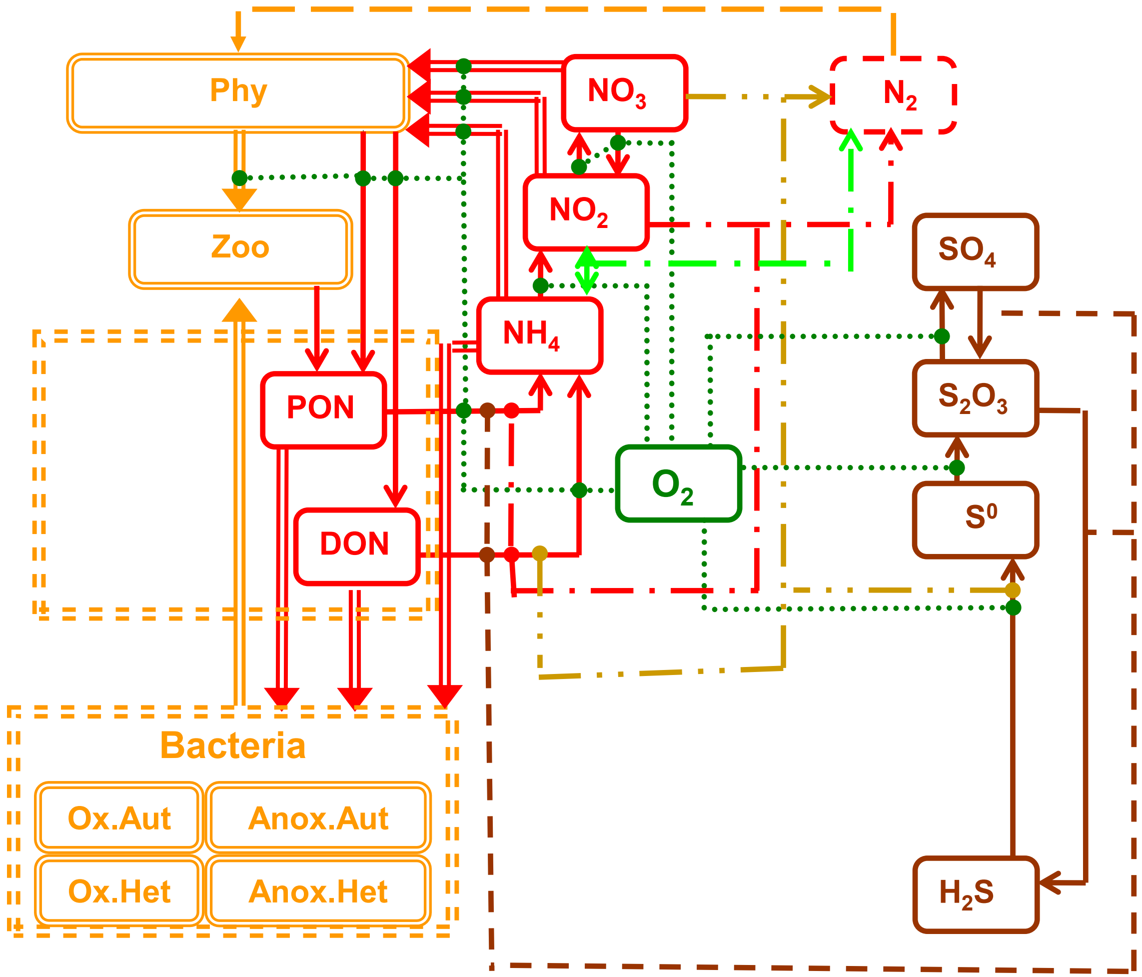
ROLM biogeochemical model



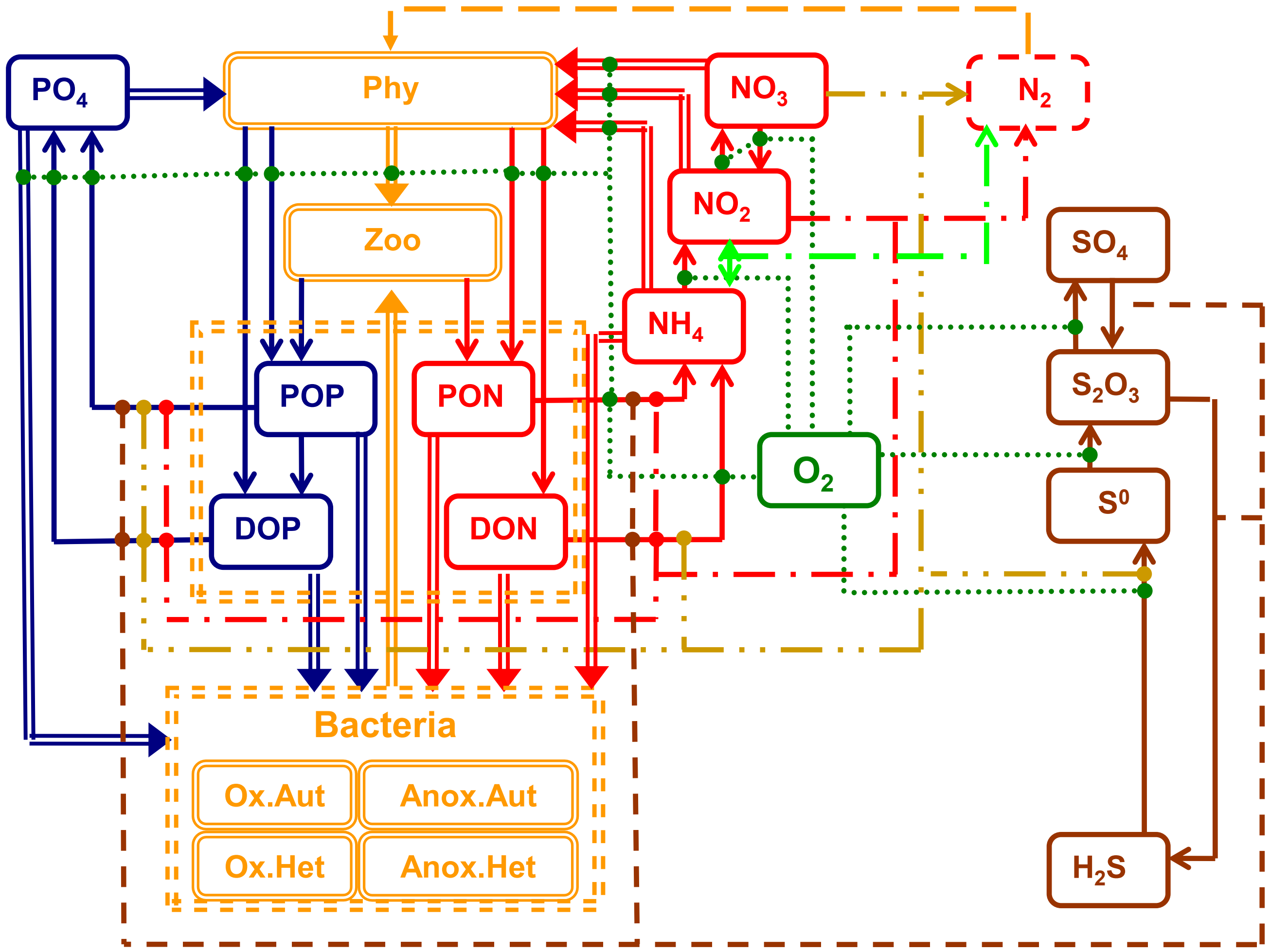
ROLM biogeochemical model



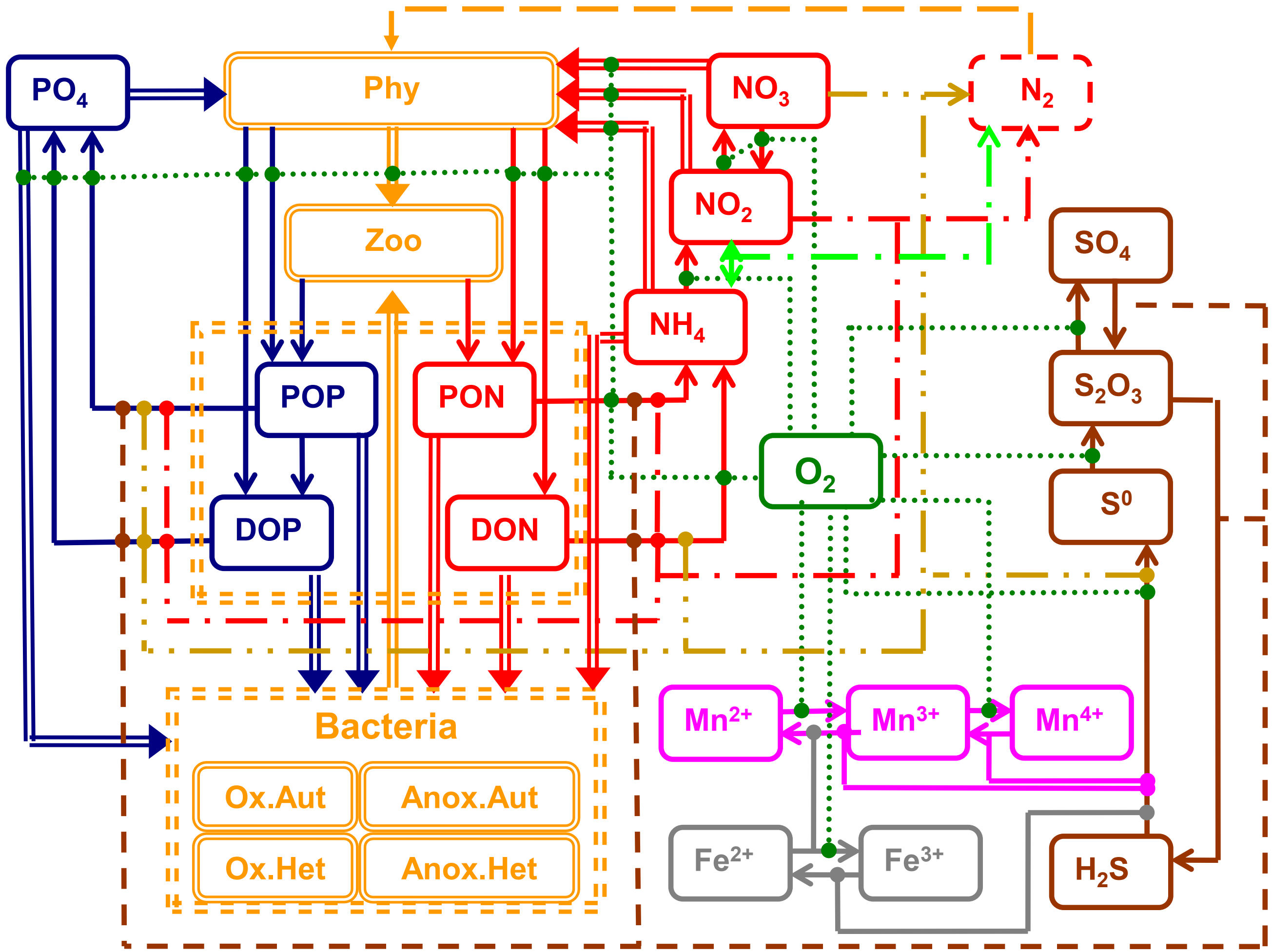
ROLM biogeochemical model



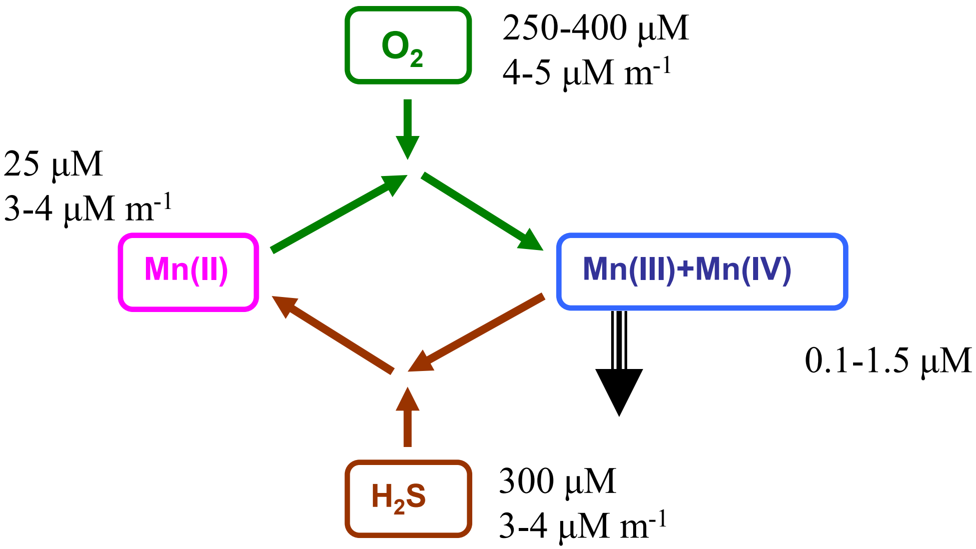
ROLM biogeochemical model



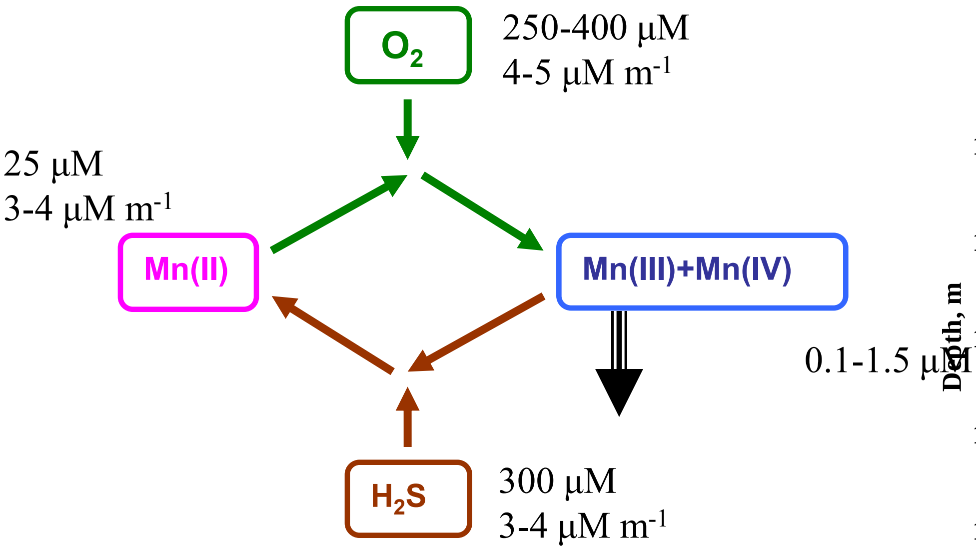
ROLM biogeochemical model

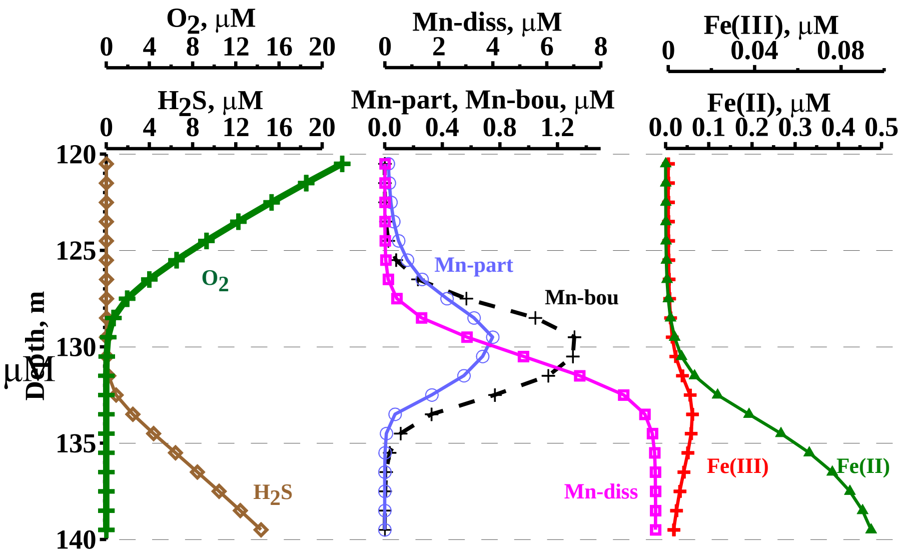


Application of the model: vertical structure (analysis)

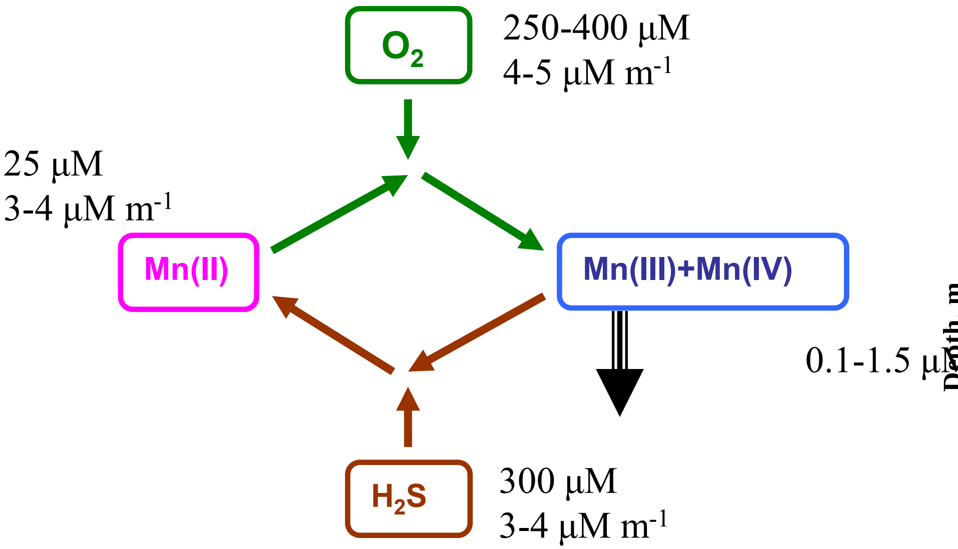


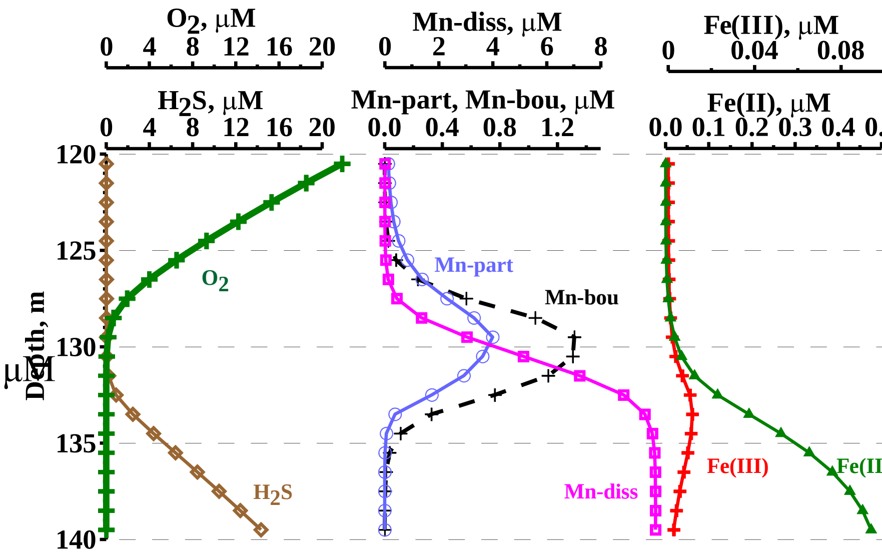
Application of the model: vertical structure (analysis)

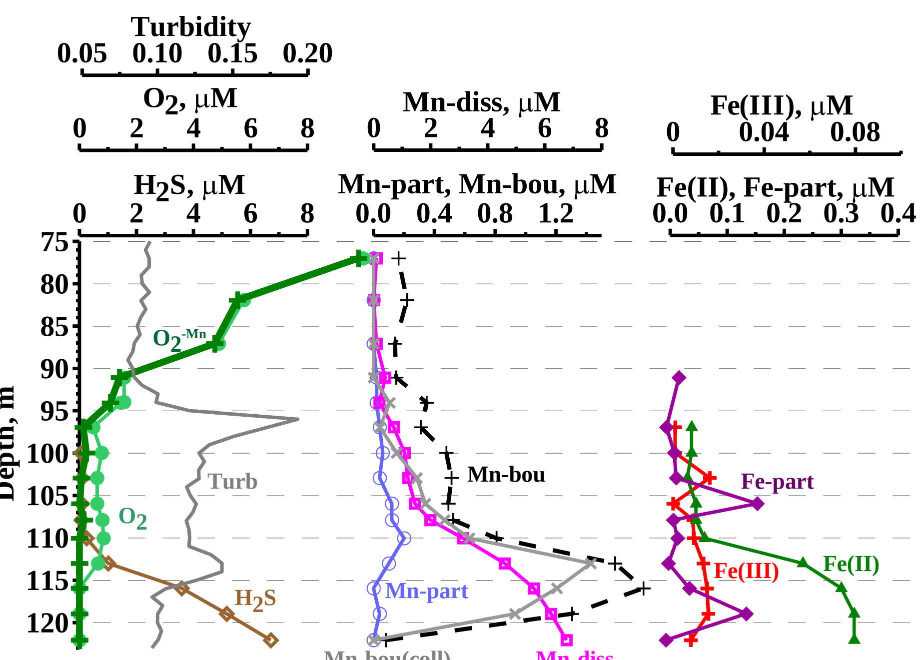




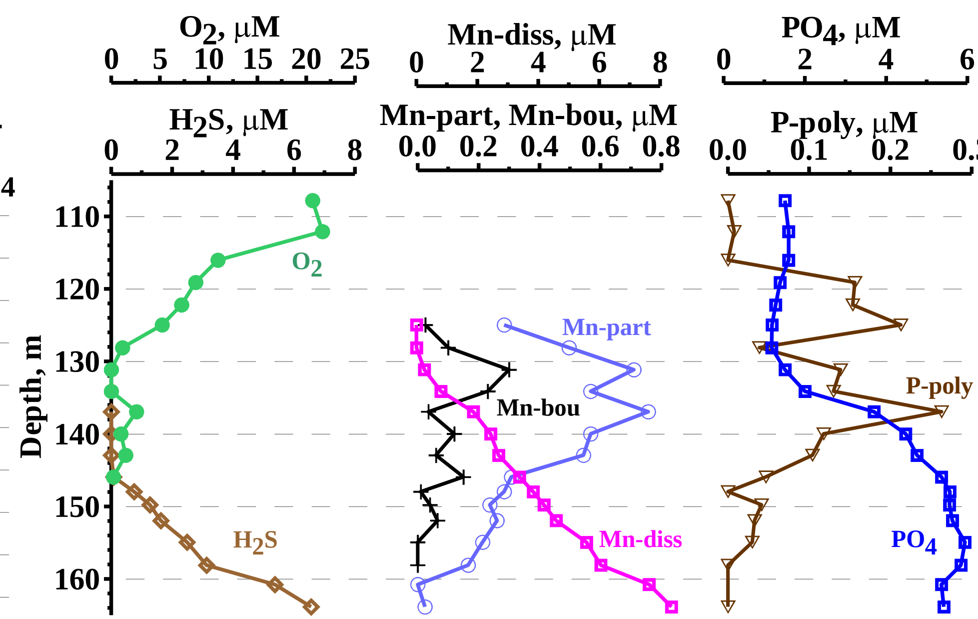
Application of the model: vertical structure (analysis)







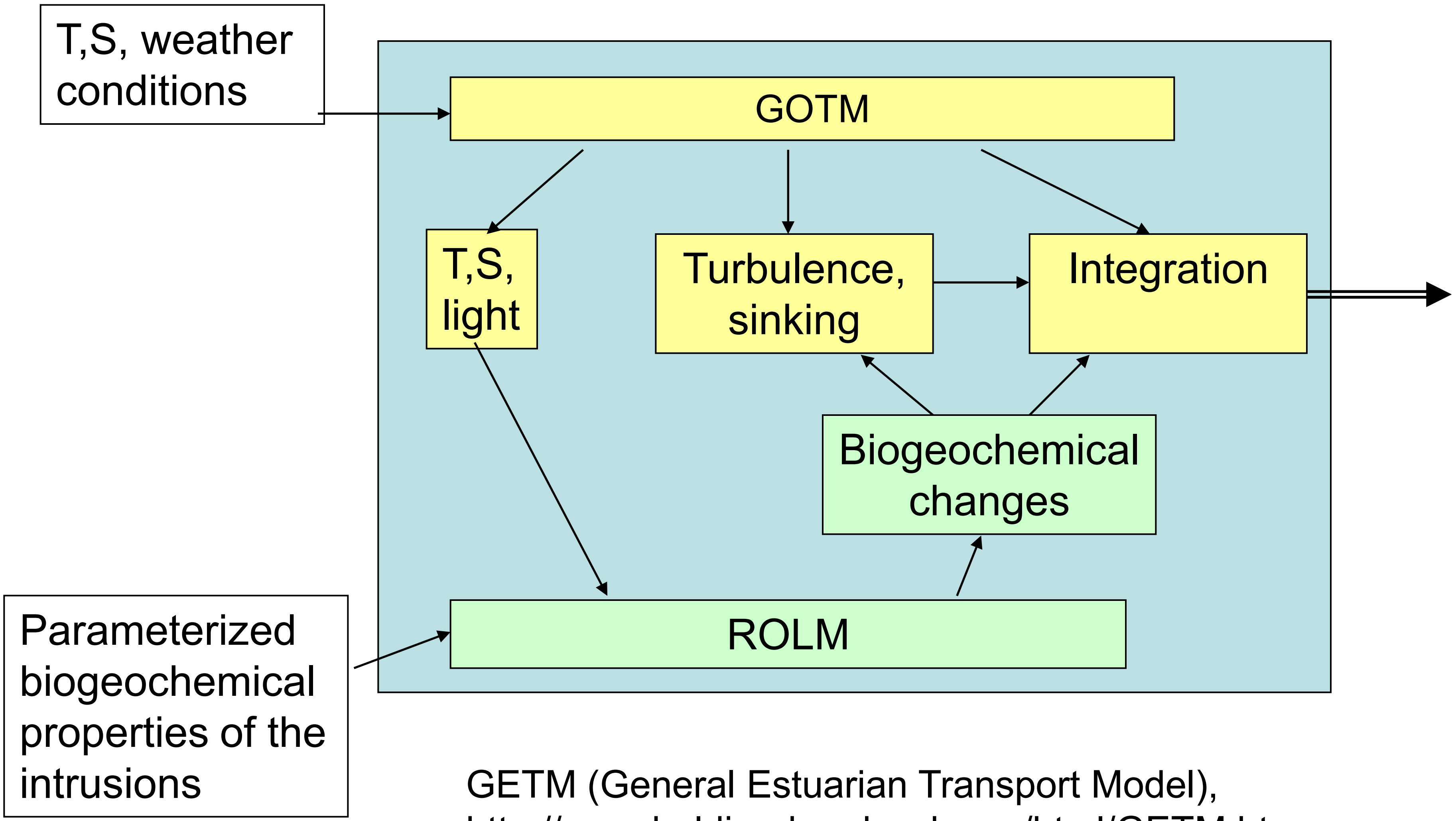
Central Black Sea, 2009



Coastal Black Sea, 2006

Application of the model: reaction on forcing (forecast)

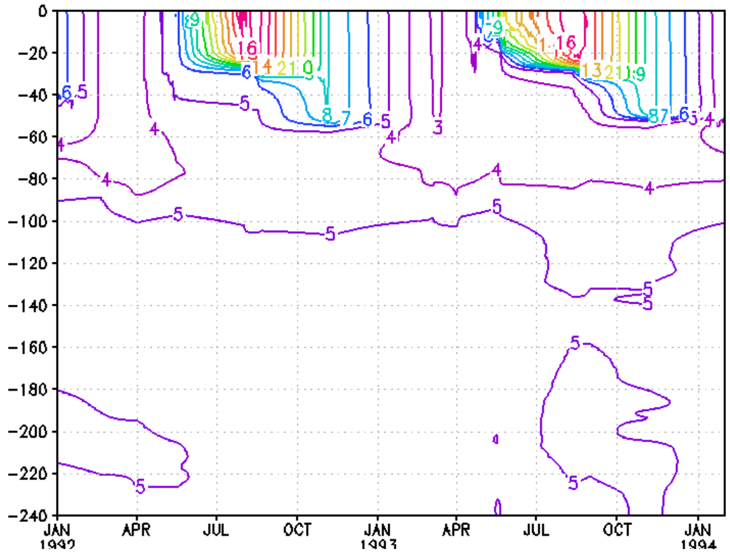
Modeling of the flushing events in the Gotland Deep



GETM (General Estuarian Transport Model),
http://www.bolding-burchard.com/html/GETM.htm

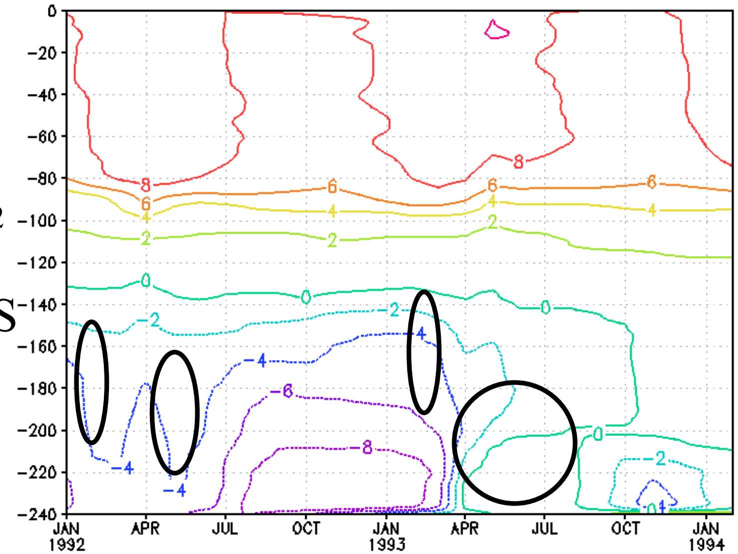
Observations in 1992-1993 (DB "ODIN"):

T

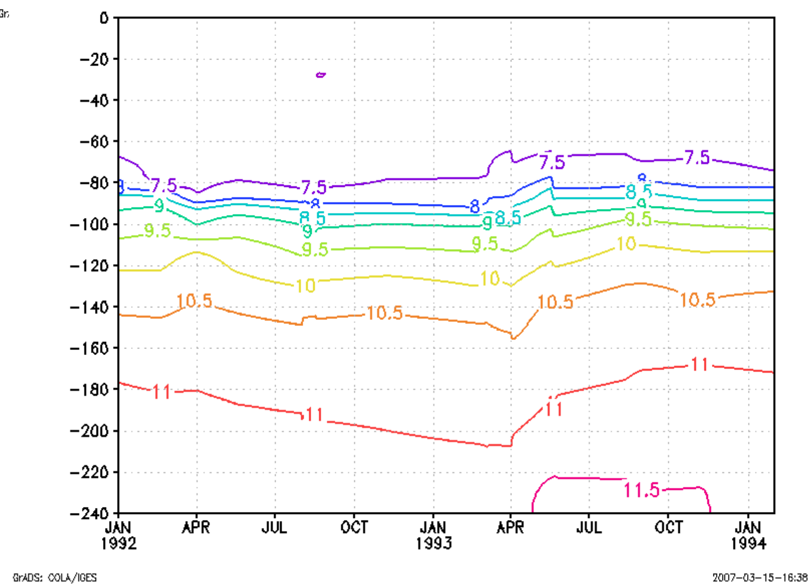


O_2

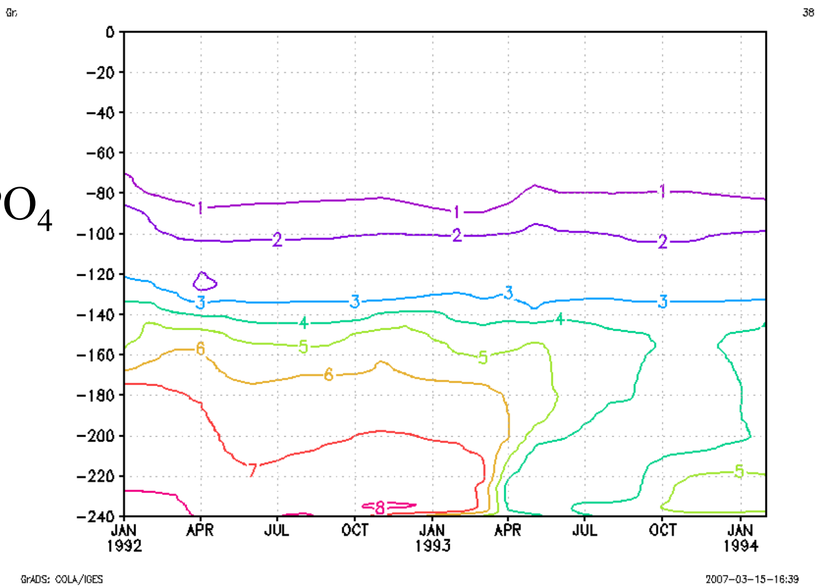
H_2S



S



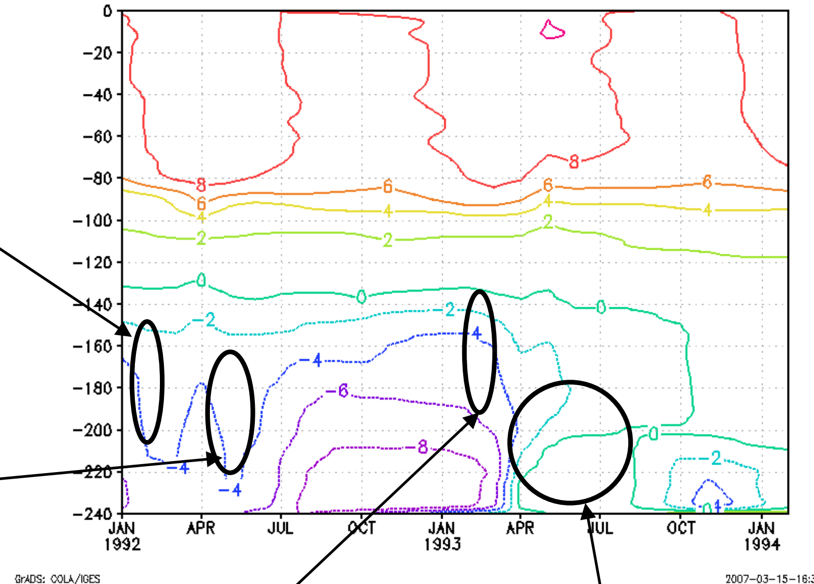
PO_4



Intrusions parameterization:

O_2= 0.1 uM
H_2S= 0.5 uM
DON= 7 uM

O_2= 1 uM
H_2S= 0 uM
DON= 5 uM



O_2= 1 uM
H_2S= 0 uM
DON= 5 uM

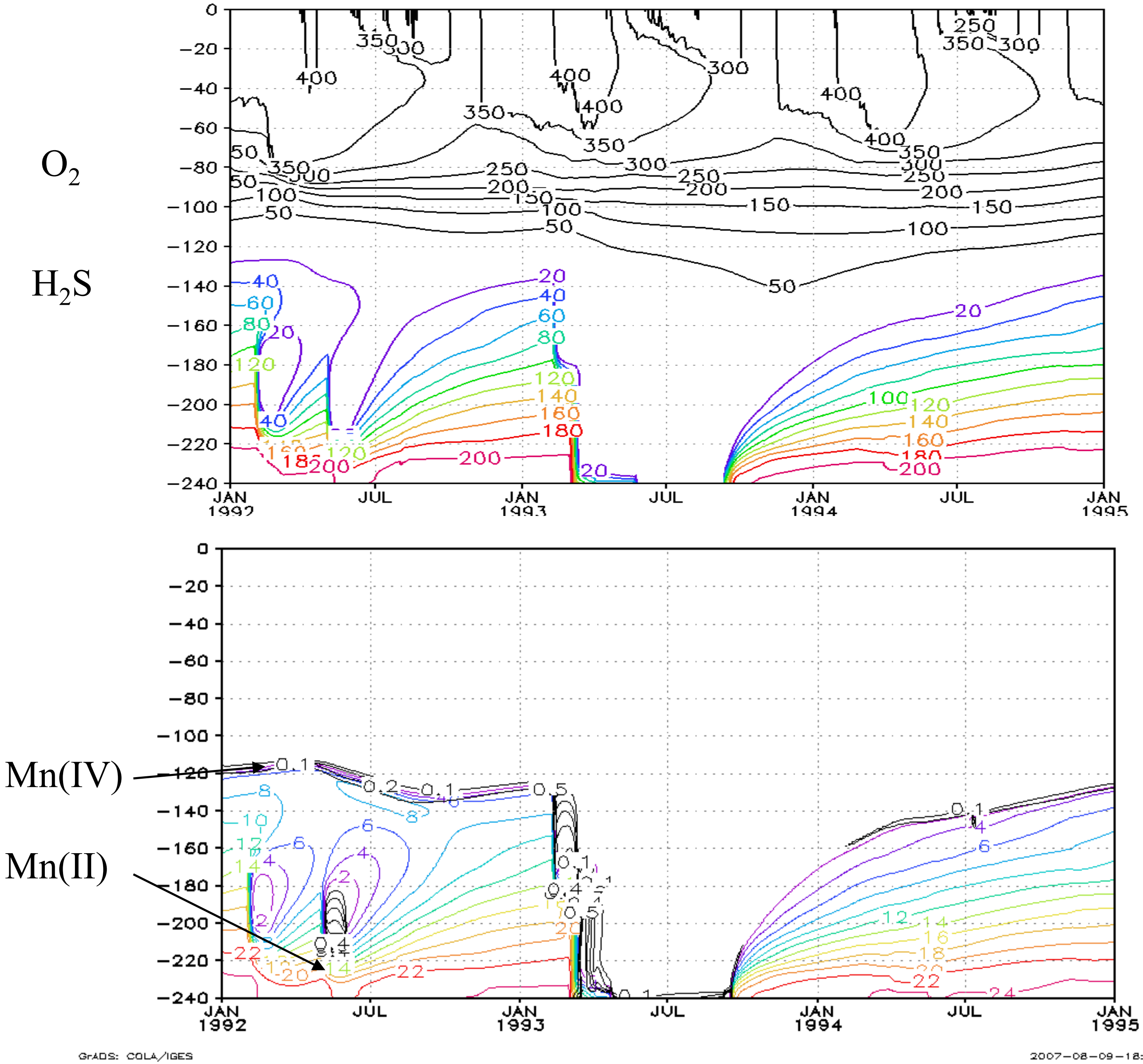
O_2= 30 uM
H_2S= 0 uM
DON= 5 uM

Parameterization of intrusions:

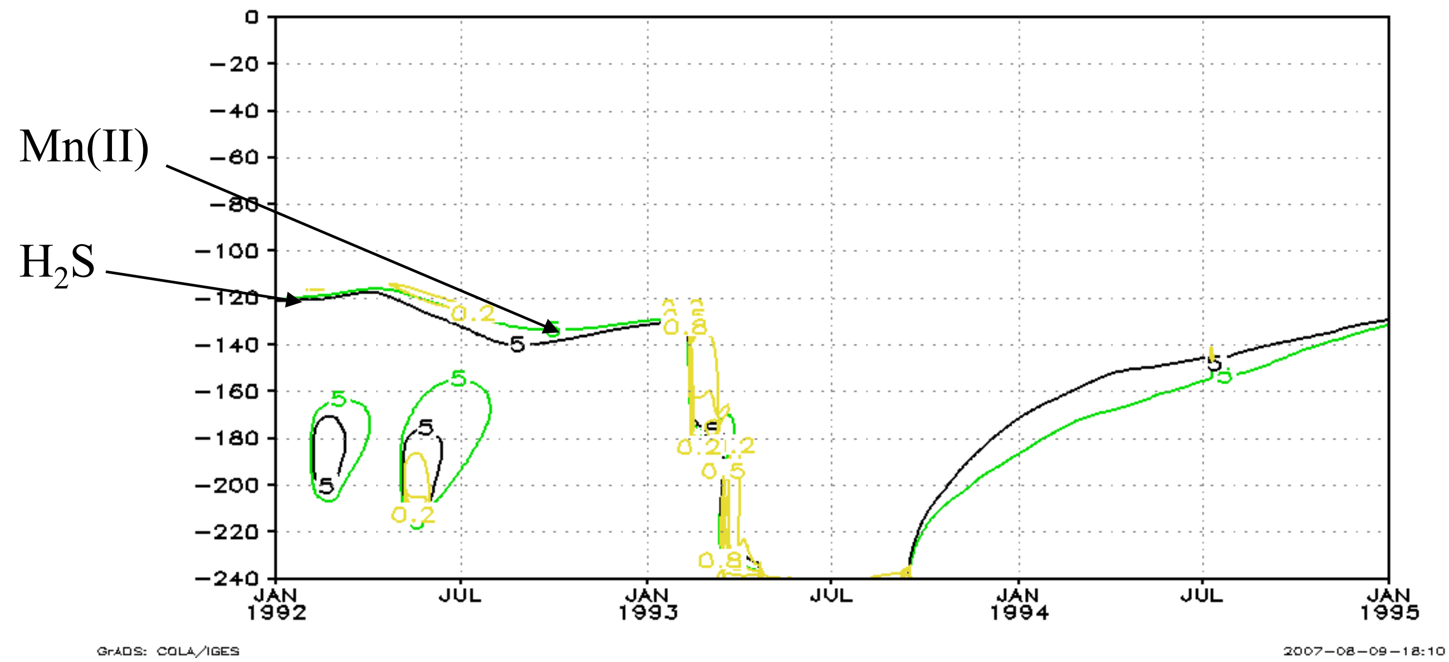
$$Q_{C_i}^{Inf} = \tau_{Inf}^{-1}(C_{Inf\,i} - C_i)Inf(t,h)$$

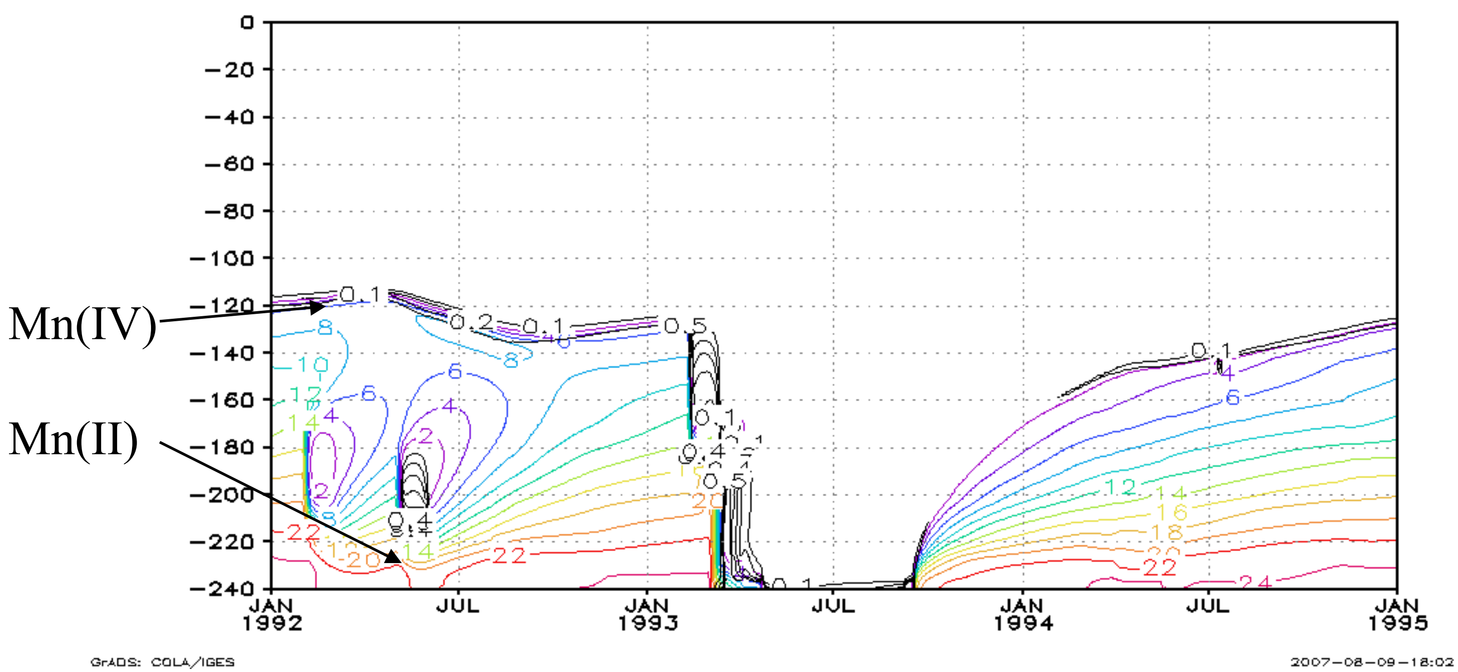
τ_{Inf}^{-1} =6000 s, is the relaxation time scale

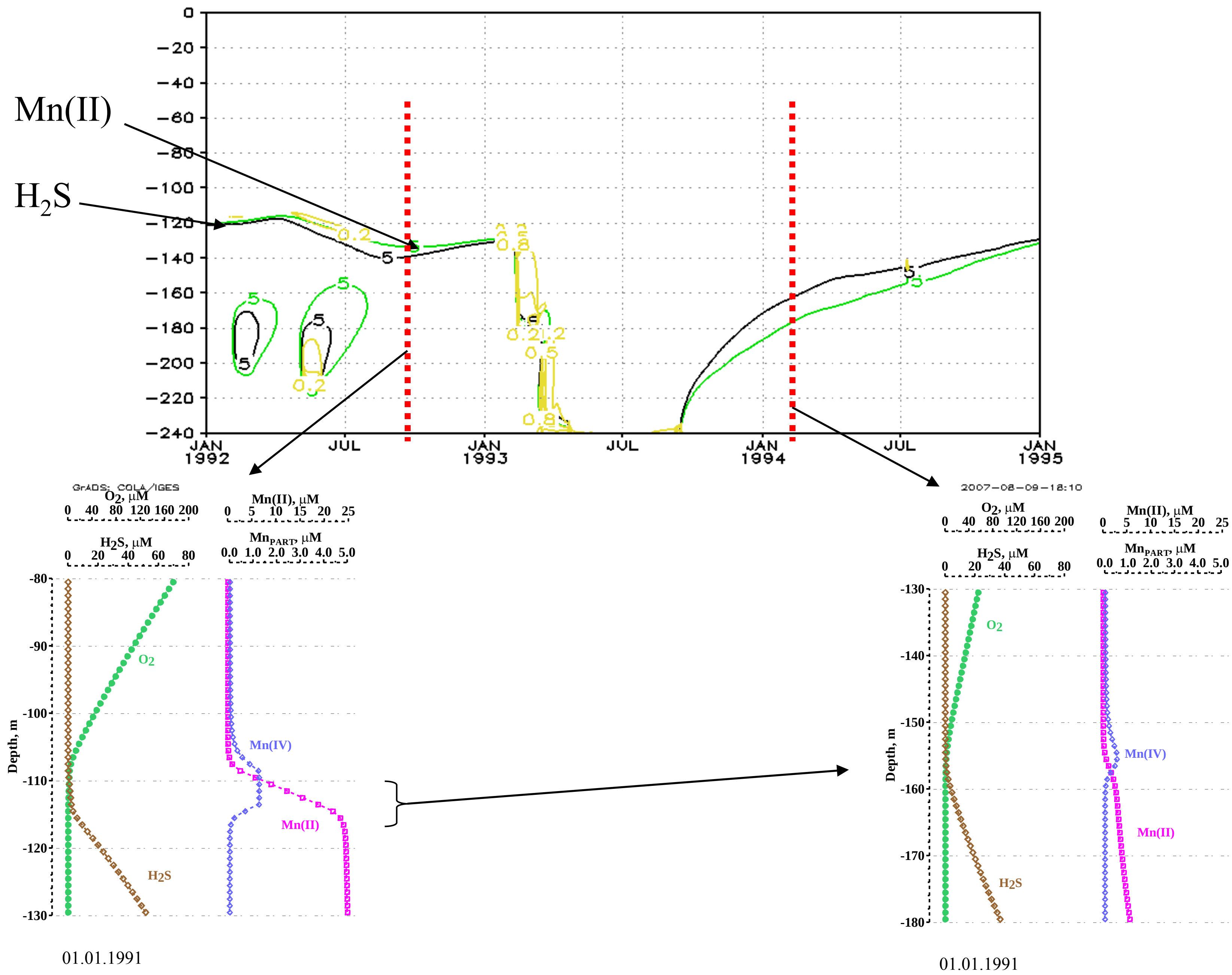
$$Inf(t,h) = \sin\left(\frac{t_i - t_{start}}{t_{end} - t_{start}}\pi\right)\sin\left(\frac{h_i - h_{start}}{h_{end} - h_{start}}\pi\right)$$ is the dependence on t and h



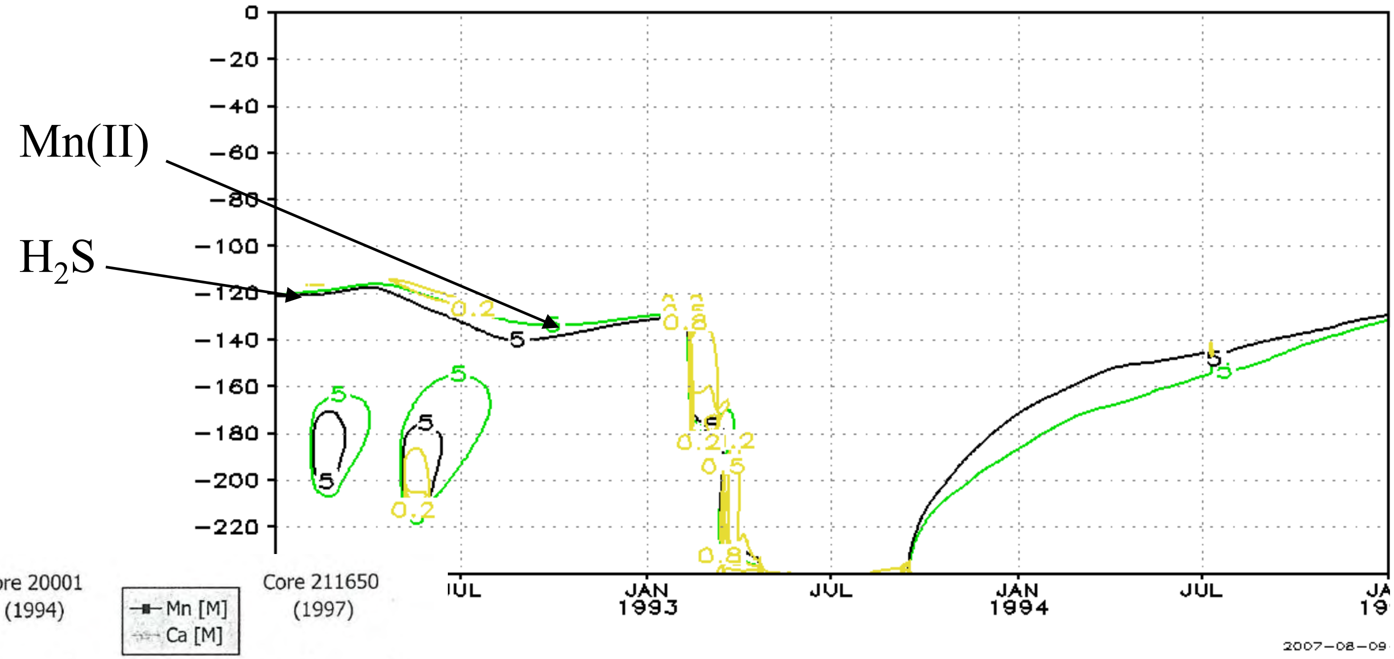
O_2
H_2S
Mn(IV)
Mn(II)
JAN 1992
JUL
JAN 1993
JUL
JAN 1994
JUL
JAN 1995
GrADS: COLA/IGES
2007-08-09-18:02

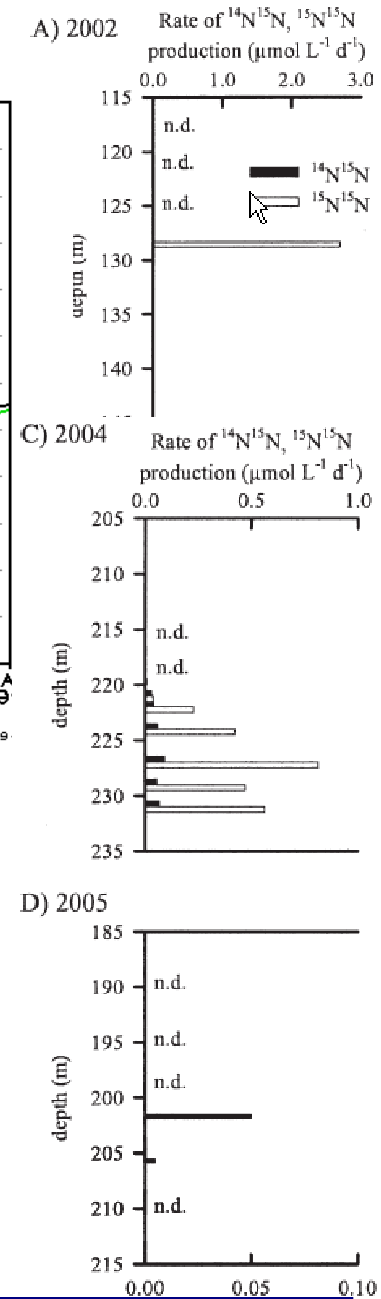

Mn(II)
H_2S
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
JAN 1992
JUL
JAN 1993
JUL
JAN 1994
JUL
JAN 1995
GrADS: COLA/IGES
2007-08-09-18:10


Mn(IV)
Mn(II)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
JAN 1992
JUL
JAN 1993
JUL
JAN 1994
JUL
JAN 1995
GrADS: COLA/IGES
2007-08-09-18:02



Mn(II)
H2S
JAN 1992
JUL
JAN 1993
JUL
JAN 1994
JUL
JAN 1995
GrADS: COLA/IGES
2007-08-09-18:10
O2, μM
H2S, μM
Mn(II), μM
MnPART, μM
Depth, m
O2
H2S
Mn(IV)
Mn(II)
01.01.1991
01.01.1991





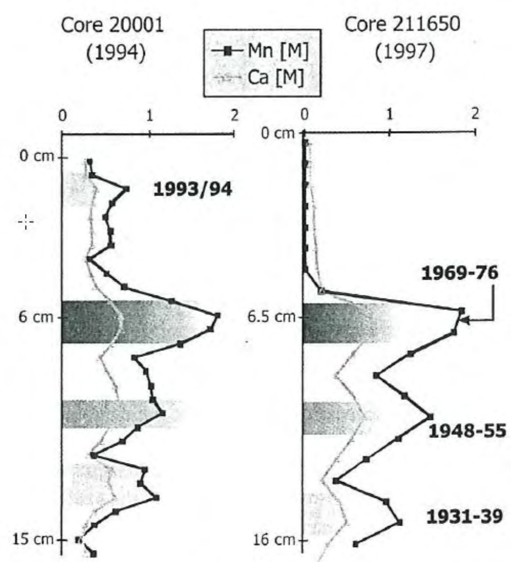


Fig. 8. Solid phase profiles of core 211650 (July 1997) and 20001 (August 1994, Neumann et al., 1997).

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 iflow (Hannig et al., 2007)

> 2 years required for the reestablishment of the stable redox interface structure (100 m thick with Kz~10^{-5} m^2s^{-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 my 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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