

# Coupling geochemical and biological approaches to assess the availability of cadmium in a natural sediment

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# Introduction

## **Context : Sediment**

- Significant storage and releasing capacities of various contaminants
- Shelter numerous invertebrate species : important for the assesement of ecological integrity of aquatic ecosystems
- DIESE (french project) develops a toolbox for the hazard assessment of sediment

## **Aim :**

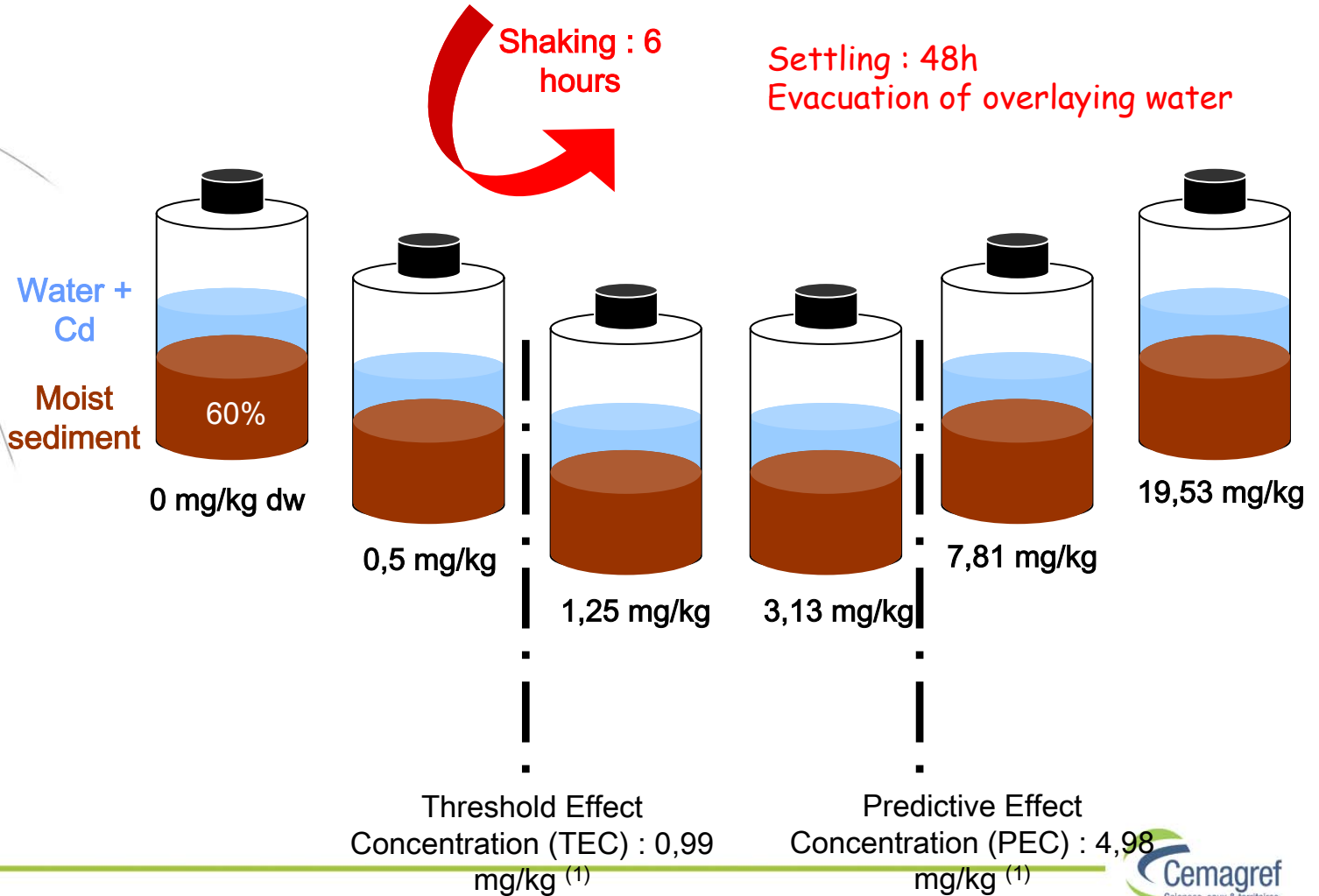
- To develop and assess the complementarity of the different tools for the evaluation of sediment toxicity : one exemple proposed here

## **Proceed :**

- Coupling geochemical and biological approaches :  
Exposition of Diffusive Gradient in Thin films (DGT) and 3 macroinvertebrates species simultaneously to a natural low contaminated sediment spiked with Cd

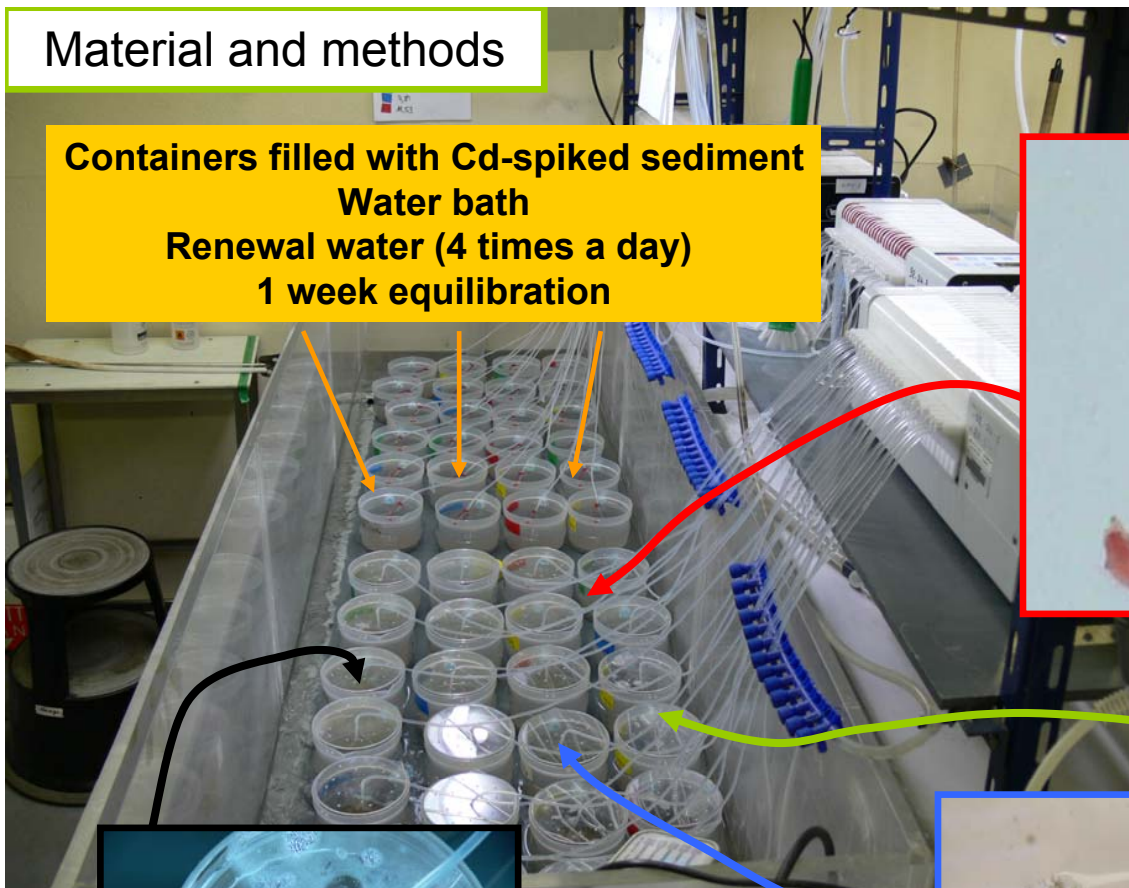
# Material and methods

Natural sediment spiking with cadmium :



# Material and methods

Containers filled with Cd-spiked sediment  
Water bath  
Renewal water (4 times a day)  
1 week equilibration



*Chironomus riparius*



*Potamopyrgus antipodarum*



*Gammarus fossarum*



Passive sampler : DGT

3 benthic organisms

## Material and methods

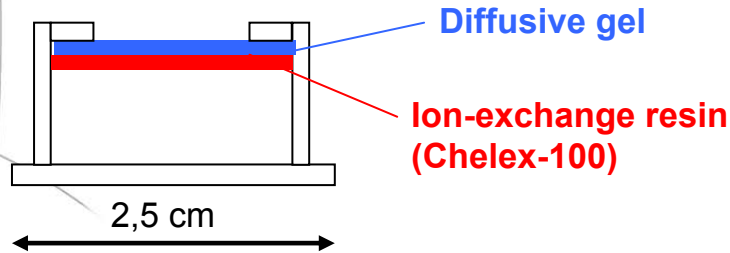
### Geochemical approach :

- Kinetic of Cd accumulation in the DGT (2H to 6 days) : measurement of labile dissolved Cd concentration and evaluation of the sediment capacity to release Cd from particles to pore water
- Extraction of pore water : measurement of total dissolved Cd concentration
- Sequential extractions of the particulate phase : to determine metal carrier phases

### Biological approach :

- Battery of organisms phylogenetically different, characterised by specific physiological and ecological traits (reproduction ; habitat ; growth ; nutrition...).
- Measurement of Cd bioaccumulation in 3 macroinvertebrate species : to estimate Cd bioavailability (7 days exposure)
- Measurement of Cd effects on life history traits related to population dynamics (e.g. reproduction or growth)

## Material and methods

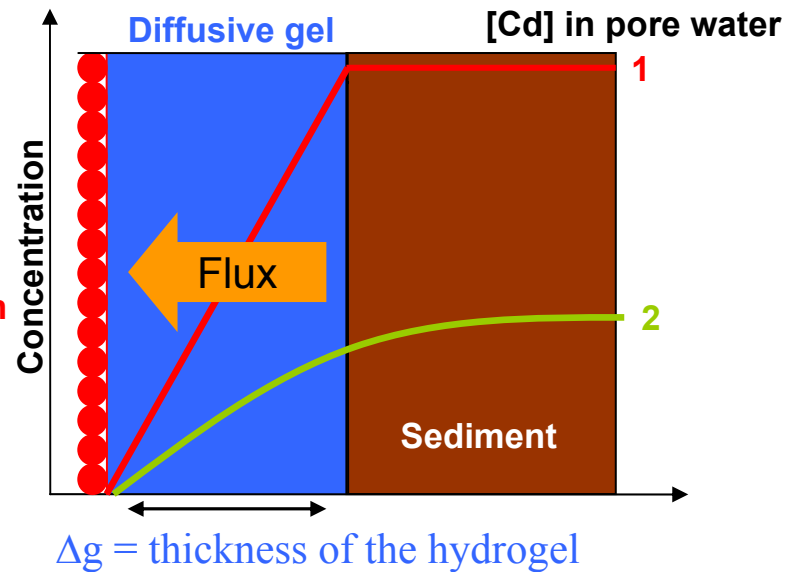


$$\text{Flux of Cd} = D \frac{dC}{\Delta g}$$

$C_{DGT}$  = dissolved labile Cd concentration in pore water

The importance of the dissolved Cd concentration decrease in pore water is given by the R ratio :

$$R = C_{DGT} / C_{\text{pore water}}$$

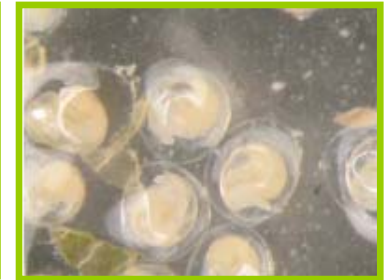


**1 : particulate contribution**  
**2 : no contribution from the particulate phase**

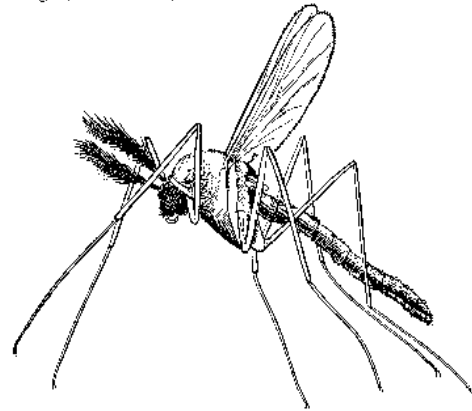
## Material and methods

### *P. antipodarum*

Growth – 6 weeks  
Reproduction – 4 and 6 weeks  
Survival



Chironomus midge (Packard #278)

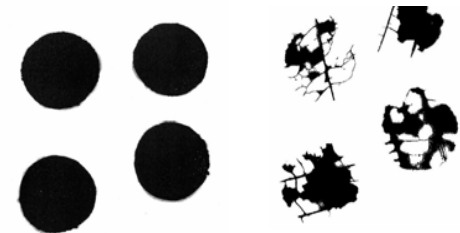


### *C. riparius*

Emergence – 28 days  
Growth – 7 days  
Survival

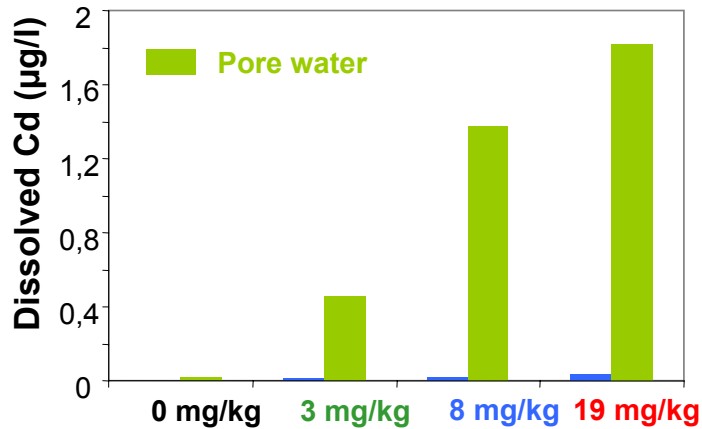
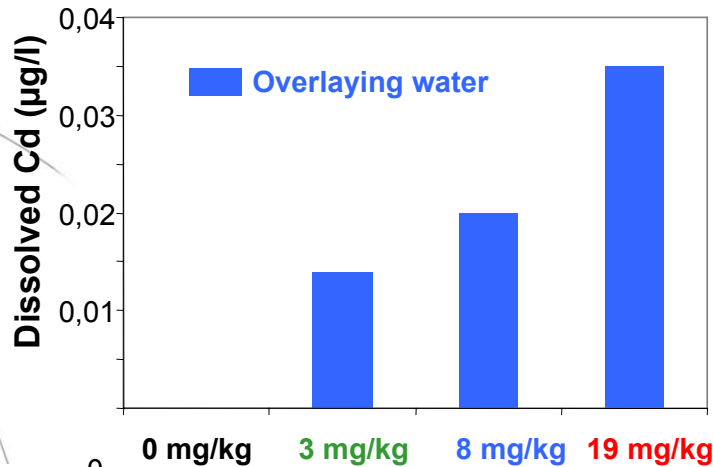
### *G. fossarum*

Feeding rate – 1 week  
Growth – 3 weeks  
Reproduction – 3 weeks  
Survival



# Results

Efficiency of Cd spiking : between 90 and 140% of nominal concentrations



Gradient of Cd pools

Particulate pool

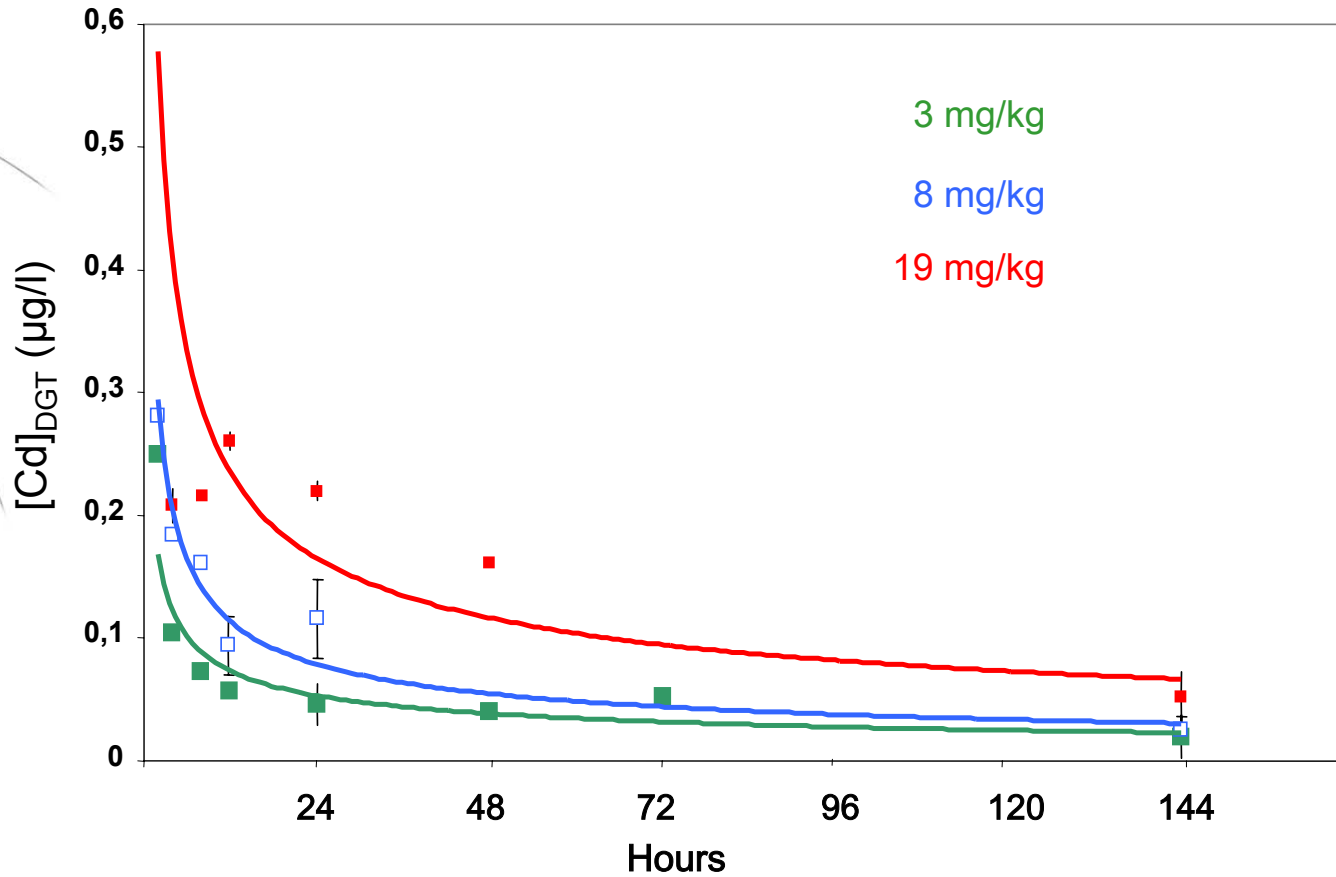
Pore water

Overlaying water



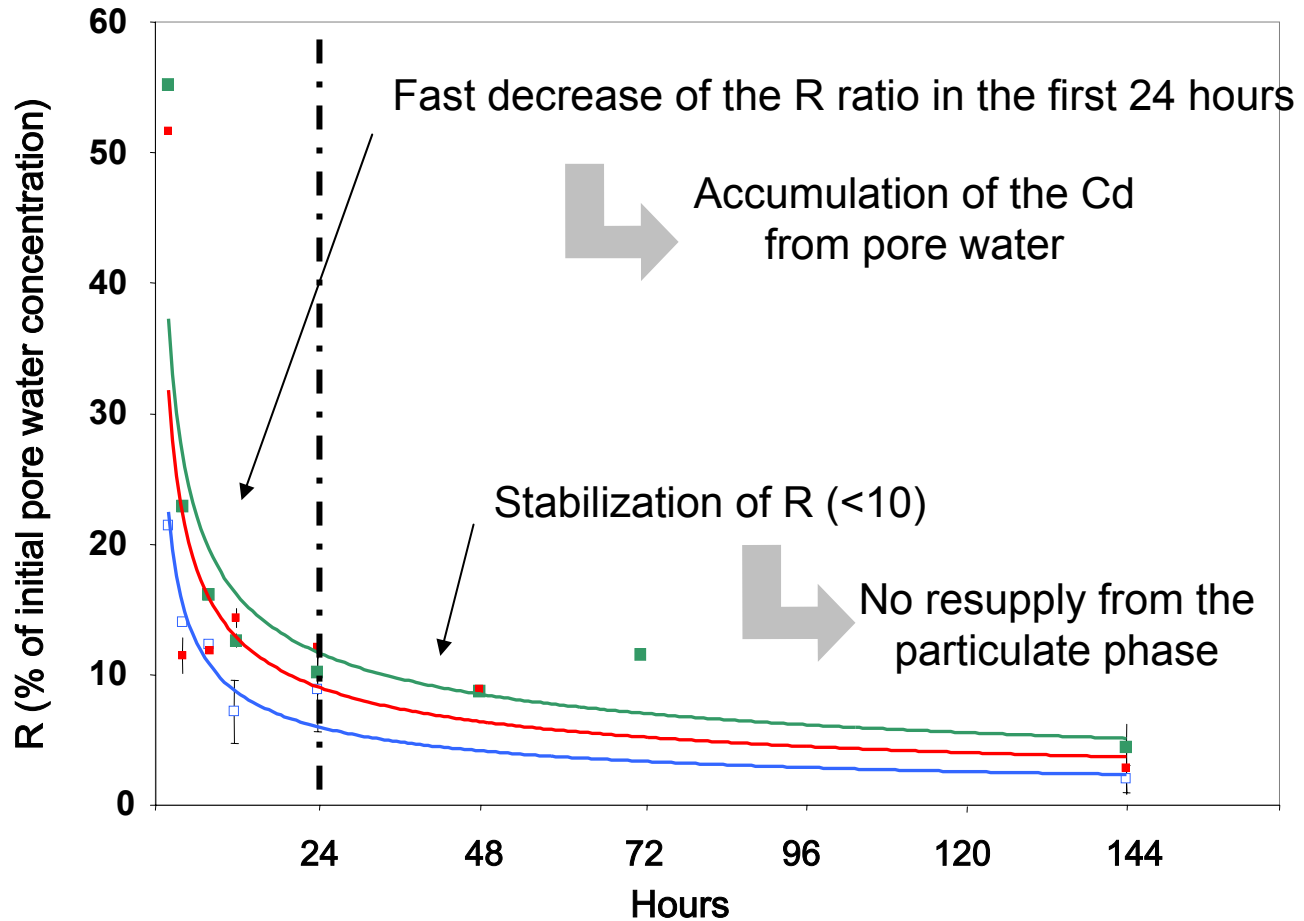
# Results

Dissolved Cd concentration =  $C_{DGT}$



## Results

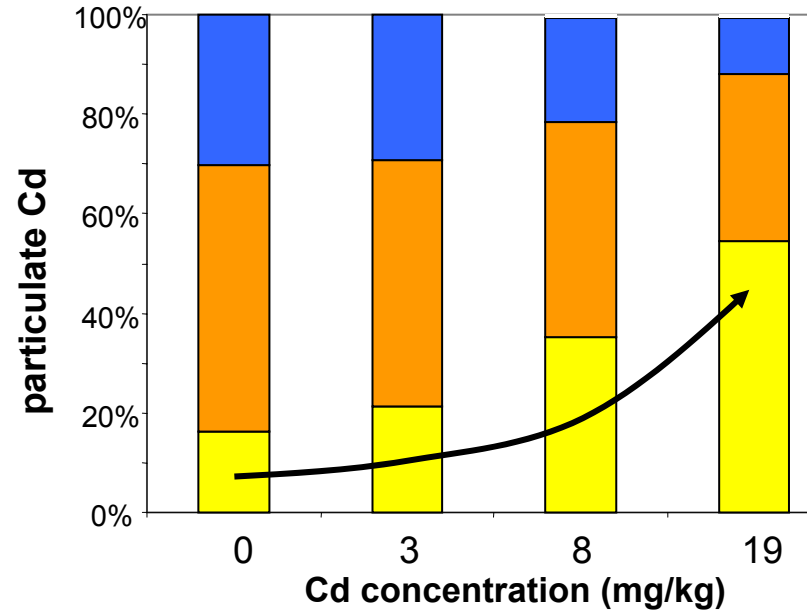
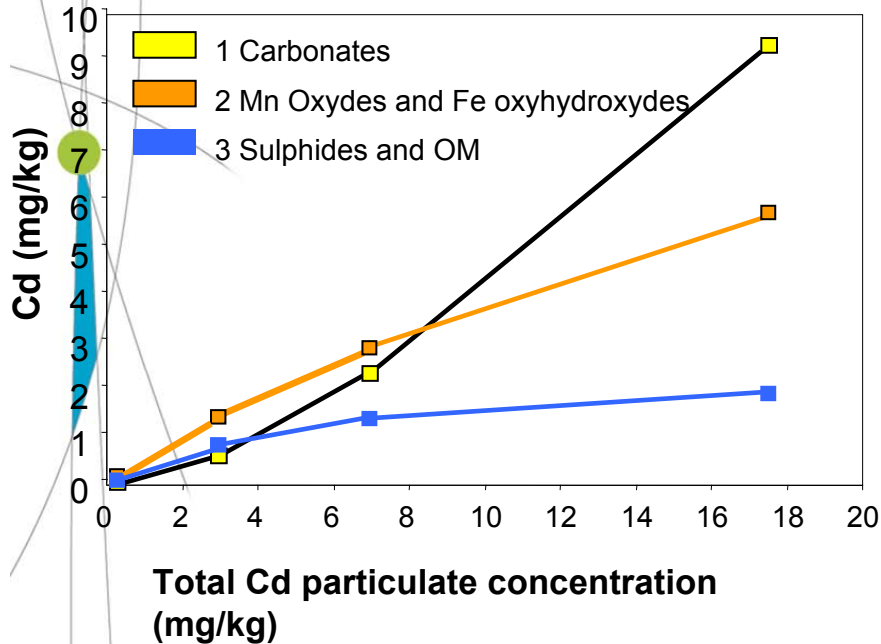
$$R = [\text{Cd}]_{\text{DGT}} / [\text{Cd}]_{\text{EI}}$$



Great similarity of the R ratio distribution for the 3 spiked level concentrations

# Results

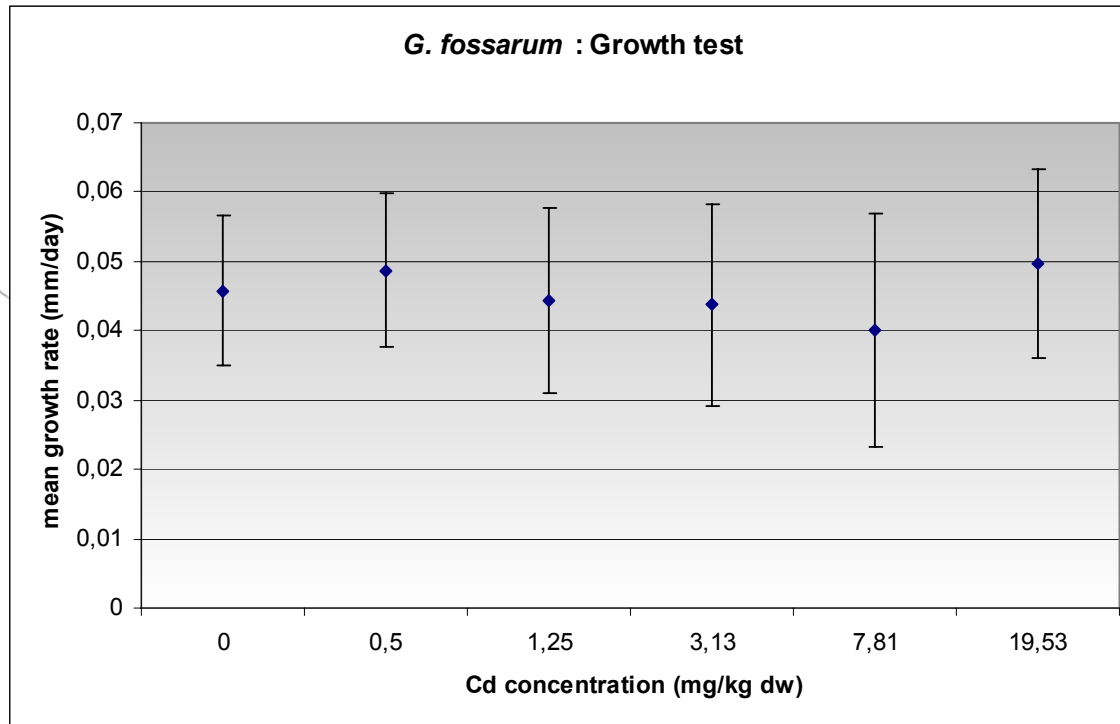
Sequential extractions : carrier phases ? What are their relative contributions?



Cd is preferentially fixed by carbonate phase  
This is in relation with the high  $\text{CaCO}_3$  content of the sediment (54%) which represents an unlimited pool of binding sites

## Results

### *G. fossarum*

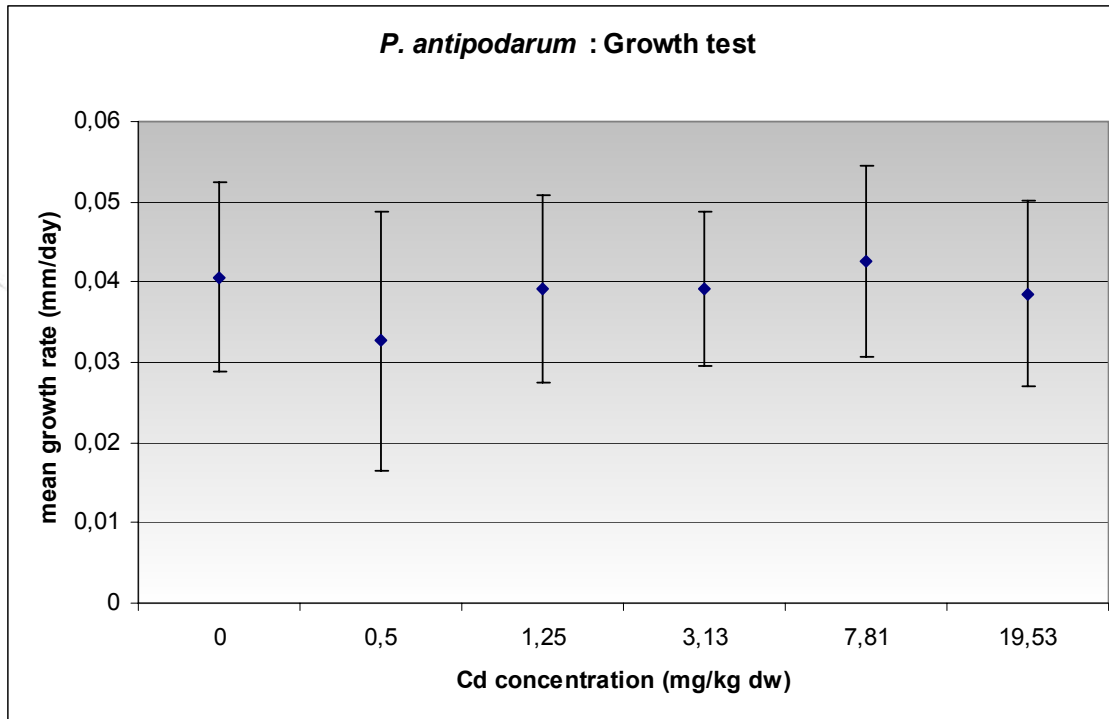


**Statistics : no difference between [0] and higher concentrations**

**Reproduction and feeding rate : no differences**

## Results

### *P. antipodarum*

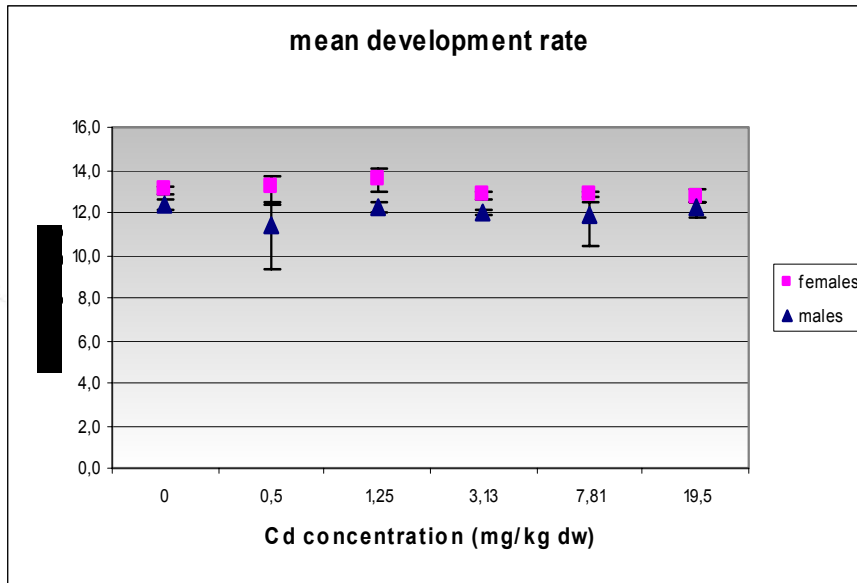


**Statistics : no difference between [0] and higher concentrations**

**Reproduction : no differences**

# Results

## *C. riparius*



Statistics : no difference between [0] and higher concentrations

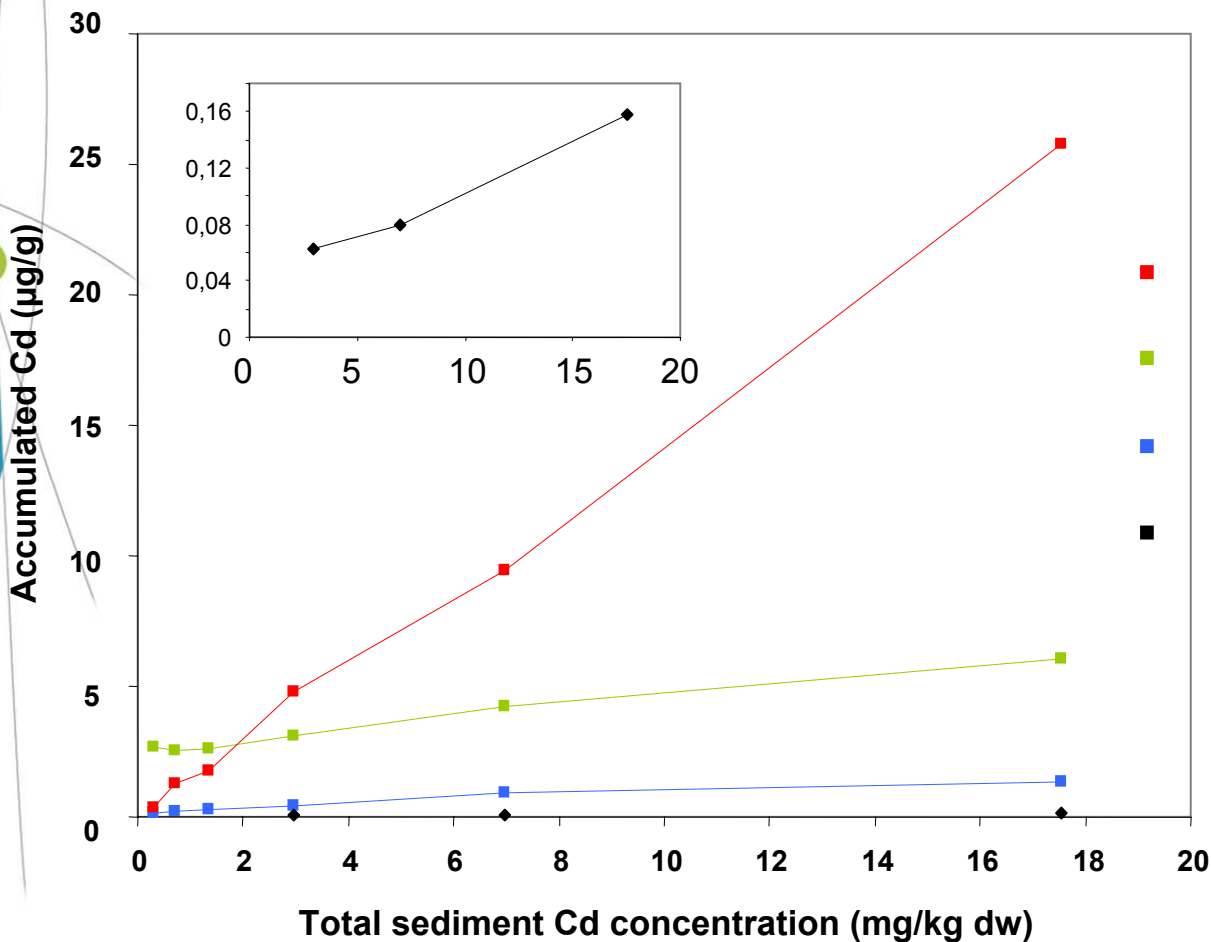
Sex ratio and growth : no differences

concentration en Cd (mg/kg dw)	emergence rate	écart type
0	0,90	0,10
0,5	0,73	0,25
1,25	1,00	0,35
3,13	0,87	0,12
7,81	0,77	0,25
19,53	0,47	0,21

$\chi^2$  19.5 vs 0 mg/kg p=0.020

Results

Bioaccumulation



- C. riparius
- P. antipodarum
- G. fossarum
- DGT

## Conclusions and perspectives

Informations provided by both methods are complementary

- DGT : Cd strongly bound to carbonate (confirmed by sequential extraction)
- biotests : only effect on emergence of Chironomids
- Bioaccumulation related to feeding habits and behaviour

What to do next?

- To make  $\text{CaCO}_3$  varied
- To test sediments naturally rich in Cd
- Tangential Ultrafiltration (UFT)
- Organisms fractionation : measurement of cytosolic concentrations

To verify both methods complementarity with other conditions

To measure which dissolved fraction of Cd is trapped by the DGT (free ions or colloids)

To estimate precisely the Cd toxicologically bioavailable

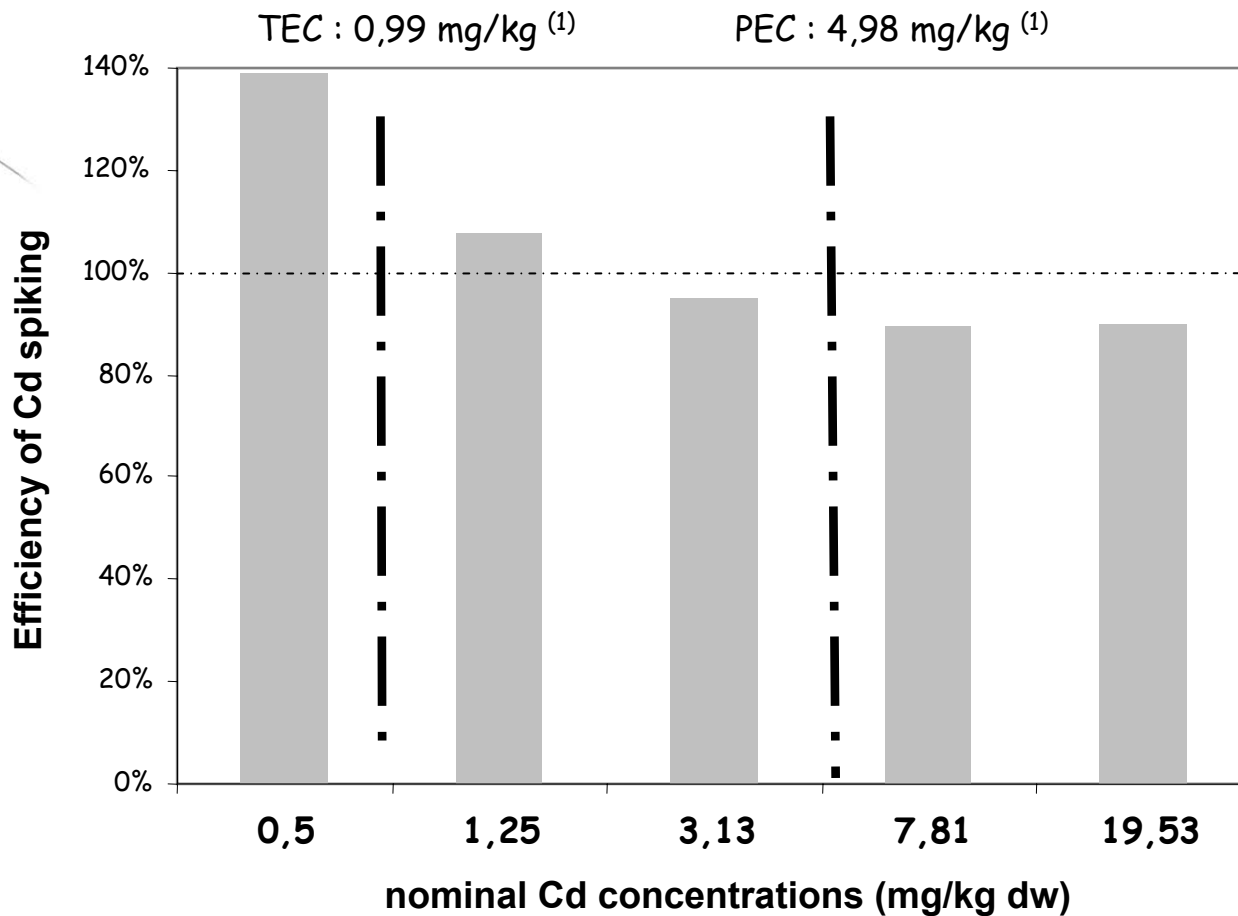




Thank you !

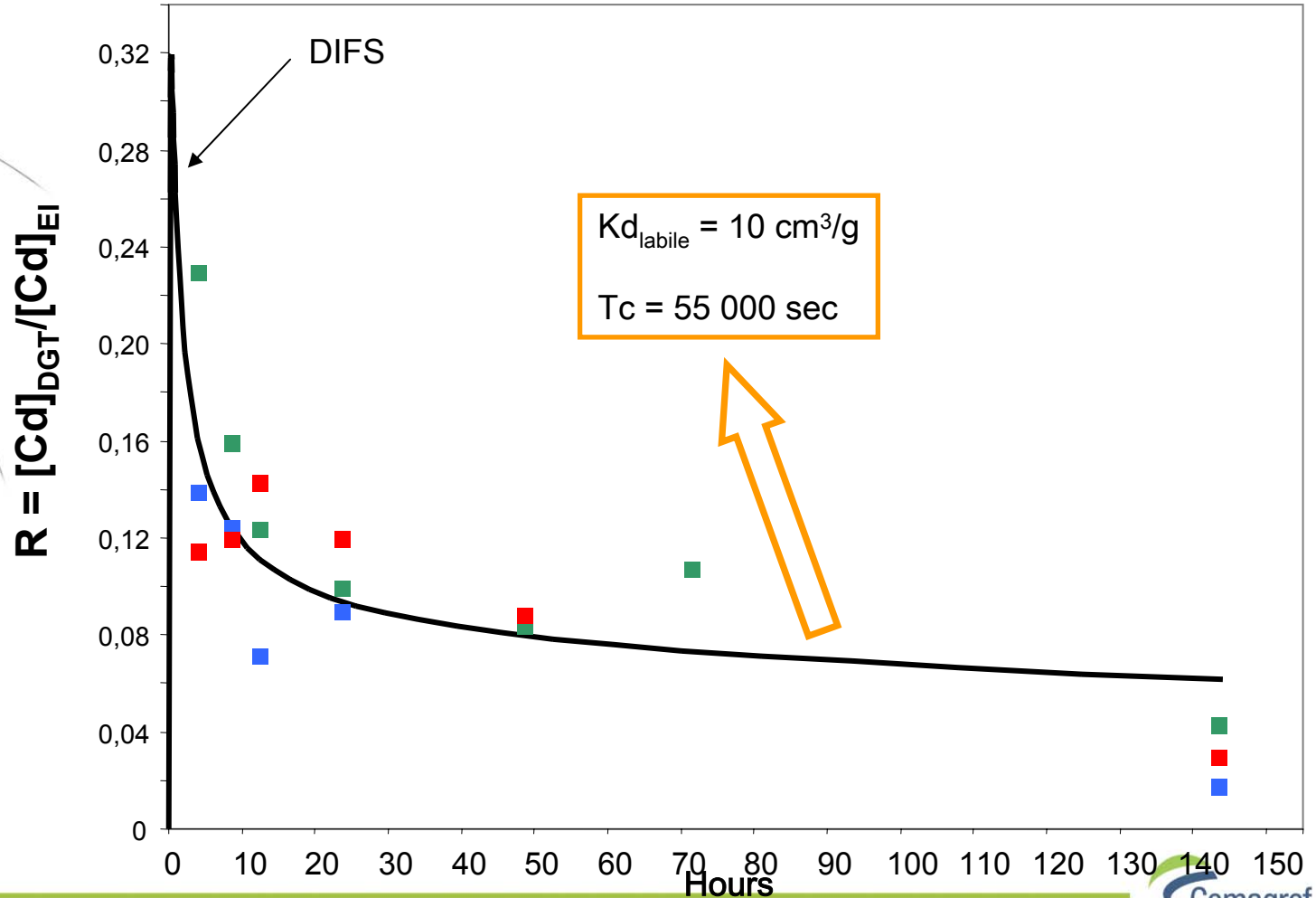
## Complementary information

### Efficiency of Cd spiking

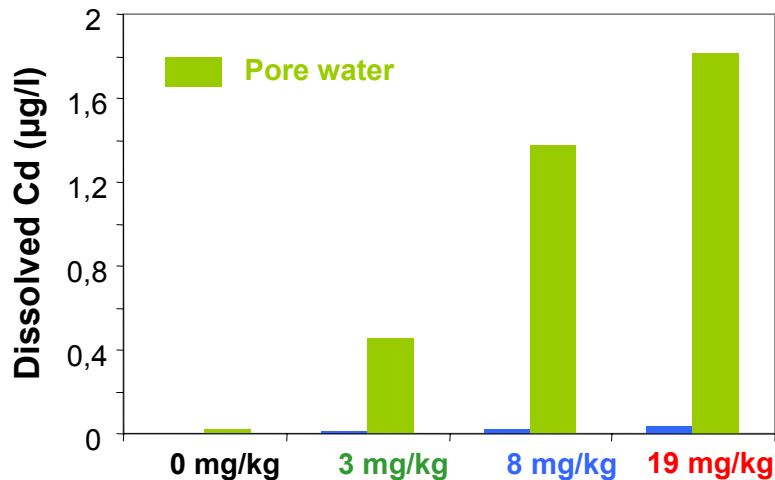
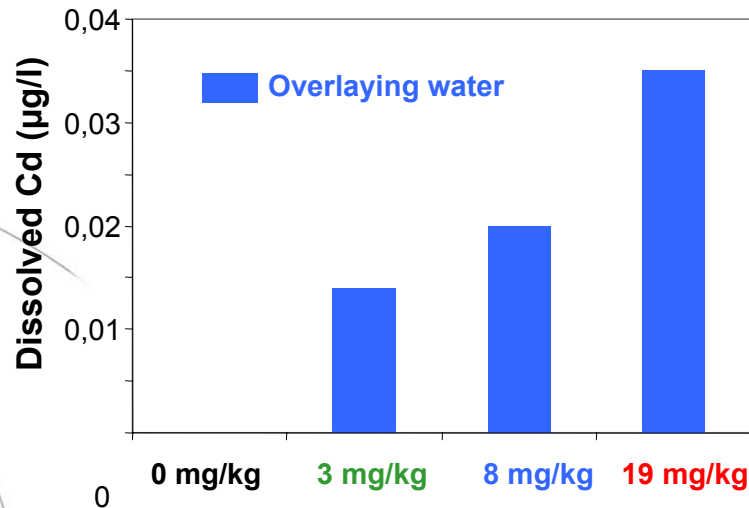


## Complementary information

R ratio modelling by DIFS model : estimation of reactivity parameters of the sediment ( $K_{d_{lab}}$  et  $T_c$ )



## Complementary information



**Cd LC50 :**

**0.07 mg/L (96h) *G. fossarum***

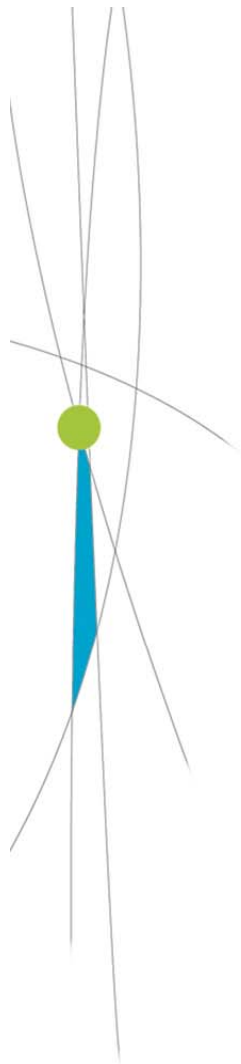
**0.3 mg/L (7d) *P. antipodarum***

**Chronic exposition : observed effects :**

**Survival rate affected at 3µg/L and feeding rate at 3 µg/L (21d) *G. fossarum***

**Reproduction rate affected at 20 µg/L (8w) *P. antipodarum***

## Complementary information



Mobility  
Reactivity

+

↑

-

- exchangeable Cd ( $\text{MgCl}_2$ )
- Cd bound to carbonates (pH 5, buffer solution acetic acid /Sodium Acetate)
- Cd bound to Mn oxydes and Fe oxyhydroxydes (pH2, hydroxylamine)
- Cd bound to sulphides and OM (pH2,  $\text{H}_2\text{O}_2$ )
- Cd bound to residual fraction (Aqua regia)