Early diagenesis in sediments, sediment-water fluxes and benthic-pelagic coupling in coastal seas

Jana Friedrich Helmholtz Zentrum Geesthacht Center for Materials and Coastal Research Askö Summerschool 2015



Black Sea, 39 m depth, March 2008 POS 363-CO1 Photo: Tim Stevens (Kongsberg Simrad 14-208 camera)

Early diagenesis in sediments, sediment-water fluxes and benthic-pelagic coupling in coastal seas

Structure of the lecture



- 1. Introduction
- 2. Early diagenetic processes in sediments
- 3. Methods and instrumentation for measurements of sediment-water fluxes
- 4. Application of benthic flux estimates
- 5. Sedimentary archives
- 6. Approaches to benthic-pelagic coupling in models
- 7. Further reading

# 1. Introduction



### Continental shelf sediments (< 65 m) are covered mainly by

- 47% sands
- 37% muds
- 6% gravel/rocks
- 6% corals
- 4% shell debris

(Eisma 1998, Hayes 1967)

Legend

Seabed\_Sediments\_German\_

Classification after Figge (1981)

Medium to coarse sand, Mud 5-

Bedrock, Mud 21-50%

Gravel/Stones, Mud 21-

Coarse sand

Medium sand Mud > 50%

# Sediments in the German Bight/North Sea

mostly fine to coarse sands m

ock. Mud 11-209

trock, Mud 5-10%

Coarse sand, Mud 5-109

Fine sand Mud 5-10%

Medium sand Mud 21-509

Gravel/Stones, Mud 11-20%

Coarse sand, Mud 21-50%

Medium sand, Mud 11-209

Gravel/Stones Mud 5-10%

Bedrock

oarse sand, Mud 21-50%

mud

ine sand, Mud > 50%

ine sand, Mud 11-20%

Fine sand

edium sand, Mud 5-10%

1:1.250.000

Source BSH

8-0.0-8

Gravel/Stones, Mud > 50%

Medium to coarse sand

Mud (more than 80%)

Fine sand, Mud 21-50%

Coarse sand, Mud > 50%

Medium to coarse sand Mud 11-20% Sector Medium to coarse sand Mud > 50% IIIII Bedrock Mud > 50%

Medium sand

Western Black Sea shelf



Panin & Jipa (2002)

mostly muddy sediments and "starved" sediments and shell debris





Black Sea, 22m, March 2008 POS 363-Phy2 Photo: Tim Stevens (Kongsberg Simrad 14-208 camera) Black Sea, 46 m water depth, March 2008 POS 363-DN10 Photo: Tim Stevens (Kongsberg Simrad 14-208 camera)





healthy benthic ecosystem with epifauna (filter feeders)

degraded benthic ecosystem due to eutrophication and hypoxia

Black Sea Photos: Tim Stevens,

#### Video-imaging of seafloor

benthic sled with C-Vision (C-Technics) system & HERO 4 Black GoPro or Kongsberg Simrad 14-208 camera geo-referenced video clips, & stills for benthic image analysis



Benthic and pelagic compartments are in close contact and in two-way interaction:



Pelagic system influences ecology and biogeochemical functioning of benthic system and vice versa

direct or indirect, at tidal or interannual timescales



Habitat for microorganisms, infauna, epifauna, -flora, demersal fishes, receive the legacy of anthropogenic perturbations

#### Proportion of benthic to total respiration depends primarily on water depth Benthic contribution varies from 40% in shallow depths to few % at 100m

(Heip et al. 1995)

# Introduction Pelagic-benthic-pelagic interactions Shelf sediments are "the memory" of the pelagic system!

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Hydrodynamic conditions and transport mechanisms into and out of the sediment determine the linkage of sedimentary processes to the overlying water. In shallow seas, sediment is the most important site for accumulation, storage and biogeochemical transormation of organic matter and contanimants



# 2. Early diagenetic processes in sediments

#### Most important benthic transport processes

- gravitational settling
- bioturbation
- burrow irrigation (bioirrigation)
- molecular diffusion
- porewater advection
- burial due to lateral sediment transport



# 2. Early diagenetic processes in sediments2.1 Transport processes

#### Linear gradient

solute concentration is controlled by diffusion from source at B to sink at A , no advection and reaction between depth A and B



#### **Concave gradient**

production or upward advection of a solute in porewater from B to A



#### **Convex gradient**

removal or downward flux of solute from A to



#### **Curved gradient**

if concentrations at A and C are equal, production generates maximum at B, consumption results in minimum at B'



# 2. Early diagenetic processes in sediments2.1 Transport processes

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Sediment porewater profiles in a perfect biogeochemist's world...









Mixing of sediment particles (with/without effect on the porositiy)

Exchange and of bottom water and porewater

201234541430121454

#### Transport processes inside a burrow caused by bioirrigating macrozoobenthos



#### **Consequences of bioirrigation:**

- ventilation of sediment and change in sediment-water chemistry



#### Bioturbation



# Consequences of bioturbation



#### mixing of substances

#### **Gravitational settling – sediment permeability**



#### Higher permeability in coarse-grained, sandy sediments

#### **Diffusion and advection**



Sediment-water exchange of matter dominated by diffusion advection

Boundary flow conditions and sediment permeability determine whether advection or diffusion dominates the sediment water fluxes.

Meio- and macrofauna enhance transport of solutes and particles by bioturbation and bioirrigation.

In coastal permable sediments biological transport can be as efficient as advective exchange.

# 2. Early diagenetic processes in sediments2.1 Transport processes

#### Advective porewater exchange due to boundary currents



sediment enclosure

# Why does it matter?

Currents due to tidal forcing and wave motion create pressure gradients that may enhance sediment-water fluxes over permeable sediments.



flow regime changes to stagnant conditions

- shift from advective to diffusive transport
- release of solutes from sediment changes

For measuring benthic fluxes, proper simulation of the flow regime is crucial for realistic results!



#### **Redox regimes in sediments**

controlled by

- supplies of organic matter,  $O_2$ ,  $NO_3^{-}$ ,  $SO_4^{2-}$  (electron acceptors)
- bottom water ventilation and near-bottom currents
- sediment permeability
- bioturbation/bioirrigation



#### **2.** Early diagenetic processes in sediments **Transformation of organic matter in sediments** 2.2

1 1

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microbial reactions (temperature and substrate dependent)					
$\rightarrow$ xCO <sub>2</sub> + yNHO <sub>3</sub> + zH <sub>3</sub> PO <sub>4</sub> + (x+y)H <sub>2</sub> O					
monas & Nitrobacter)					
5CO <sub>2</sub> + 69NH <sub>3</sub> + 53H <sub>2</sub> O (DNRA) g bacteria)					
06CO <sub>2</sub> + 55.2N <sub>2</sub> + 177.2H <sub>2</sub> O					
$\Rightarrow xCO_2 + 2xMn^{2+} + yNH_3 + zH_3PO_4 + 2xH_2O$					
$\rightarrow xCO_2 + 4xFe^{2+} + yNH_3 + zH_3PO_4 + 3xH_2O$					
bactilus, Beggiatoa, Thioploca)					
→ 2xHCO3- + xH <sub>2</sub> S + yNH <sub>3</sub> + 2zH <sub>3</sub> PO <sub>4</sub>					
$xCH_4 + 2yNH_3 + 2zH_3PO_4$					
fter Aller 1982 Dalsgaard et al. 2003)					

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### Close up of nitrogen cycle



after Kuypers et al. (Nature 2003)



 $(CH_2O)_{106}(NH_3)_{16} + 53HNO_3 \rightarrow 106CO_2 + 69NH_3 + 53H_2O$ 

**DNRA = major N reduction pathway in coastal ecosytems** 

DNRA is favored over denitrification at increased C loads (high C<sub>org</sub>/NO<sub>3</sub> ratios), increased sulfate reduction rates, increased temperatures

#### Eutrophication & climate warming support DNRA → of critical importance for predicting eutrophication trajectories!

# 3. Methods and instrumentation for measurements

### of sediment-water fluxes

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### 3.1 Ex-situ: Sediment sampling – surface sediments (slurries)

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Van-Veen grab



e.g. fauna analysis grain-size analysis permeability volumetric oxygen consumption slurry incubations



### 3.1 Ex-situ: Sediment sampling – surface sediments 0-40 cm

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#### **Box corer**

e.g. fauna analysis grain-size analysis permeability core subsampling







# 3.1 Ex-situ: Sediment sampling – surface sediments 0-40 cm

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# **Multicorer (MUC)**

#### **Ex-situ:** Incubation of sediment cores in ship's cool lab 3.2

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Oxygen uptake and nutrient release from sediment under laboratory conditions



German Bight, HE432, Neumann et al. EGU2015-1296



Benthic primary production from changes in oxygen concentrations in the sediment overlaying water

- **h** height (m) of the water column in the enclosure
- d[C]/dt accumulation rate  $(mmol m^{-3} d^{-1})$
- **F** flux at sediment water interface  $(mmol m^{-2} day^{-1})$

### 3.2 Ex-situ: Needle-type oxygen optodes on microprofiler



Example:

High-resolution  $O_2$  profiles at water-sediment interface  $O_2$  penetration depth into sediment



German Bight, sandy sediment

Janssen & Friedrich, HE383

#### O<sub>2</sub> profiles under different oxygen regimes



photo J. Friedrich

Crimean Shelf, Black Sea (Lichtschlag et al., submitted)

# **3.2.1** Calculation of diffusive benthic fluxes from microprofiles

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#### Fick's First Law

Diffusive benthic fluxes across the (sediment-water ) interface is proportional to the concentration gradient and the diffusion coefficient

$$J = -\phi D_s \frac{dC}{dx}$$

J - flux (mmol m<sup>-2</sup> day<sup>-1</sup>)  $\phi$  - porosity (ml cm<sup>-3</sup>)

 $D_s = \frac{D}{\phi F} \qquad D_{\text{s}} - \text{effective diffusion coefficient in the sediments} \\ D - \text{molecular diffusion coefficient in seawater at 5°C} \\ (Furrer and Wehrli, 1996)$ 

*F* - sediment resistivity (Berner, 1980); (Christensen et al., 1987) and is given by an empirical relationship to  $\phi$  (Manheim, 1970)





Ullman & Aller 1982

Fig. 3. Relationship between F and  $\phi$ ;  $\Box$ —Mud Bay, station 5;  $\odot$ —Long Island Sound, station NWC;  $\triangle$ —Florida Bay, Captain Key Bank;  $\diamond$ —from

### **3.3** Ex-situ: Sediment porewater sampling with rhizones

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Fig. 1. (A) Schematic diagram of a Rhizon (length 5 and 10 cm, respectively, outer diameter 2.5 mm, dead volume 0.5 mL, pore size 0.1 µm) and the devices used for porewater extraction (vacuum tubes, syringes, and peristaltic pumps, I-III). Modes of application are (B) sampling of porewater with a Rhizon and a syringe from an open sediment core, (C) insertion of Rhizons through predrilled holes in a liner used for sediment sampling or for micro-cosm experiments, and (D) combined flux and porewater studies using a benthic chamber and an array of Rhizons inserted into the sediment. Typically, 2 mL porewater was sampled from sediments.

Seeberg-Elverfeldt et al. 2005

# 3. Methods and instrumentation3.3.1 Example: Sediment porewater profiles from rhizones

#### Porewater concentrations and gradients differ depending on sediment composition



(porewater concentrations in  $\mu$ mol L<sup>-1</sup>) 1000 500 0 5 0 80 100 120 40 60 -5 -10 --- PO4 -15 -Si(OH)4 -20 -25 -30 -35



Helgoland starved dunes







Friedrich et al., EGU2015-9199

# 3. Methods and instrumentation3.4 In-situ techniques: Eddy correlation/covariance

#### Benthic oxygen uptake



after Holtappels et al. 2013, Berg et al., 2003 MPI Bremen



#### In-situ techniques: Eddy-correlation 3.4



# 3.5 In-situ techniques: microprofiler lander and laser scanner

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Ahmerkamp et al. in prep.

#### Measurements

- Current velocity
- Topography
- Bedform migration
- O<sub>2</sub> depth profiles
- O<sub>2</sub> flux dynamics in the field





# 3.6 In-situ techniques: Benthic flux chamber lander

deep-sea battery

weights

# Measurement of solute fluxes across the sediment-water interface

#### Principle

#### sediment-bottom water enclosure



FLUXSO lander, HZG

# 3.6 In-situ techniques: Benthic flux chamber lander

#### Calculation of benthic fluxes across the sediment-water interface



change in solute concentration in chamber over time



linear regression to the change in concentration over time in the flux chambers/microcosms

- *h* height (m) of the water column in the enclosure
- **d[C]/dt** accumulation rate (mmol m<sup>-3</sup> d<sup>-1</sup>)
- F flux at sediment water interface (mmol m<sup>-2</sup> day<sup>-1</sup>)

$$F = h \frac{d[C]}{dt}$$

0.66 mmol  $NH_4^+ m^{-2} day^{-1}$ 0.11 mmol  $NO_3^- m^{-2} day^{-1}$ 

NOAH-E Sep 2014 fine sand, epi- /infauna

Friedrich et al., EGU2015-9199

# 3.6 In-situ techniques: Benthic flux chamber lander

#### Example: HZG Chamber lander "FLUXSO" – Fluxes on Sands Observatory



2 chambers, equipped with:

stirrer disk (variable speeds) oxygen optode CO<sub>2</sub> optode pH sensor Hamilton conductivity sensor syringe sampler for tracer injection and sampling from chamber

outside chamber:

CTD with fluorescence & turbidity sensors, PAR, oxygen optode, pH sensor Hamilton z-pulse doppler current sensor

# 3.6 In-situ techniques: Benthic flux chamber lander

# Wiggling chamber for sandy and consolidated sediments



Janssen et al. 2005

#### Chamber lid with sensors and stirrer disk



Appropriate simulation of hydrodynamic regime is crucial for reliable measurement of fluxes on permeable sediments!



# 3.6 In-situ techniques: Benthic flux chamber lander

# FLUXSO on fine sand North Sea, 27 m water depth





# 3.6 In-situ techniques: Benthic flux chamber lander

25

25



chamber 1



7.8

0

5

10

hours

15

20

25

Example: FLUXSO on the Dogger Bank, June 2015 DCS Korrigierte Strömungsrichtung 360 - X 400 30 Current Abs Speed cm/s (57) 350 25 -6 per. Mov. Avg. (Korrigierte Strömungsrichtung 360 - X) current direction (degree) 005 120 120 120 120 20 (cm/s) 15 15 current speed (cm/s) & direction current sp 5 눉 100 5 50 0. n chamber 2 0 10 20 25 5 15 hours 350 **O**<sub>2</sub> 330 O<sub>2</sub> (μM) 310 000 oxygen in 500 270 מאלפח -16.4 mmol m<sup>-2</sup> day<sup>-1</sup> 250 230 210 5 10 15 20 0 K2CO2 C1RPh(Deg) (101) 61 CO2 60.9 60.8 **CO**<sub>2</sub> 60.7 pН 60.6 (raw data) 60.5 60.4 60.3 60.2

60.1 60

5

10

hours

15

20

### 4. Application of benthic flux estimates

# 4.1 Comparison of benthic and pelagic fluxes in the North Sea



#### **Influences on North Sea**

- Atlantic (North Atlantic / Fair Isle current Channel)
- Rivers (Rhine, Maas, Elbe & Weser etc)
- anti-clockwise circulation driven by semi-diurnal tides & wind



#### **Hypothesis**

In the German Bight (DB), 10-30% of total remineralisation occurs in sediments, depending on water depth

(after Heip et al.1995)

4. Application of benthic flux estimates

4.1 Comparison of benthic and pelagic fluxes in the North Sea

### Comparison of benthic and pelagic respiration

German Bight (27 m): weakly permeable sand with infauna & epifauna





#### Integrated pelagic O<sub>2</sub> respiration

September 324 mmol m<sup>-2</sup> day<sup>-1</sup>

### Integrated pelagic O<sub>2</sub> respiration

May 84 mmol m<sup>-2</sup> day<sup>-1</sup>

õ



#### **Application of benthic flux estimates** 4.

#### Sediments contain the legacy of eutrophication 4.2

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# **Example from the Black Sea western shelf**









#### Bottom water oxygen in western Black Sea shelf



Friedrich et al. 2010

Borysova et al. 2005

# 4.2 Sediments contain the legacy of eutrophication

#### Changes in nitrate in the surface water of the western Black Sea shelf in the 1990s and 2000s



Winter 1990-1995



Winter 2005-2010

1990s = eutrophication 2000s = recovery from eutrophication

data from Black Sea database <u>http://sfp1.ims.metu.edu.tr/ODBMSDB/</u>) 2006 and 2008 data from Friedrich et al. P363 cruise report.

#### Changes in sediment-water nutrient fluxes in the 1990s and 2000s



Sediment nutrient release is an internal source for productivity.

Despite decrease in eutrophication, sediment nutrient release continues for longer than the legislation period of politicians!

#### Shelf sediments contain legacy of eutrophication!

# 5. Sedimentary archives

### Dating the last 100 years with <sup>210</sup>Pb and <sup>137</sup>Cs



# 5. Sedimentary archives

## <sup>210</sup>Pb and <sup>137</sup>Cs pathways to sediments



Example: Core from the western Black Sea shelf (F1)



Friedrich & Laptev EGU2010-15234



<sup>241</sup>Am – independend time marker for 1963

high <sup>137</sup>Cs peaks mark Chernobyl event and floods



#### 5. Sedimentary archives

# 5.1 Example from thewestern Black Sea shelf

Example: dated sediment core from the western Black Sea shelf (F1)

CRS model - Constant Rate of Supply (Appleby 2008) Mass accumulation rates (MAR) =  $0.1 - 1.2 \text{ g cm}^{-2} \text{ year}^{-1}$ 





Coupling sediment and water column dynamics...

Earth-Science Reviews 51 (2000) 173–201 On the coupling of benthic and pelagic biogeochemical models

Karline Soetaert<sup>\*</sup>, Jack J. Middelburg, Peter M.J. Herman, Kerst Buis Netherlands Institute of Ecology, Centre for Estuarine and Coastal Ecology, PB 140, Yerseke 4400 AC, Netherlands Received 17 February 1999; accepted 7 December 1999



Level (4): vertically resolved

- dynamic, **vertically resolved**, biogeochemical model of the sediment coupled with a vertically resolved dynamic model of the water column

- Particles sinking is incorporated into the sediment by burial and bioturbation

- Solute exchange via molecular diffusion /advection near the sediment–water interface

- considers faunal irrigation
  - considers distinct layers of the sediment
- e.g., C, O and N cycle at a shelf-break site Soetaert et al., 2000)

#### Level (3): vertically integrated



- dynamic **vertically integrated** model for the sediments coupled with a water column model
- Particles settling to the seafloor are added to sediment layer
- exchange of dissolved constituents is described as a function of the particulate transformation rate
- e.g., C incorporated in a thin sediment layer and Cmineralisation is translated in corresponding O<sub>2</sub> demand (global ocean carbon cycle model of Maier-Reimer 1993)

#### Level (2): reflective



- the sediment interface is represented as a **reflective boundary**
- particles arriving at the sediment surface are instantaneously transformed into nutrients and CO<sub>2</sub>
- Partitioning of the return flux is parameterised but may be calculated based on steady-state diagenetic modelling (Lancelot and Billen, 1985)
- most often used in global ocean biogeochemical models because of its computational efficiency

#### Level (1 a): Flux imposed



Level (1 b): BW conc imposed



- either the sediment–water exchange rate (e.g., Chapelle et al., 1994) or the bottom-water concentration of dissolved substances (e.g., Sharples and Tett) is imposed, usually based on data
- includes lower boundary conditions where solute flux, or the gradient at the lower boundary, equals 0 (e.g., Kühn and Radach, 1997)
- widely used and akin to the specifications commonly imposed at open boundaries in water column models

#### Level (0): no bottom



- no particulate material arrives at the sediments
- reactive material just accumulates in the lowermost water layer or is exported along the lateral boundaries

Summary of model characteristics for the various levels of sediment-water exchange parameterisation (+) Accounted for; (-) not accounted for or not appropriate;  $(\pm)$  partially accounted for, depending on the exact formulation.

Level	Mass conser- vation	Retention capacity	Speciation characteristics of efflux	Short- and medium-term response	Long-term effects	Initialisation of sediment	Parameter requirements	Calibration and validation data	Computational demand
4 — Fully coupled diagenetic model	+	+	+	+	+	Special attention for slow- reacting components	Bioturbation, irrigation, advection rate	Vertical profiles; in situ fluxes	High
3 — Vertically integrated model	+	+	±	±	+	Special attention for slow-reacting components	Speciation characteristics of return flux	In situ fluxes	Low
2 — Reflective boundary	+	+	±	-	-	_	Speciation characteristics of return flux	Long-term averaged fluxes	Insignificant
1 — Solute flux or BW concentration imposed	-	+	-	-	-	-	Bottom water concentrations or sediment fluxes	-	Insignificant
0 — Sediment ignored	+	-	-	-	-	-	None	-	None

# 6. Approaches to benthic-pelagic coupling in models

Effect of different levels of sediment–water exchange formulations on the total sediment DIN efflux (DIN+N<sub>2</sub>)



- computationally inexpensive
- only integrated concentration of 2 fractions of sedimentary solid substances is described prognostically
- offers the possibility to reproduce sediment response on both short- and long-term scales

#### Why coupled benthic-pelagic models?

Understanding of biogeochemical processes

Understanding the role of ecosystem components for assessments of ecosystem functioning

Extrapolation of point measurements for budget estimates

Assessment of ecosystem state drivers and forecasts scenarios for decision making Modeling benthic-pelagic nutrient exchange processes and porewater distributions in a seasonally hypoxic sediment: evidence for massive phosphate release by *Beggiatoa*?

A. W. Dale, V. J. Bertics, T. Treude, S. Sommer, and K. Wallmann

Modeling eutrophication and oligotrophication of shallow-water marine systems: the importance of sediments under stratified and well-mixed conditions

Karline Soetaert · Jack J. Middelburg

Nitrogen budget of the northwestern Black Sea shelf inferred from modeling studies and *in situ* benthic measurements

M. Grégoire<sup>1,3,\*</sup>, J. Friedrich<sup>2,4</sup>

Drivers, mechanisms and long-term variability of seasonal hypoxia on the Black Sea northwestern shelf – is there any recovery after eutrophication?

A. Capet<sup>1,2</sup>, J.-M. Beckers<sup>1</sup>, and M. Grégoire<sup>2</sup>

# 7. Further reading



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