Effects of the CO_2 acidification in sediments: the role of pH values in the bioaccumulation of metals in *R. philippinarum*.

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RAVENNA 2009. WORKSHOP F: 'INNOVAZIONE ECO-DESIGN IMPRESE'

Scientists determine what can be done, but the Governments determine how it can best be done.

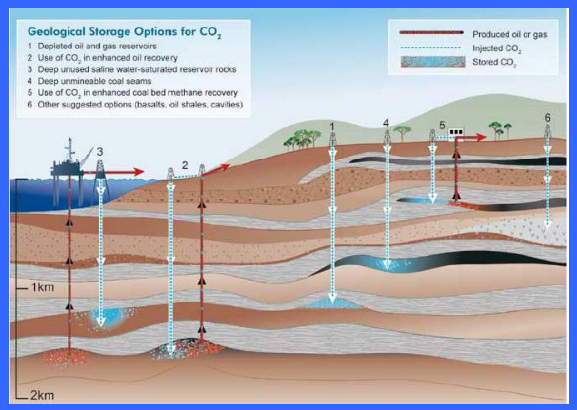
The ultimate goal of the UNFCCC is to stabilise the concentrations of greenhouse gases in the atmosphere at a level that avoids dire consequences from human interference with the climate system.
Stern 2007.

The last 30 years has been the warmest surface temperatures in recorded history. Scientists are documenting the rapid melting of glaciers. Ocean temperatures have warmed, sea levels have risen…Scientists have concluded that human activity, primarily the burning of fossil fuels, is the major driving factor in global warming.(IPCC)

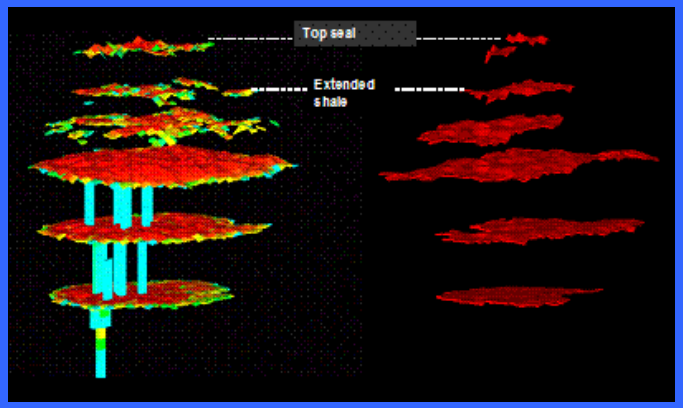
http://www.bbc.co.uk/climate/policies/
http://global-warming.accuweather.com

INTRODUCTION

The urgent need to reduce the greenhouse emissions to the atmosphere has lead to study new systems to capture and store CO_2 (CCS) → The sequestration of CO_2 in marine geological formations system.



Different alternatives for the injection and storage of carbon dioxide in geological formations: Source IPCC, 2005.



Simulation of carbon dioxide bubbles (on the left) and observed carbon dioxide bubbles (on the right) using seismic methodology after 3 years of injection and storage of this gas in Sleipner platform (North Sea). Source: IPCC, 2005 (Sleipner CO2 injection Project).

- **LONDON CONVENTION AND PROTOCOL**

  In November 2006 the text of the convention was amended to allow the storage of CO_2 in marine geological structures.
  Framework and waste assessment guideliness for CO_2 sequestration developed

- **OSPAR CONVENTION**

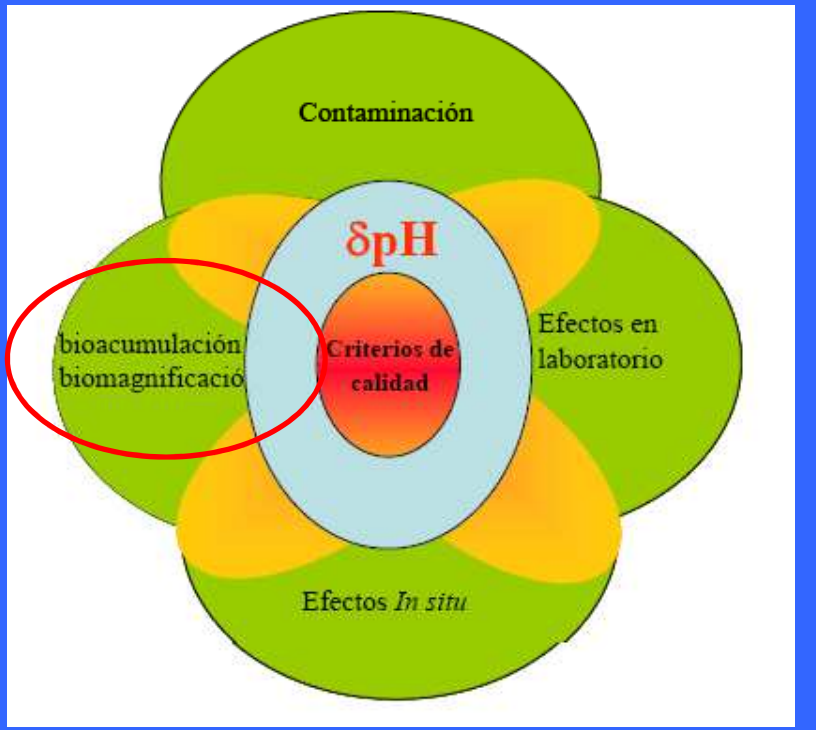
  In June 2007, the text of the convention was amended to allow the storage of CO_2 in marine geological structures, and oblies the contract countries to apply the risk assessment and management guidelines formulated by the convention.

- **BARCELONA CONVENTION**

  It is expected that during this year 2009, CO_2 capture and storage in marine geological formation will be discussed and regulated.

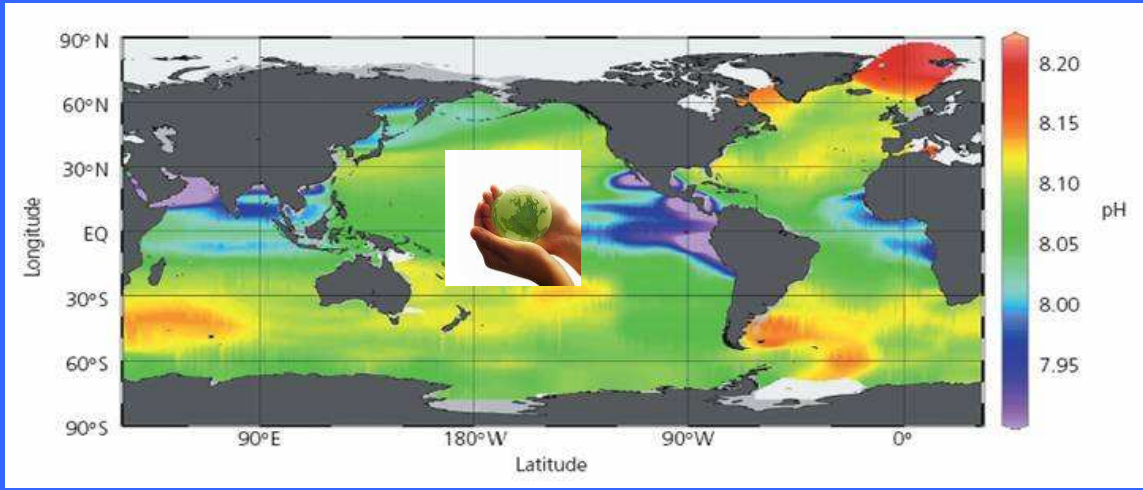
- **EUROPEAN COMISSION**

  A new EU Directive on CCS has been approved Dec. 2008



Hypothesis:

The acidification resulted of potential leakages during CO_2 capture and storage (CCS) in the ocean is one of the main **effects** associated with this technology. Models predict that decrease of pH in surface sediments results in higher mobility of metals in sediment pore water and overlying water. This hypothesis has been tested in an exposure sediment bioassay using the clam *R. philippinarum*.



s-p.mit.edu/.../Environment-1244063123.jpg; www.appinsys.com/.../image001.jpg

Objectives:

-The influence of pH on metal accumulation exposing juvenile clams (*R. philippinarum*) to sediments with different degrees of metal contamination within a pH range of between 6.5 and 8.5.

-Concentrations of Zn, Cd, Pb, Cu, Ni, Cr, Hg and As were determined within the sediments, and within the tissues of whole clams, providing insights into the interaction between sediment pH and bioaccumulation.

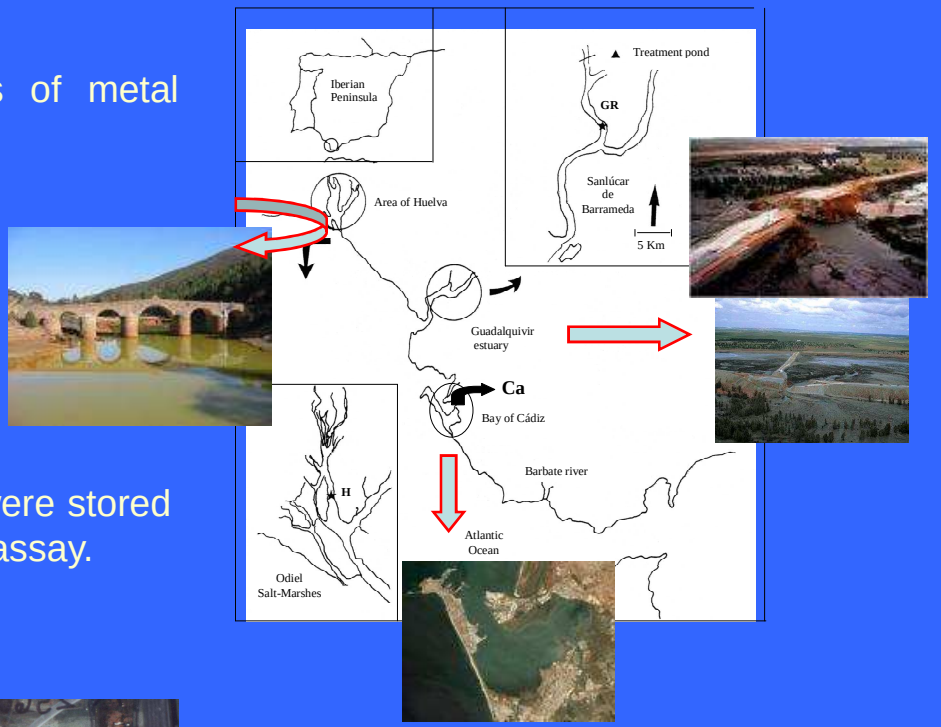
- Show the importance of this tool for environmental impact assessment during CCS, including human risk assessment by consumption of contaminated species.

MATERIAL AND METHODS

❖ 3 estuarine areas with different degrees of metal contamination:

- The Guadalquivir estuary (GR),
- Huelva (H)
-The Gulf of Cádiz (Ca)

❖ DIL 0.3; DIL 5.

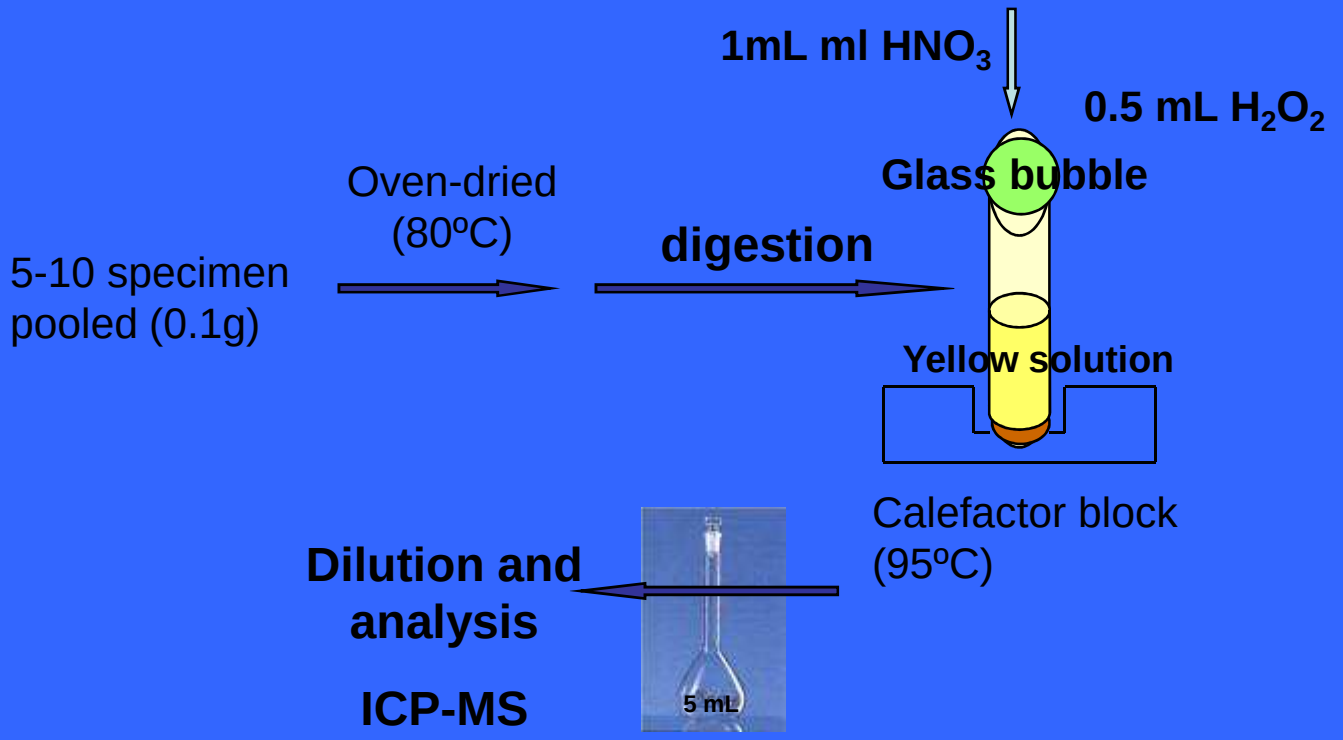


Sediment were homogenized and sub-sample were stored for chemical quantification and bioaccumulation assay.

Ruditapes philippinarum; shell length approx. 0.01 m, mean weight approx. 0.42 g

- **The pH (6.5, 7.5 and 8.5) of the seawater used in the clam incubation chambers (20 L aquaria) was adjusted using the buffer capacity of the carbonate system in oceanic waters as reported by Mount and Mount (1992) adapted by Riba et al. (2003a, 2004).**
- **Sediment-water ratio (1:2 v/v). (DelValls et al, 2002)**
- **40 organisms in each of the 3 replicate.**
- **Exposed to sediments for 28 days.**
- **Endpoint: % mortality and metal concentration in homogenised tissues (Zn, Cd, Pb, Cu, Ni, Cr, Hg and As).**

Seawater pH (SWS or sea water scale) was measured with a potentiometric analyzer (Metrohm, 670, Berchem, Belgium) with a glass combination electrode (Metrohm, ref. 6.0210.100).



Samples (whole soft bodies of 5-10 specimens pooled) were digested 1 hour, 95ºC and analyzed using inductive coupled plasma mass spectrometry (ICP-MS) (Amiard et al., 1987).

RESULTS AND DISCUSSION

Sediment	Cu	Zn	Cd	Pb	As	Ni	Cr	Hg	Fe	Mn	C_{org}	Fines
Ca	1.34	6.28	0.03	4.60	1.85	1.7	3.47	0.1	0.5	163	1.07	49
DIL5	191	1700	2.45	650	301	4.90	4.45	2.21	3.9	166	1.06	48
DIL0.3	14.0	100	0.18	87.3	22.1	1.82	3.51	0.1	5.6	155	0.97	49
H	2012	2551	1.76	423	343	33.1	64.8	2.32	4.1	354	3.20	85
GR	30.0	152	0.34	35.4	9.36	31.3	50.1	2.32	3.2	812	2.10	90

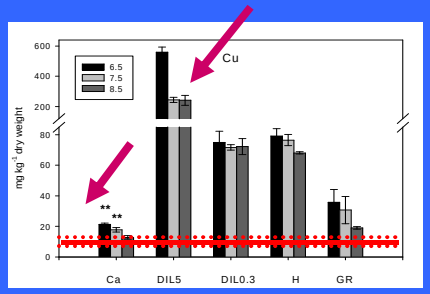
Table 1. Summarized results for sediment physico-chemical characteristics used in the bioassay tests. All concentrations expressed as mg kg-1 dry weight, except the organic carbon content (Corg), fines and Fe in %.

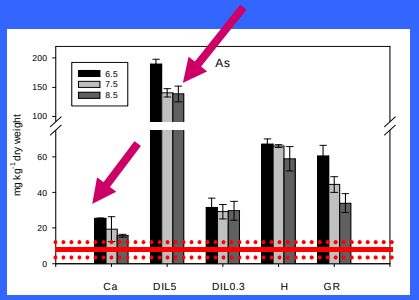
CA had lower metal concentration

Sediment of H contained high level of Cu, Zn and As

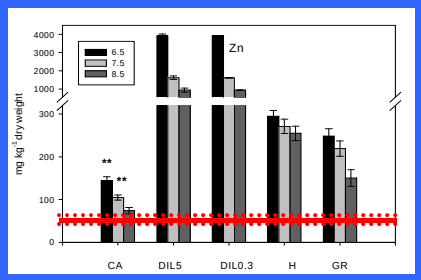
Levels of Ni, Cr and Hg are high in H and GR

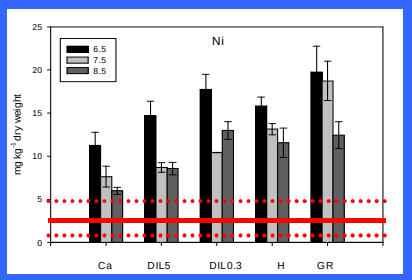
INFLUENCE OF SEDIMENT ACIDIFICATION ON THE BIOACCUMULATION OF METALS IN *Ruditapes Philippinarum*



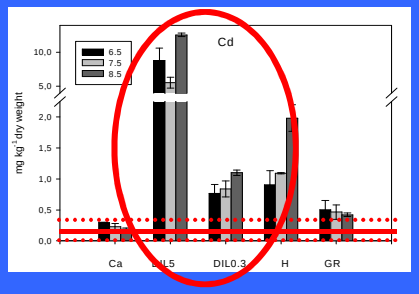


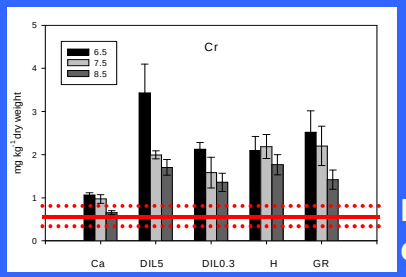
❖In general the highest metal concentrations were measured in clams exposed to the sediment DIL5, although this sediment was not the most contaminated. High metal concentrations within the tissues of clams exposed to DIL5 are in line with the enhanced clam mortality (28% and 55% at pH 7.5 and 6.5 respectively).





❖ The lowest accumulated values were found in clams exposed to CA.

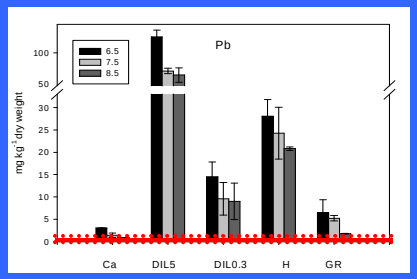


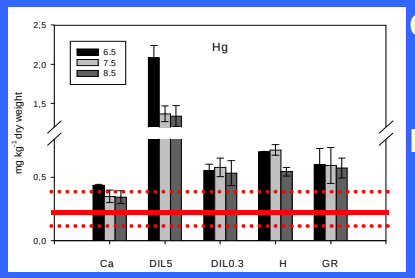


❖ Cu, Zn, Cd, Pb present higher concentration accumulated in H than in GR but As, Ni, Cr and Hg are similar accumulated.

Influence of sediment acidification on metal bioavailability

In general a decrease in pH value produce higher concentration of metal in organisms, except Cd.





Cd uptake increased as pH increased for H and DIL5, DIL0.3.

-Cd has affinity with carbonates and other ligands: less bioavailability to organisms

CONCLUSIONS

❖ **Concentrations of metals in clams *R. philippinarum significantly* ($p<0.1$) increased upon lowering of pH except for Cd**

❖ **Acidification of sediments increases environmental risk in areas selected for CCS increasing the bioavailibility of metals and (potentially) other contaminants.**

❖ **Consumption of commercial species located in these areas could be associated with human risk if contaminated species are identified**

Bioaccumulation is a very strong tool to address the impact of CO_2 leakages in CCS both in the environment and in humans. It is included in International Convention guidelines as part of a framework to address the impact assessment in areas selected for CCS in the ocean.

This tool will improve the innovation and eco-design in enterprises/firms that must take into account this kind of studies for an integrated impact assessment in CCS process.