

Organic matter in the Baltic

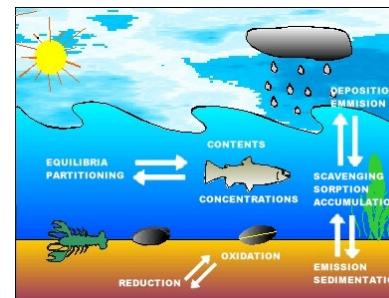
J.Pempkowiak, A.Szczepańska,
A.Maciejewska, K.Kuliński

Marine Biogeochemistry Section

Institute of Oceanology PAS, Sopot, Poland

Summary

1. What is organic matter?
2. Sources of OM in marine environment
3. Role organic matter plays in mar.envir.
4. OM amounts
5. OM in the carbon cycle
6. Baltic_C; WP4
7. Seawater acidification

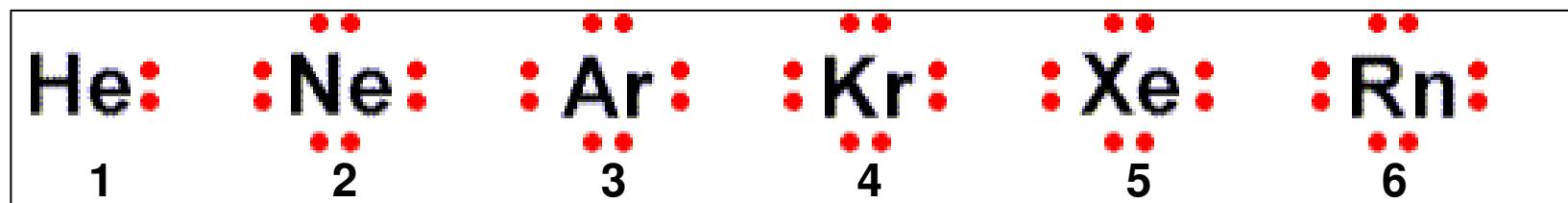
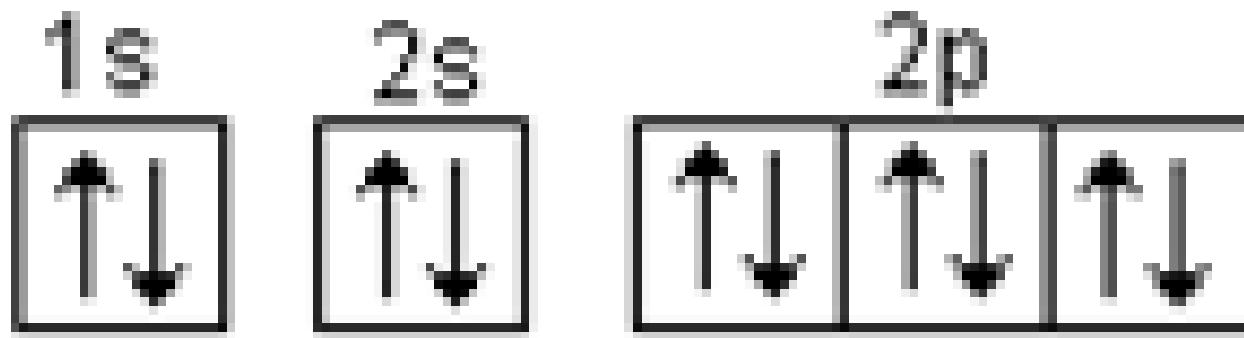


Organic substances vs organic matter



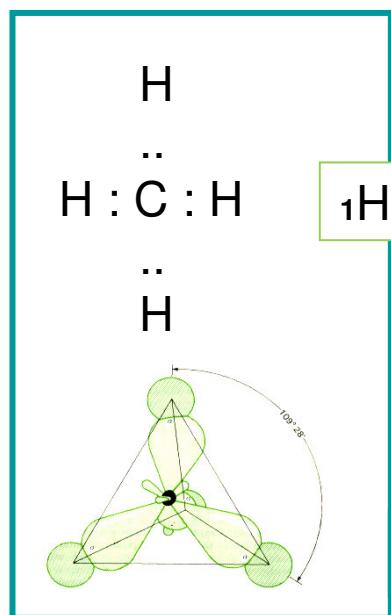
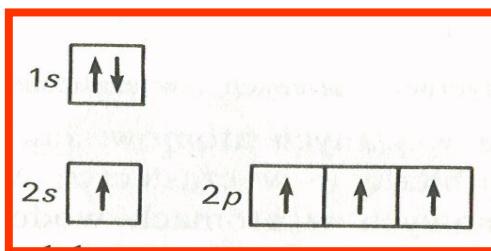
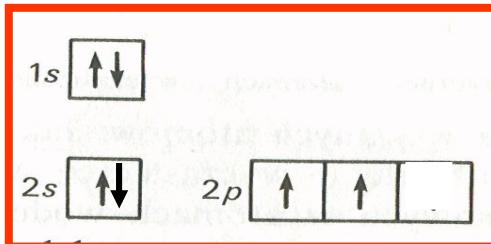
Distribution of electrons within shells

- neon: $1s^2 2s^2 p^{3 \times 2}$ (${}^{20}_{10} \text{Ne}$)
- Within shells electrons are distributed on orbitals (max. 2 electrons on one orbital)

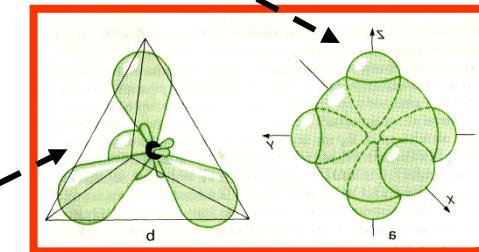
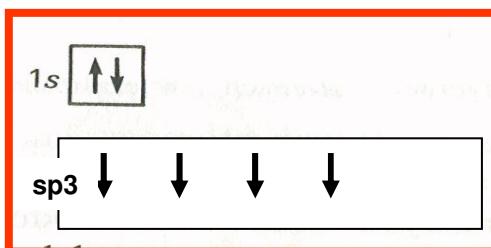


¹²
6
carbon

1s2 2s2 p2

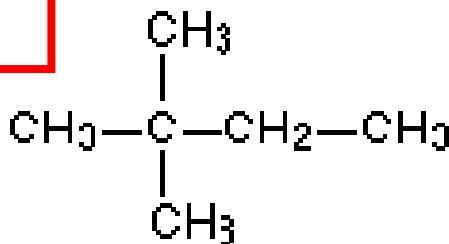
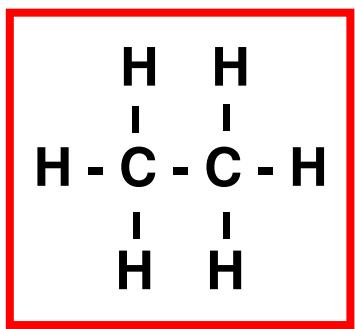
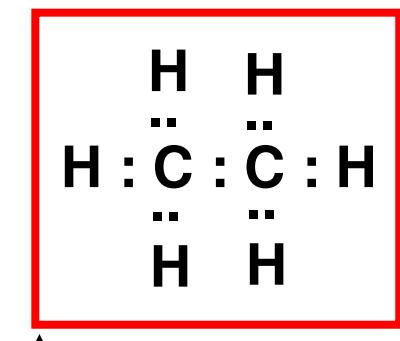


sp₃ hybridization



Metan- CH₄, the result of the *sp₃ hybridization*

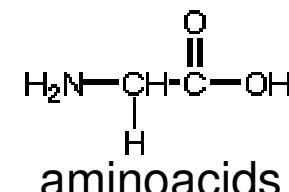
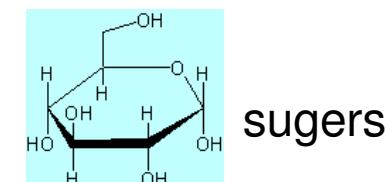
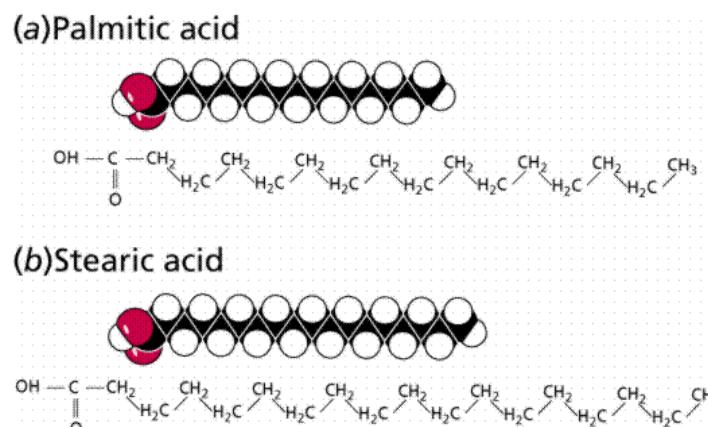
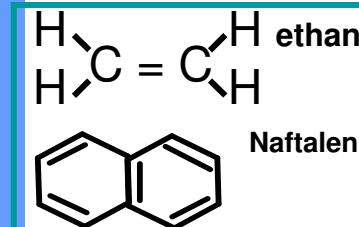
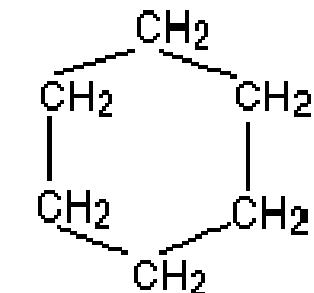
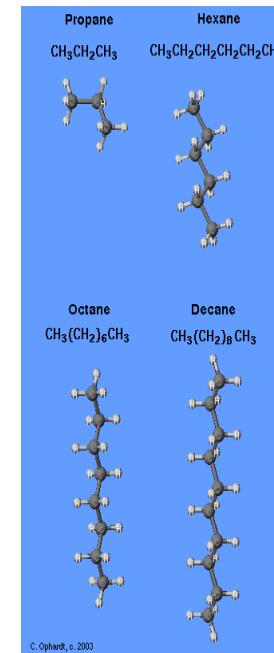
The wide world of organic substances



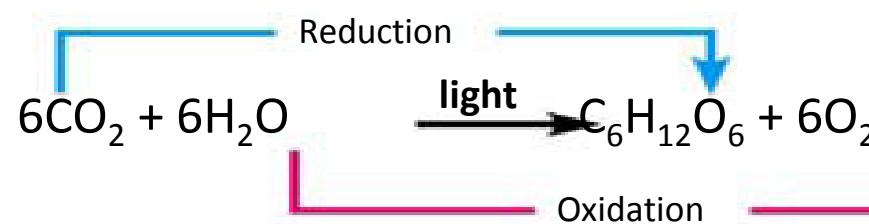
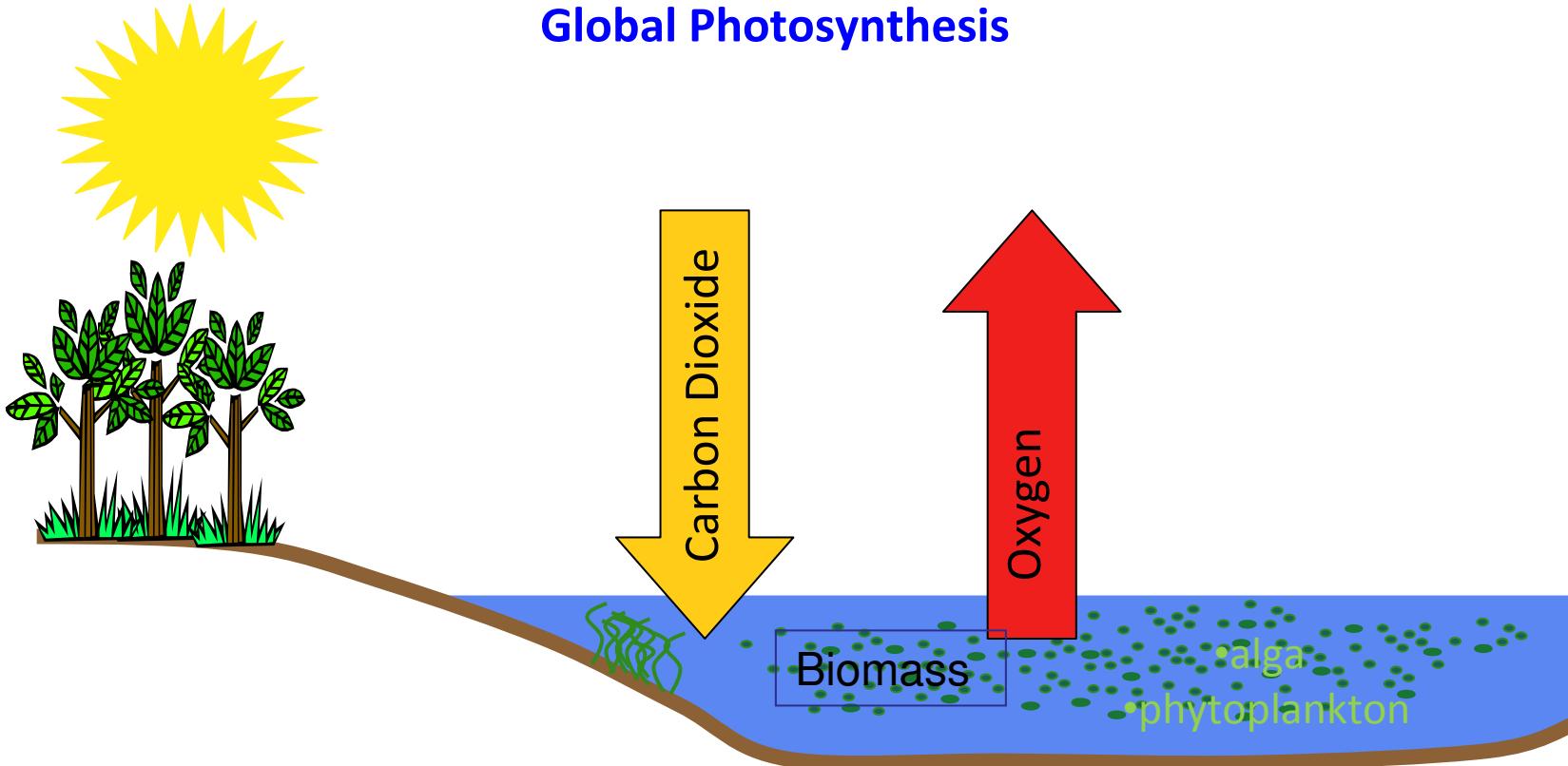
hydrocarbons

-OH
 $\text{CH}_3 - \text{OH}$ alkohols

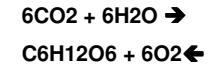
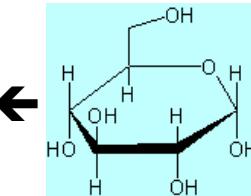
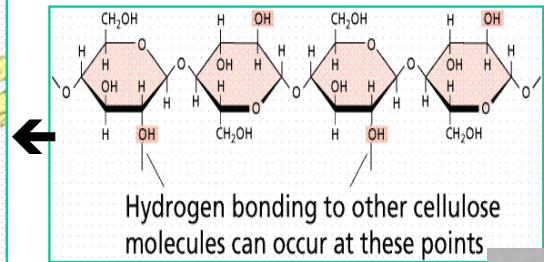
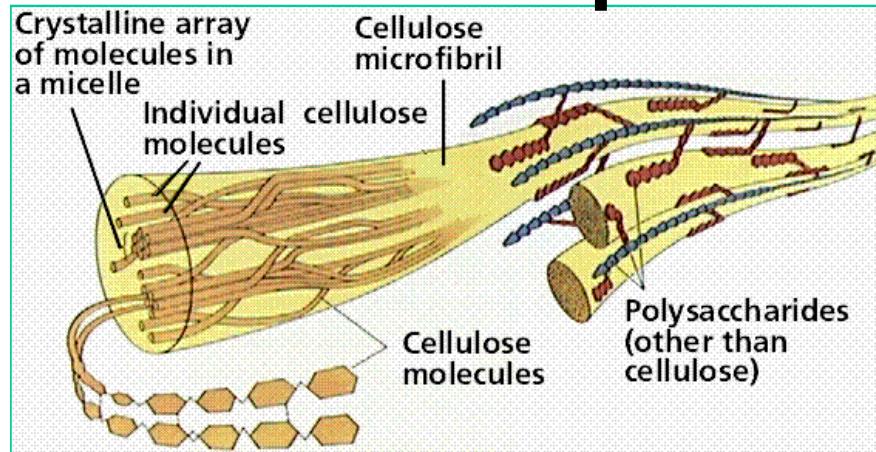
-COOH
 $\text{CH}_3 - \text{C} \begin{matrix} \nearrow \text{O} \\ \searrow \text{OH} \end{matrix}$ acids



Global Photosynthesis

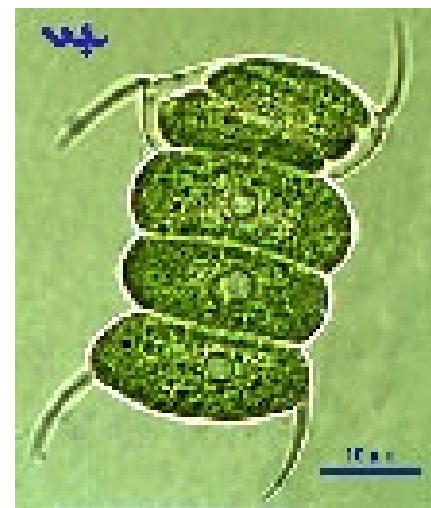
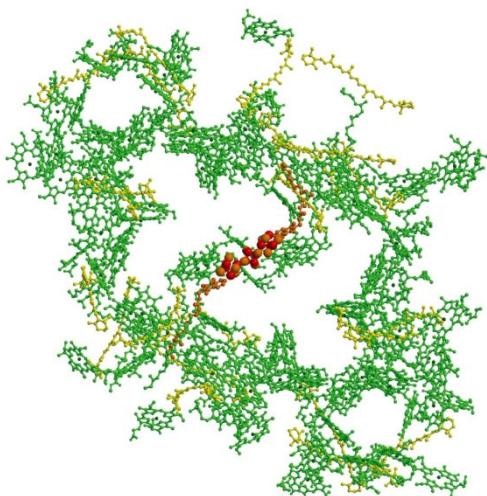


Bio-polymers vs geo-polymers



/ białka, kw.nukleinowe, polisacharydy, lipidy

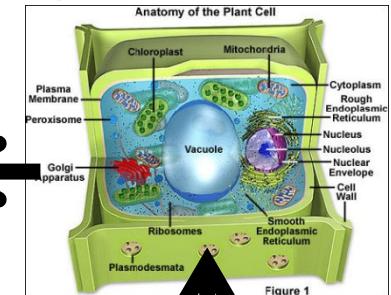
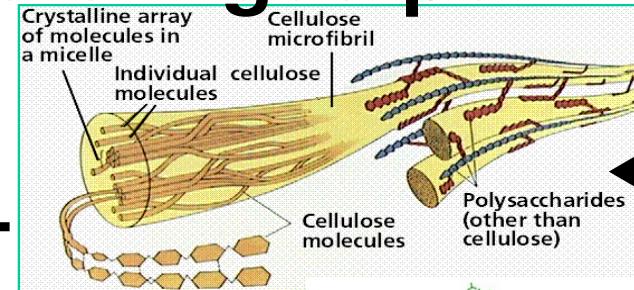
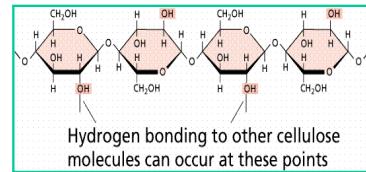
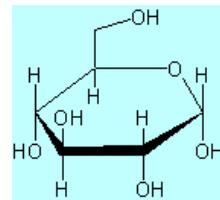
Biopolimery



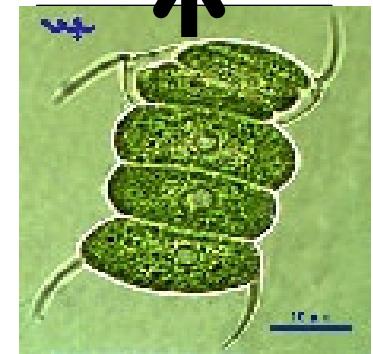
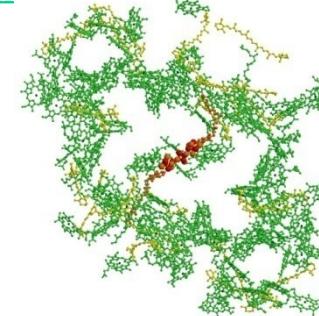
Nodularia spumigena



Bio-polymers vs geo-polymers

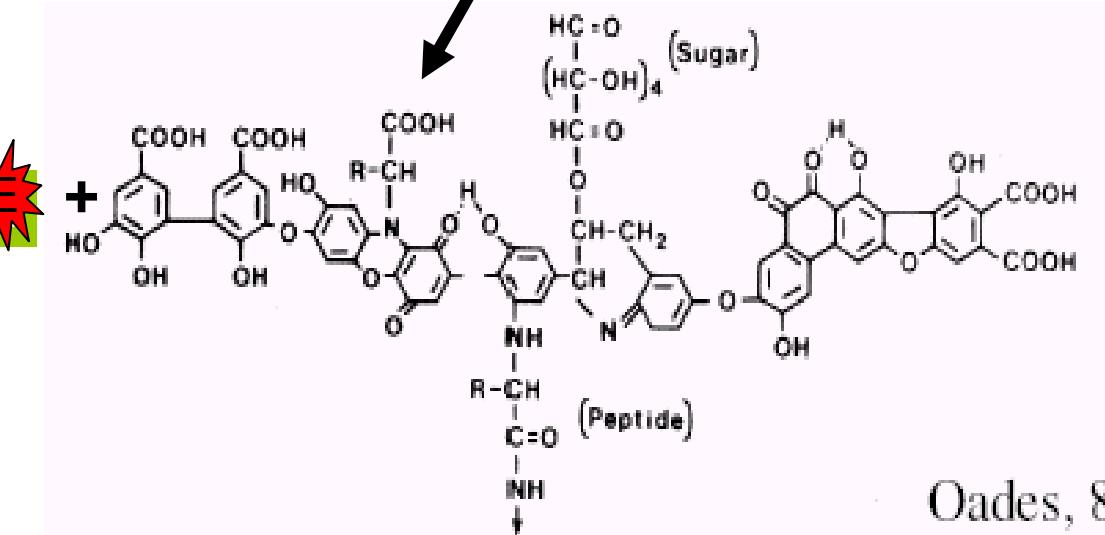


Biopolimery
/ białka, kw.nukleinowe,
polisacharydy, lipidy



Geopolimery / Kw.humusowe, bitumy, węgle

biochemical degradation

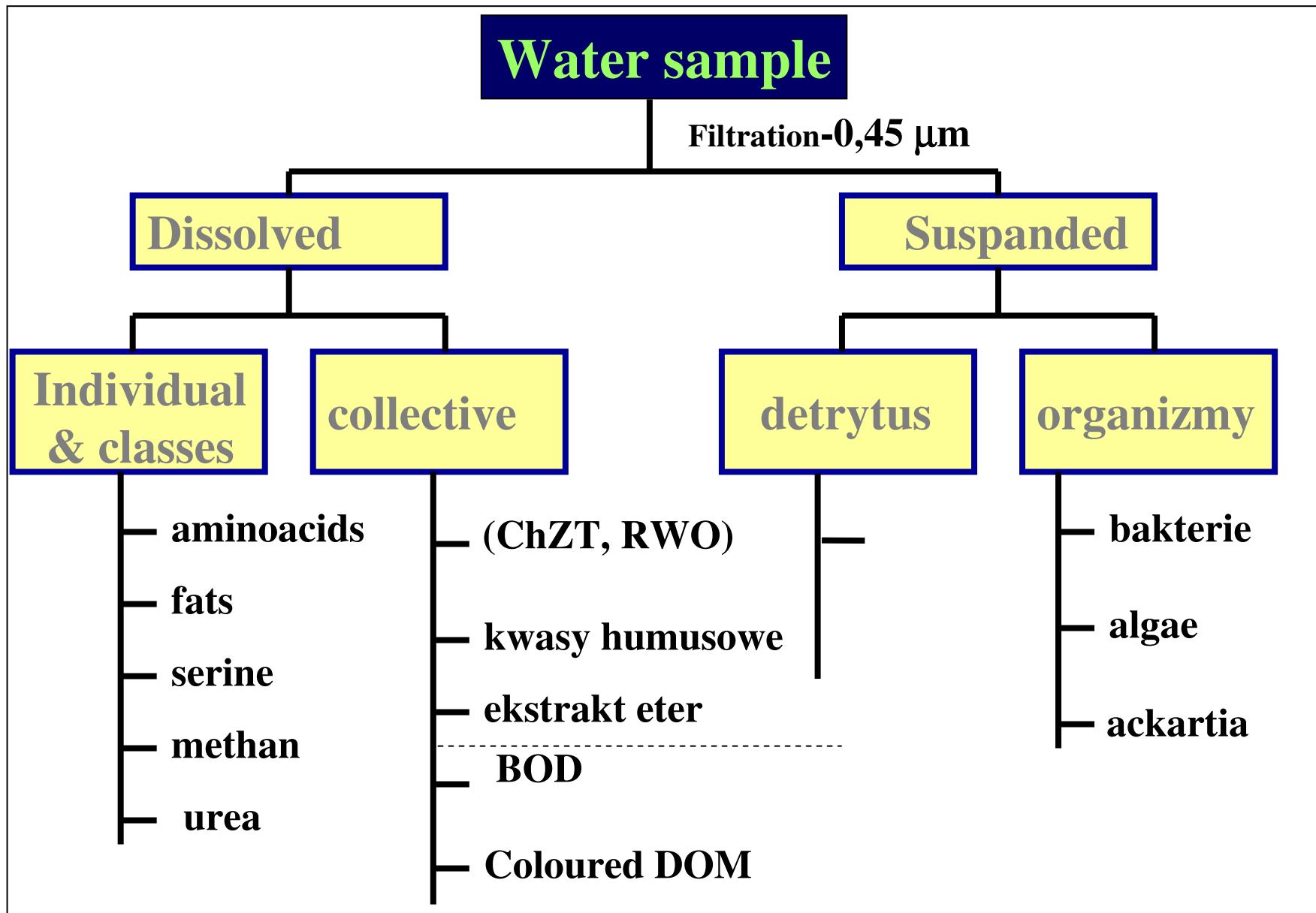


Oades, 89

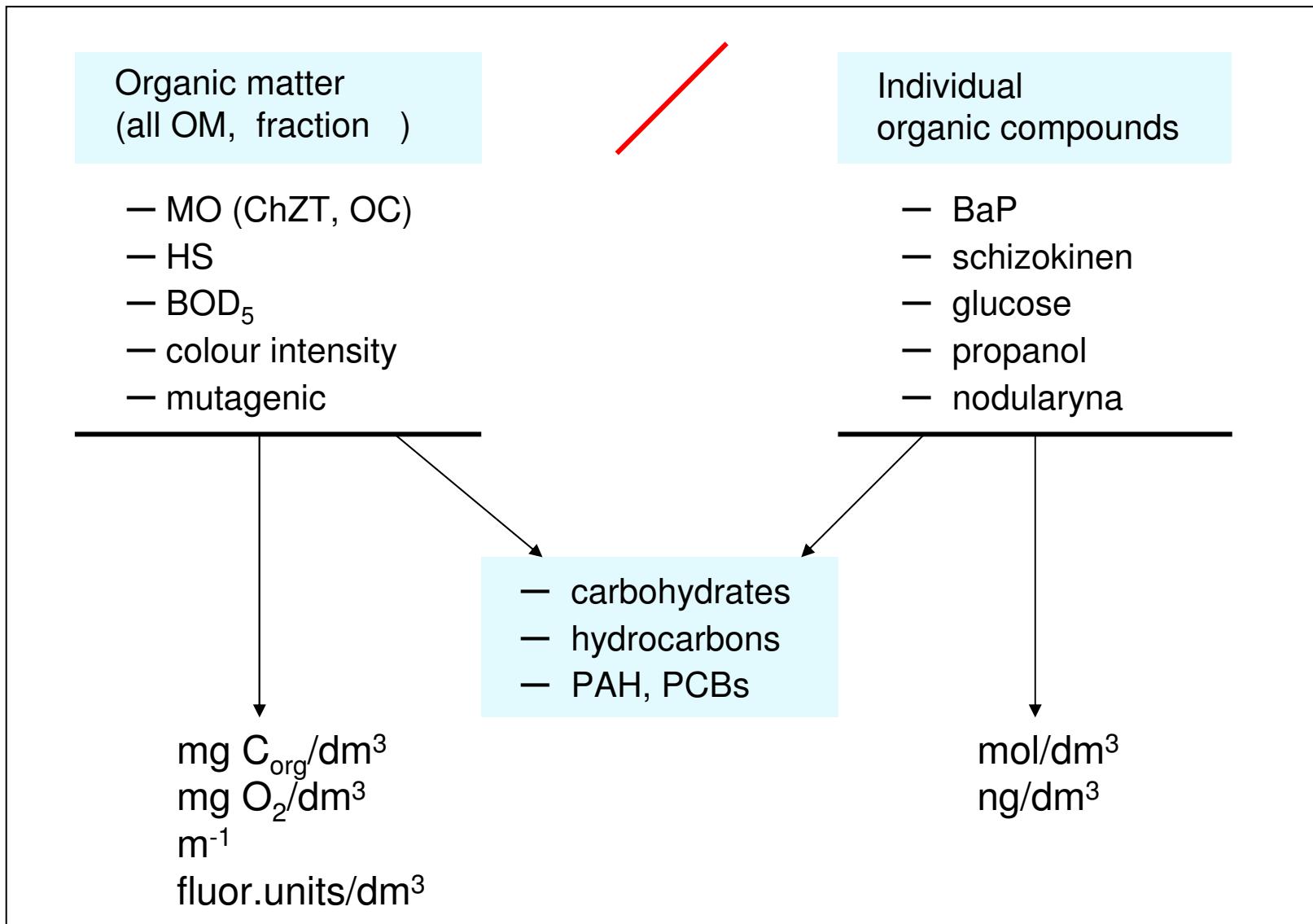
Measures of organic matter



Organic matter in sea-water



PROBLEM → all compounds vs thousands of individual organic compounds

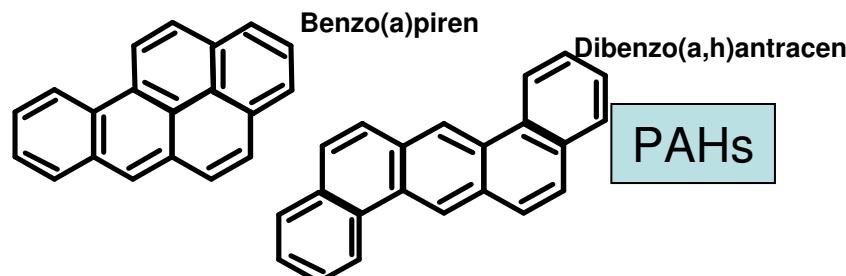
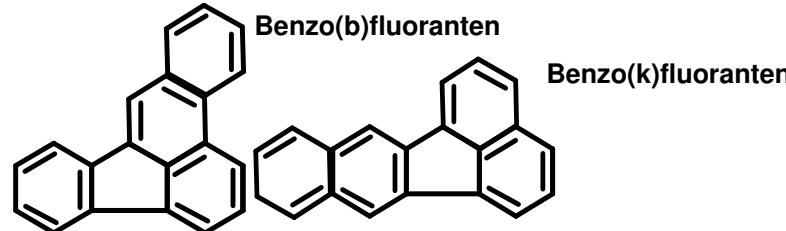


Measures of particulate organic matter

- **POC(POM)**
 - $POM = 2.12 (+/- 0.08) POC$
-

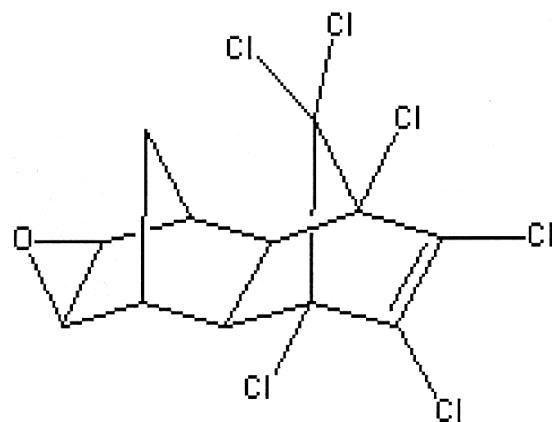
- BOD → LDOM (mgO₂/dm³)
- Nitrogen → mg/mg (%)
- HS content → mg/mg

Persistent organic pollutants- POP's

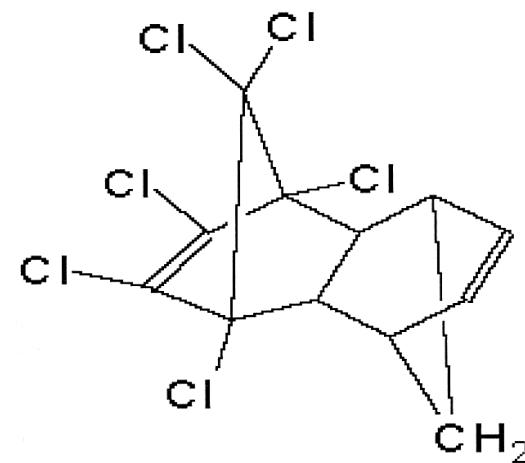


PAHs

- Toxic
- Bio-accumulated/magnified
- Trace concentrations (ng- μ g/l)

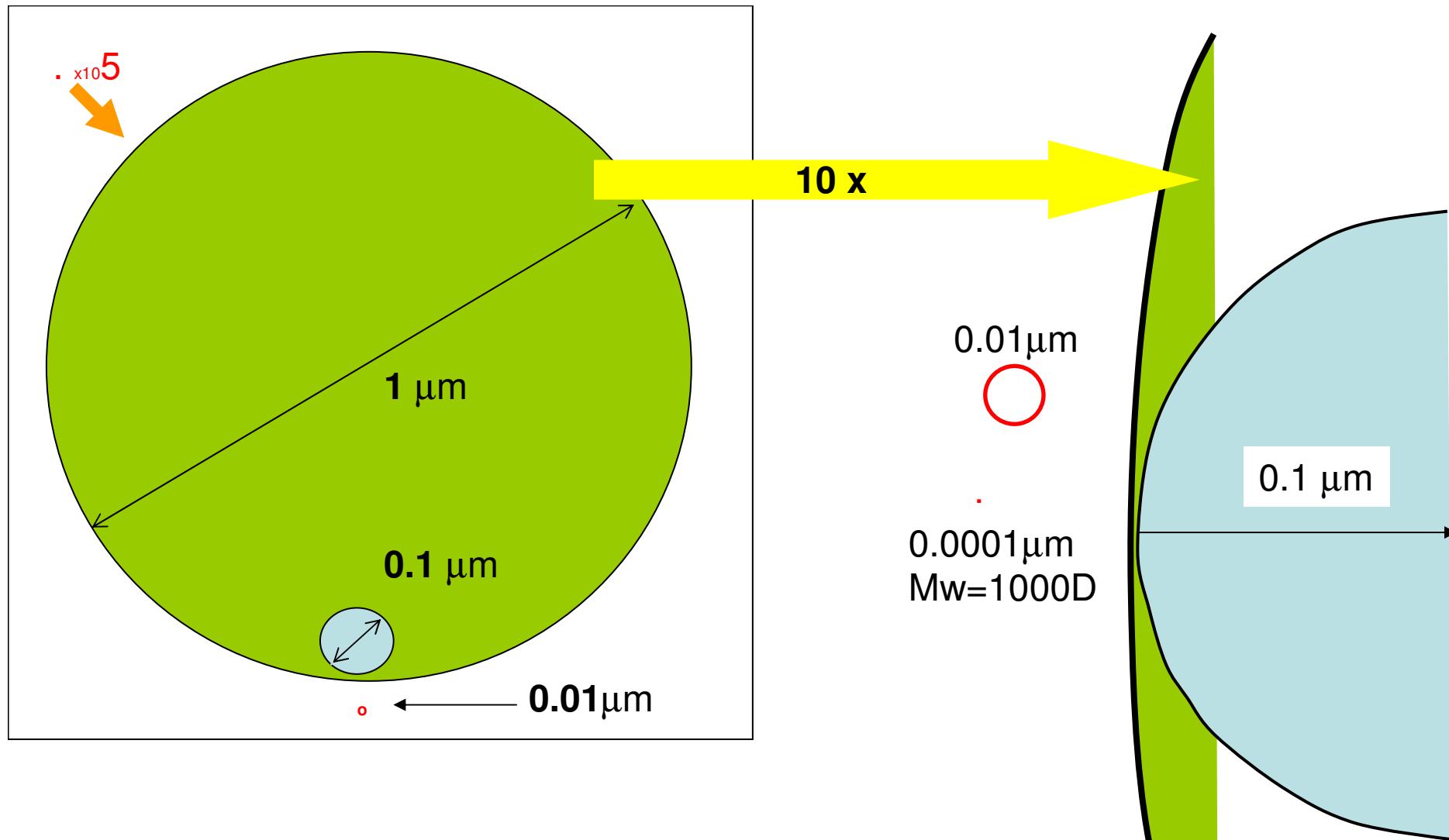


Insecticides
•aldrine
•deldrine



Dissolved vs Particulate OM- sizes





Założenie:

$0.1 \text{ ug/dm}^3 - 10^{-9} \text{ mol/dm}^3$

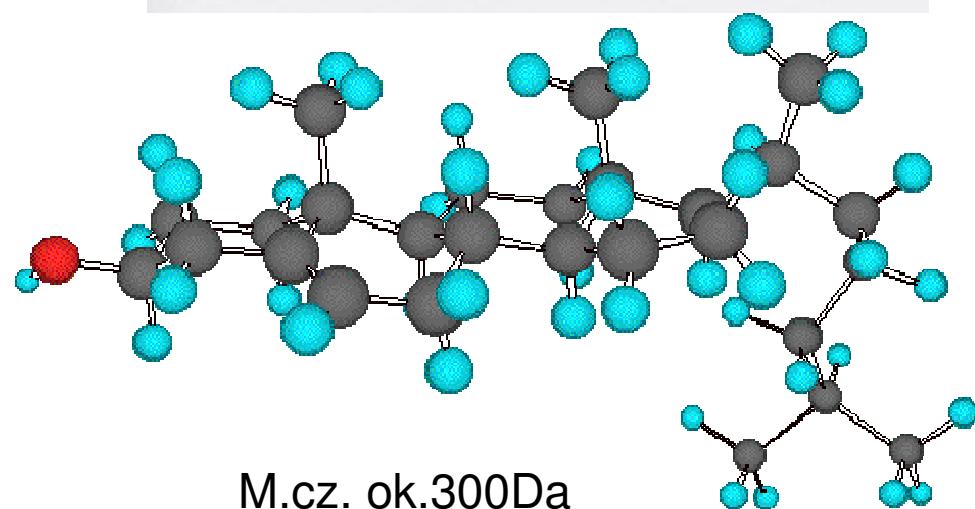
liczba cz. w przestrzeni o promieniu $0.01 \mu\text{m}$?

10^{-6}

czyli w przestrzeni o promieniu $0.1 \mu\text{m}$ będzie ich.. 1

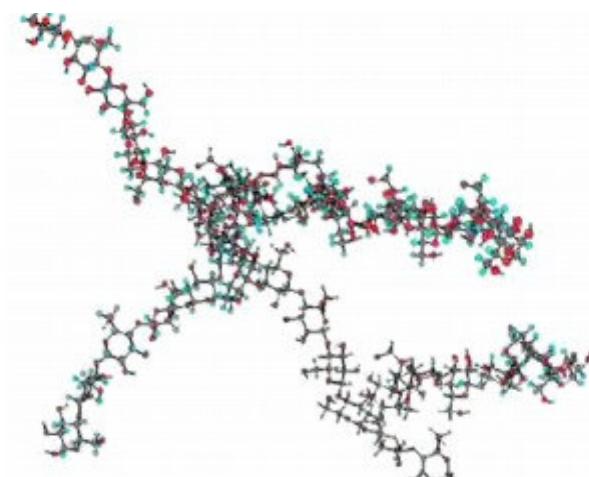
M.cz. ok. 4000Da

M.cz. ok. 1500Da

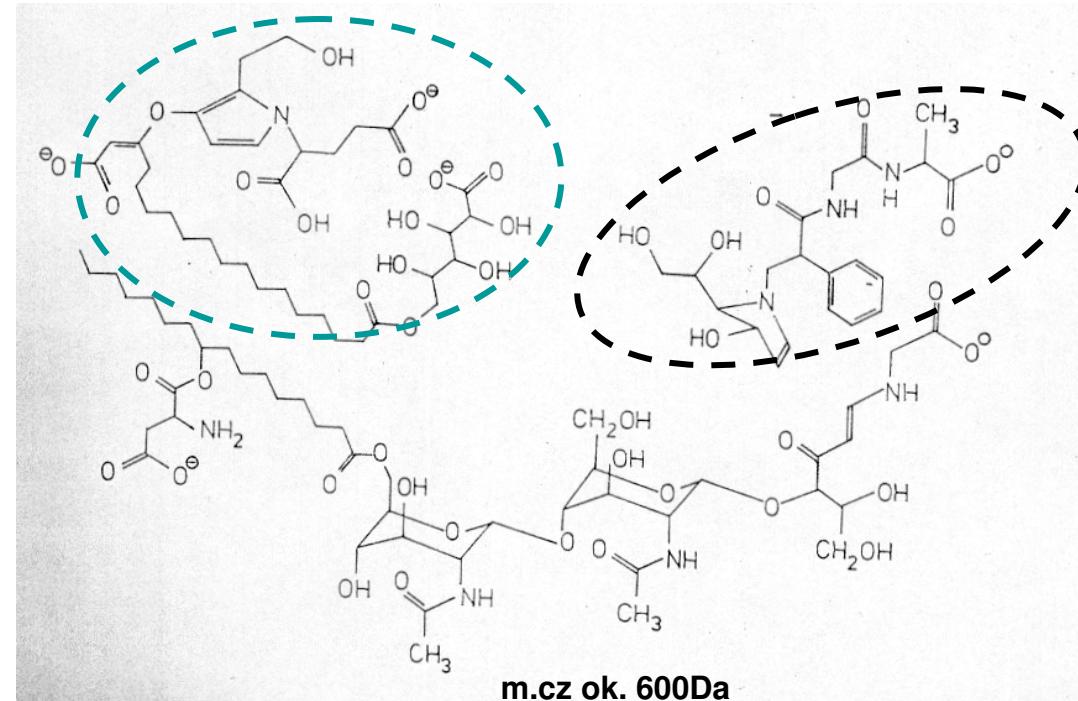


CH₄

M.cz. 16D (12 +4x1=16)

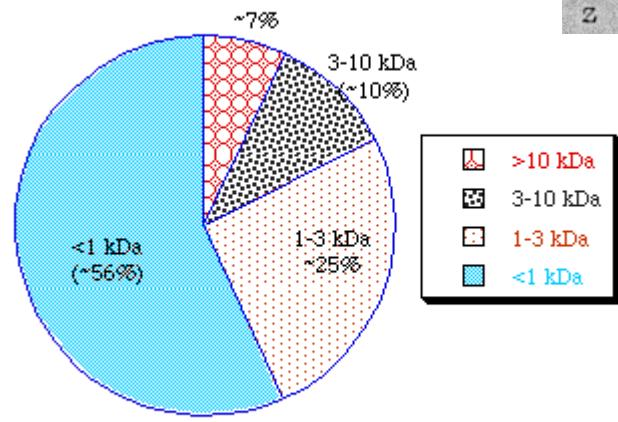


Chemical structure



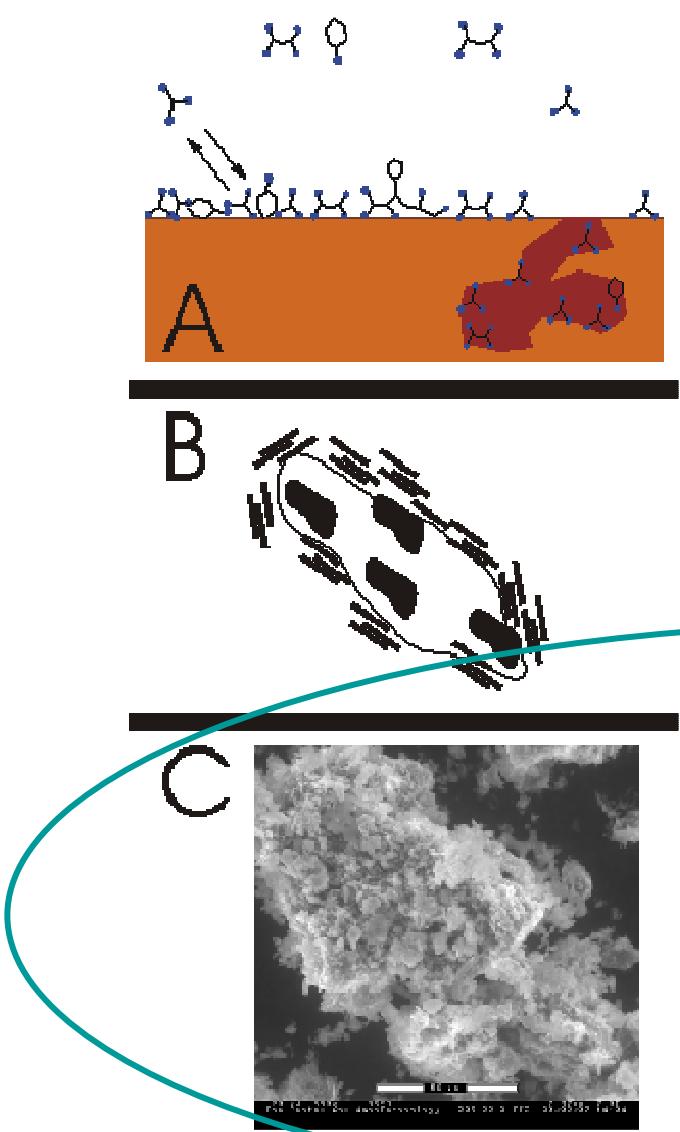
m.cz ok. 600Da

Rys.6. Hipotetyczne struktury cząsteczek kwasów humusowych z wody oceanicznej [174] Stourmer, 1975



Molecular weight distribution
Narrangaset Bay (Darret, 1998)

Baltic O.C.>10kD – 2%
Brown(~ 1975)



Panel A
shows the potential interactions between organic molecules and surfaces.

Panel B
is a conceptual diagram of the organic-mineral onion in which organic matter is protected within a mineral sheath, largely composed of clay minerals, especially the expandable clays.

Panel C
shows a ESEM image of one such organo-clay onion isolated from the Mexican Margin. The aggregate has a density between $1.05 - 1.2 \text{ g cm}^{-3}$ and is roughly 45% organic matter by weight. The size of the cluster is $\sim 50 \times 100 \text{ microns}$.



Role OM plays in marine environment

- **Produkcja pierwotna**
- **Marker**
- **Reg.N/P**
- **Stęż. O₂**
- **Pożywienie**
- **Pole światła, mnutrienty**
- **Kompl.subst toksycznych**



Sources of OM in marine environment

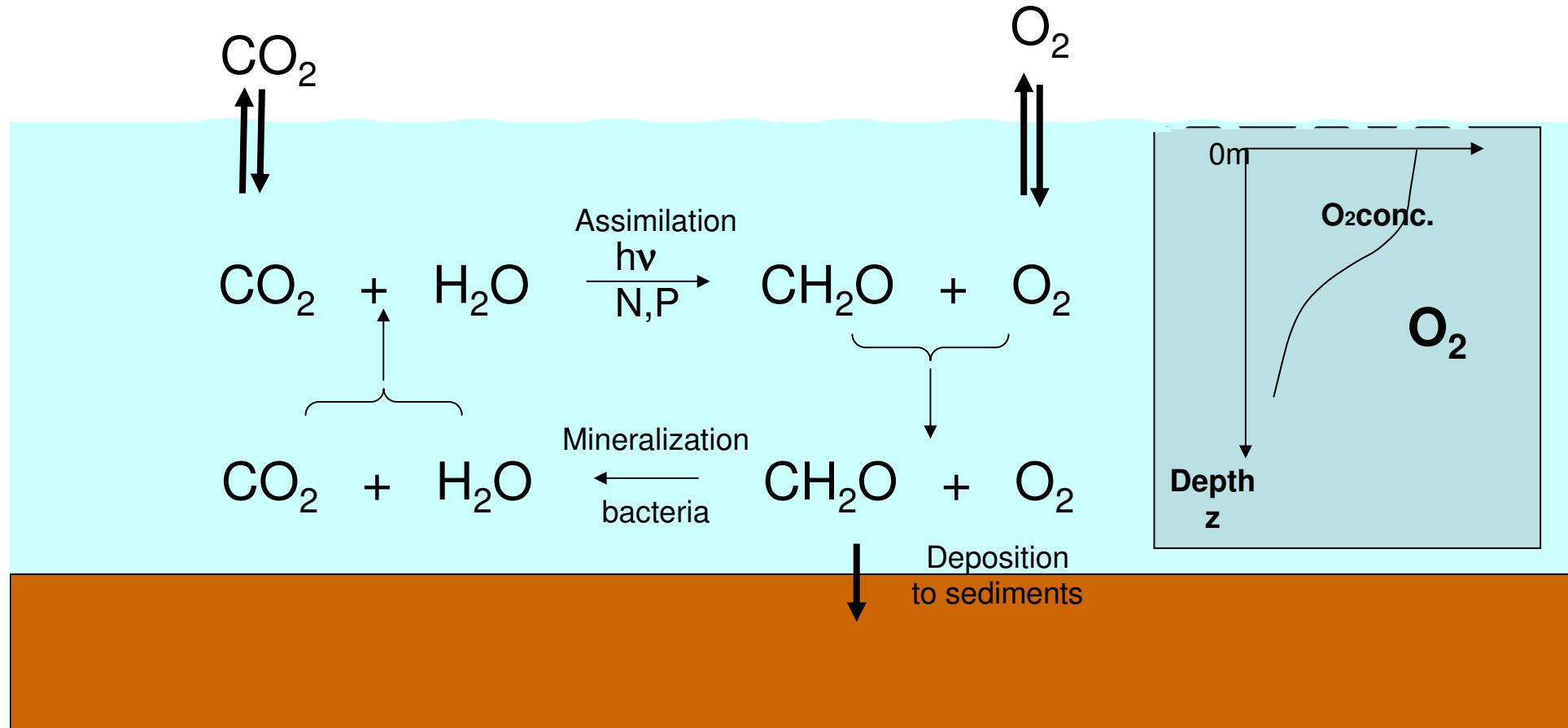
- Primary productivity/ biota
- River run-off
- Precipitation
- Sediments

Fate of organic matter in the sea



Factors controlling oxygen concentration

1. CO₂ assimilation/OM mineralization

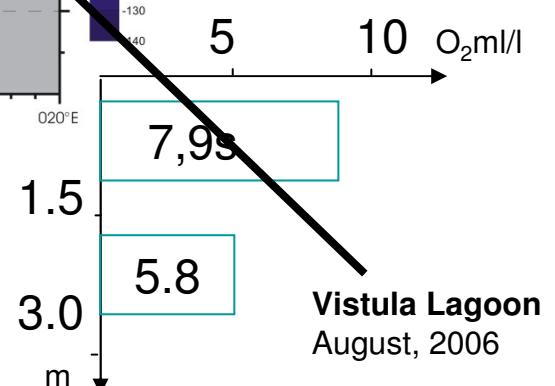
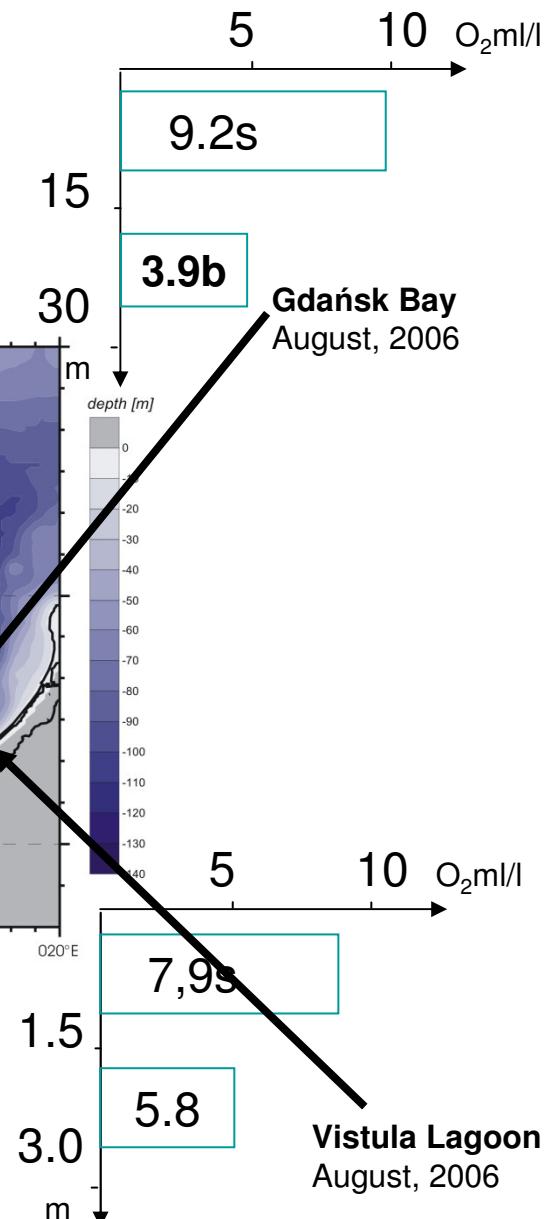
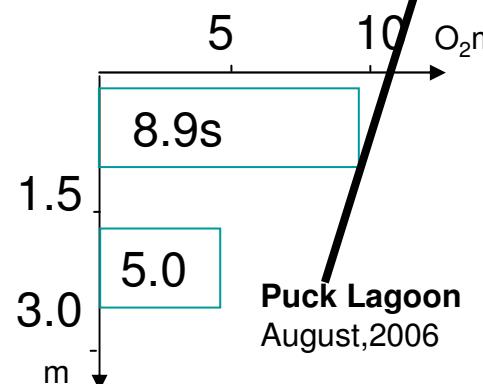
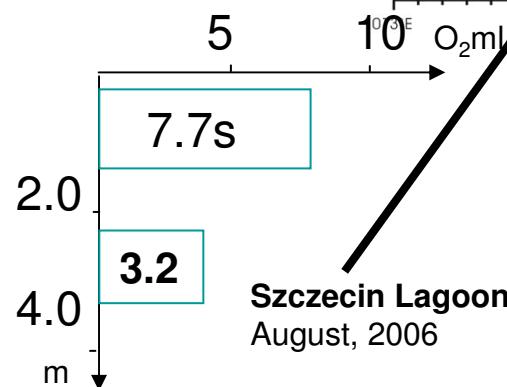
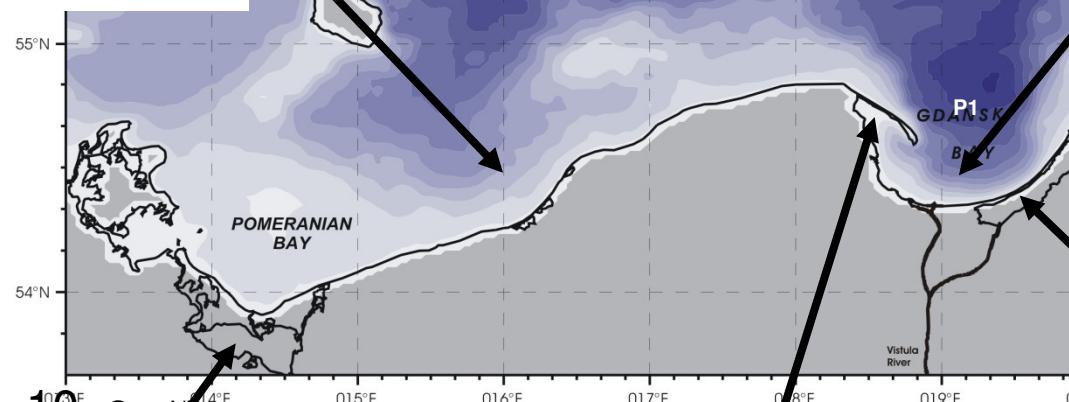
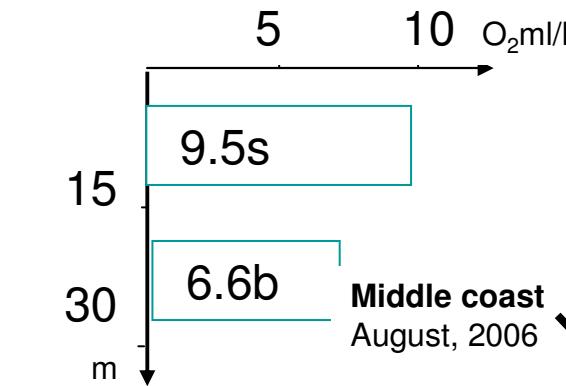


2. Oxygen saturation disequilibria

- Temperature oscillations
- Supersaturation

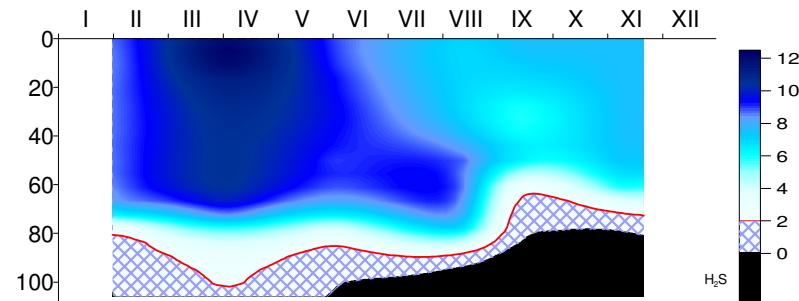
Oxygen concentrations – **coastal** (*Pastuszak,2007*)

- surface(0-2m) vs bottom (2-0.5m above bottom)

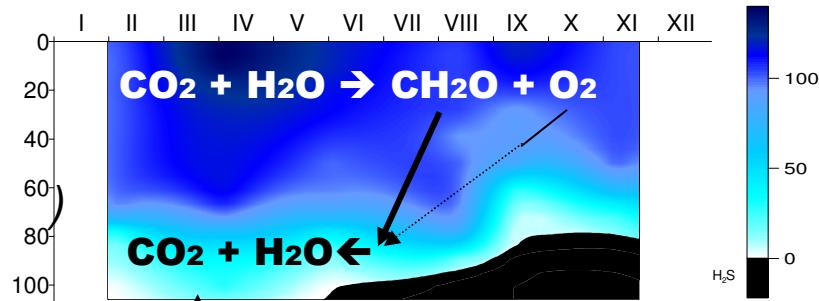


Oxygen concentrations – offshore (Pastuszak,2007)

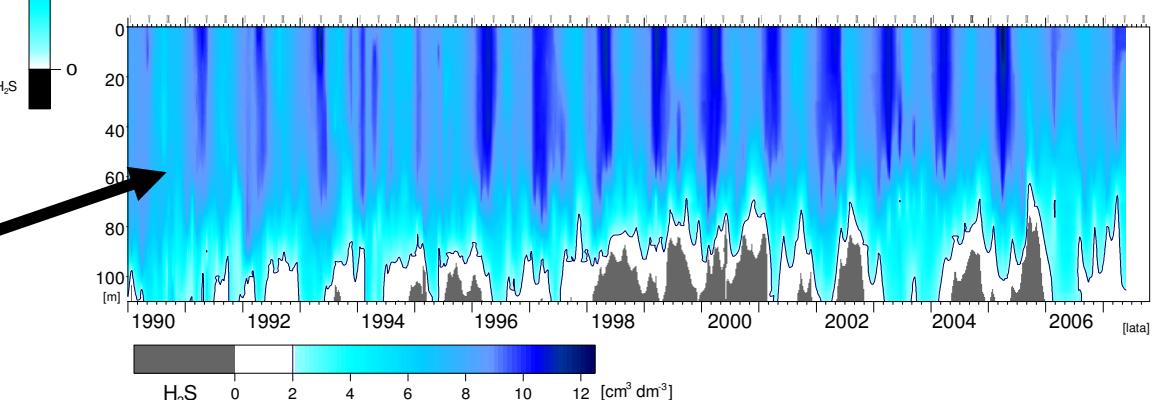
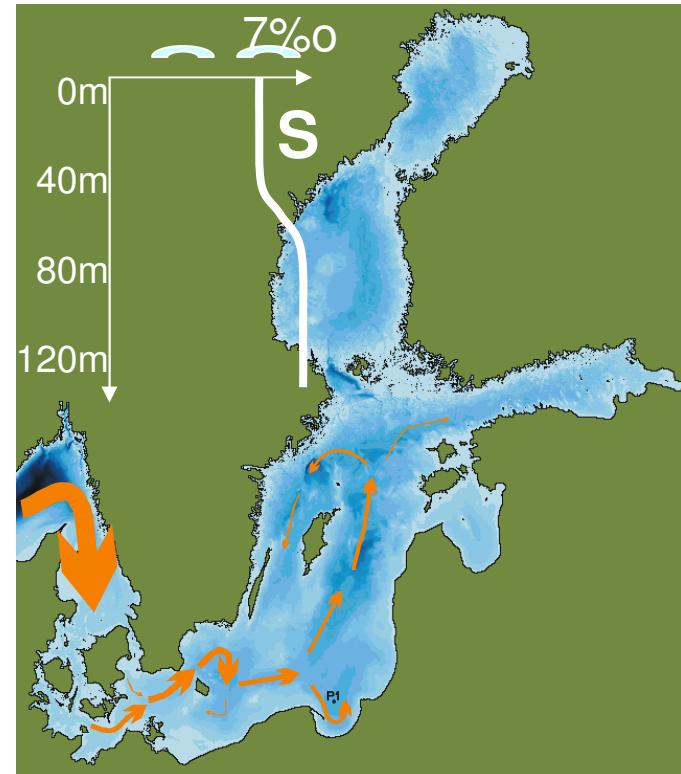
Gdańsk Deep, P1 station
a) concentration (ml/l)



b) saturation index (%)



•2005
•1990-2006

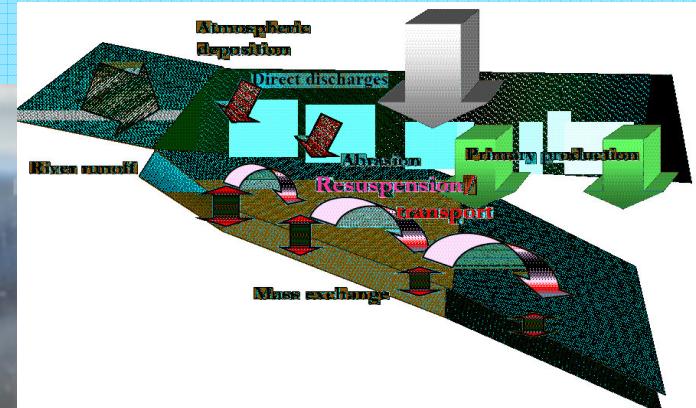


Fluffy Layer Suspended Matter -FLSM

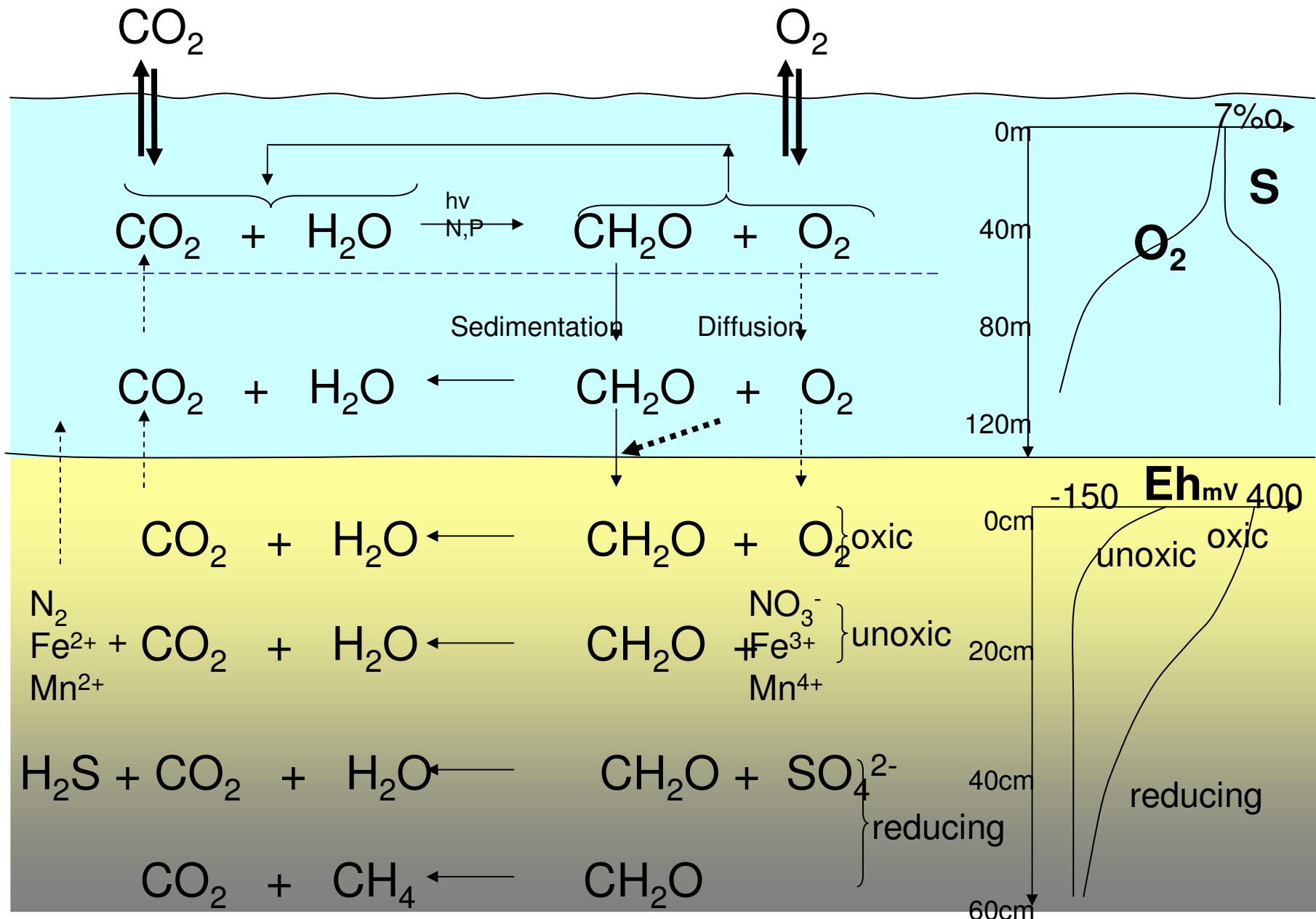
Sediment/Water interface
-2-3 cm thick layer

Concentr.- 1-4mg/ml

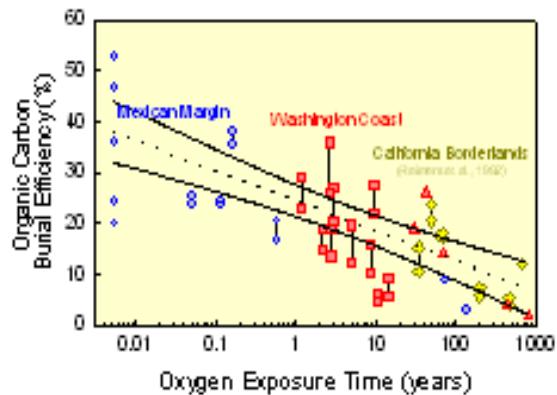
Resuspension- 4-5cm/s/



Processes



Organic matter/carbon burial rates

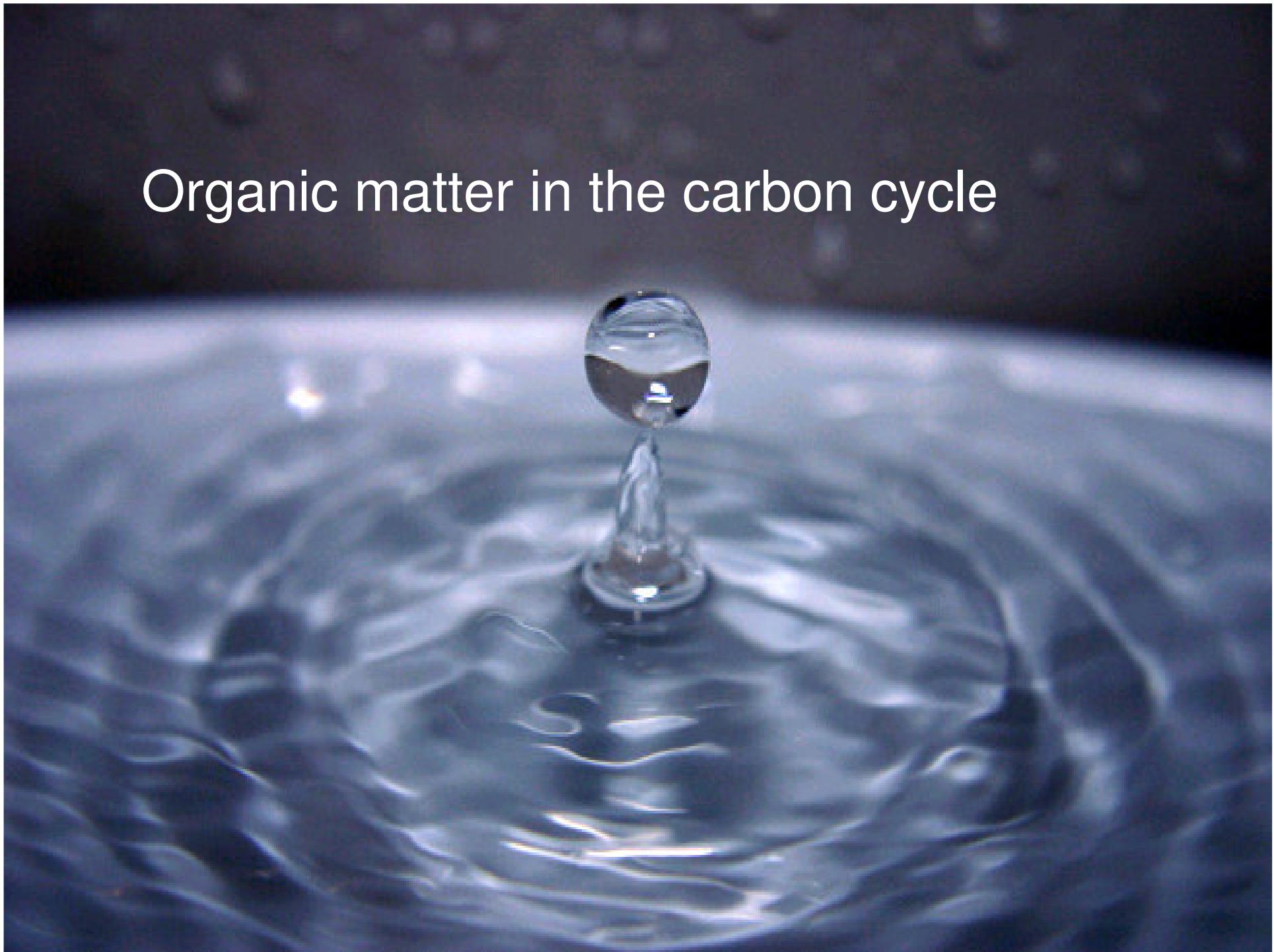


In the Baltic sediments

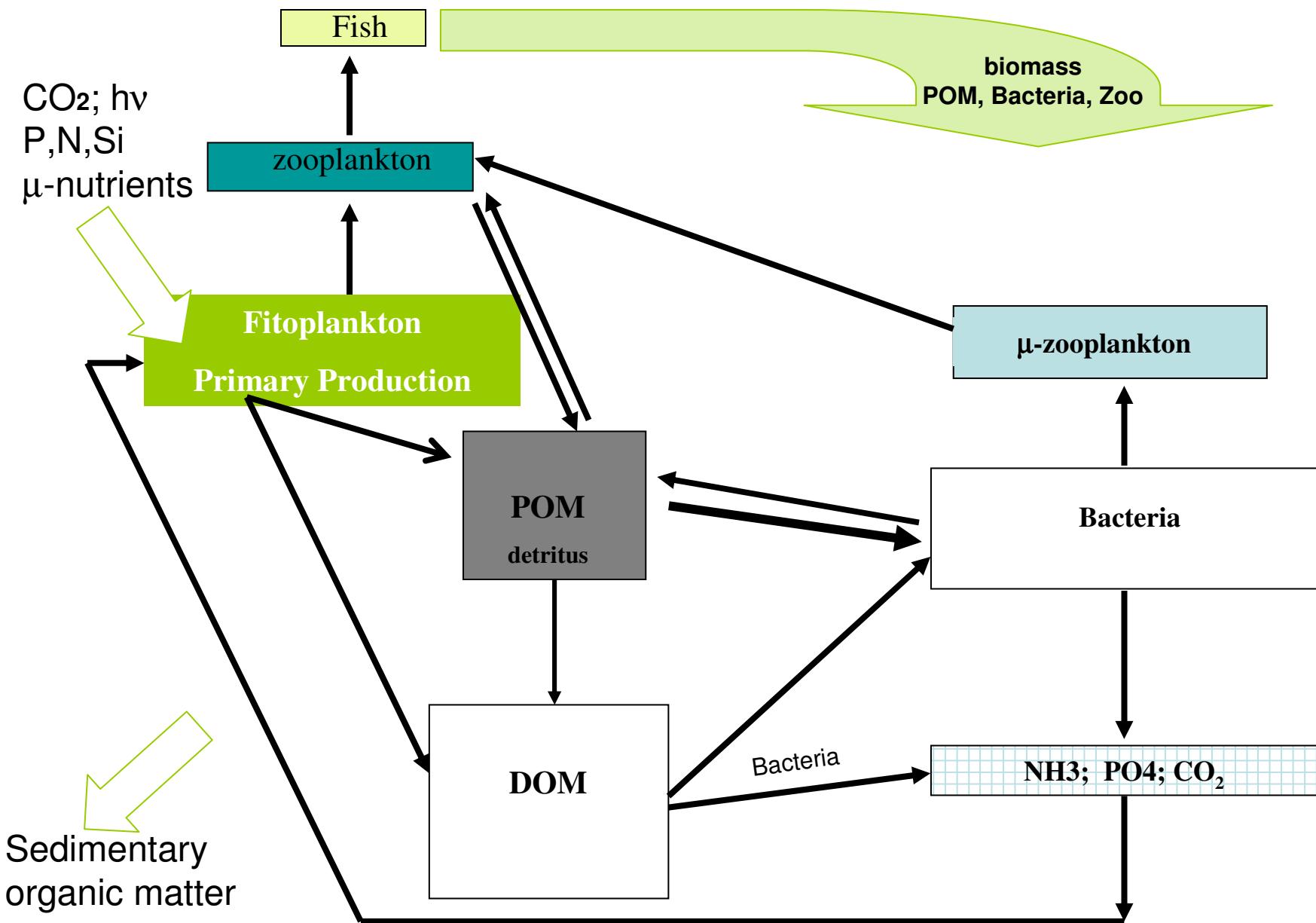
- $T_{1/2} \sim 5\text{-}8\text{ years}$
- Burial efficiency ?
10-30%

Hartnett, H.E., Keil, R.G., Hedges, J.I. and Devol, A.H., 1998.
Influence on oxygen exposure time on organic
carbon preservation in continental margin sediments.
Nature, 391: 372-374

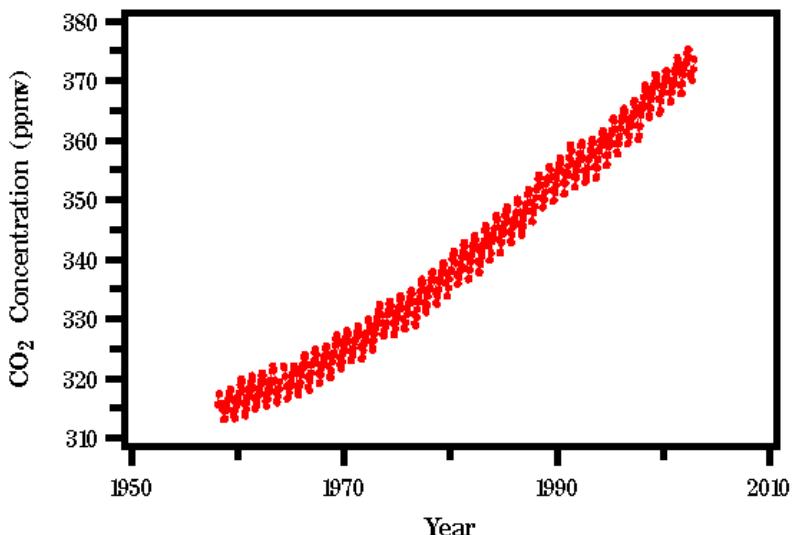
Organic matter in the carbon cycle



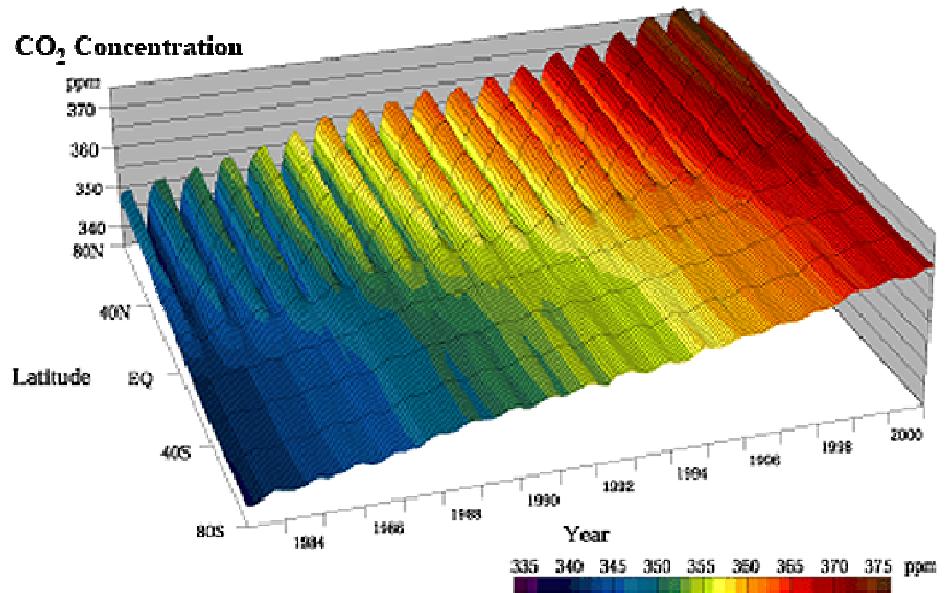
POM and DOM cycling



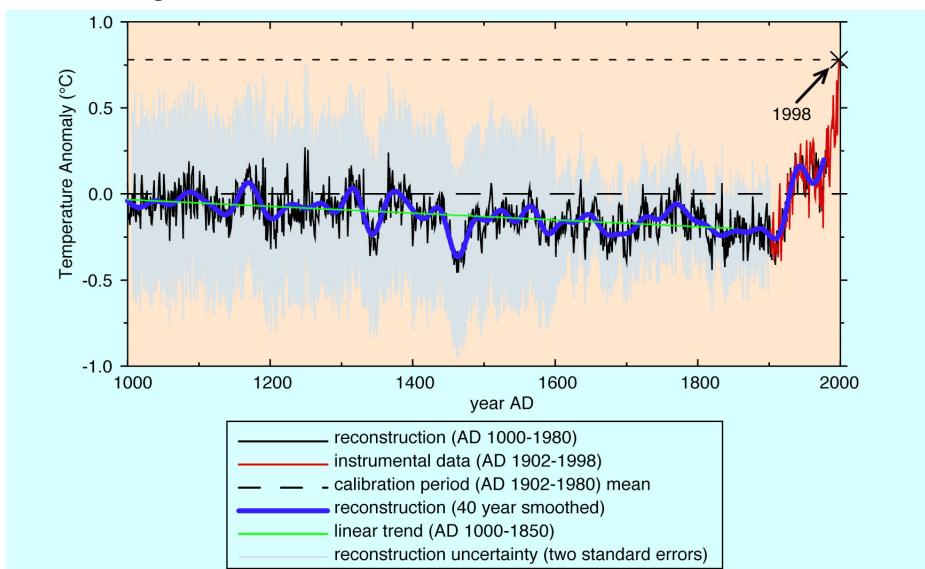
Global warming



Keeling's Curve, Mauna Loa, Hawaii

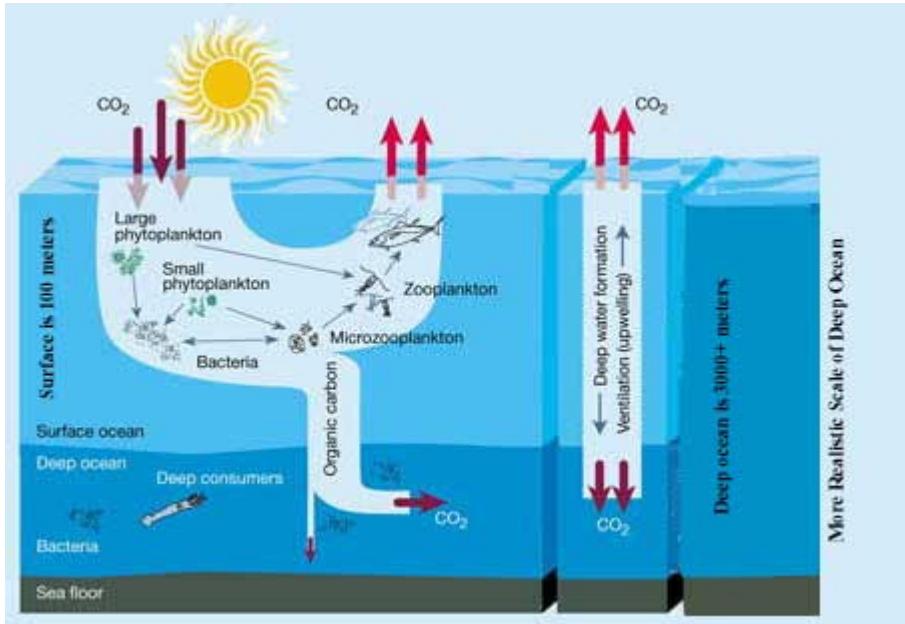


World Data Centre for Greenhouse Gases, Japan

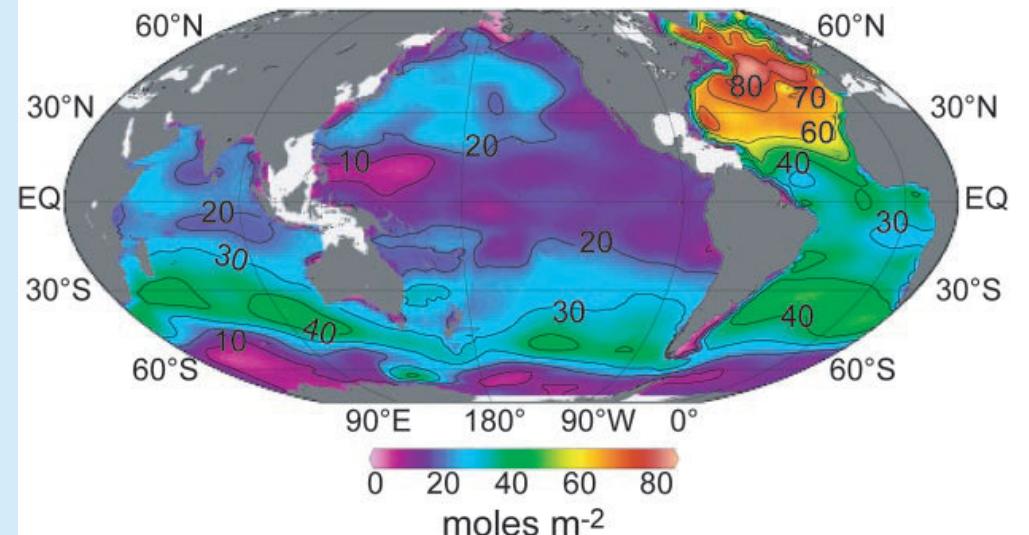


Bradley 2003 after Mann et al. 1999

Marginal seas in the global carbon cycle



Biophysical pump, PLANKTOS

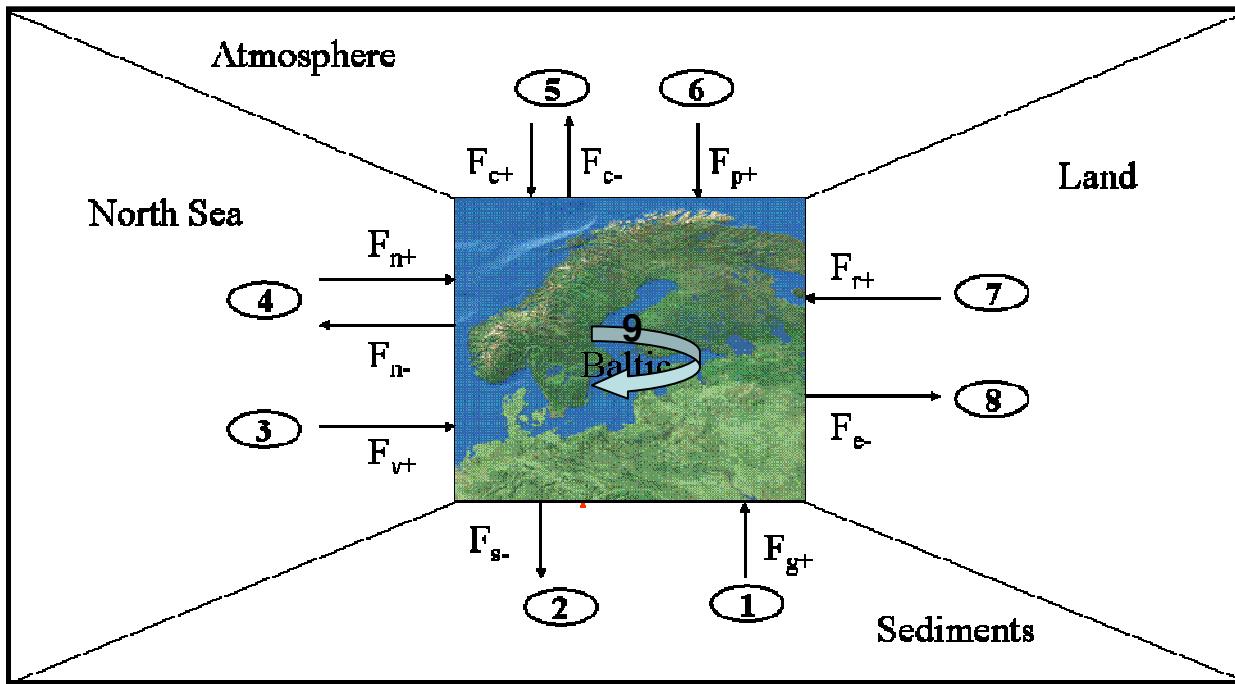


Oceans CO₂ uptake, Sabine et al. 2004

Role of the marginal seas in the global CO₂ uptake ???

- **mariginal-** 0,4 Pg C year⁻¹ (Thomas et al., 2004) ;
1,0 Pg C year⁻¹ (Tsunogai et al., 1999)
- **global-** 2,0 Pg C year⁻¹ (Cai et al., 2003)

Baltic Sea carbon cycle



- ① Groundwater seepage
- ② Sedimentation +
- ③ Ships discharge
- ④ North Sea + Baltic Sea water exchange
- ⑤ Air / Sea CO₂ exchange
- ⑥ Precipitation
- ⑦ Riverine runoff
- ⑧ Extraction

F... Carbon fluxes as a product of material fluxes
and carbon concentration

Carbon fluxes in the Baltic Sea,

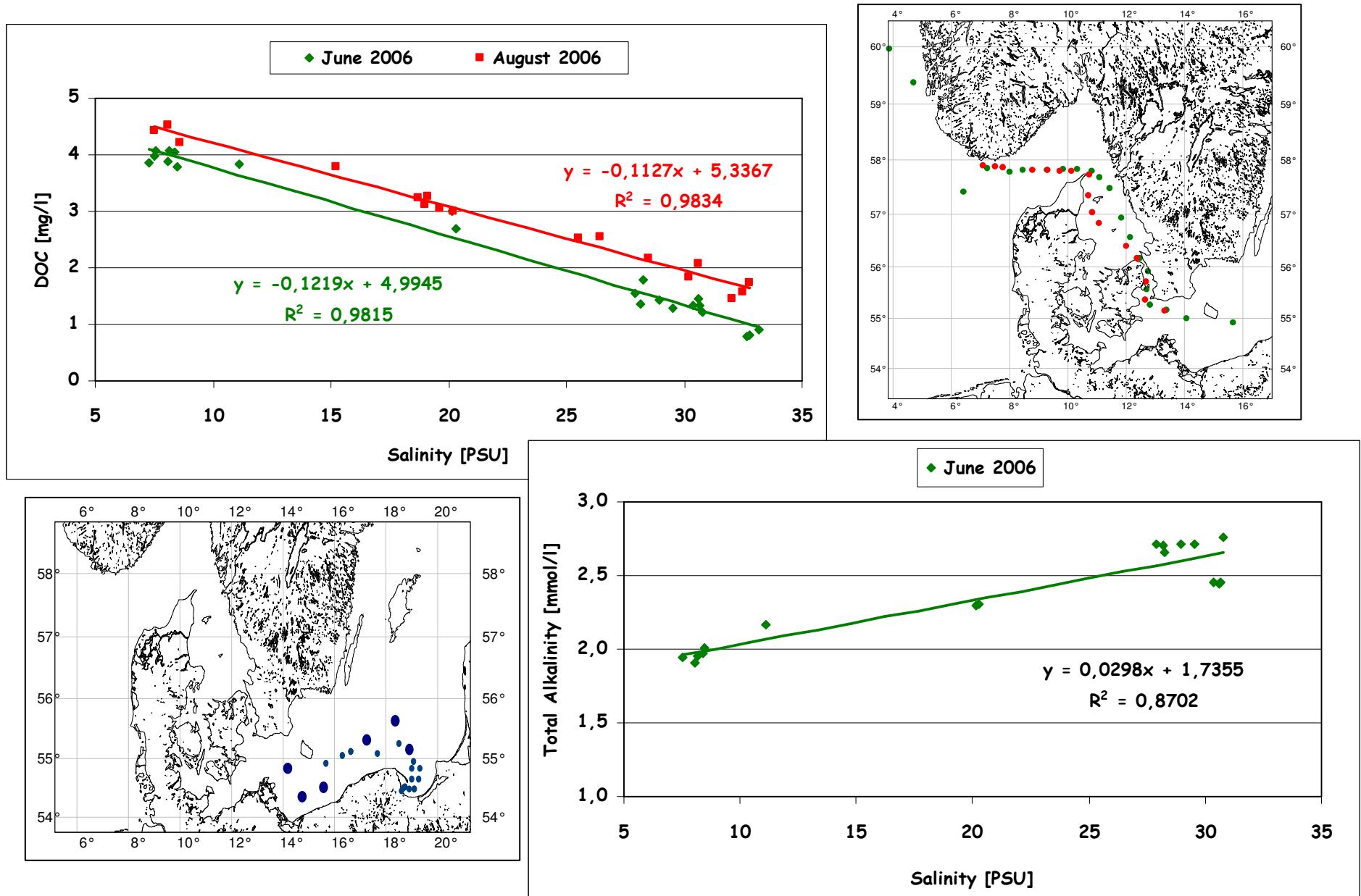
*Pempkowiak 1977; Peltonen 2002; Thomas & Schnider, 2000
Thomas et al. 2003a; Thomas et al. 2003b; Smailys 2005;
HELCOM 2004, 2006; SMHI 2003*

9. Primary production/mineralization

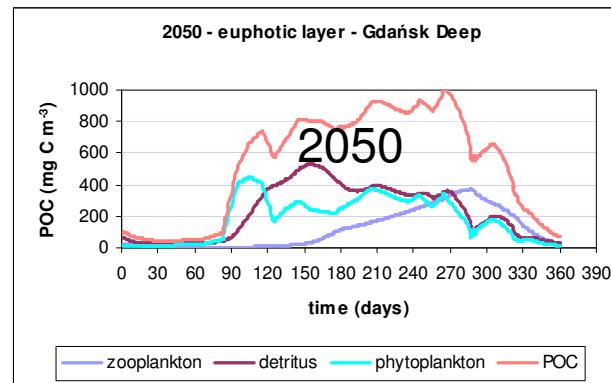
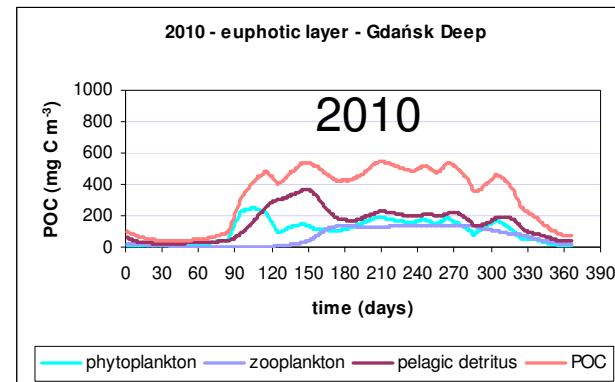
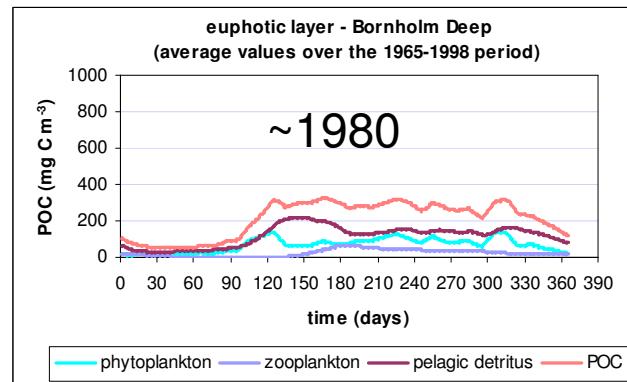
Concentration of OM



Baltic Sea Cruise 2006 / AREX 2006



POC modelling



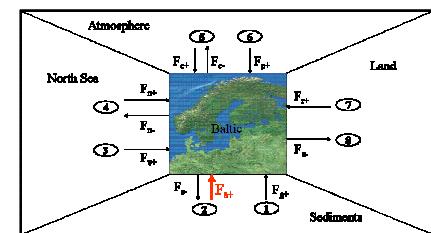
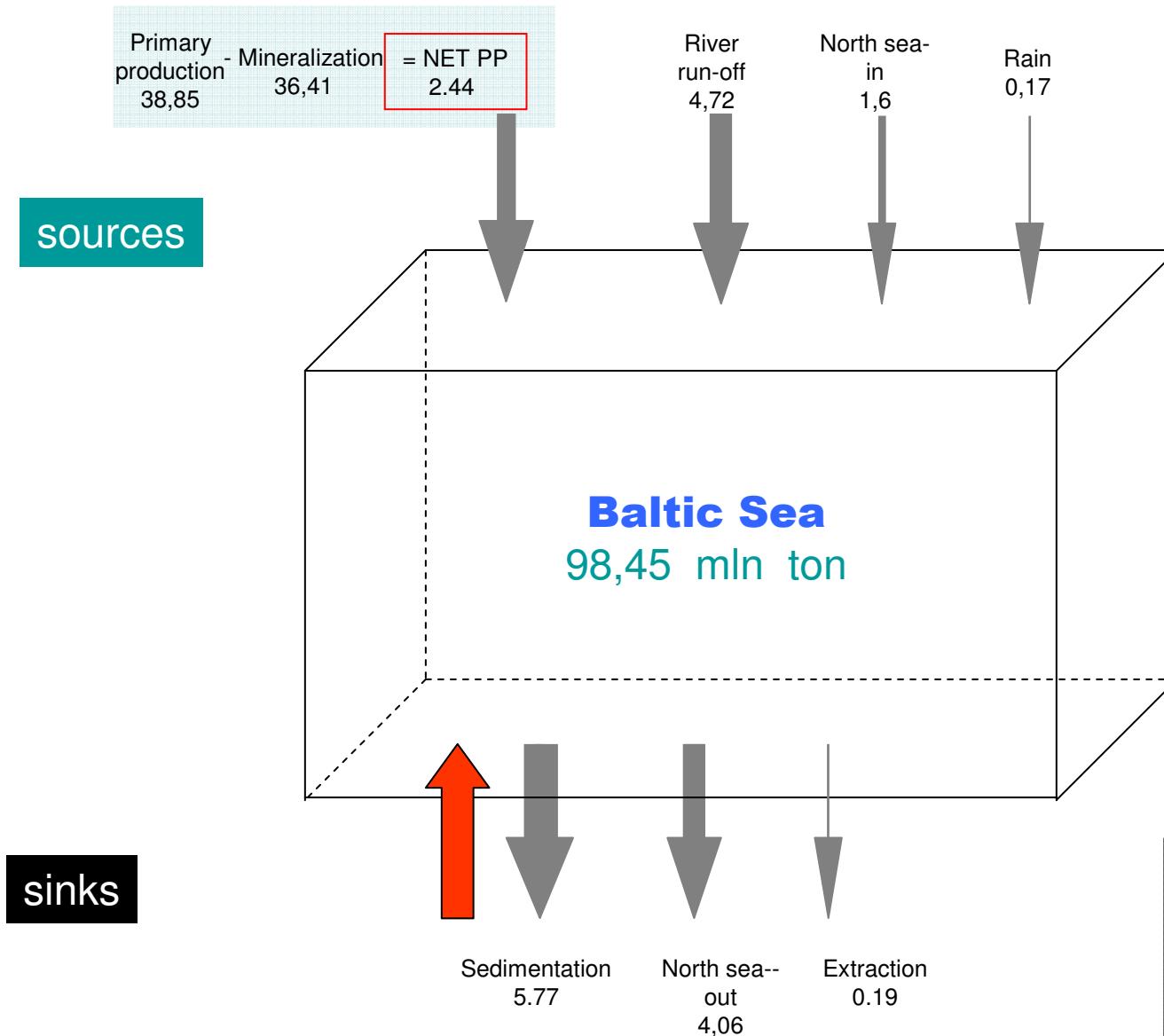
Anna Maciejewska
Lidia Dzieżbicka
Karol Kuliński

OM burial rates in sediments



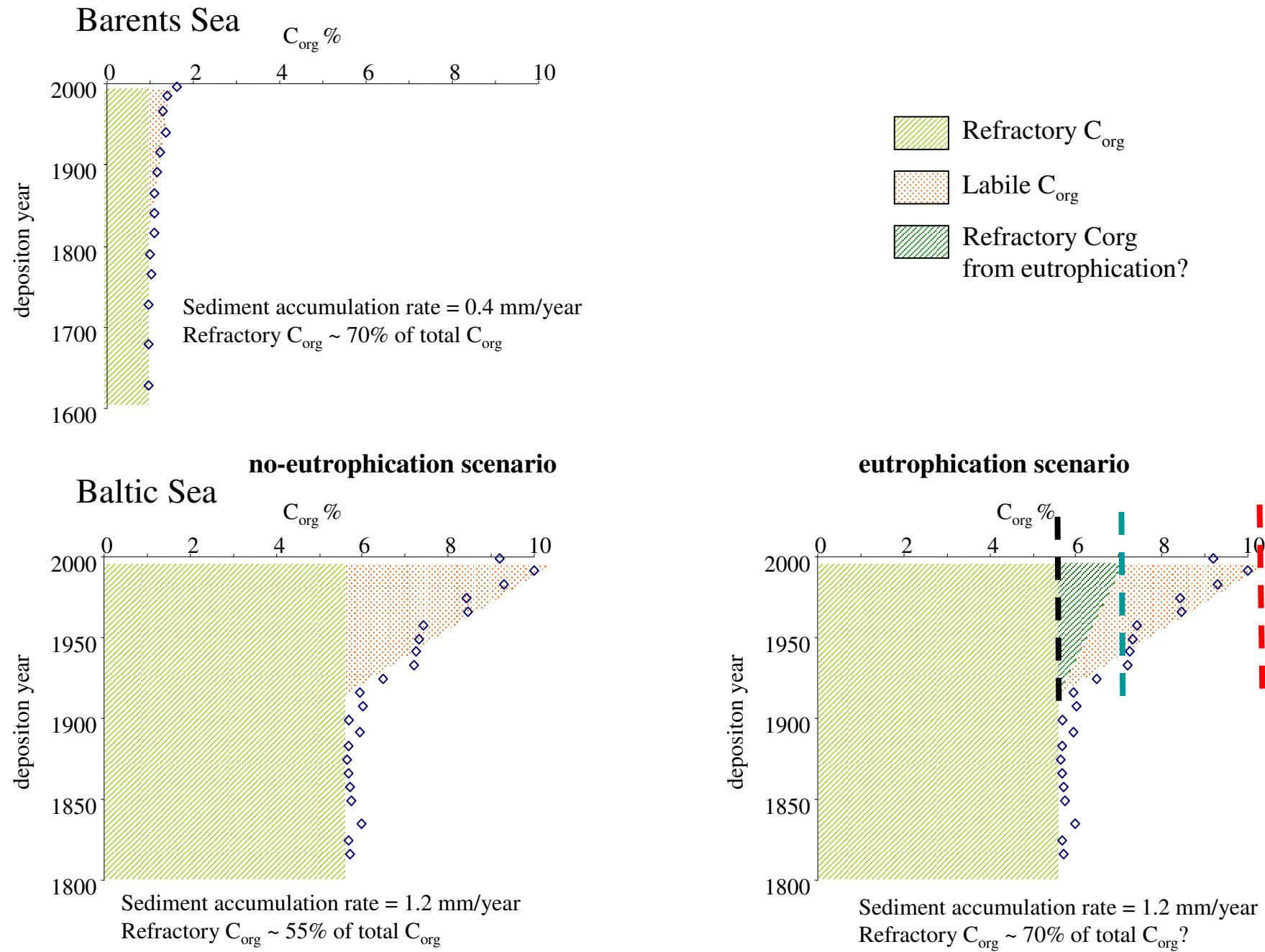
Organic carbon in the Baltic -

yearly fluxes (10⁶ ton/year)
standing stock (10⁶ ton/year)



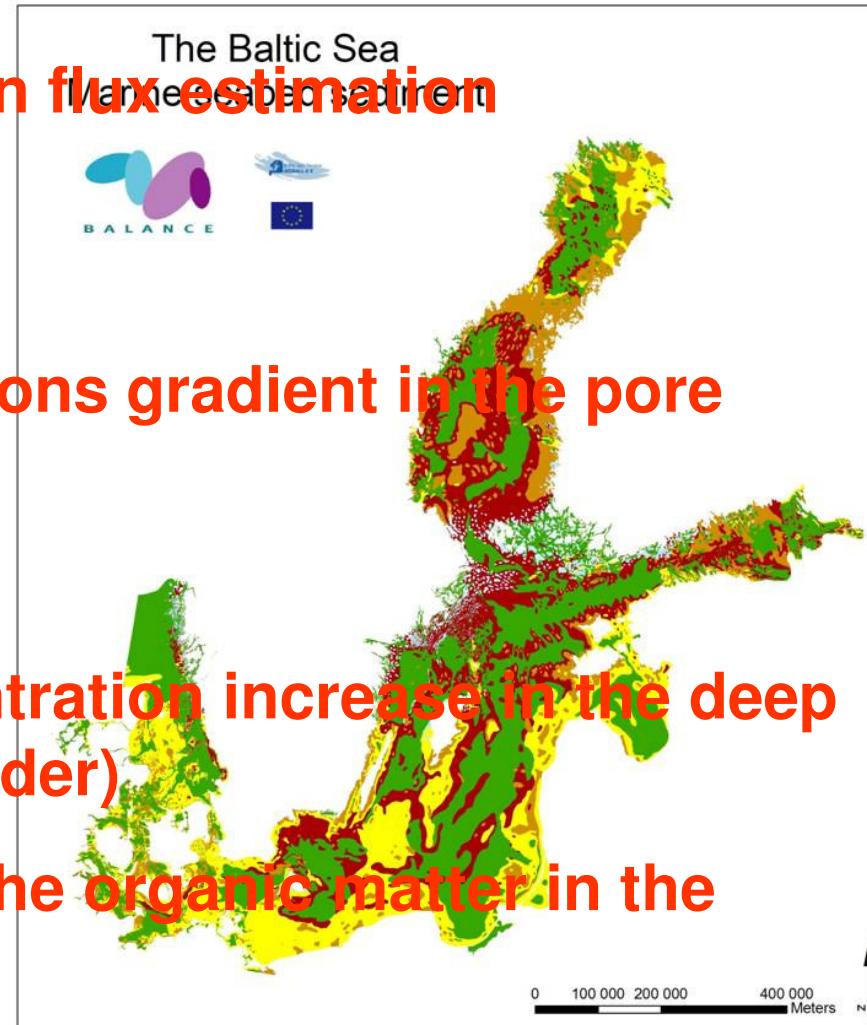
Baltic carbon budget

Fresh o.m. production impact on sedimentary organic carbon



Methods of the carbon return flux estimation from the bottom sediments:

1. DIC and DOC concentrations gradient in the pore waters
2. „Time Capsule” (I and II)
3. Dissolved carbon concentration increase in the deep water layer (Bernd Schneider)
4. Isotopic composition of the organic matter in the sediments
5. Thermogravimetry (TG-IR)



CONCLUSIONS

Amount returning to seawater as a consequence of organic matter decompositoion

PROCESS	F	Flux				Budget (10^6 ton)	
		F_i		F_o			
		o	i	o	i		
Sediment./Diff.	F_s	-	(1.88)	3.89 5.77	0.10		
Dischar./extr.	F_D	0.21	0.02	0.41	0.00		
Run-off	F_R	3.12	9.44	-	-		
Prec./aeros	F_P	0.17	0.02	0.01	-		
Water exch.	F_W	1.62	10.62	4.10	18.45		
Total	ΣF	5.12	20.10	8.41 10.79	18.55		
		25.22		26.96 28.84			

$$\begin{aligned}
 F_g &= \Sigma F \\
 &= -\cancel{3.62} \times 10^6 \text{ t/a} \\
 &= \cancel{9.43} \text{ g/m}^2 \text{a}
 \end{aligned}$$

Estimated yearly carbon fluxes in the Baltic Sea,

Pempkowiak 1976; Peltonen 2002; Thomas et al. 2003a; Thomas et al. 2003b; Smailys 2005; HELCOM 2004, 2006; SMHI 2003)

Baltic_C





Baltic_C bussiness

Baltic-C: Building predictive capability regarding the Baltic Sea organic/inorganic carbon and oxygen systems



WP 4: Quantification of carbon species fluxes through sediment-water interface. 463136

Organic matter in the Baltic sediments

- deposition rates
- remineralization rates
- burial rates



LEIBNIZ
INSTITUTE FOR
BALTIMORE SEA RESEARCH
WARNEMÜNDE

iow



FINNISH
METEOROLOGICAL
INSTITUTE



UPPSALA
UNIVERSITET

LUND
UNIVERSITY



Deliverables List			
Del. No.	Deliverable Name	WP no.	Delivery date (month)
D1	Estimating environmental costs of change in the acid-base balance (pH).	1	12
D2	Assessment of Baltic Sea CO ₂ system.	1	36
D3	The Baltic-C data base.	1	36
D4	Lecture and notes on the Baltic Sea CO ₂ system under climate change.	1	12
D5	Seasonally resolved pCO ₂ fields for the entire Baltic Sea.	2	12
D6	Seasonally resolved pCO ₂ fields for the entire Baltic Sea: Update.	2	24
D7	Improved process parameterizations (biomass production, nitrogen fixation).	2	12
D8	CO ₂ gas exchange balance.	2	24
D9	Concentrations of inorganic/organic carbon species in the major model sub-basins.	2	12
D10	Compilation of existing CO ₂ /carbon data.	2	6
D11	Trend analysis for CO ₂ /carbon variables.	2	12
D12	River inflow of: alkalinity, pH, total organic carbon, total inorganic carbon, and calcium: Initial database.	3	6
D13	River inflow of: alkalinity, pH, total organic carbon, total inorganic carbon, and calcium: Updated database.	3	18
D14	Calculate remineralisation rates of organic matter based on existing data.	4	6
D15	New stratified sediment samples collected covering Arkona Deep, Bornholm Deep, Gotland Deep, Coastal areas.	4	12
D16	Mineralization rates at the sediment water interface and in the deep water.	4	12
D17	Mineralization rate at different redox conditions. Collected cores analyzed.	4	12
D18		4	18
D19	Mineralization rates established for a range of environmental conditions.	4	18
D20	Loads of carbon deposited to sediments and return flux of carbon from sediments for the entire Baltic Sea established.	4	24
D21	Carbon burial rates in the Baltic sediments established.	4	30

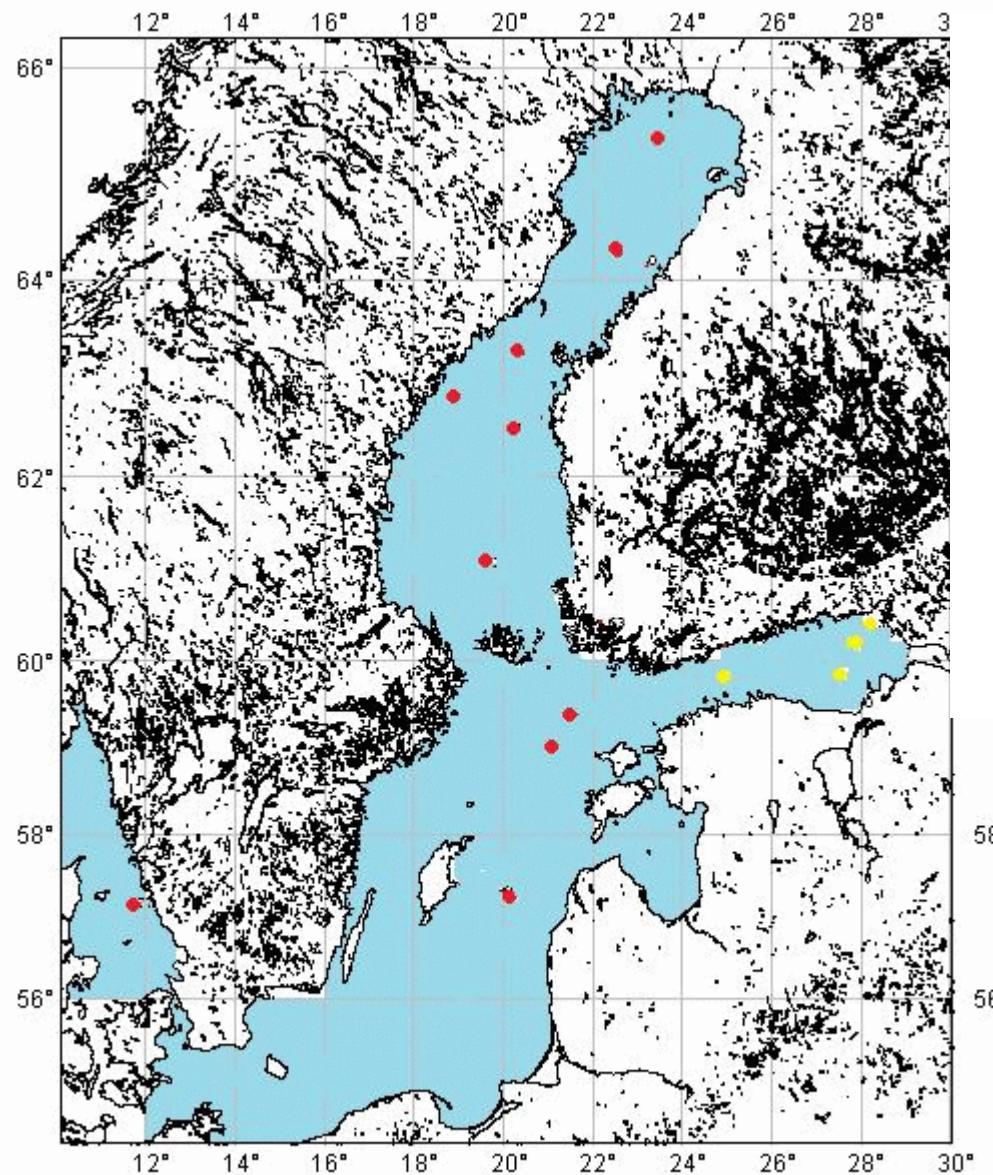
Deliverables List			
Del. No.	Deliverable Name	WP no.	Delivery date (month)
D22	Data base consisting of C _T depth profiles measured in the central Gotland Sea.	4	36
D23	Report concerning mechanisms of carbon flux to the Baltic sediments.	4	36
D24	Improved parameterisation of the gas exchange transfer velocity.	5	18
D25	Measurements from the first 12 month of the project taken at the Östergarnsholm station.	5	18
D26	Acidic deposition for the Baltic Sea drainage basin.	5	8
D27	Compiled present and future scenario land use data for the Baltic Sea drainage basin.	5	12
D28	Set up and validation of the vegetation model with implementation of DOC export algorithm and coupling to river runoff model.	6	18
D29	Modelling present and past changes in vegetation, CO ₂ exchange and DOC production on watershed basis for the Baltic Sea drainage basins.	6	18
D30	Modelling future changes in vegetation, CO ₂ exchange and DOC production on watershed basis for the Baltic Sea drainage basis	6	24
D31	Data set on A _T , C _T , Ca and C _{org} inputs to the Baltic Sea.	7	6
D32	Model describing A _T , C _T , Ca and C _{org} inputs from 83 major watersheds for the period 1990-2000.	7	12
D33	Model runs and data set A _T , C _T , Ca and C _{org} fluxes from 83 watersheds as a function of land cover changes.	7	24
D34	Model runs and data set on N and P fluxes from 83 watersheds as a function of land cover changes.	7	24
D35	Model runs and data on N and P fluxes from 83 watersheds as a function land use changes.	7	24
D36	Modelling present and past changes of Baltic Sea CO ₂ system.	8	18
D37	Modelling possible future changes in the Baltic Sea CO ₂ system.	8	24

WP4 Most pressing deliverables

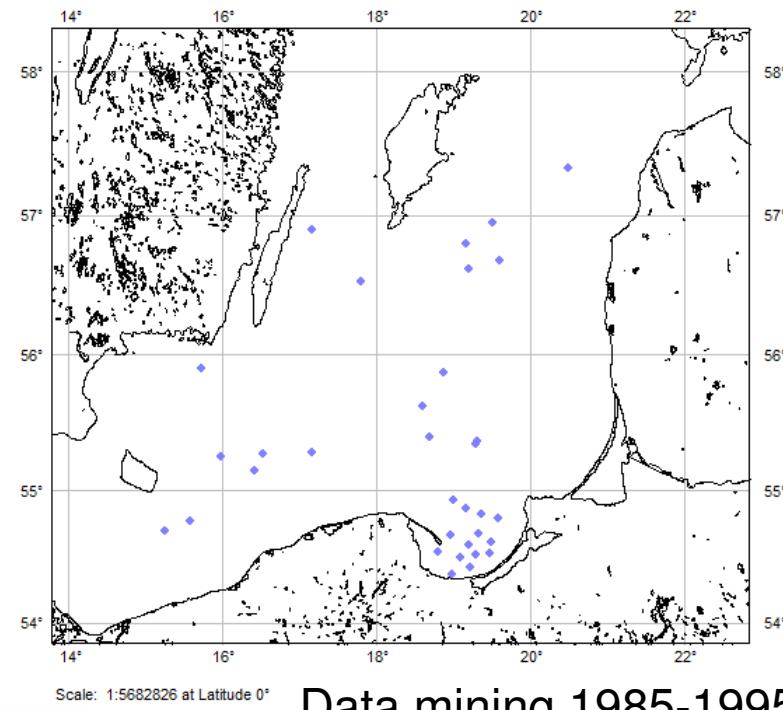
D.14 Calculate remineralization rates of organic matter basing on existing data	M 6
D.15 New stratified sediment samples collected	M12
D.16 Mineralization rates at the sediment water interface and in the deep water	M12
D.17 Mineralization rates for different environmental conditions.....	M18

D.14 → Karol Kuliński will talk about remineralization rates
Aleksandra Szczepańska will show results of 'data mining'

D.15 → Sediment cores collected (Aranda, Oceania), Anna Maciejewska
D.16 → Bernd Schneider (?)

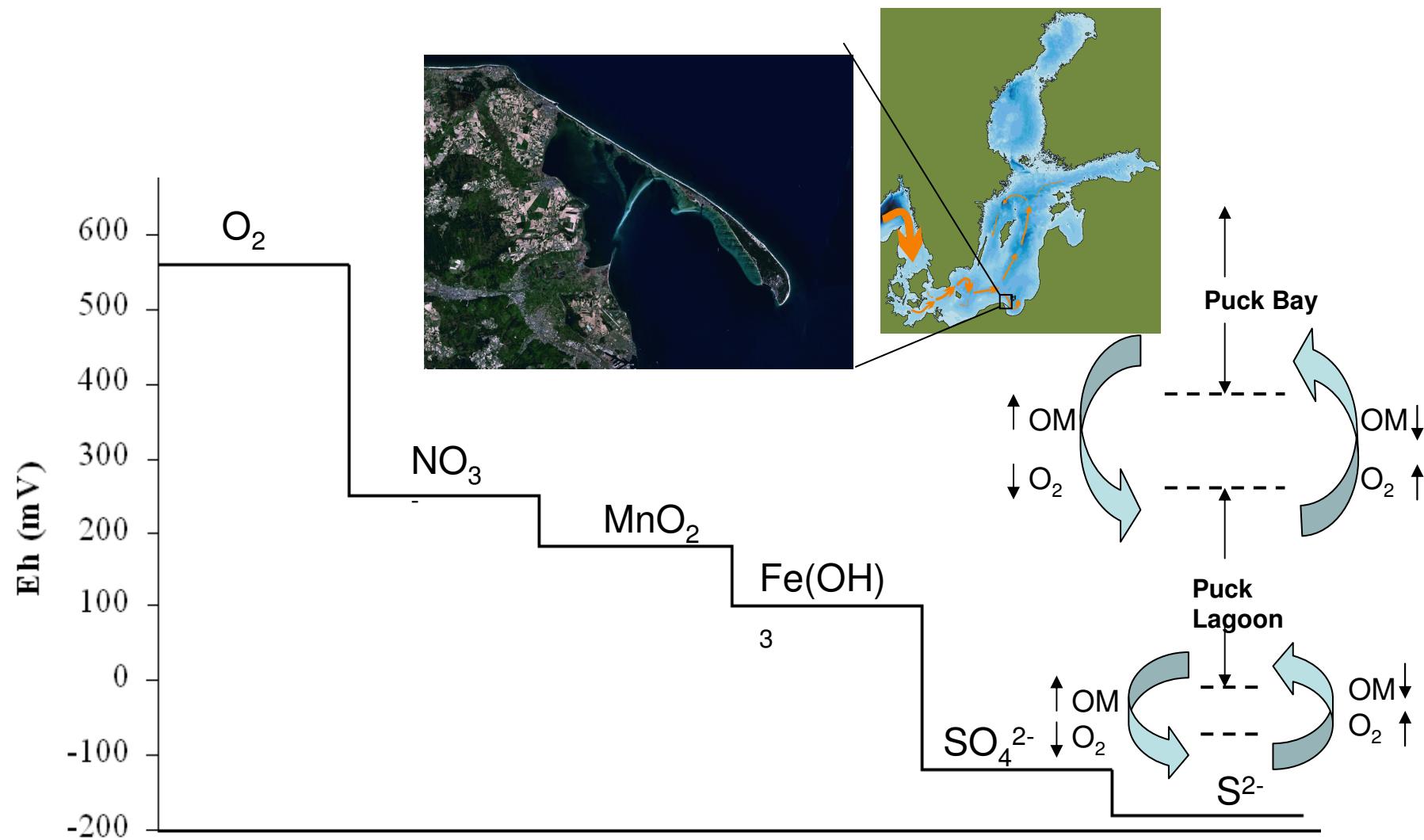


Scale: 1:14005068 at Latitude 0° „Aranda” January’s cruise
„Oceania” April’s cruise



Data mining 1985-1995

Oxidation-reduction potential in surface sediments (Pempkowiak, 1995)





Organic matter in the high CO₂ world

- sea-water acidification
- increased supply of CO₂ to algae

