Dissolved heavy metal fluxes at sediment-water interface in polluted sediments of the Adriatic Sea

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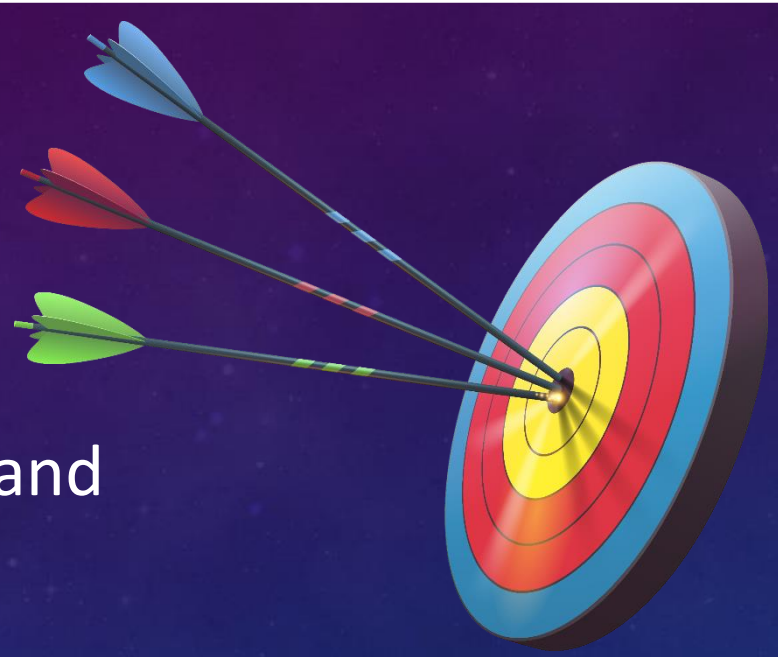
Aims

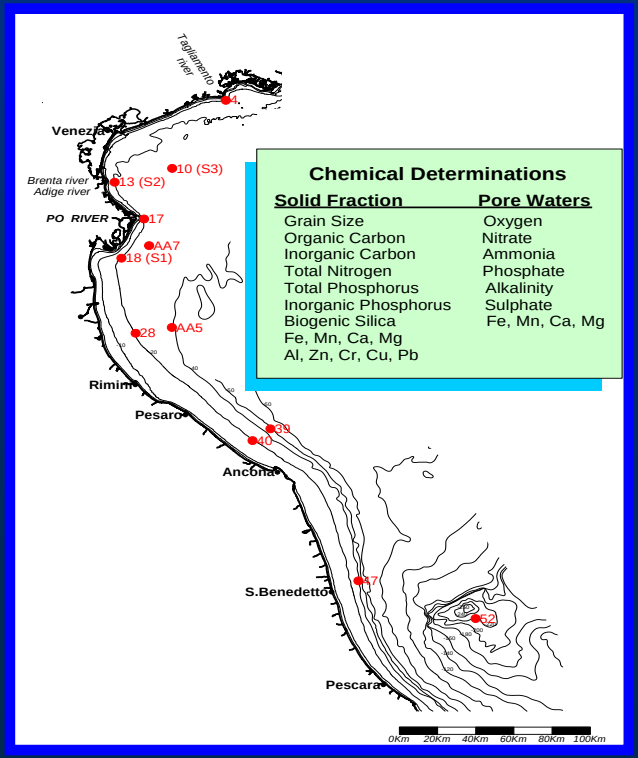


- Evaluate the role of sediments in the contamination and eutrophication of the western Adriatic Sea
- Recycling of heavy metals in polluted marine sediments
- Measurements of dissolved benthic fluxes of nutrients and heavy metals in sea bottom near and far from Po river outflows
- Study of the early diagenesis processes generating the dissolved benthic fluxes

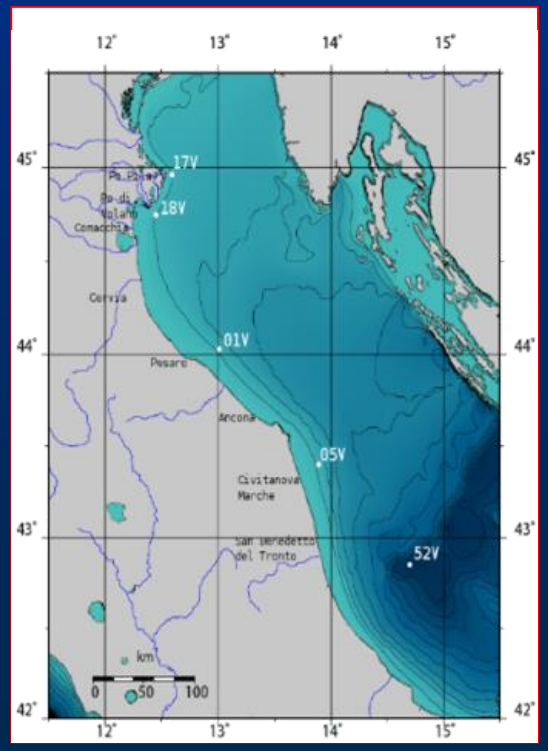
Methods

Several studies have been carried in the Adriatic Sea in last few years to measure the fluxes of dissolved substances at the sediment-water interface and to study the early diagenesis processes leading to these fluxes

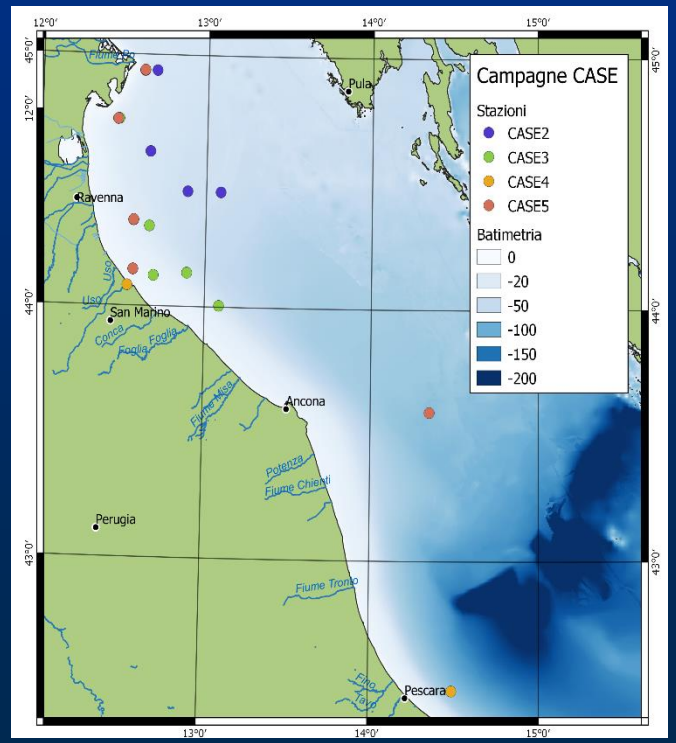
PRISMA1: 1993-1996



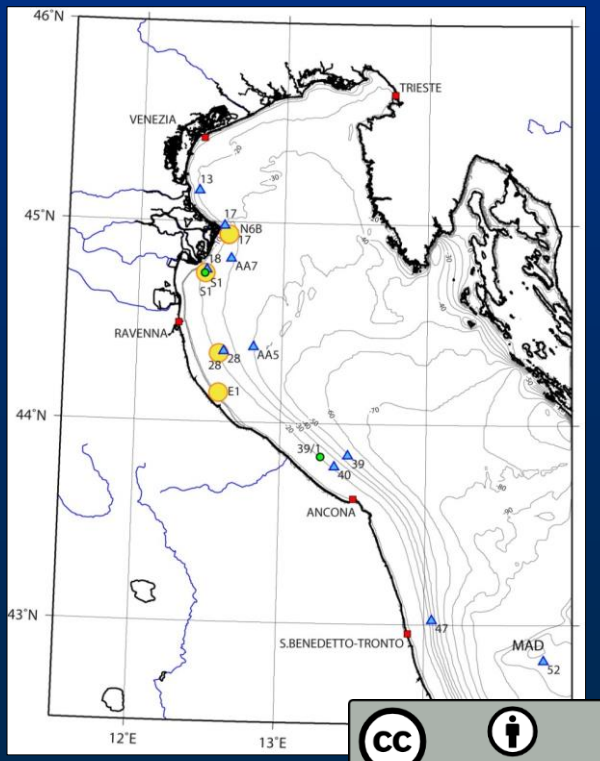
VECTOR: 2006-2009



CASE: 2010-2014



PERSEUS: 2012-2016



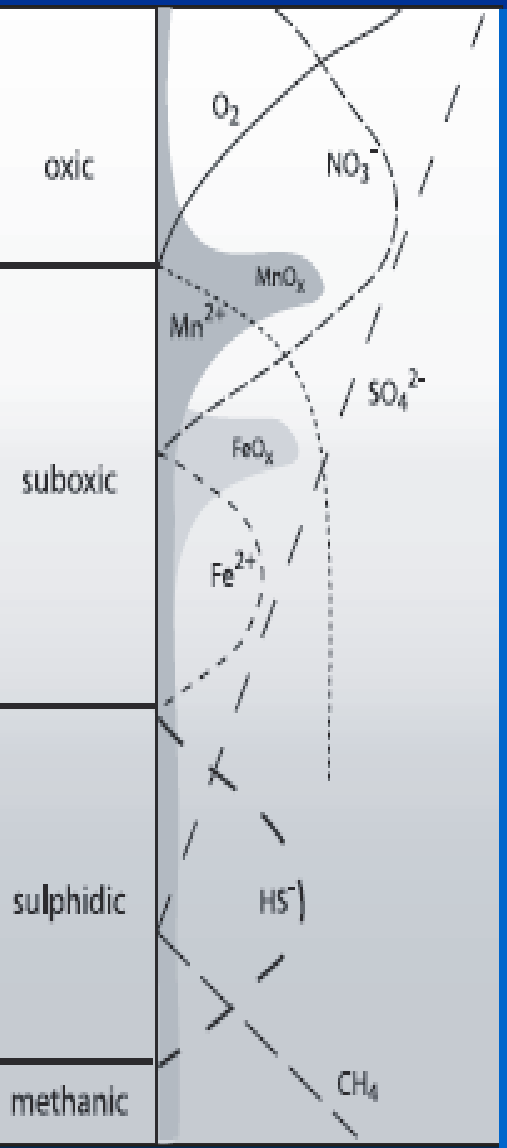
Methods

Early diagenesis Processes

- **The biogeochemical reactions and processes occurring in the upper cm of the sediment**
  - **Due to** the organic matter deposition and **degradation;**
  - **Using,** in decreasing order of free energy, O_2 , NO_3, Mn_xO_y, Fe_xO_y, SO_4, CH_2O
  - **Mineral dissolution**
  - **Mineral precipitation**

- **Early diagenesis processes generate dissolved fluxes at the sediment-water interface**
  - **Outward the sediment**
  - **Inward the sediment**

Early diagenesis processes



- **Aerobic biodegradation:**

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+138\,O_2 \rightarrow 106\,CO_2+16\,HNO_3+H_3PO_4+122\,H_2O$

- **Anaerobic degradation:**
- Denitrification (Nitrate reduction):

$5(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+472\,HNO_3 \rightarrow 276\,N_2+520\,CO_2+5\,H_3PO_4+886\,H_2O$

- Oxi-hydroxi-Mn reduction:

$5(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+236\,MnO_2+472\,H^+ \rightarrow 236\,Mn^{2+}+106\,CO_2+8\,N_2+H_3PO_4+336\,H_2O$

- Oxi-hydroxi-Fe reduction:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+212\,Fe_2O_3+848\,H^+ \rightarrow 424\,Fe^{2+}+106\,CO_2+8\,NH_3+H_3PO_4+530\,H_2O$

- Sulfate reduction:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+55\,SO_4^{2-} \rightarrow 106\,CO_2+16\,NH_3+55\,S^{2-}+H_3PO_4+106\,H_2O$

- Methanogenesis:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53\,CH_4+53\,CO_2+16\,NH_3+H_3PO_4$

Berner Sequence (1980)

EARLY DIAGENESIS AND BENTHIC FLUX STUDY METHODS

Methods

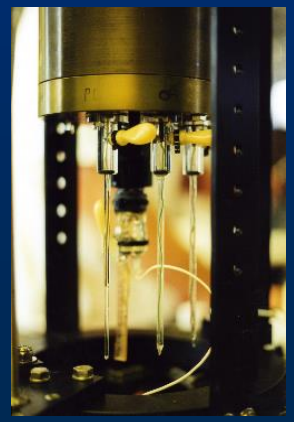
Early diagenesis

IRBIM-CNR on deck laboratory

- Pore ware analysis:
- Elaboration, interpretation and modeling.

Sea-water corer

Microprofiler



Dissolved benthic fluxes

IRBIM-CNR benthic chambers

- Benthic chamber deployments;
- Core incubations on deck;
- Pore water profile modeling.

Comparison of calculated and measured benthic fluxes

Methods

Pore Water chemical Analysis

Final electron acceptors:

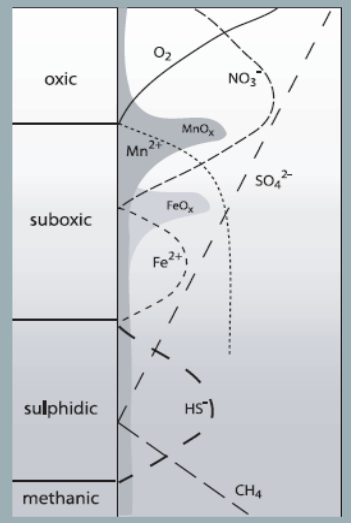
- O_2,
- NO_3,
- Fe,
- Mn,
- SO_4.

Organic matter degradation products

- NH_4,
- DIC,
- PO_4,
- Alcalinity,
- CH_4.

Others:

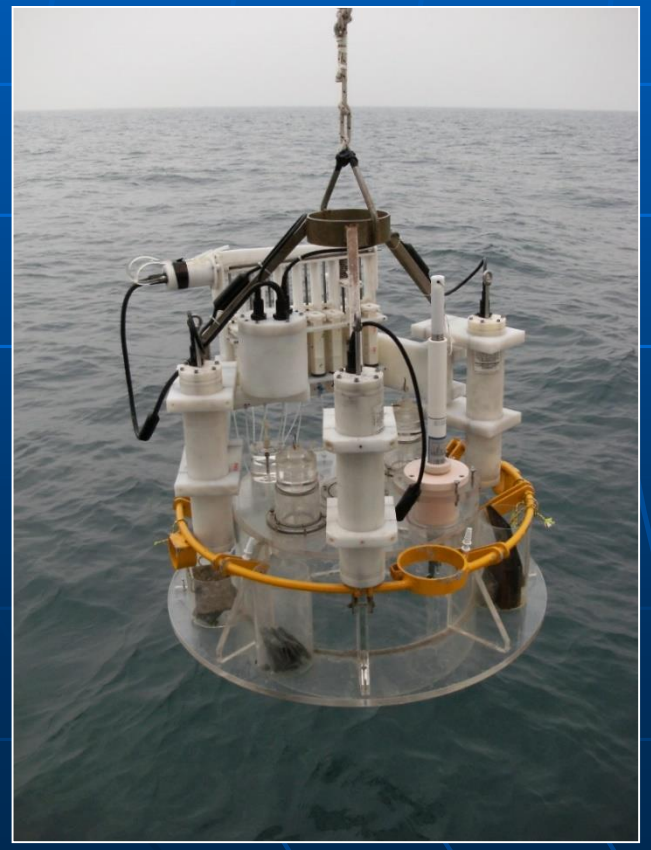
- Ca;
- Mg;
- Silica ($Si(OH)_4$);
- Sulphide (HS^-).



Ada N.: the automatic benthic chamber realized by the IRBIM-CNR

The automatic benthic chamber (CBA) is made by a polymethylmethacrylate cylinder (80 cm ID, 33 cm h) closed on the top and open on the bottom

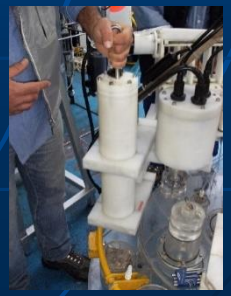
The CBA can operate on the continental shelf (up to 200 m depth)



Spagnoli et al., 2019

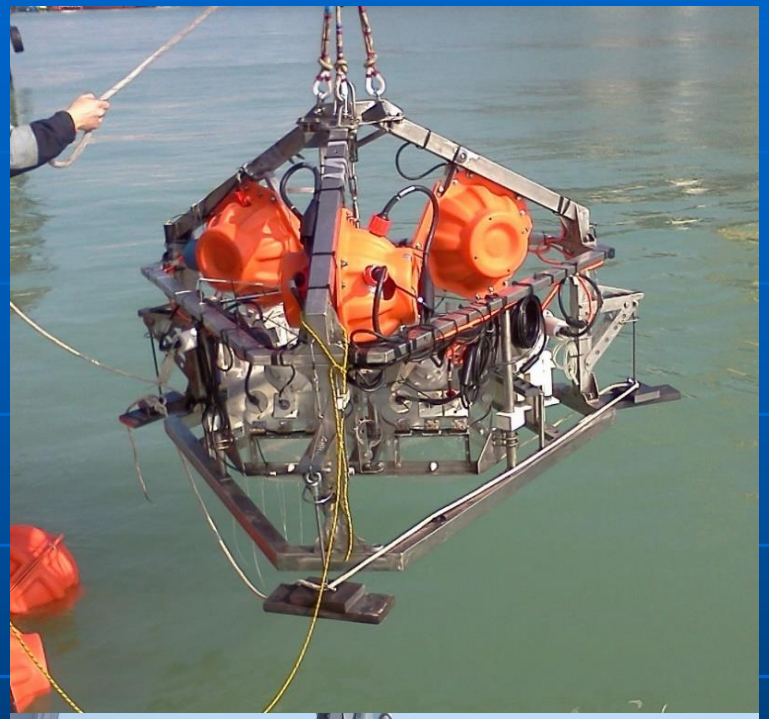
The CBA is equipped with:

- **A device for collecting water samples inside or outside the chamber or to inject a tracer inside the chamber (the VAMPIRE);**
- **A multiparametric probe (Hydrolab MS5) to measure oxygen, pH, Eh, temperature, conductivity (i.e. salinity) inside the chamber;**
- **Simple and commercial available electronic (Idec MicroSmart FC6A PLC) and batteries.**



Spagnoli et al., 2019

The Amerigo Lander



Main characteristics

- Amerigo is a lander (able to reach and operate on the sea bottom and return to the surface autonomously).

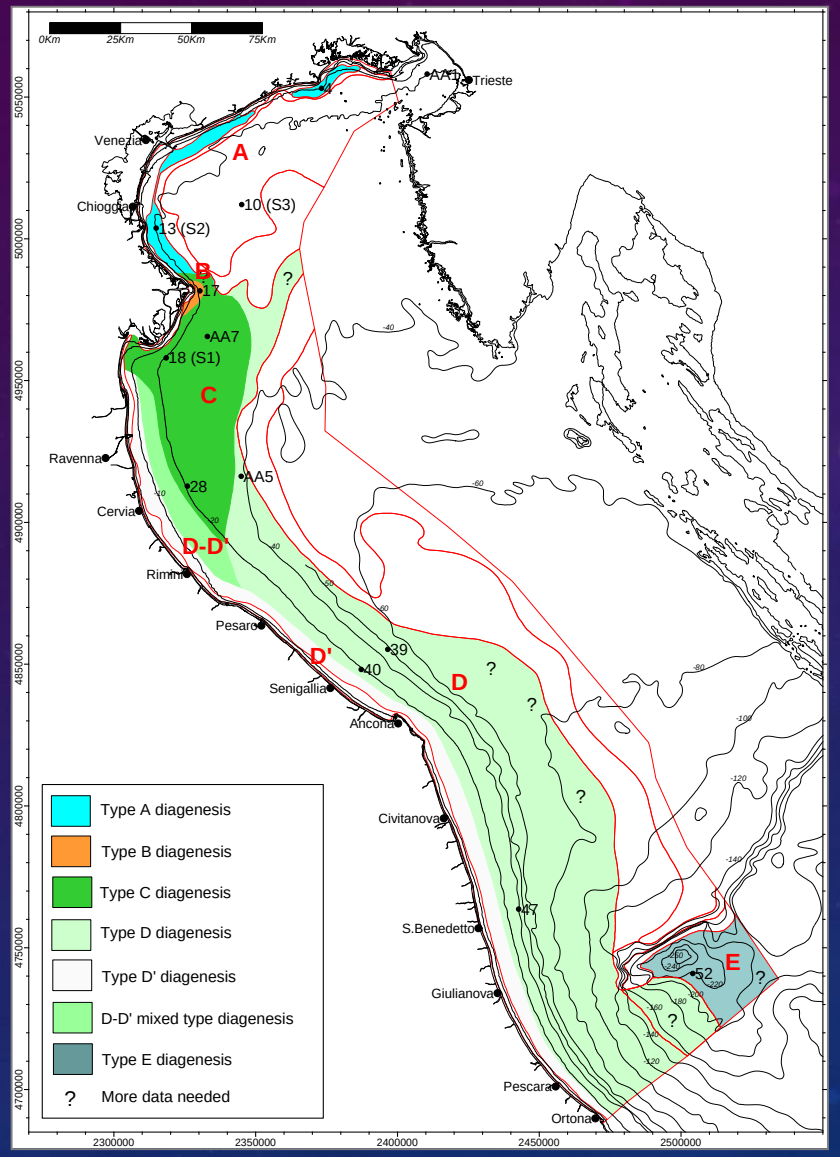
-At present is configured for the measurement of dissolved benthic fluxes at the sediment-water interface, including dissolved gases, nutrients, metals and pollutants;

- it is prepared to host other instruments for different monitoring and measurement studies:

- sensors for water column (oxygen, pH, methane, PAHs, pCO_2, H_2S, turbidity, fluorimeter);
- Instruments: microprofiler, (sediment-water interface properties), penetrometer (mechanical properties of the surface sediments), gravimeter, wave and current meter, corer.

Amerigo can operate from continental shelf to abyssal plain (up to 6000 m depth).

Main early diagenesis process environments of the Adriatic Sea



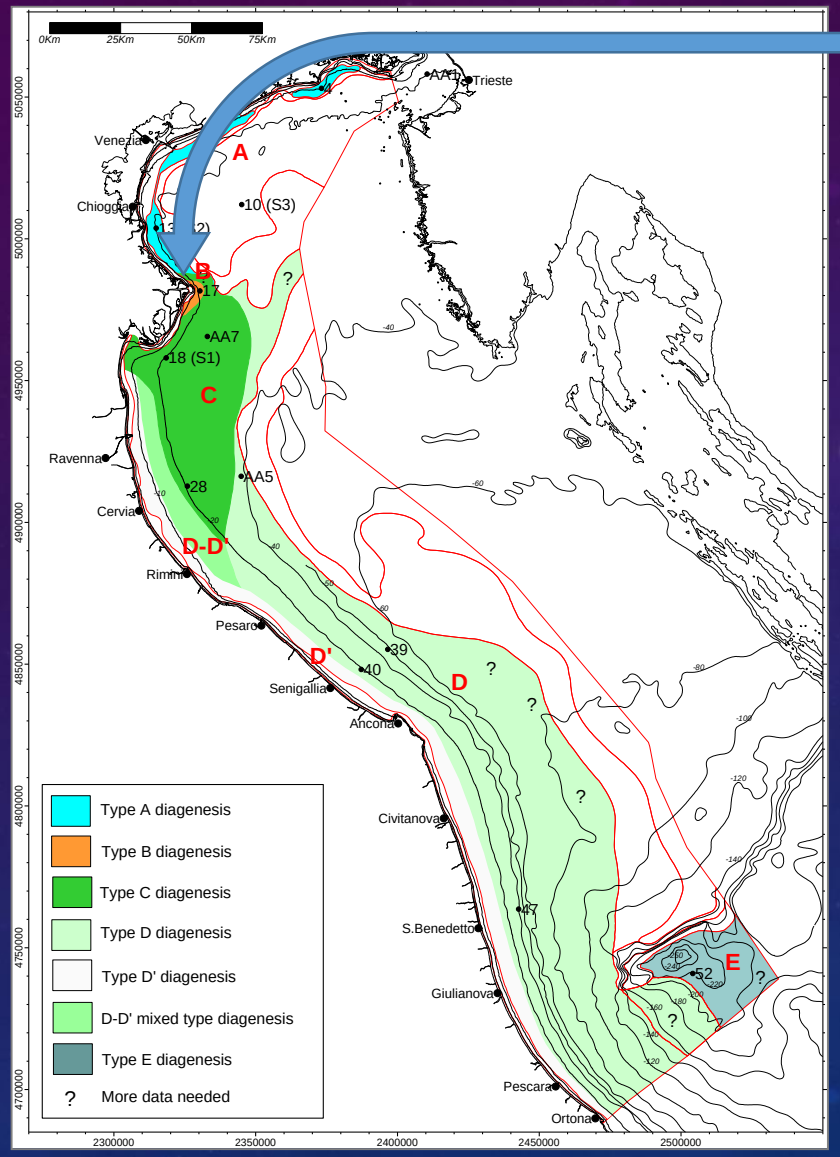
Diagenetic Reactivity

Main early diagenesis process environments of the Adriatic Sea

Type A
Type B
Type C
Type D
Type D’
Type D-D
Type E

Decreasing intensity from the Po River to the Middle Adriatic Depression

Main early diagenesis process environments of the Adriatic Sea



B: In front of the Po River

High solid inputs from Po River and strong primary production

Producing

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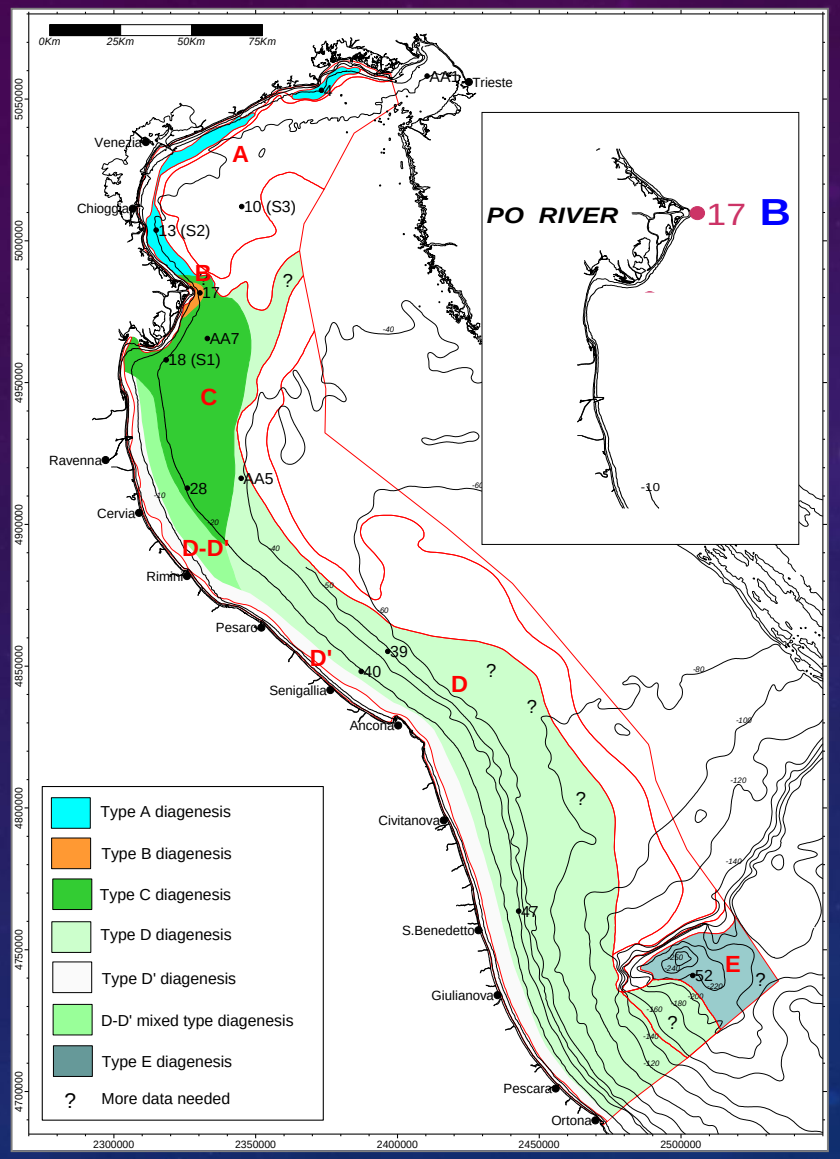
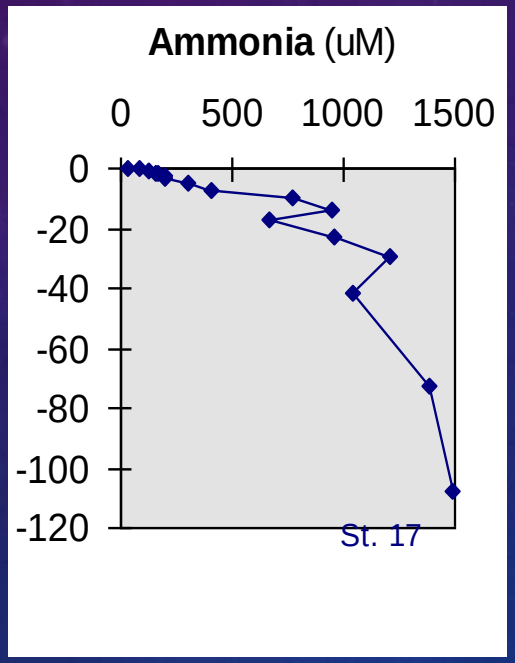
Main early diagenesis process environments of the Adriatic Sea

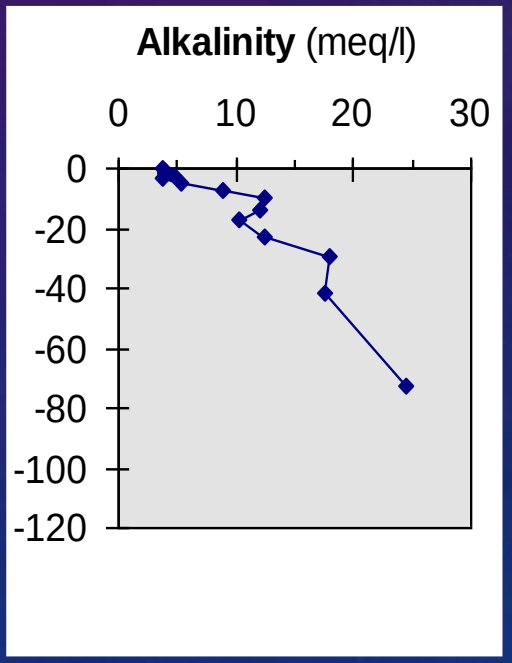


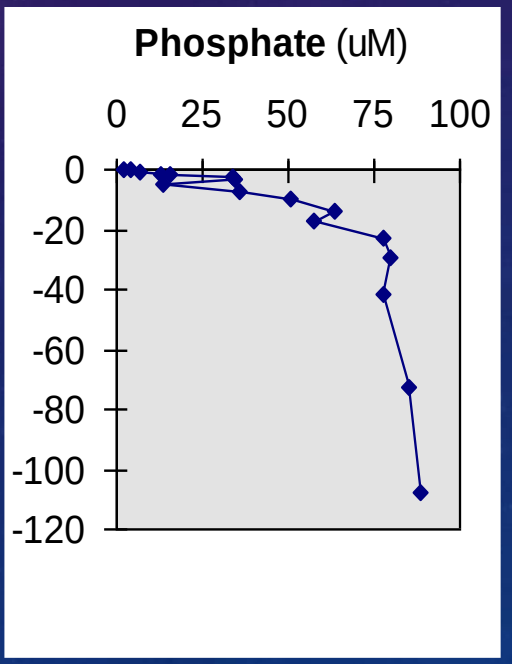
B: In front of the Po River

Producing

High pore water organic matter degradation product concentrations and benthic fluxes

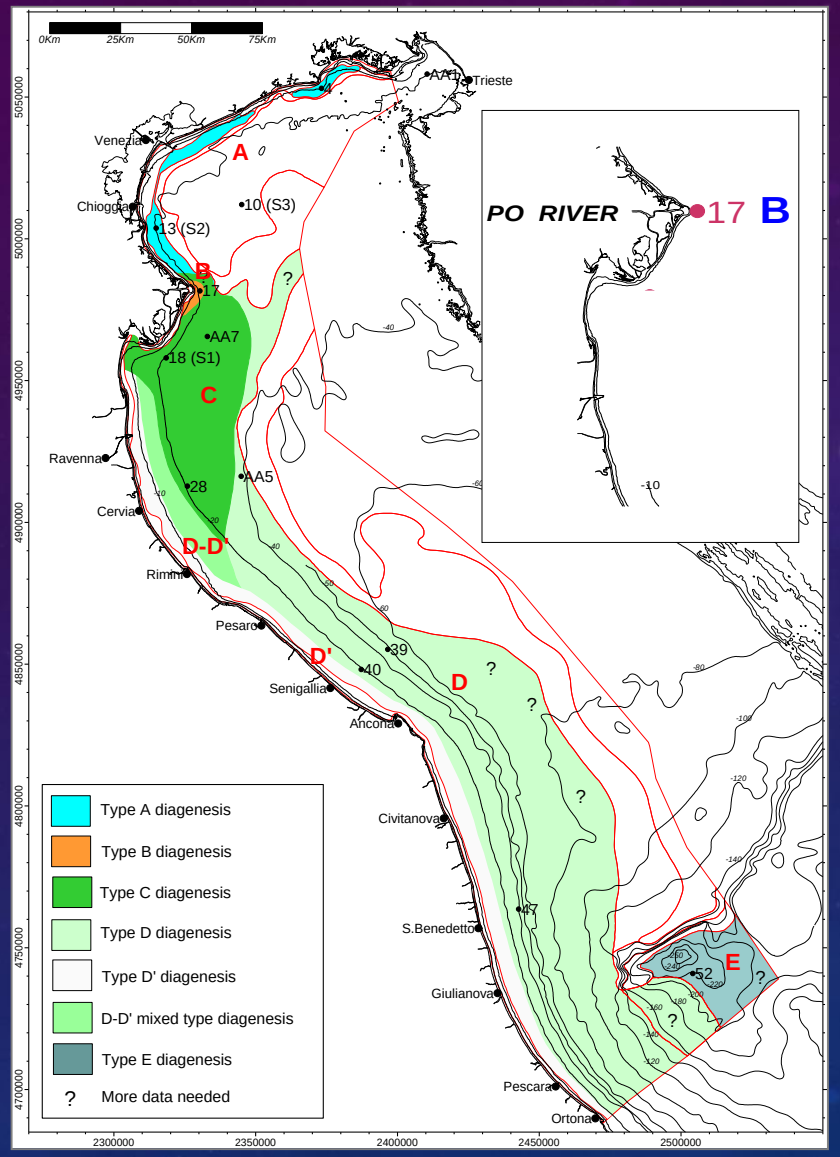






Organic matter degradation products

Main early diagenesis process environments of the Adriatic Sea

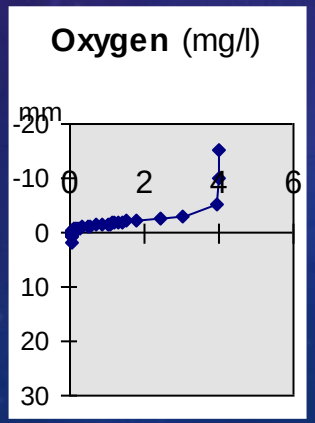


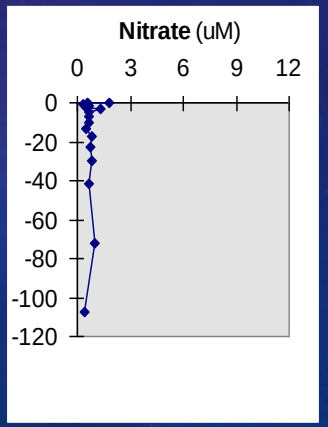
B: In front of the Po River

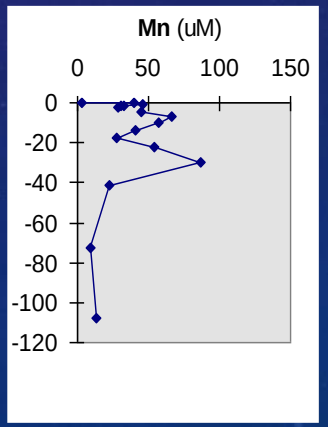
Fine Siliciclastic sediments

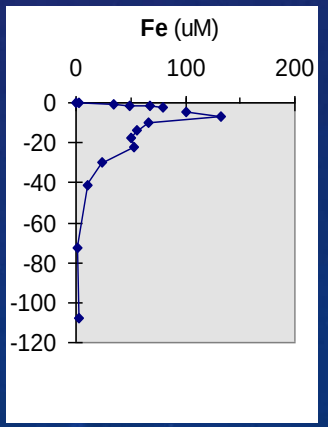
Producing

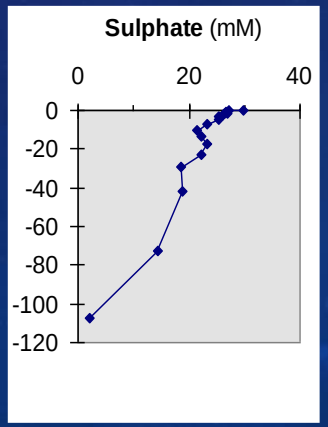
- Oxygen and nitrate reduction in the first millimetres
- Fe and Mn oxy-hydroxide reductions in the upper centimetres
- Strong sulphate reduction
- Anoxic environment near surface











Final electron acceptors

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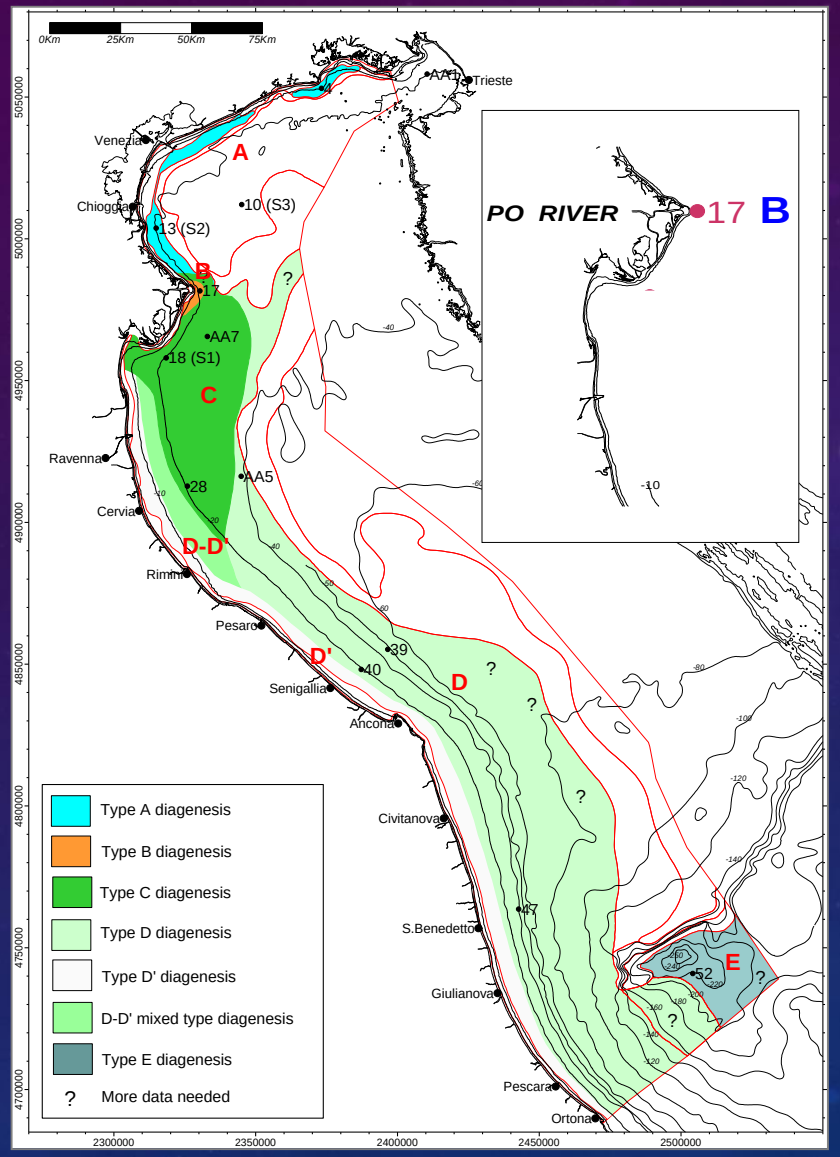
Main early diagenesis process environments of the Adriatic Sea



B: In front of the Po River

Fine Silicoclastic sediments

- High sedimentation rates
- high reactive and degraded organic matter contents
- high Fe-oxy-hydroxide contents
- anoxic-non sulfidic-methanic environments
- **very high benthic fluxes (NH_4, PO_4, DIC) for degradation of high organic matter**

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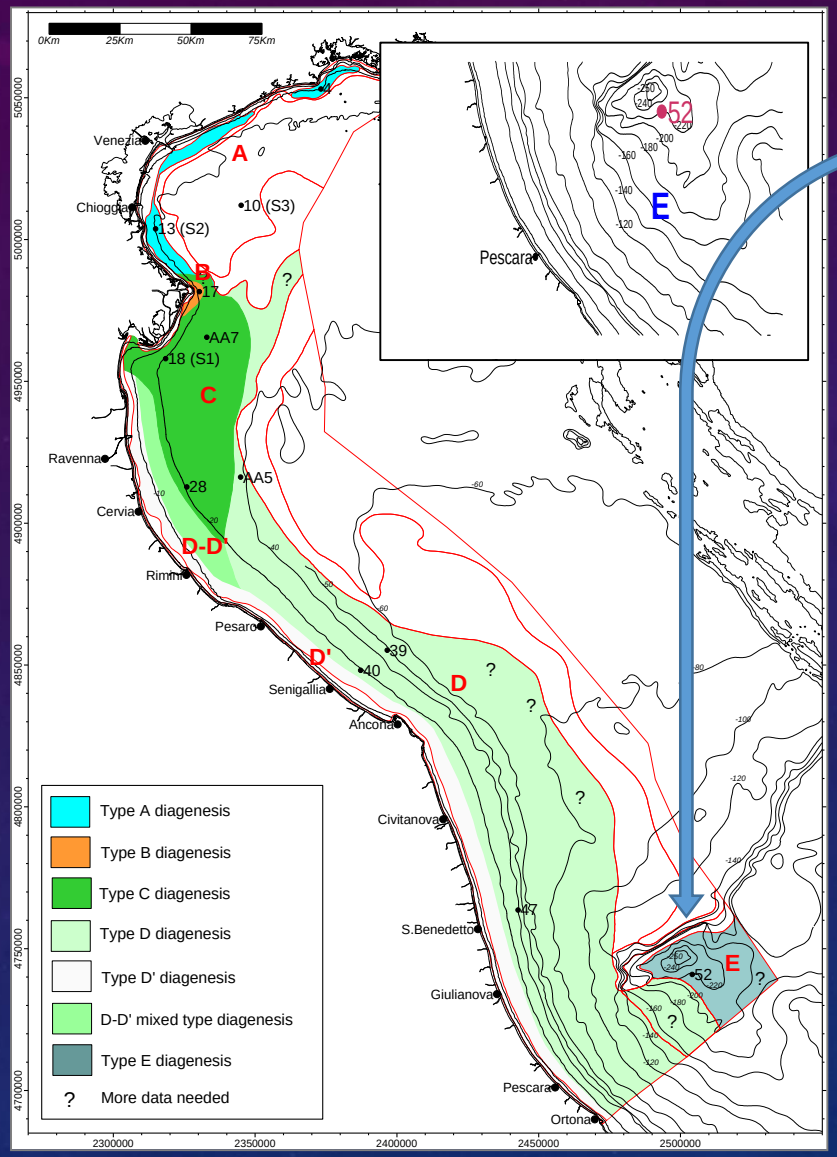
Main early diagenesis process environments of the Adriatic Sea



Type E diagenetic processes

- Basin area (Mid-Adriatic Depression)
- Far from the Po River and other continental inputs
- Mixed fine carbonatic and silicoclastic sediments highly reworked
- Low sedimentation rate
- Low inputs of reactive organic matter
- greater depths
- low reactive organic matter contents

Producing

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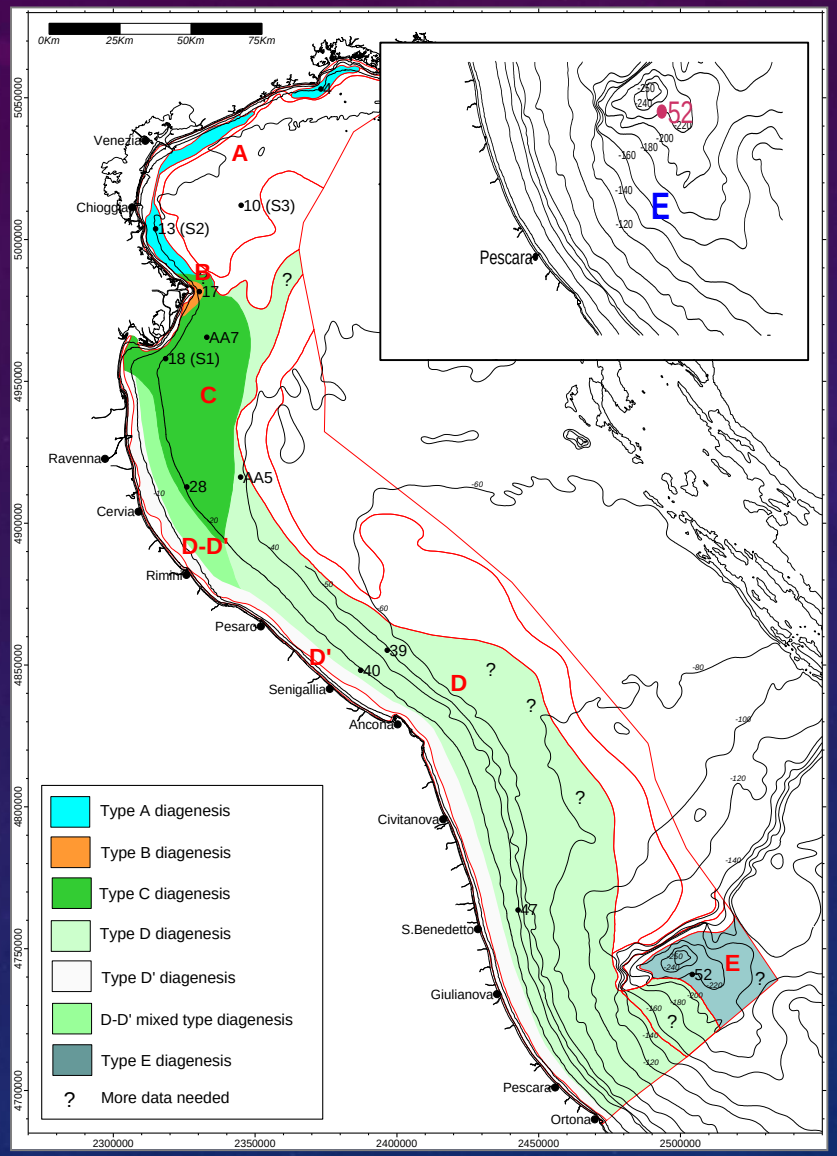
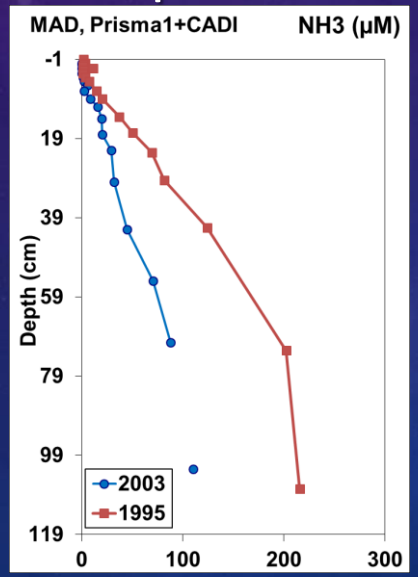
Main early diagenesis process environments of the Adriatic Sea

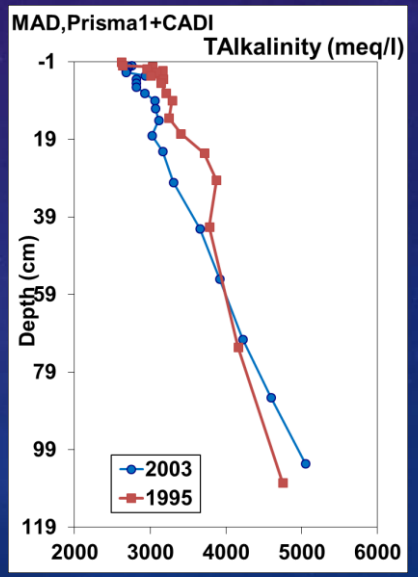


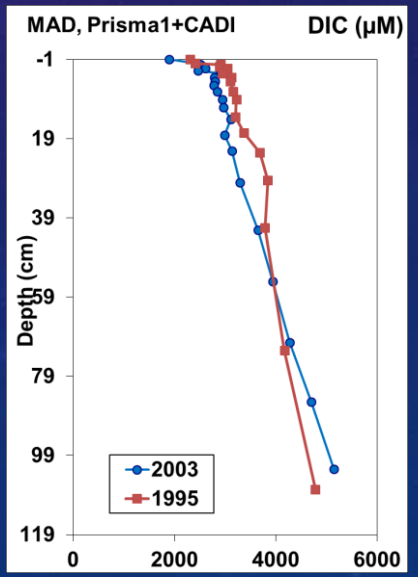
Producing

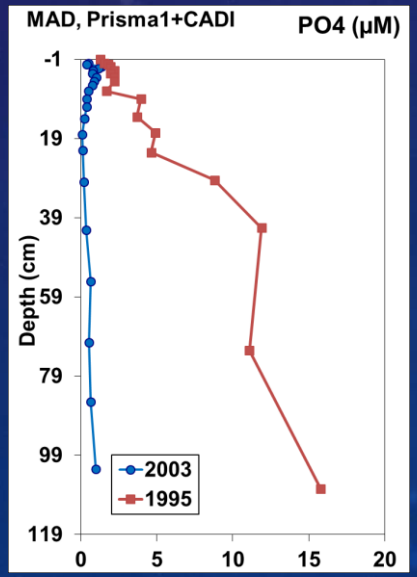
Type E diagenetic processesIn basin areas away from the Po River

- Low pore water organic matter degradation product concentrations and benthic fluxes
- Weak increase of ammonia, alkalinity and phosphate with depth









Organic matter degradation products

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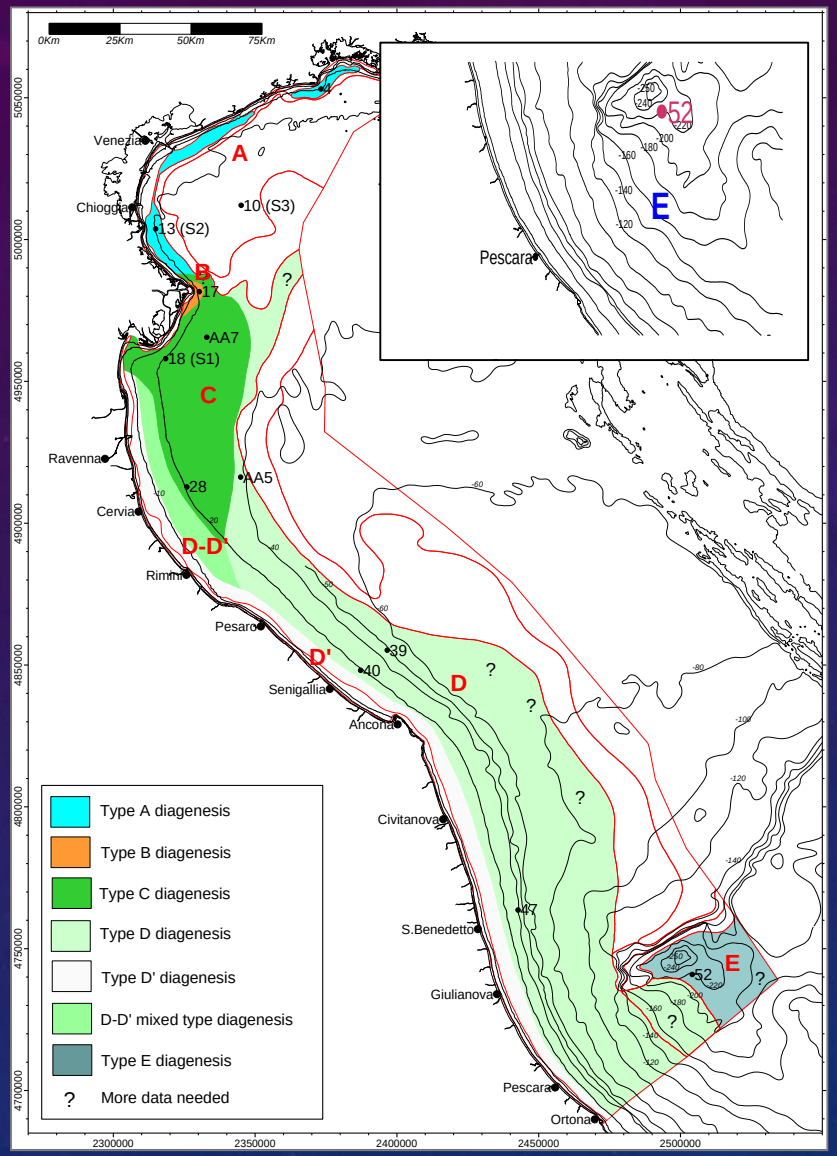
Main early diagenesis process environments of the Adriatic Sea

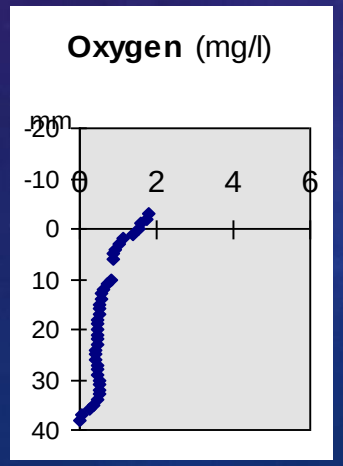


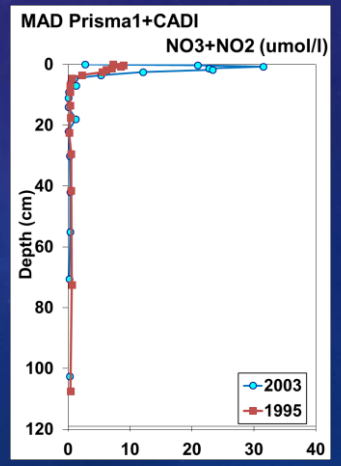
Producing

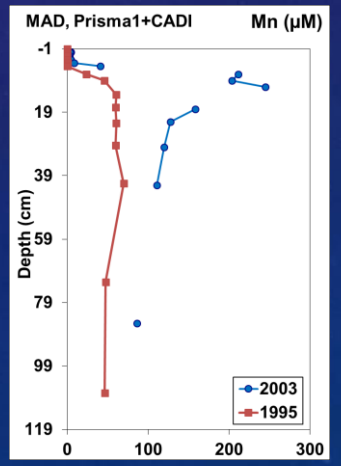
Type E diagenetic processesIn basin areas away from the Po River

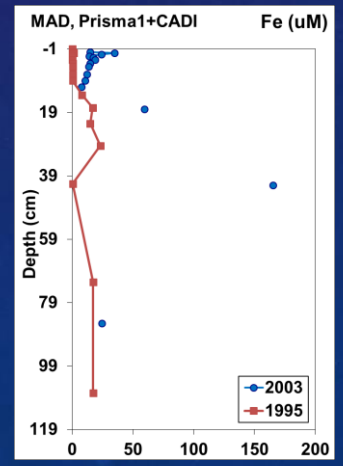
- Oxygen decrease after 3 centimetres
- strong decrease of nitrate in the upper centimetres
- Mn and Fe oxy-hydroxide reductions after few centimetres
- weak sulphate decreasing with depth
- Oxic environment near surface

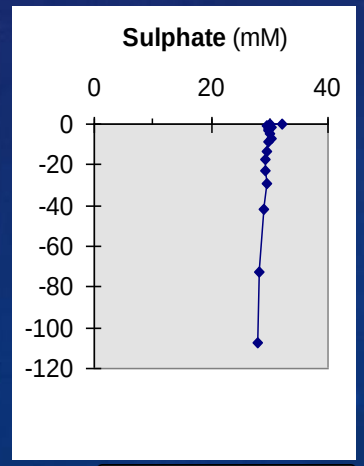
17





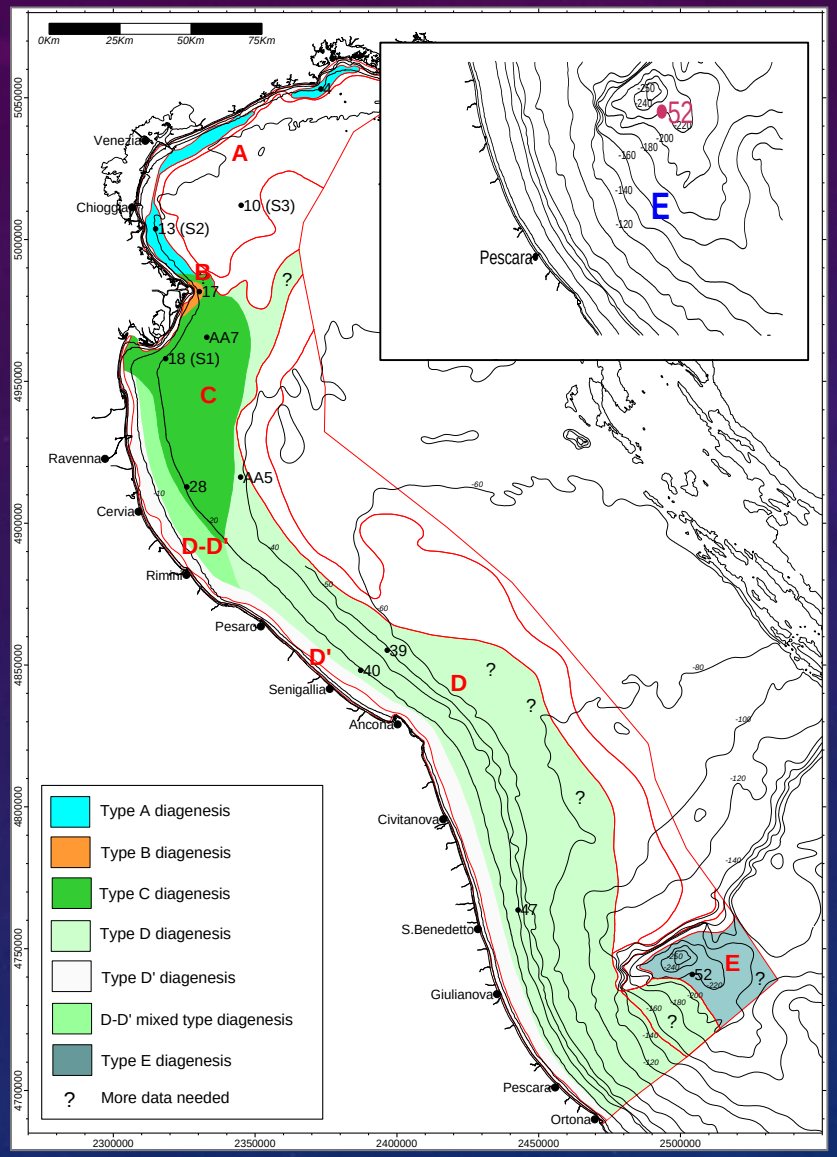






Final electron acceptors

Main early diagenesis process environments of the Adriatic Sea



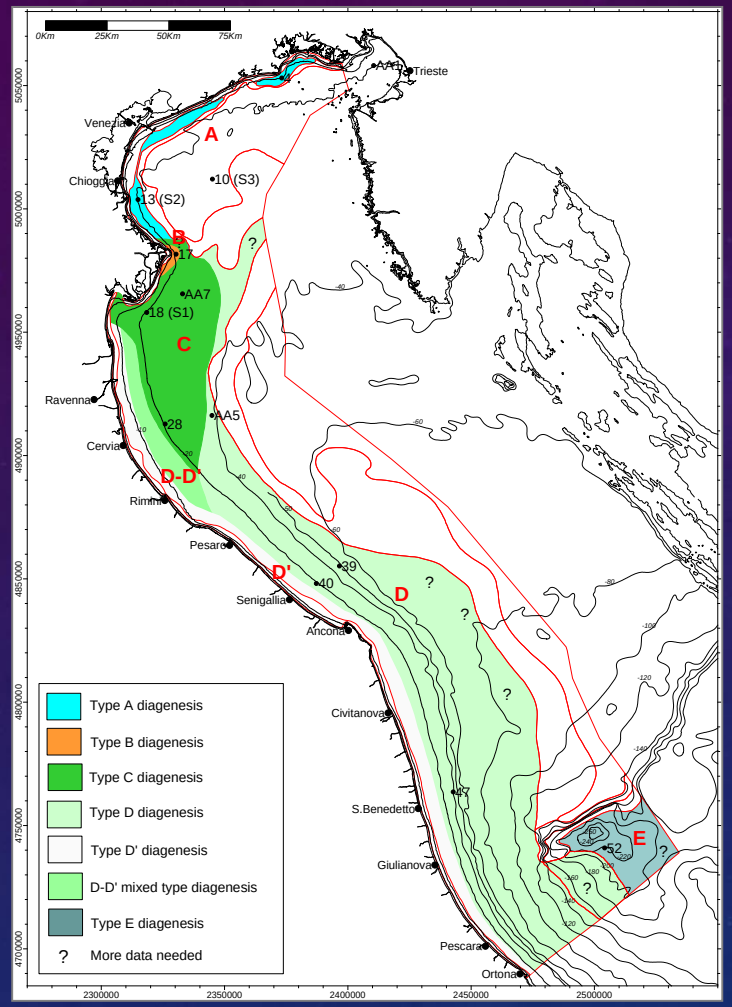
Producing

Type E diagenetic processesIn basin areas away from the Po River

18

- main degradation at sediment-water interface
- oxic environments up to 10 cm
- Fe and Mn oxy-hydroxides precipitation in first centimetres
- organic matter degradation by sulphate with depth
- **very weak diagenetic processes and benthic fluxes**

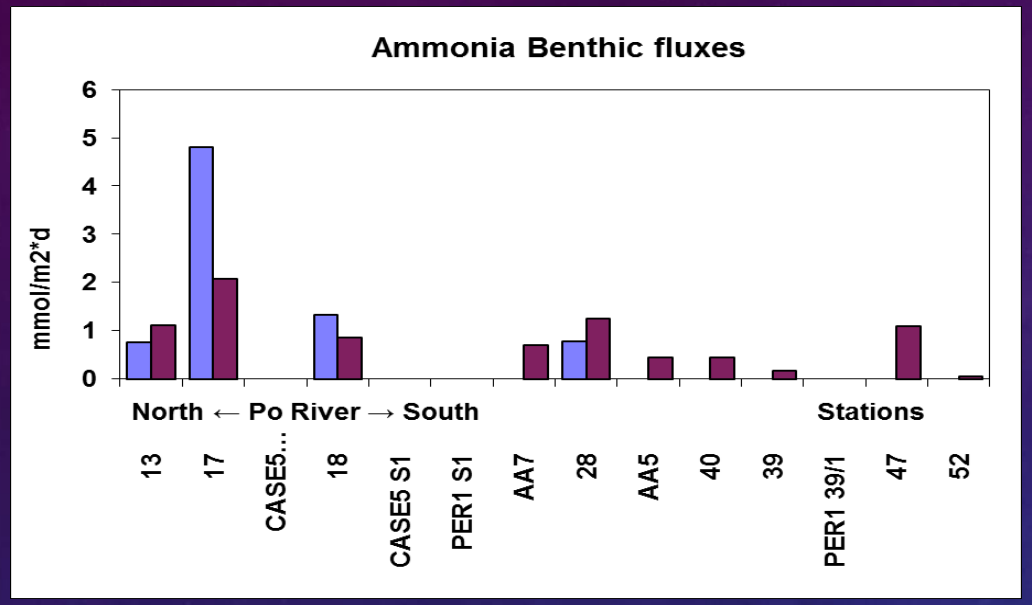
Main early diagenesis process environments of the Adriatic Sea

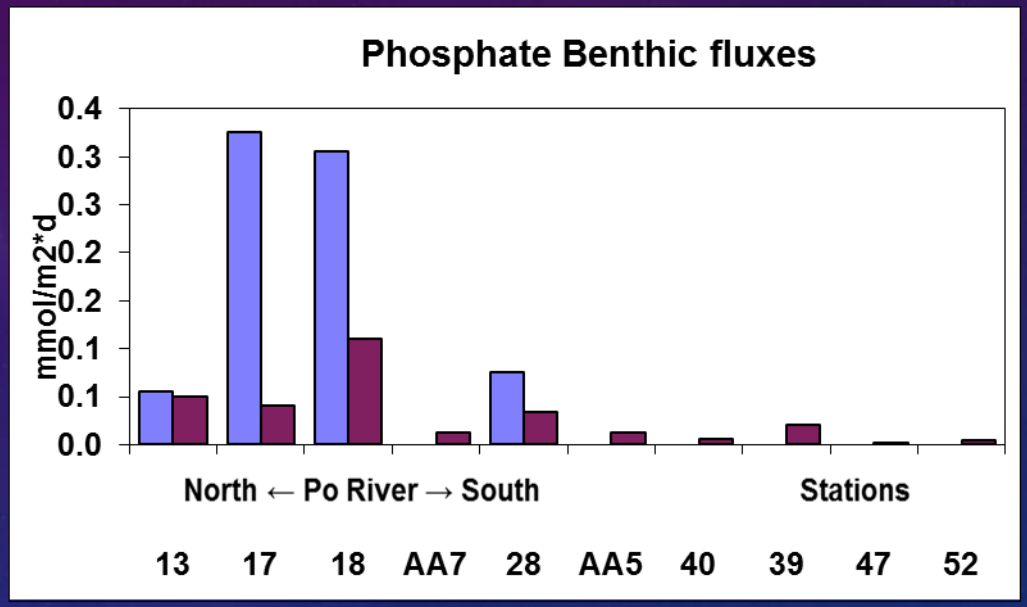


Benthic Fluxes

Fluxes at the sediment-water interface of nutrients and trace metals are activate by the early diagenetic processes.

NUTRIENT BENTHIC FLUXES IN THE ADRIATIC SEA



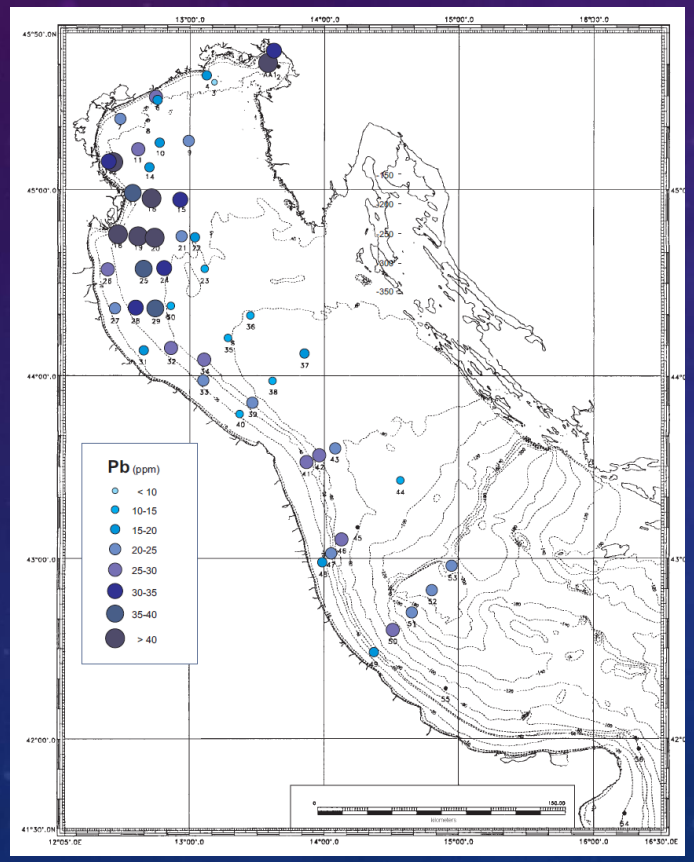


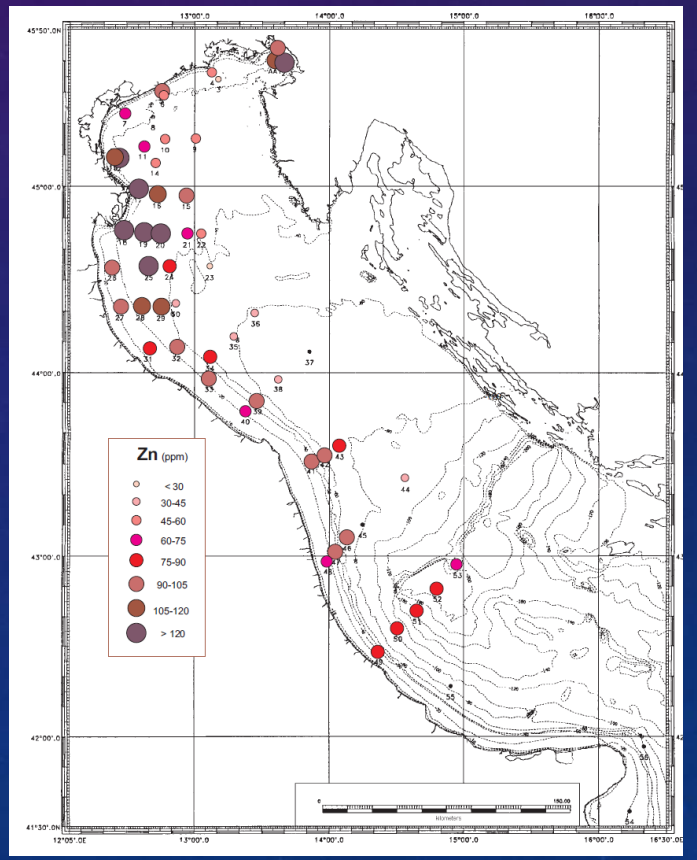
- Maximum benthic fluxes are located in front of Po River (Stations 17 and 18); minimum fluxes are present in Mid Adriatic Depression sediments (station 52).
- Nutrient benthic fluxes decrease away from Po River mouths northward and southward because of the increasing distances from main sediment and nutrient sources and the continuous sediment reworking and lower primary production that decrease the reactive organic matter inputs in the surface sediments;

SURFACE SEDIMENT HEAVY METAL POLLUTION

Pollution in the Adriatic Sea

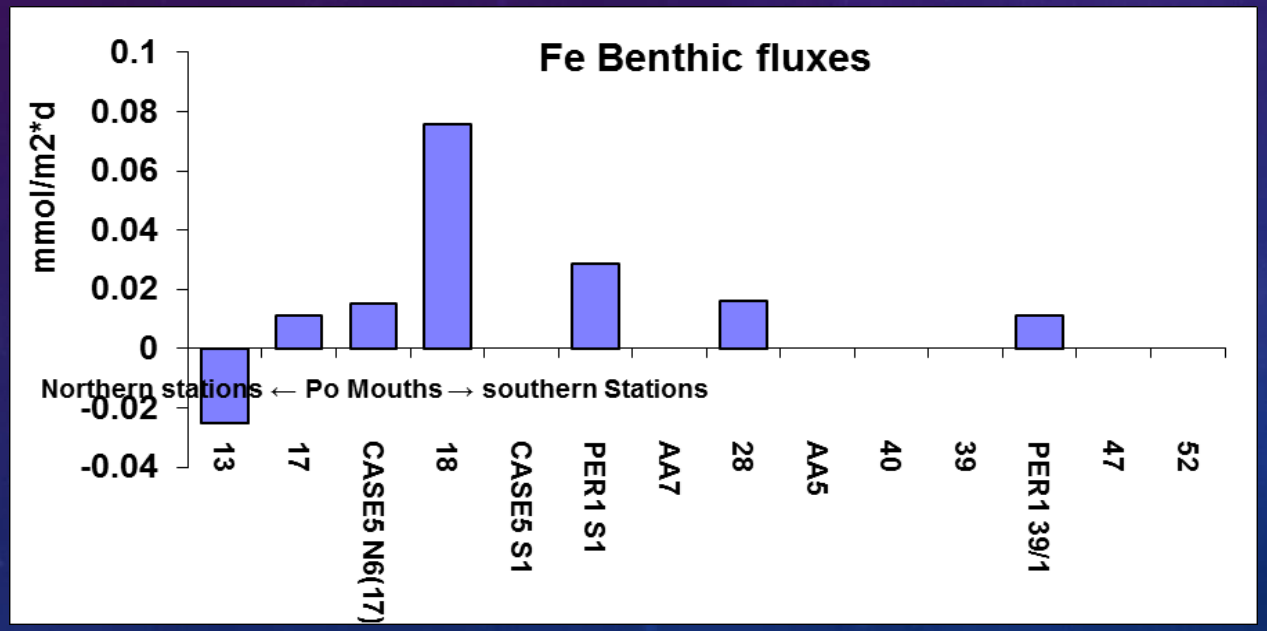
The heavy metal concentrations in surface sediments of the western Adriatic Sea indicate a consistent pollution deriving from the Po River inputs as can be seen by the decreasing heavy metal concentrations from the Po River mouths northward and southward.

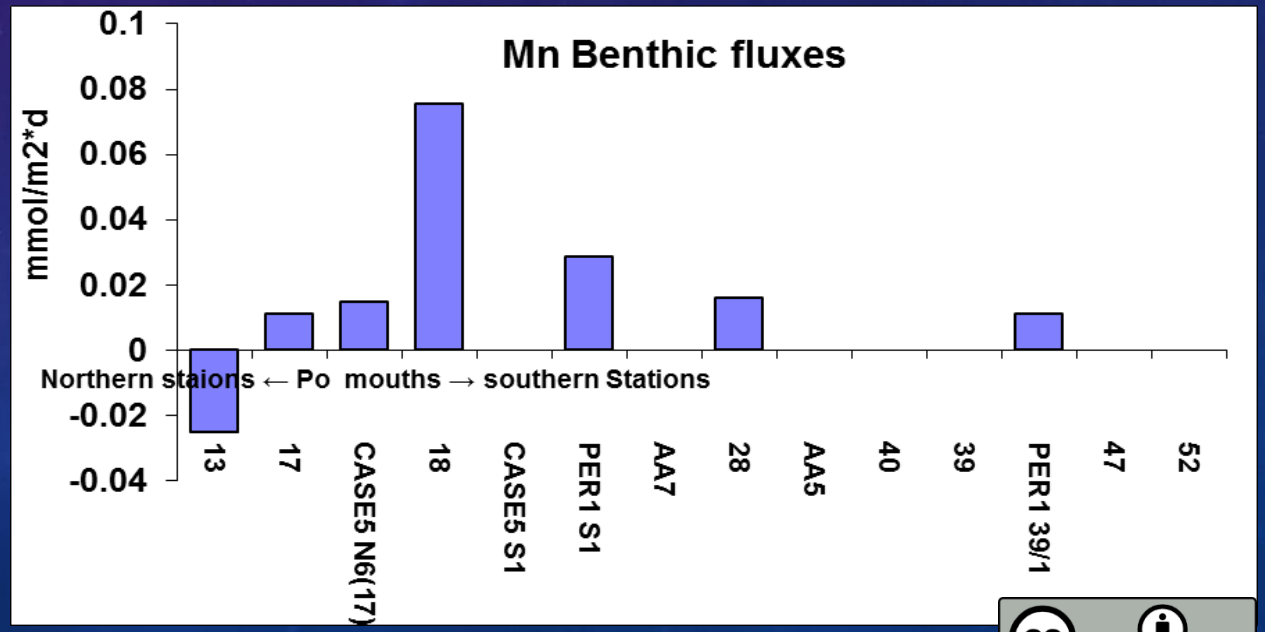




DISSOLVED HEAVY METAL BENTHIC FLUXES

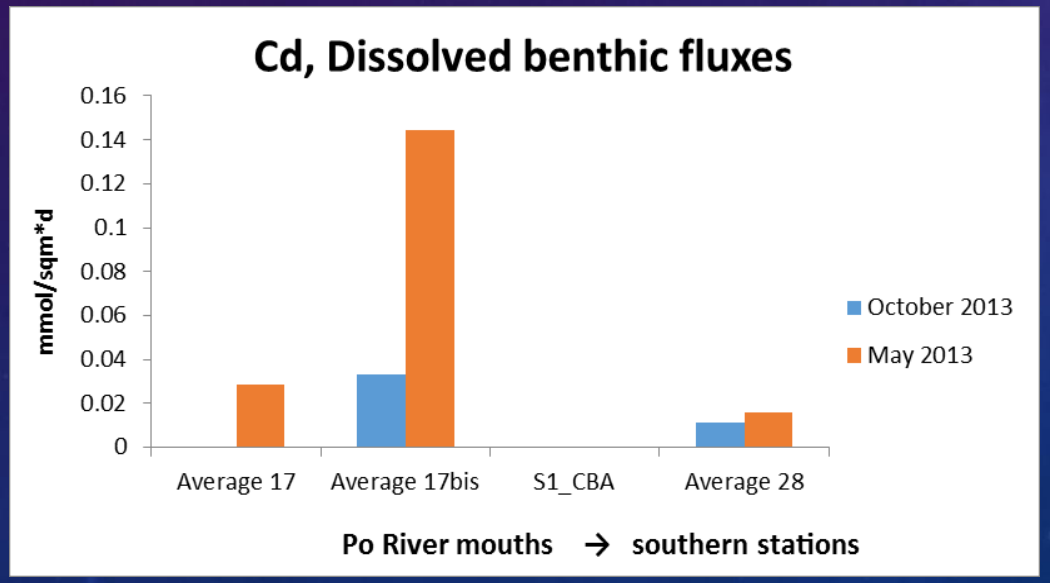
- Fe and Mn dissolved benthic fluxes decrease from the Po River mouths southward and northward
- This trend is attributed to of the high Po River metal inputs that deposit in the surface sediments of the Po prodelta and of the high early diagenesis processes that take place near the Po River mouths for the high inputs of fresh autochthonous and allochthonous organic matter

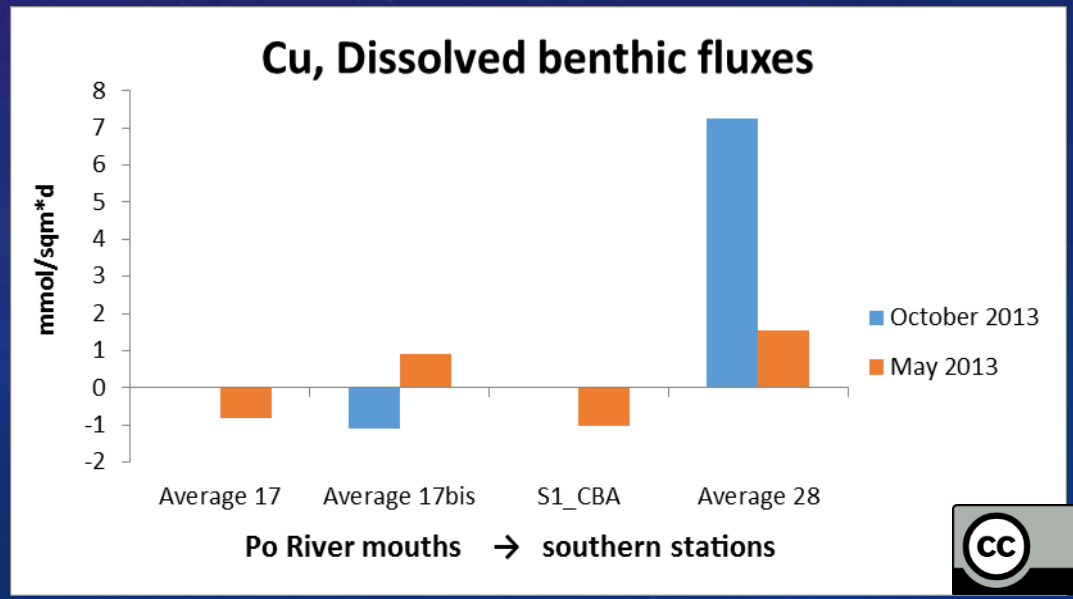




DISSOLVED HEAVY METAL BENTHIC FLUXES

- Dissolved benthic fluxes of other heavy metals (Co, Ni, Zn, Cu, Cd, Pb) indicate that:
  - Elements such as Cd show a southward decreasing trend suggesting a behaviour affected by the Po River inputs and Fe-Mn-oxyhydroxide cycle
  - some elements such as Cu doesn't show a clear north–south trend suggesting that they are affected by local inputs;





Conclusions

Researches on early diagenesis process studies and dissolved benthic flux measurements in the Adriatic allowed:

The individuation of areas with different types of early diagenesis processes generating characteristic benthic fluxes

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This variability reflects different sedimentary settings determined by variations in some factors such as:

- sedimentation rate;
- reactive organic matter inputs (fresh marine and continental organic matter);
- hydrodynamic of the water column;
- particulate and dissolved continental inputs;
- oxygenation of near bottom waters;
- distances from main sediment sources (mainly the Po River);
- bottom sediment composition (carbonate or silicate);
- depths (more or less resuspension events, increasing pressure with depth).

Conclusions

- Heavy metal distribution and early diagenesis studies in the surface sediments of the North and Central Adriatic Sea highlight the presence of heavy metal polluted areas producing high heavy metal dissolved benthic fluxes in front of the Po River mouths with decreasing values northward and southward
- The higher release of heavy metals from the sea bottom near the Po River mouths are consequence of the Po River inputs and early diagenesis processes
- Other elements seem to be affected my local processes and inputs

Conclusions

The study of the early diagenesis and of the benthic fluxes allowed also:

- To understand the mechanisms responsible of the recycle or sinking of nutrients, carbon and heavy metals at the sediment-water interface
- To quantify nutrient, DIC and some metal fluxes at sediment-water interface

Thank You

Sunset from Dallaporta