Estuaries in a Changing World
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Metal geochemistry of the sediments and benthic fluxes in a Galician ria (Vigo Ria, NW Iberian Peninsula)

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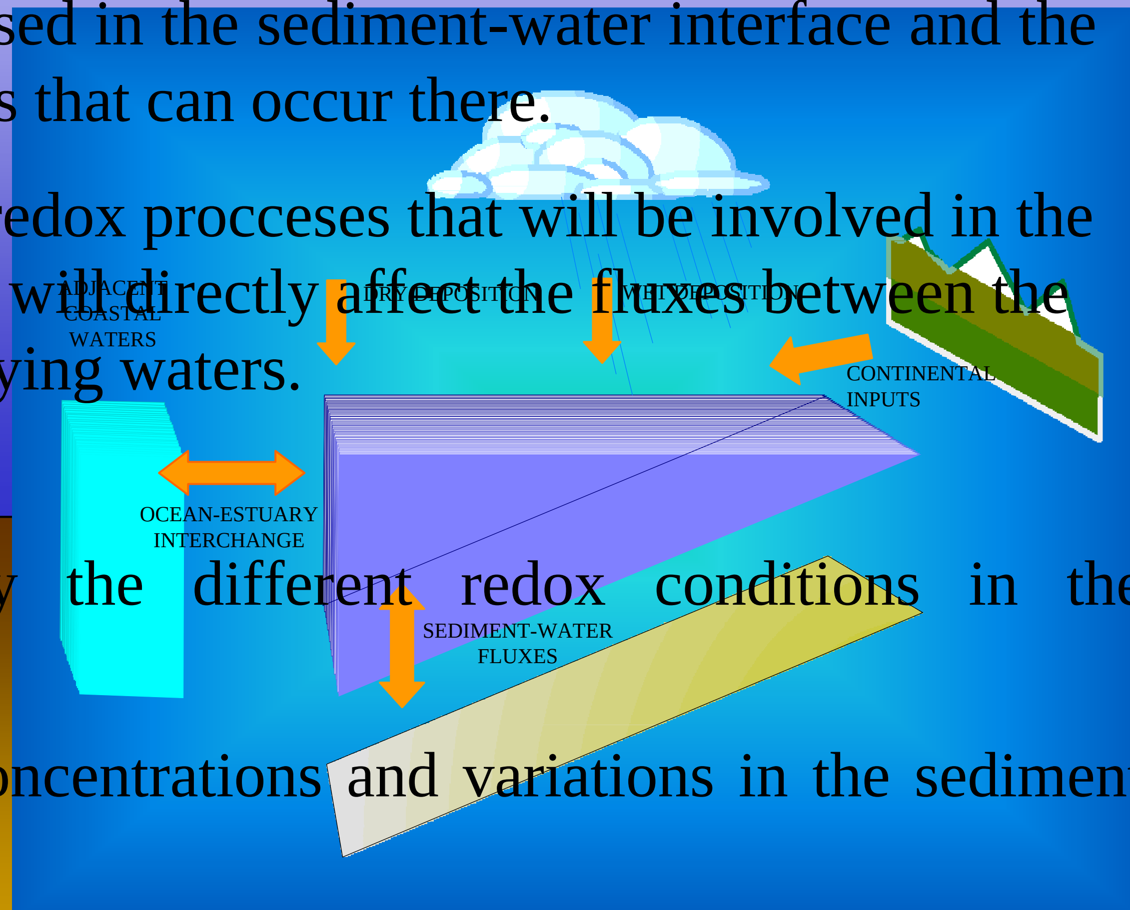
INTRODUCTION: Background and objectives

- Estuaries are located between the open ocean and the continent. Thus, trace elements can be exchanged between the estuary and the sorrounding ambients through various frontiers.

- This study will be focused in the sediment-water interface and the exchanges of trace metals that can occur there.

- The geochemistry and redox procceses that will be involved in the sediment-water interface will directly affect the fluxes between the porewaters and the overlying waters.



Objectives:

1) Describe and study the different redox conditions in the sediments

2) Study trace metal concentrations and variations in the sediment and porewaters

3) Estimate trace metal fluxes in the sediment-water interface

STUDY AREA : Vigo Ria

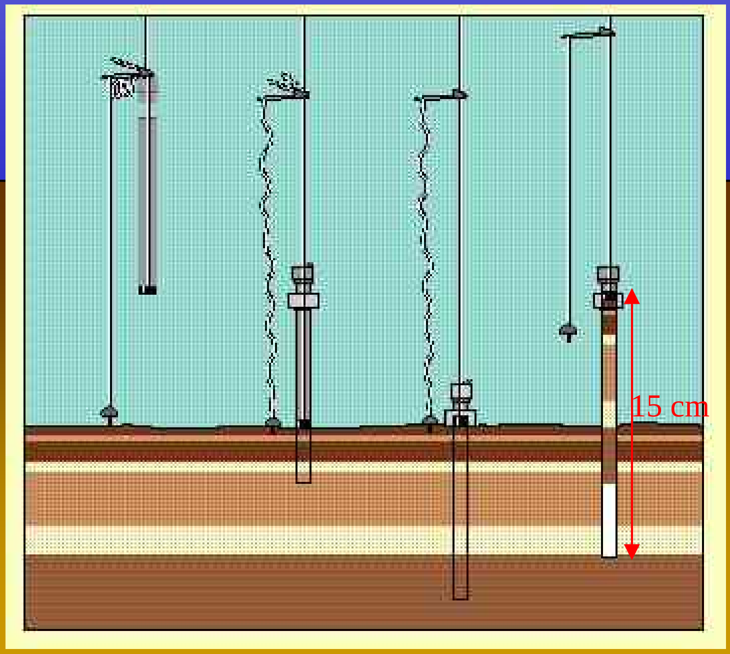
MATERIAL AND METHODS: Sampling strategy

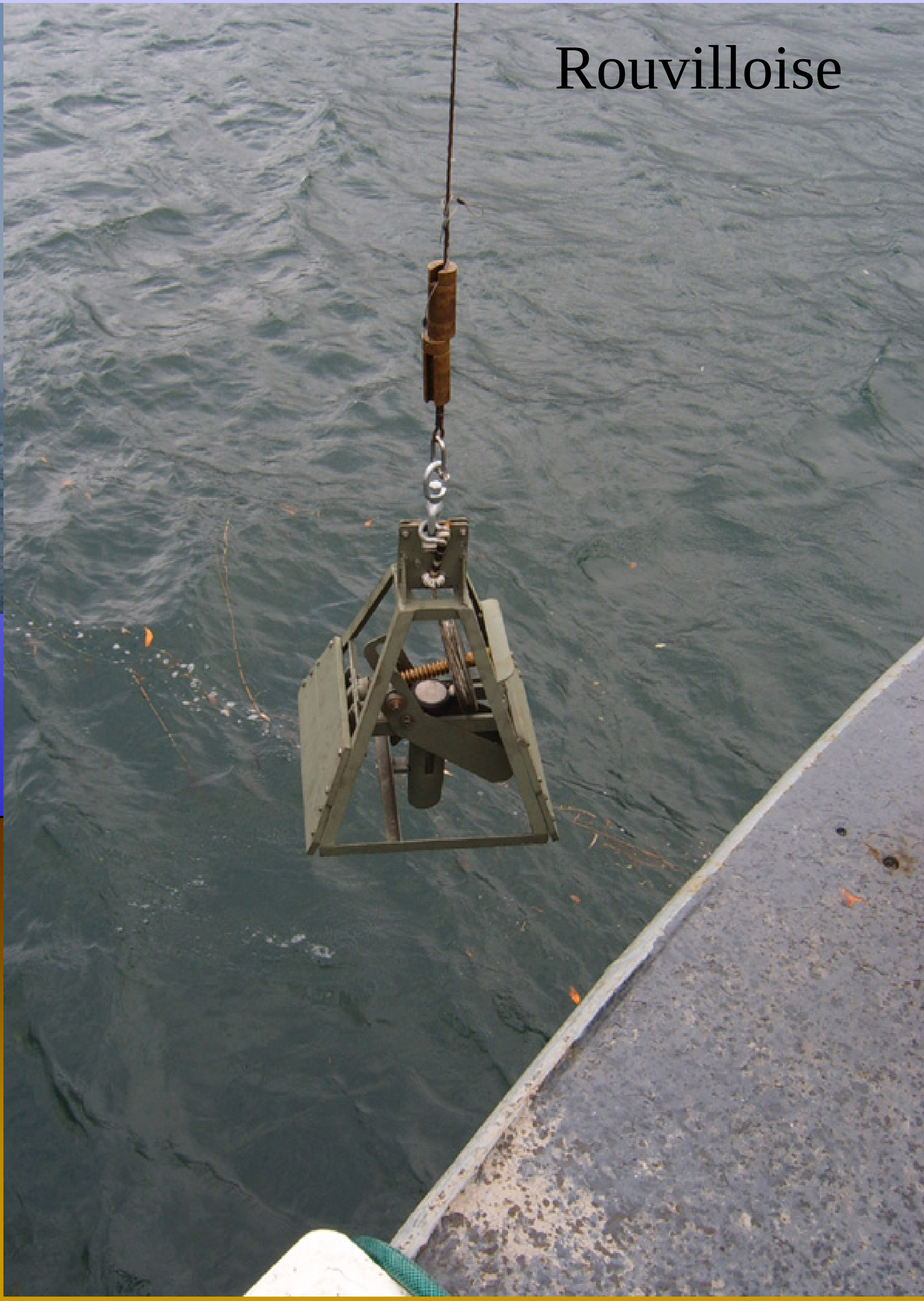
Three different seasons during 2004:

-Winter (February)

-Spring (May)

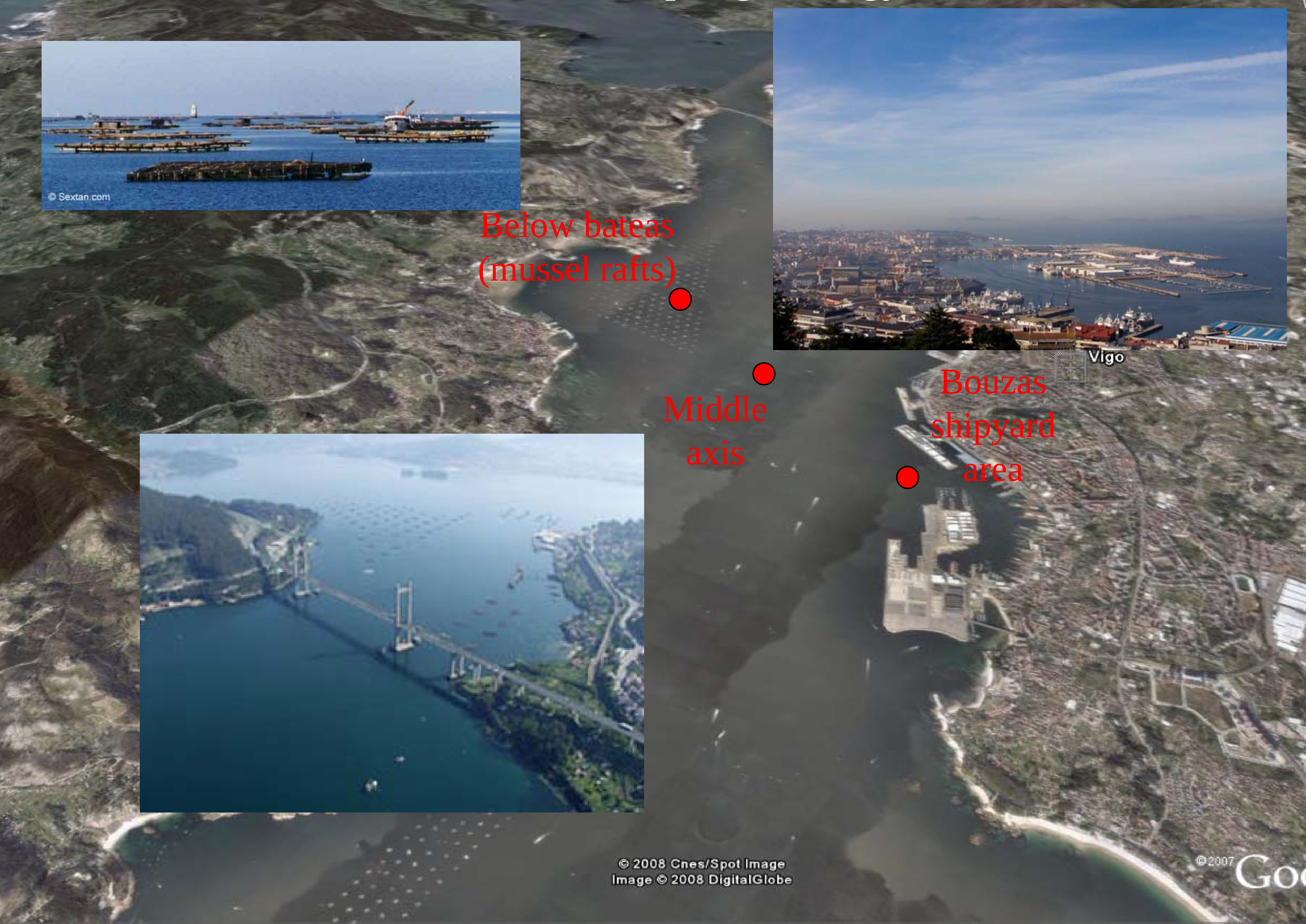
-Summer (July)



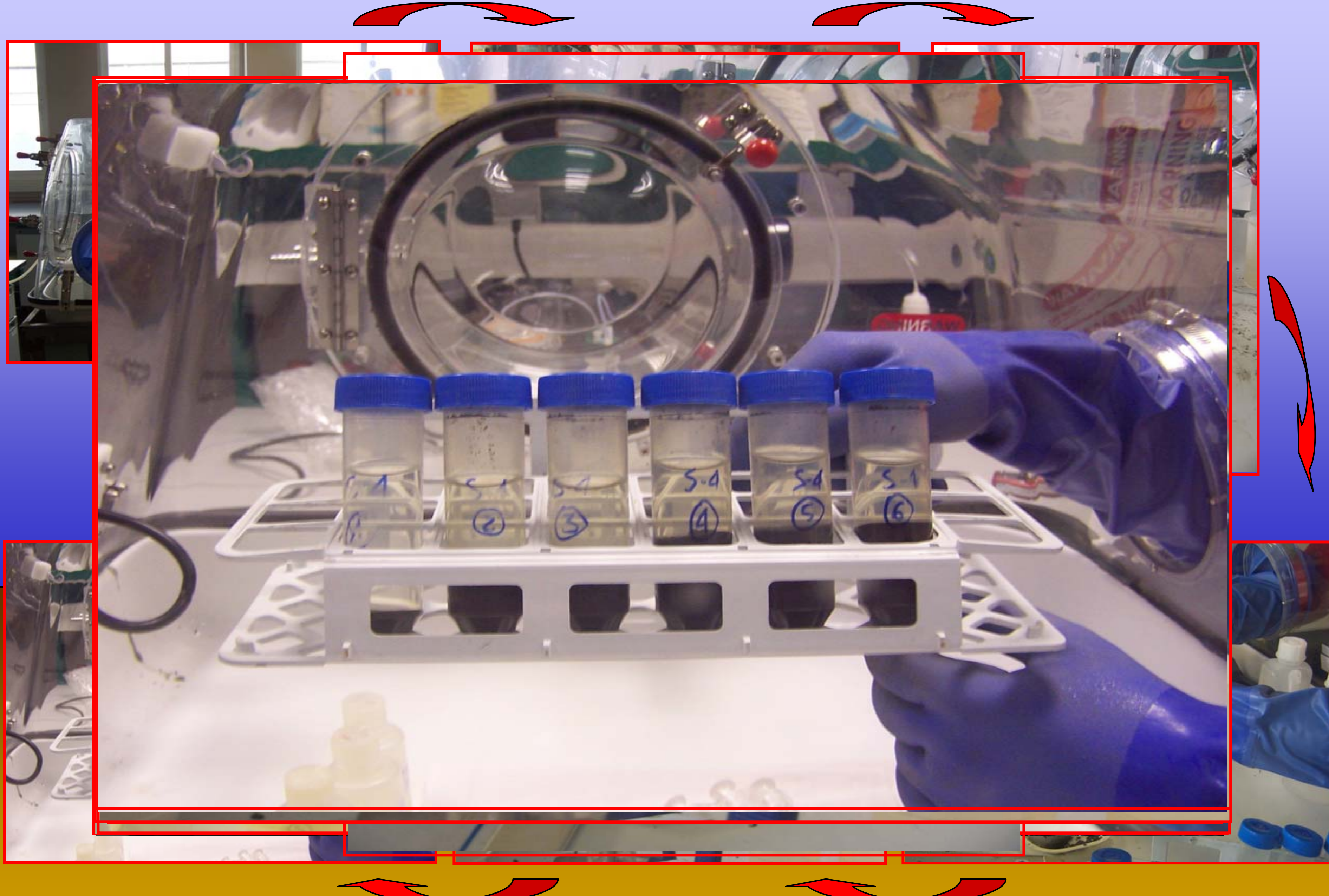


Rouvilloise

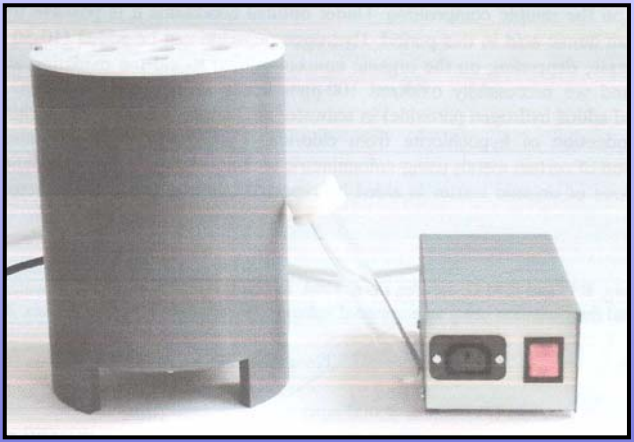
MATERIAL AND METHODS: Sampling strategy



MATERIAL AND METHODS: Sample pretreament



MATERIAL AND METHODS: Overlying and pore waters

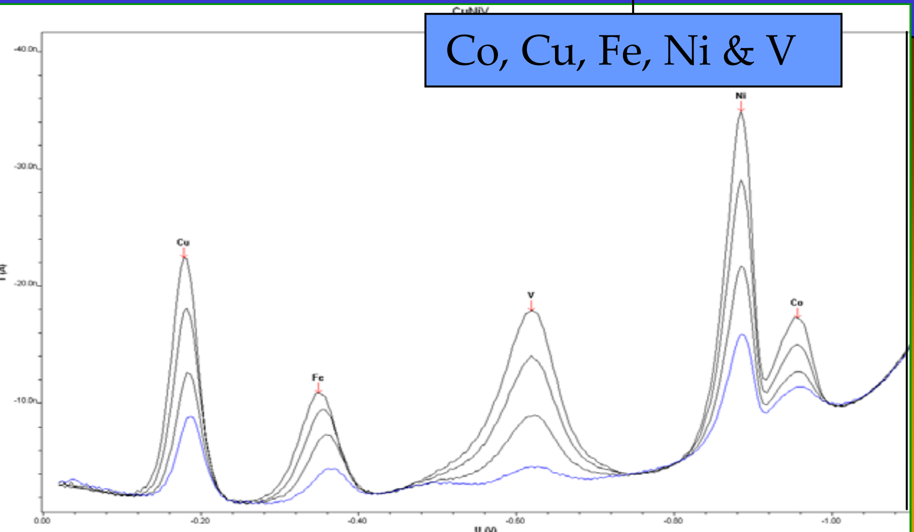


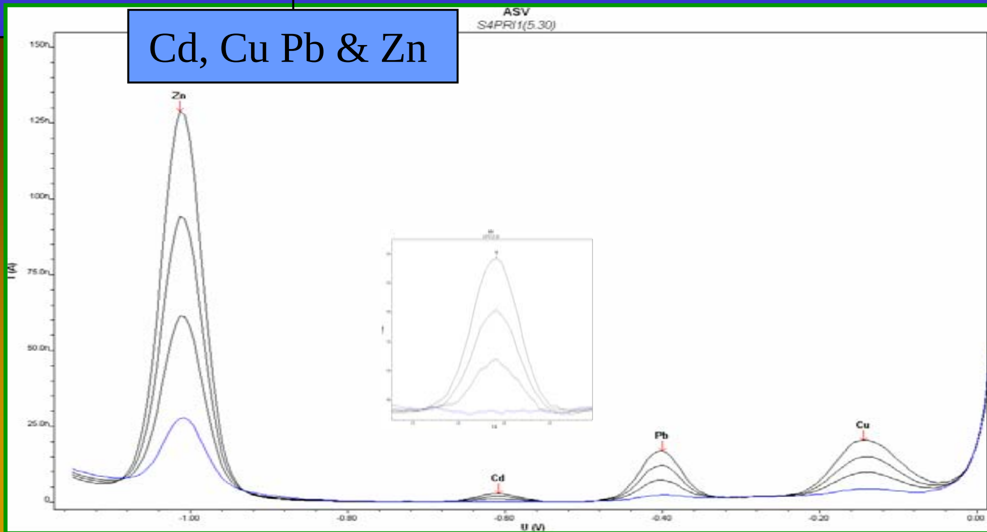
WATER

Filtration 0,2 µm

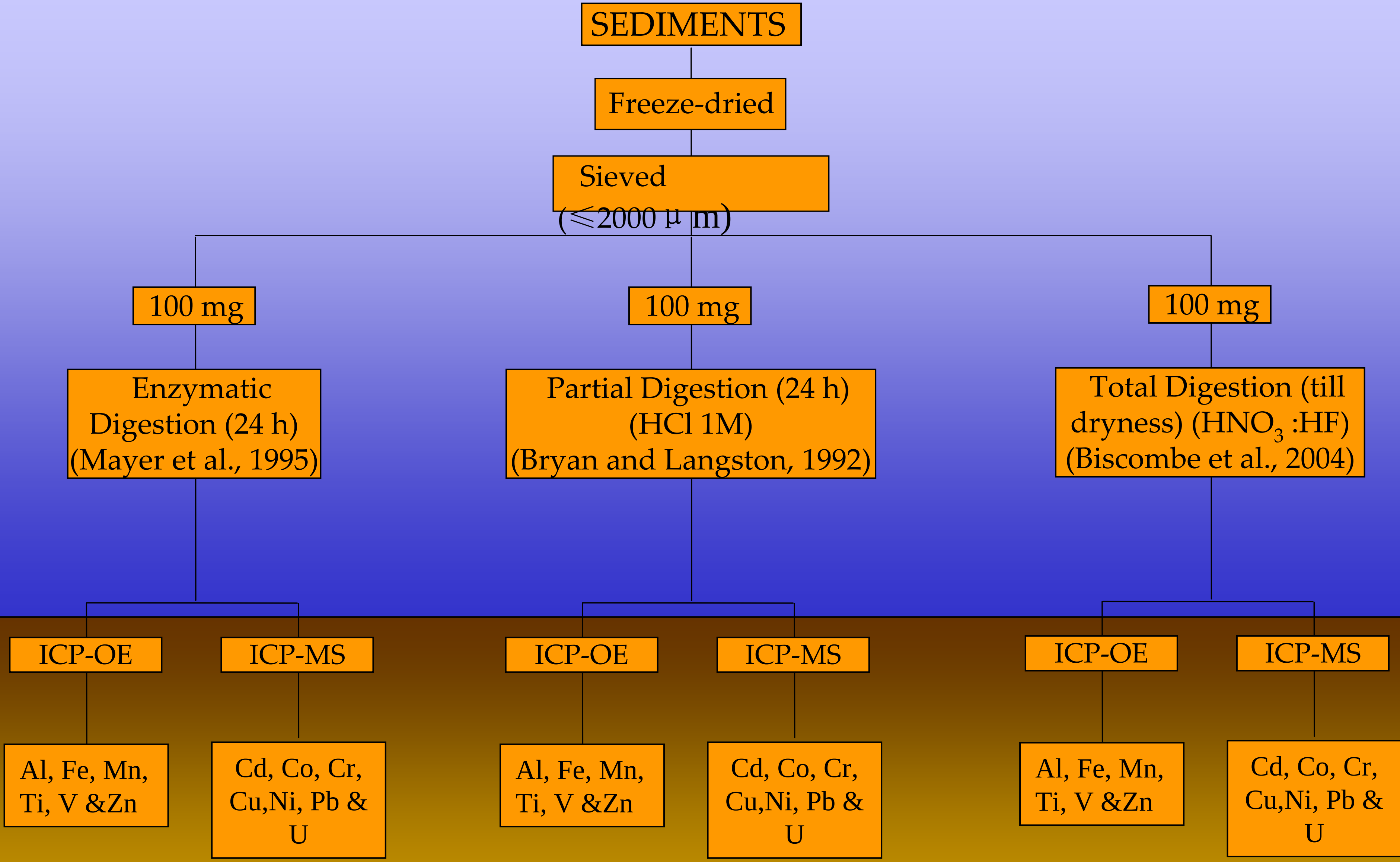
UV digestion (Achterberg and van den Berg, 1994)

- F-AAS
  - Fe&Mn
- Cathodic Stripping Voltammetry (Cobelo-García et al., 2005)
  - Co, Cu, Fe, Ni & V
- Anodic Stripping Voltammetry (Gardiner and Stiff, 1975)
  - Cd, Cu Pb & Zn





MATERIAL AND METHODS: Sediments



MATERIAL AND METHODS: Sediment-water fluxes prediction

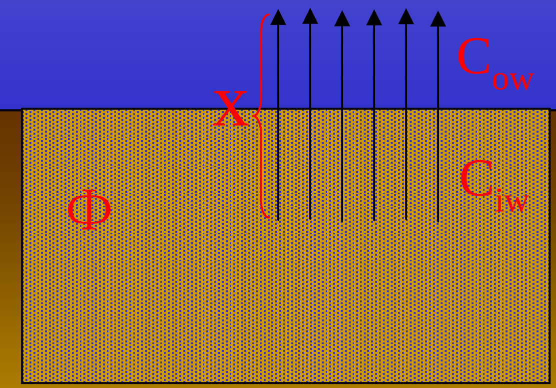
Fick´s law

$$J_i = -\Phi D_s^i \left(\frac{dC_i}{dx} \right)$$

- J_i = Trace metal flux (10^{-6} nmol m^{-2} d^{-1})
- Φ = Sediment porosity
- D_s^i = Difusson coefficient of metals (cm^2 s^{-1})
- C_i = (overlying water – interstitial water) concentration (nM)
- x = distance between overlying and interstitial waters (cm)

$$\Phi_i = \frac{V_{IW}}{(V_{IW} + V_S)}$$

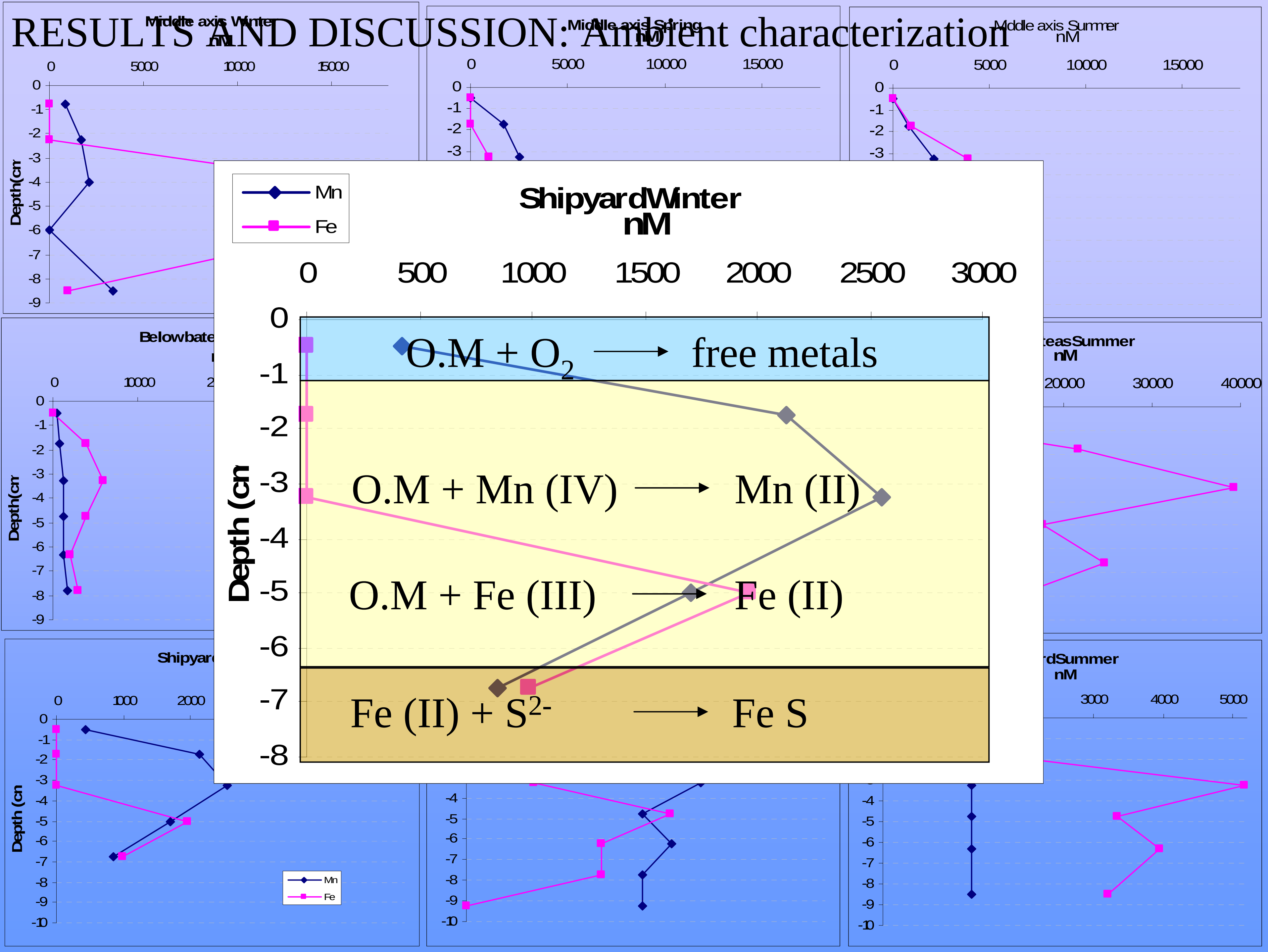
- V_{IW} = interstitial water volume
- V_s = sediment solids volume



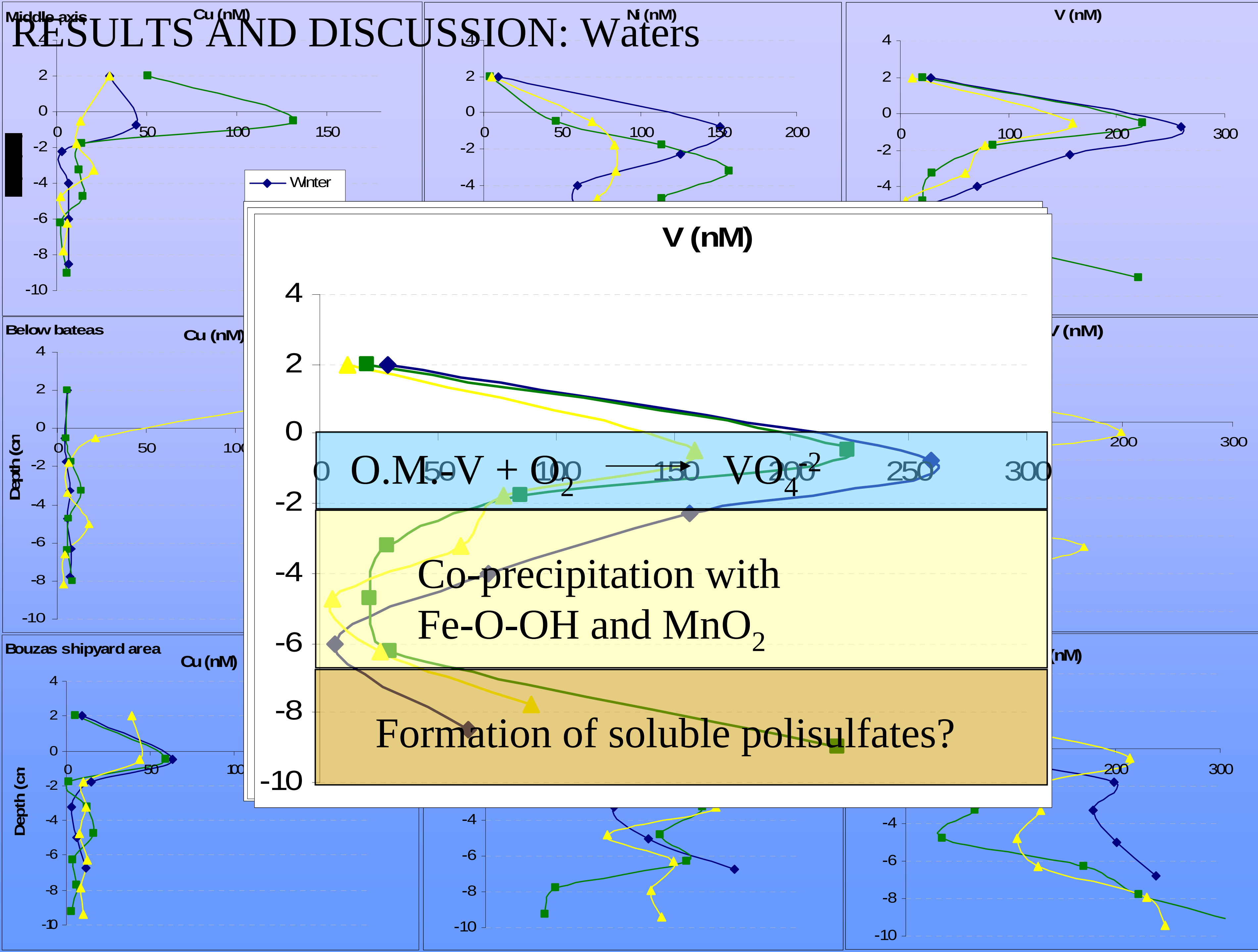
$$D_s^i = \Phi^2 D_0^i$$

- D_0^i = Difusson coefficient of metal at a given Temperature (calculated from Li and Gregory (1974))

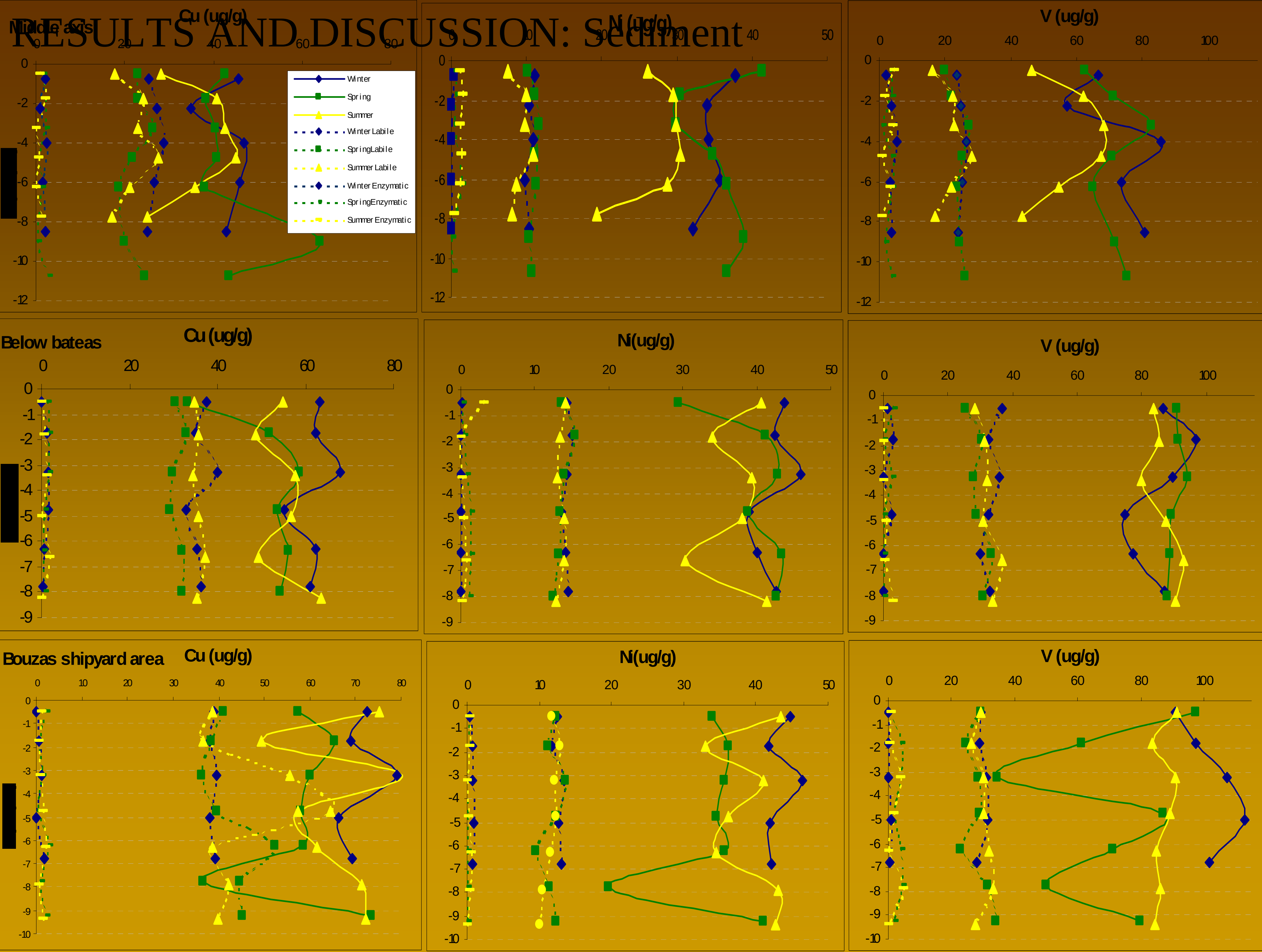
RESULTS AND DISCUSSION: Ambient characterization



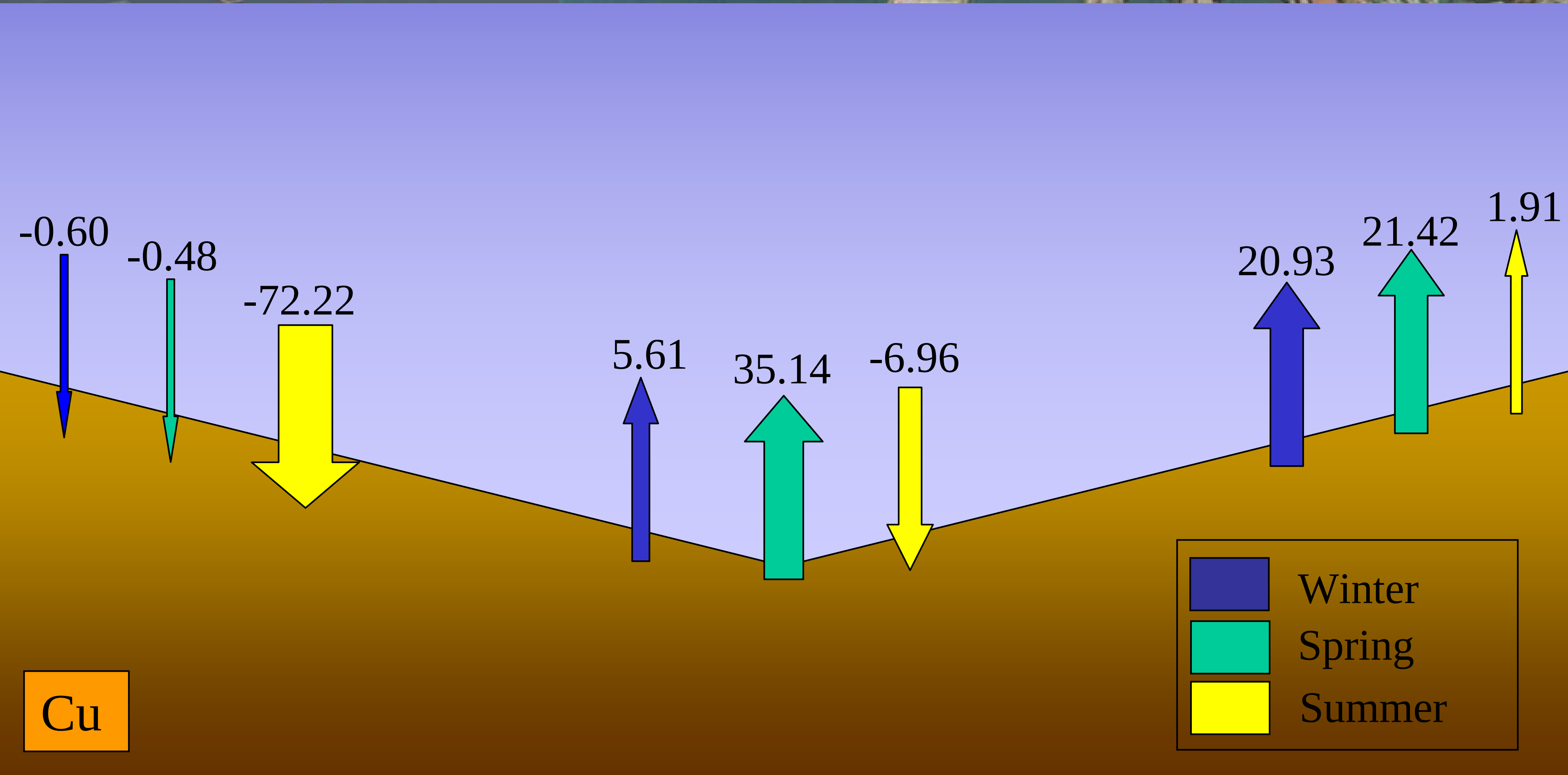
RESULTS AND DISCUSSION: Waters



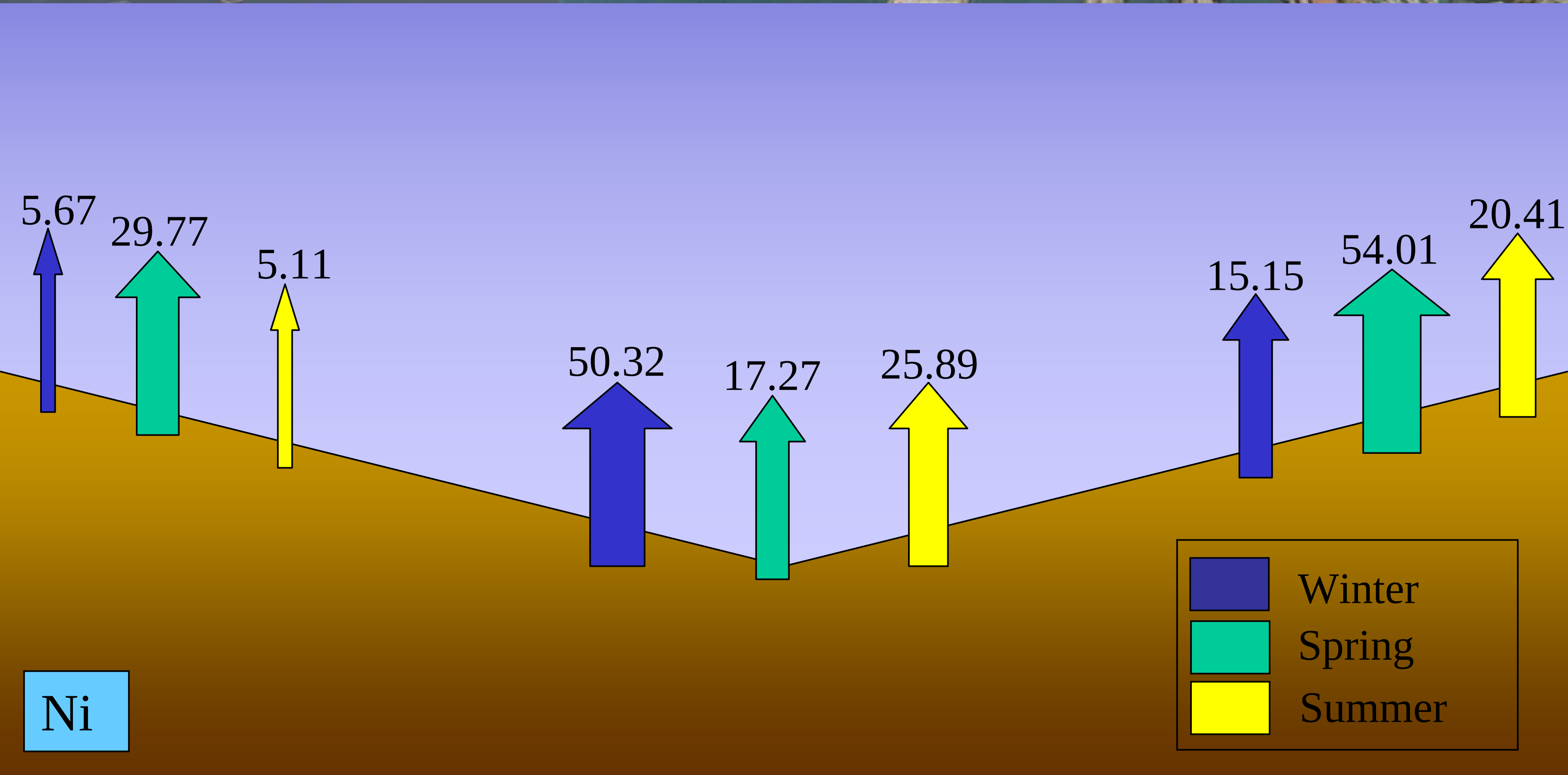
RESULTS AND DISCUSSION: Sediment



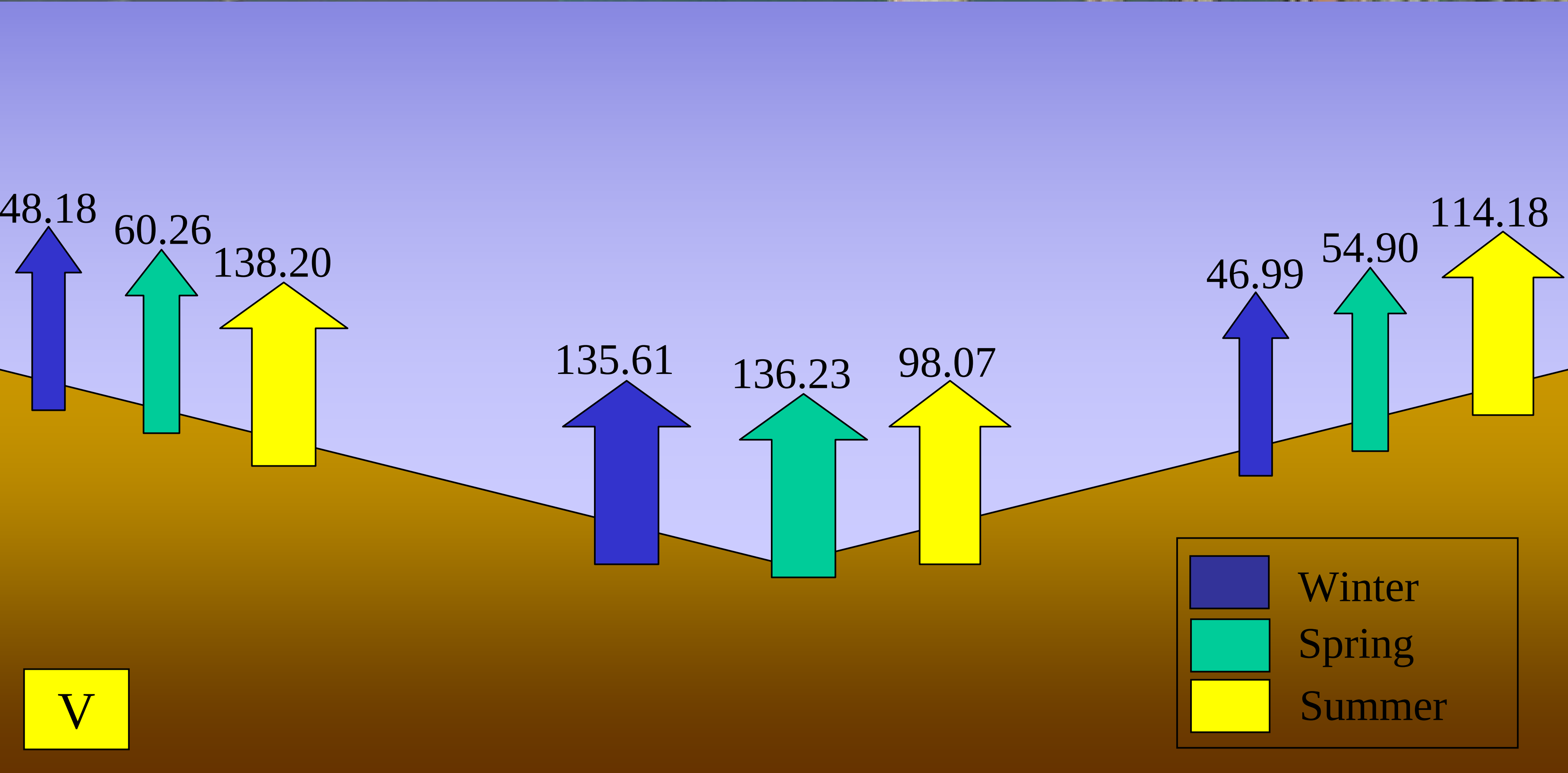
RESULTS AND DISCUSSION: Estimation of Copper Fluxes (10^{-6} nmol m^{-2} d^{-1})



RESULTS AND DISCUSSION: Nickel Fluxes (10^{-6} nmol m^{-2} d^{-1})



RESULTS AND DISCUSSION: Vanadium Fluxes (10^{-6} nmol m^{-2} d^{-1})



CONCLUSIONS

- Particulate metal levels are, usually higher in the shipyard area than below bateas or the middle axis.

- The lability of trace metals in the solid phase is higher for copper than for nickel or vanadium.

- Porewater dissolved metal levels are, in general higher in the shipyard area than in the middle axis and below bateas. Probably due to anoxic conditions below bateas that precipitate the dissolved metals into the particulate phase.

- Trace metal fluxes (Cu and Ni) are higher in the shipyard area than in the middle axis or below bateas. In the case of V the highest fluxes were found in the middle axis.

- All this reactions between solid-liquid phase in the sediment and the subsequent fluxes are controlled by the redox conditions present in each area.

THANK YOU FOR YOUR ATTENTION.

Aknowledgements. We acknowledge to the crew of R/V Mytilus and the personal participating in the project for the kind cooperation in the sampling. Juan Santos-Echeandía thanks the Basque Government for financial support (pre-doctoral grant). This work is a contribution to the LOICZ-Spain program and it was supported by CICYT "*Biogeochemical budget and modelling of heavy metal fluxes in a Galician ria (METRIA)*", ref. REN2003-04106-C03.

CERTIFIED REFERENCE MATERIALS

Waters

Table 1. Accuracy of the analytical procedure: AdCSV determination of Co, Cu, Fe, Ni, and V and ASV of Cd, Pb and Zn in seawater reference material CASS-4 nearshore seawater) compared with the certified values (replicates in brackets).

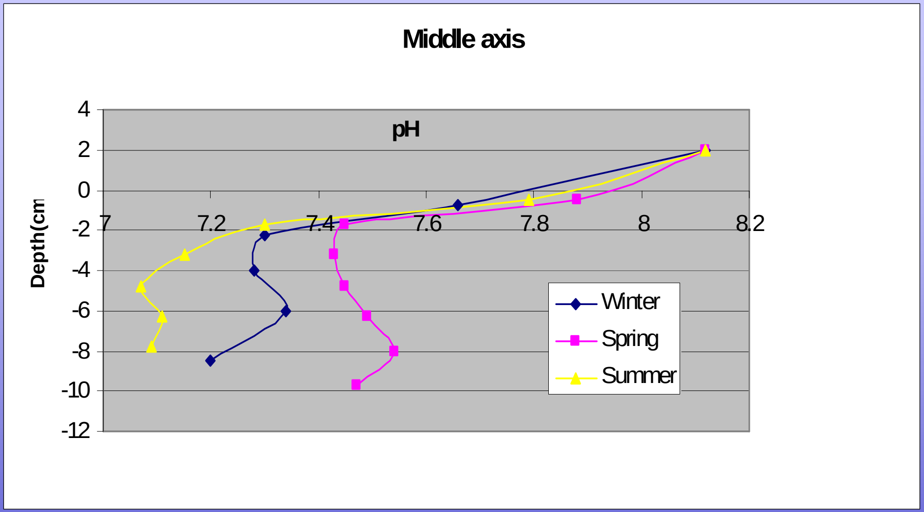
	Cd (pM)	Co(pM)	Cu(nM)	Fe (nM)	Pb(pM)	Ni(nM)	V(nM)	Zn(nM)
Obtained	236±33 (n=13)	480±80 (n=6)	9.4±0.5 (n=6)	13.08±3.09 (n=6)	68±12 (n=13)	5.6±0.7 (n=6)	21.0±1.8 (n=6)	5.8±1.0 (n=13)
Certified	231±27	440±50	9.3±0.8	12.8±1.0	47±17	5.4±0.5	23.2±3.1	5.8±0.9

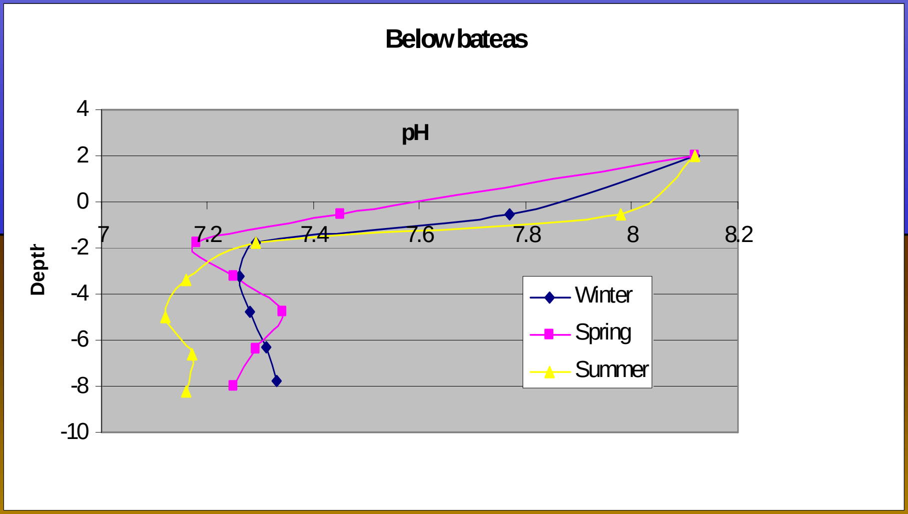
Sediments

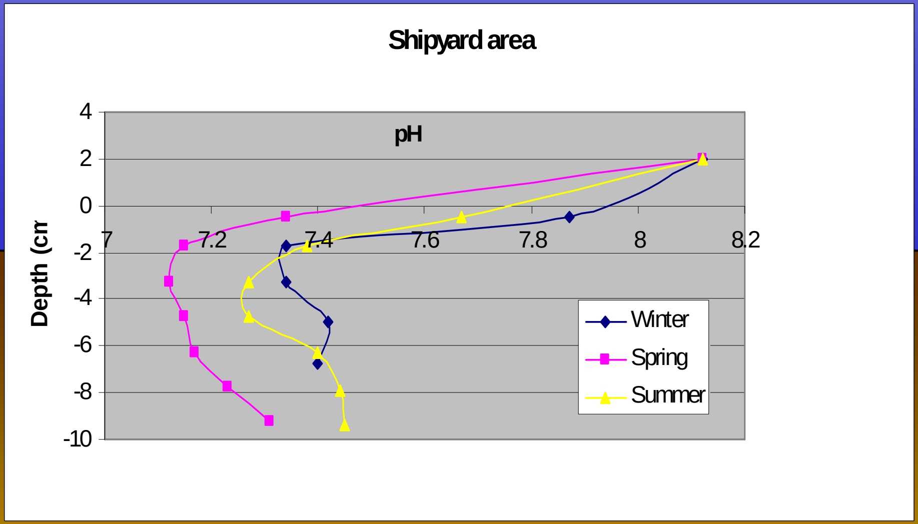
PACS-2 certified reference material

	Cd (ug/g)	Co (ug/g)	Cu (ug/g)	Fe (mg/g)	Pb (ug/g)	Mn (ug/g)	Ni (ug/g)	Zn (ug/g)	V (ug/g)
Obtained	2.28±0.14	13.1±1.8	299.5±3.8	43.9±1.3	166.9±.2	472.6±29.8	40.3±3.6	376.4±77.1	141.8±31.5
Certified	2.11±0.15	11.5±0.3	310±12	40.9±0.6	183±8	440±19	39.5±2.3	364±23	133±5

pH MEASUREMENTS







Fe y Mn labile in the sediment