SedNet Conference Venice 6-9 April 2011
Sediments and Biodiversity:
bridging the gap between science and policy

"The MIRACLE Project: an Interdisciplinary Research on Mercury in the Marano & Grado Lagoon (northern Italy)"

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[7]ISPRA, Chioggia, Italy
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Northern Adriatic: double input of Hg contamination

1) historical:

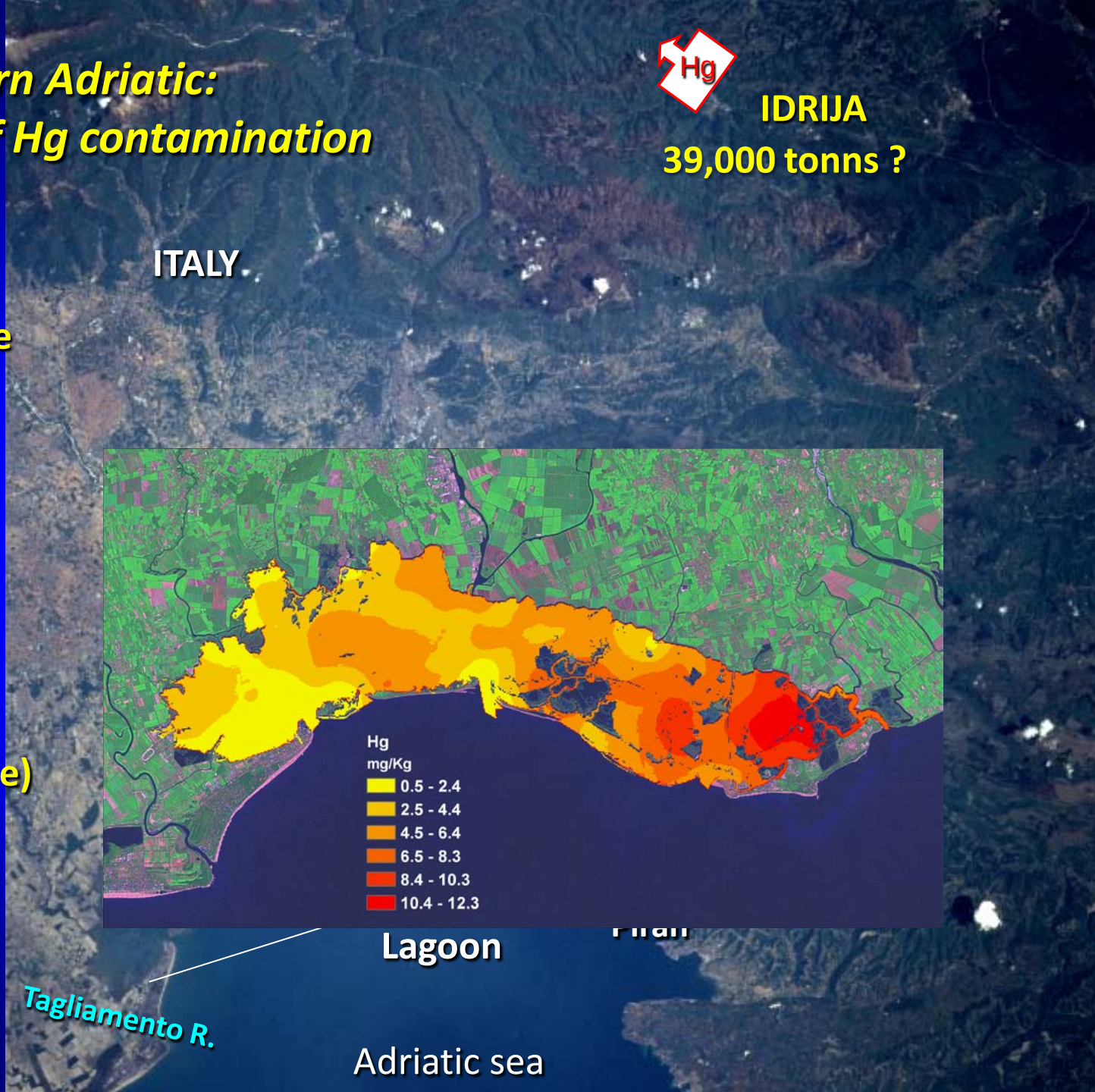
Idrija mercury mine

⬇

Isonzo River (about 500 years)

2) recent:

chlor-alkali plant at Torviscosa (Udine) ('30-'80)



Why an extensive research project on Hg In the Marano & Grado Lagoon ?

The **MIRACLE** project was launched by *Commissario Delegato (a Deputy Commissioner)* for the state of socio-economic and environmental emergency of the Marano & Grado Lagoon in 2008, in order to verify, under scientific basis, whether suitable environmental conditions can be found in the lagoon environment for clam farming extension without risk of Hg bioaccumulation in bivalves.

Duration: 18+2 months
Starting date: 28 April 2008
Conclusion: 31 October 2009
Revised final Report: March 2010

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The project involved an international collaboration between Italian researchers,…..

DiGEO (ex DiSGAM) - Trieste University - ref. Stefano Covelli
Coordination, planning and sampling; geochemistry of sediments, benthic chamber experiments (water-sediment interface)

ARPA FVG Regional Env. Agency - ref. Sergio Predonzani
Hg analyses in water and sediment; clams sampling

ISPRA National Env. Agency, Chioggia (Venice) - ref. Michele Giani
Humic acids, $\delta^{13}C$ sediments; biometrics and stabulazione clams, Hg in clams, bioaccumulation risk assessment

AUTORITÀ DI BACINO Friuli Venezia Giulia - ref. Katia Crovatto
Planning and logistics

OGS – Dept. of Biological Ocean. Trieste - ref. Cinzia De Vittor
Water chemistry (nutrients, DIC, DOC, O_2), technical assistance

Dept. BIOLOGY – Venice University - ref. Franco Baldi
Microbiology (Hg-resistant bacteria in sediments and clams)

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…Slovenian and US scientists, applying a broad range of expertise at various scales.

"Jožef Stefan" Institute

"Jozef Stefan" **Institute, Ljubljana (SLO) – ref. Milena Horvat**
Sampling, Hg and Metil-Hg analyses in sediment, water and clams
and
Marine Biology Station, Piran (SLO) – ref. Jadran Faganeli
Technical support, S and nutrients analyses, biogeochimical cycles of Hg and nutrients

UMASS

University of Massachusetts Lowell (USA) – ref. Mark Hines
Methylation, Demethylation and sulphate-reduction rates measurements with radiotracers

…and with the valuable cooperation of the local fishermen cooperatives involved in clam farming.

Project planning

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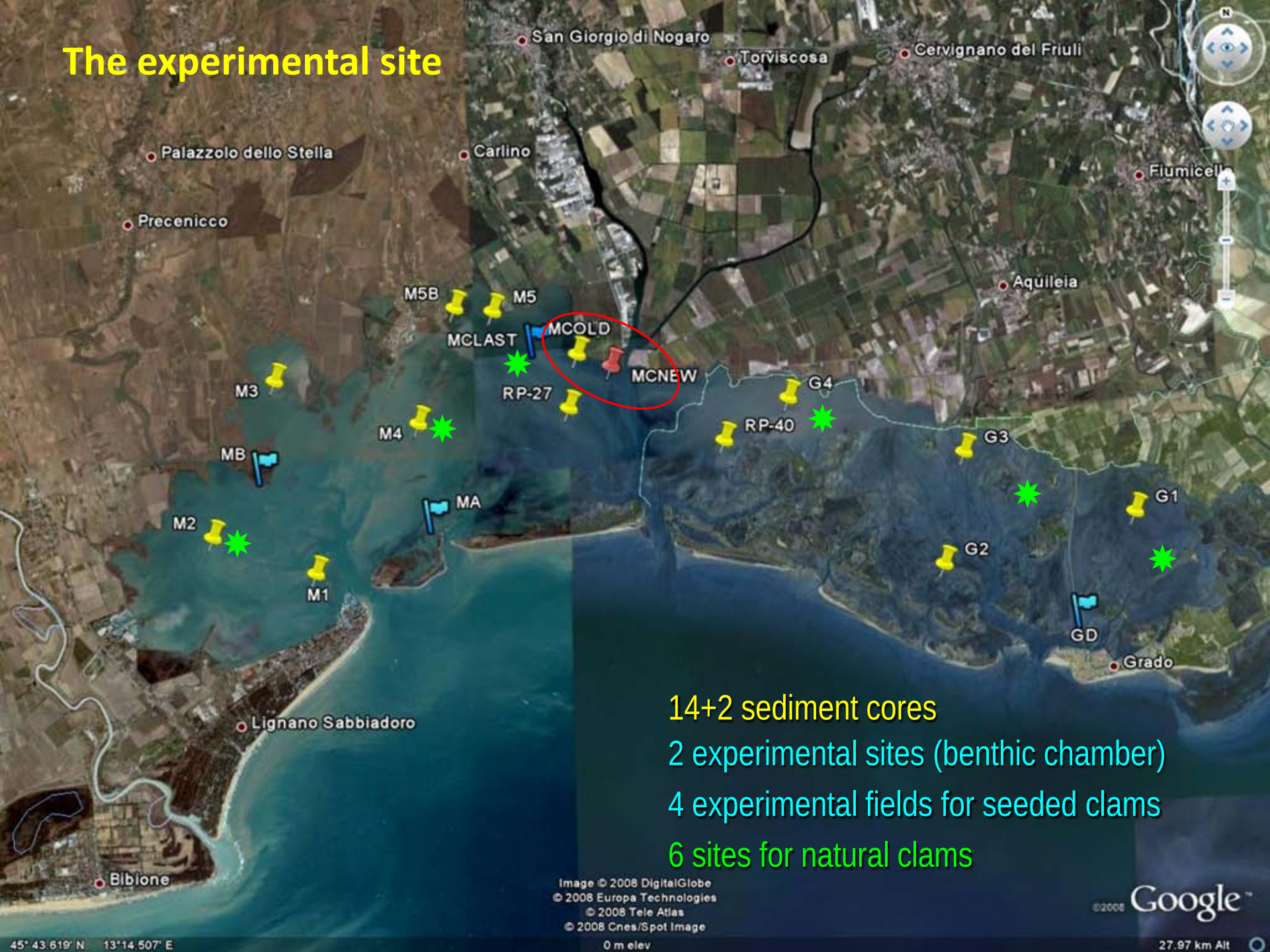
Subtasks

Geochemistry of bottom sediments	Hg spatial and historical distribution, Hg speciation, Hg current and past accumulation fluxes, inventory and burial.
Biogeochemical processes at water/sediment	Methylation/Demethylation and sulphate reduction processes, benthic fluxes of Hg species, Hg resistant bacteria activity.
Bioaccumulation of Hg in bivalves	Spatial variability of Hg and Metil-Hg bioaccumulation in *Tapes Philippinarum* (natural population, "farming" areas and potentially new farmed areas).
Remobilization of Hg from sediments	Assessment of Hg release into the water column due to physical resuspension of lagoon bottom sediments induced by natural or artificial events (*in lab simulation*).


The experimental site
San Giorgio di Nogaro
Torviscosa
Cervignano del Friuli
Palazzolo dello Stella
Carlino
Fiumicello
Precenicco
Aquileia
M5B
M5
MCLAST
MCOLD
MCNEW
M3
RP-27
G4
RP-40
M4
G3
MB
MA
G1
M2
G2
M1
GD
Grado
Lignano Sabbiadoro
Bibione
14+2 sediment cores
2 experimental sites (benthic chamber)
4 experimental fields for seeded clams
6 sites for natural clams
Image © 2008 DigitalGlobe
© 2008 Europa Technologies
© 2008 Tele Atlas
© 2008 Cnes/Spot Image
©2008 Google
45° 43.619' N 13°14.507' E
0 m elev
27.97 km Alt

Results overview: sediment geochemistry

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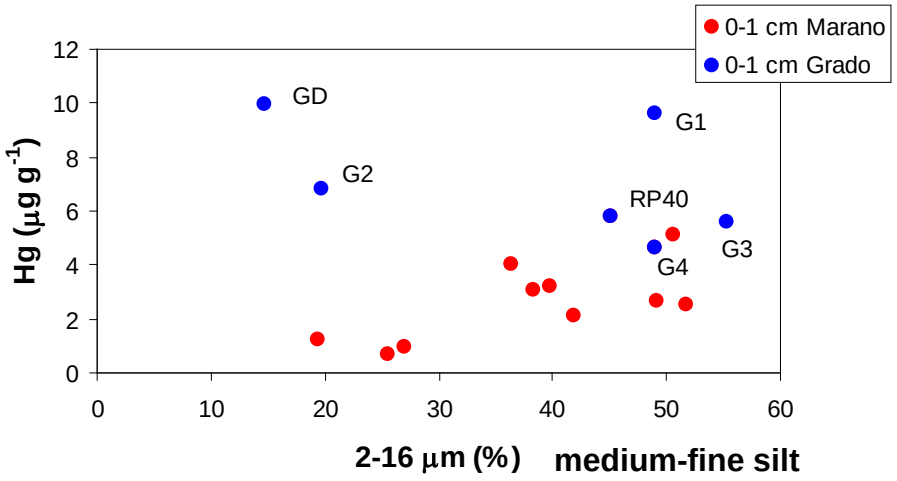
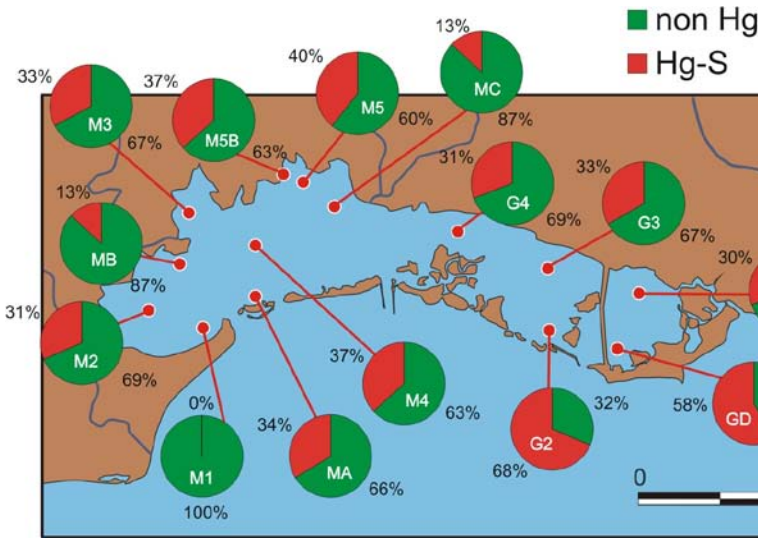
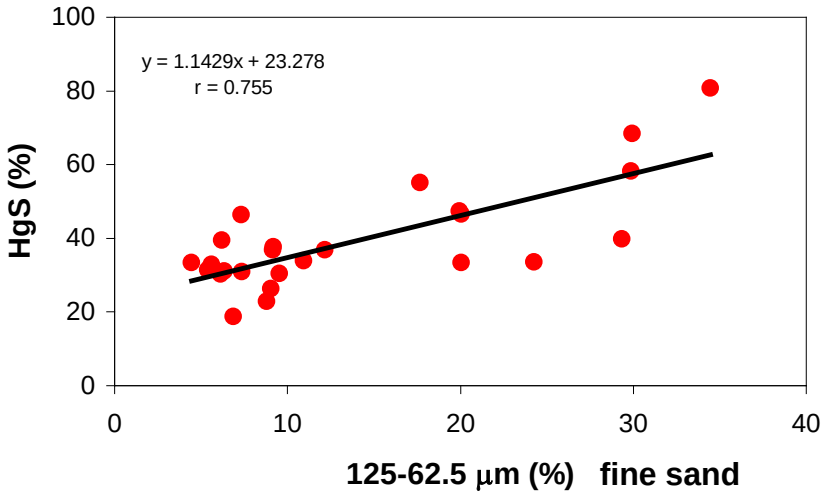
Hg is primarily **associated with fine-grained sediments (2-16 µm)** and it is **transported** and dispersed in suspension **by littoral and tidal currents.**

Coarser sediment particles are **correlated with** the percentage of Hg present as **sulfide (HgS).**
The Hg-rich coarse fraction would be composed by detritic Hg (**microcrystalline cinnabar**), settling where hydrodynamism is strongest.







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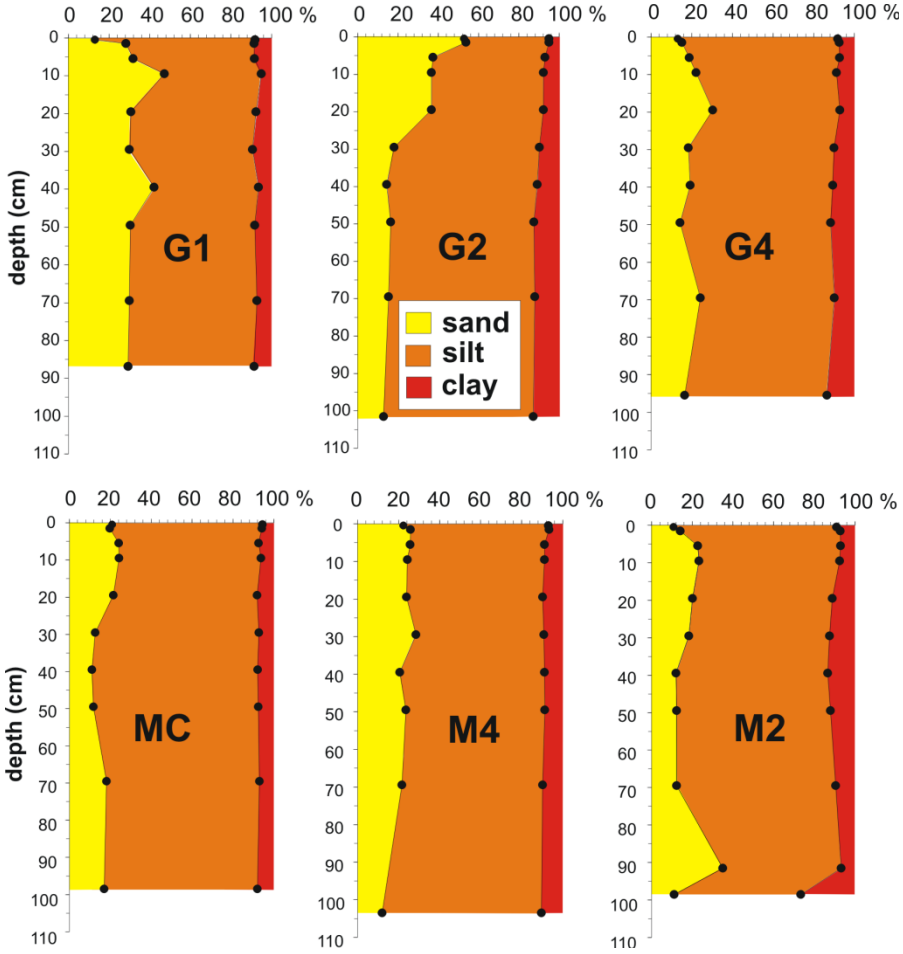
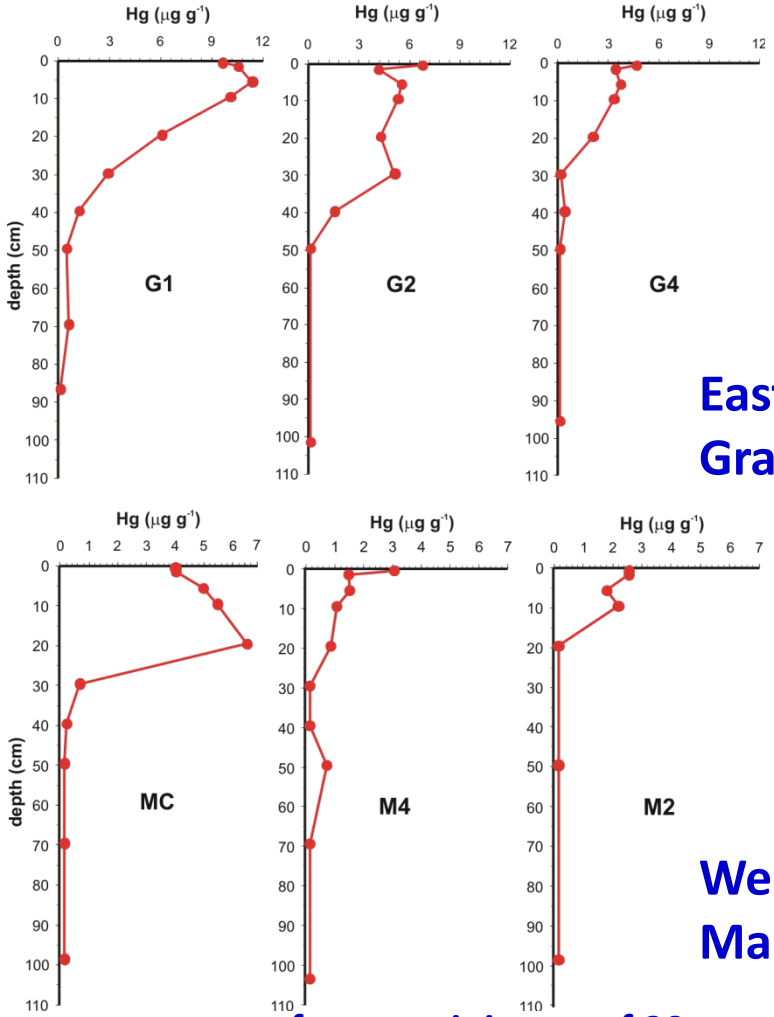
Sediment long cores





- **The anthropogenic input of Hg affects the sedimentary sequence from a minimum of 20 cm to a maximum of 100 cm (local sediment reworking?).**
- **However, in most of the sites, "natural background" (0.13 µg g^{-1}) was found between 0.5 and 1 m.**

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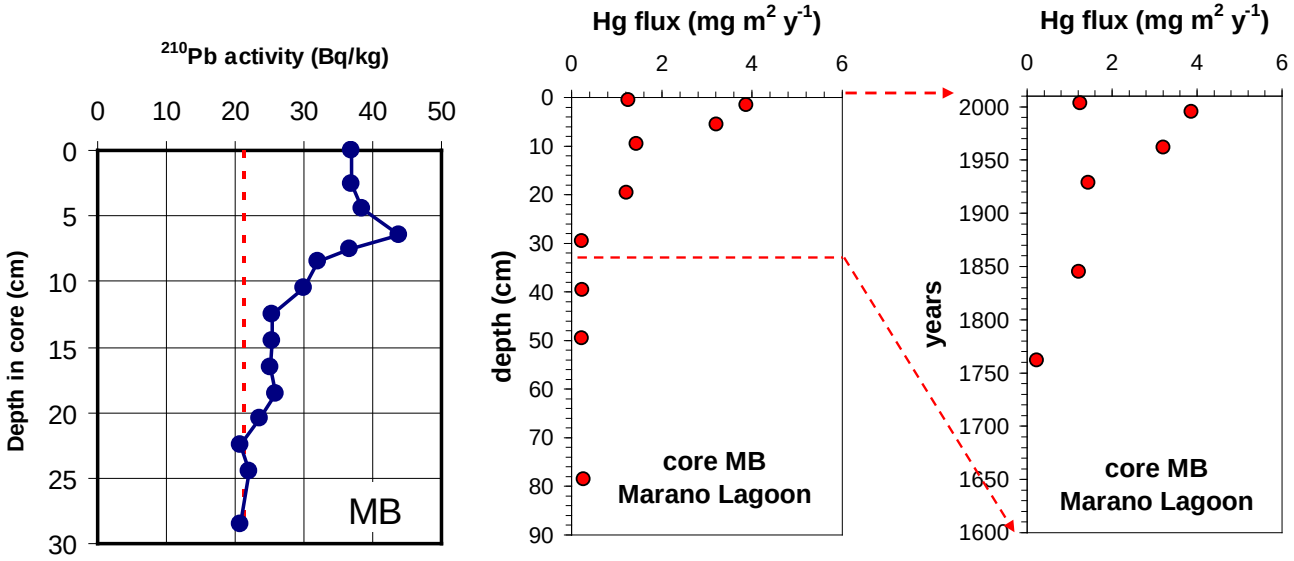
Historical Hg fluxes in Marano & Grado Lagoon: an example

$FHg = \omega (Hg)_s$

$con\ \omega = (1-\phi)\ S\ \rho_s$

$(Hg)_s$ mercury concentration (µg
ϕ porosity
S sedimentation rate (mm y^{-1})
ρ_s density (g cm^{-3})



- Recent Hg flux: 29-8 mg m^2 y^{-1} (eastern sector) and 4-1 mg m^2 y^{-1} (western sector).
- The historical flux of Hg seems to have been affected by mining activity (Idrija) since 1800, in agreement with what previously observed in the Gulf of Trieste (*Covelli et al., 2006 Mar. Geol.*).
- After 1950, the occurence of Hg in the upper portion of the sedimentary sequence could be due to both sources, industrial and mining, at least in the central-western sector of the basin (Marano).

Cumulated Inventory and ammount of Mercury "buried" in the sediments

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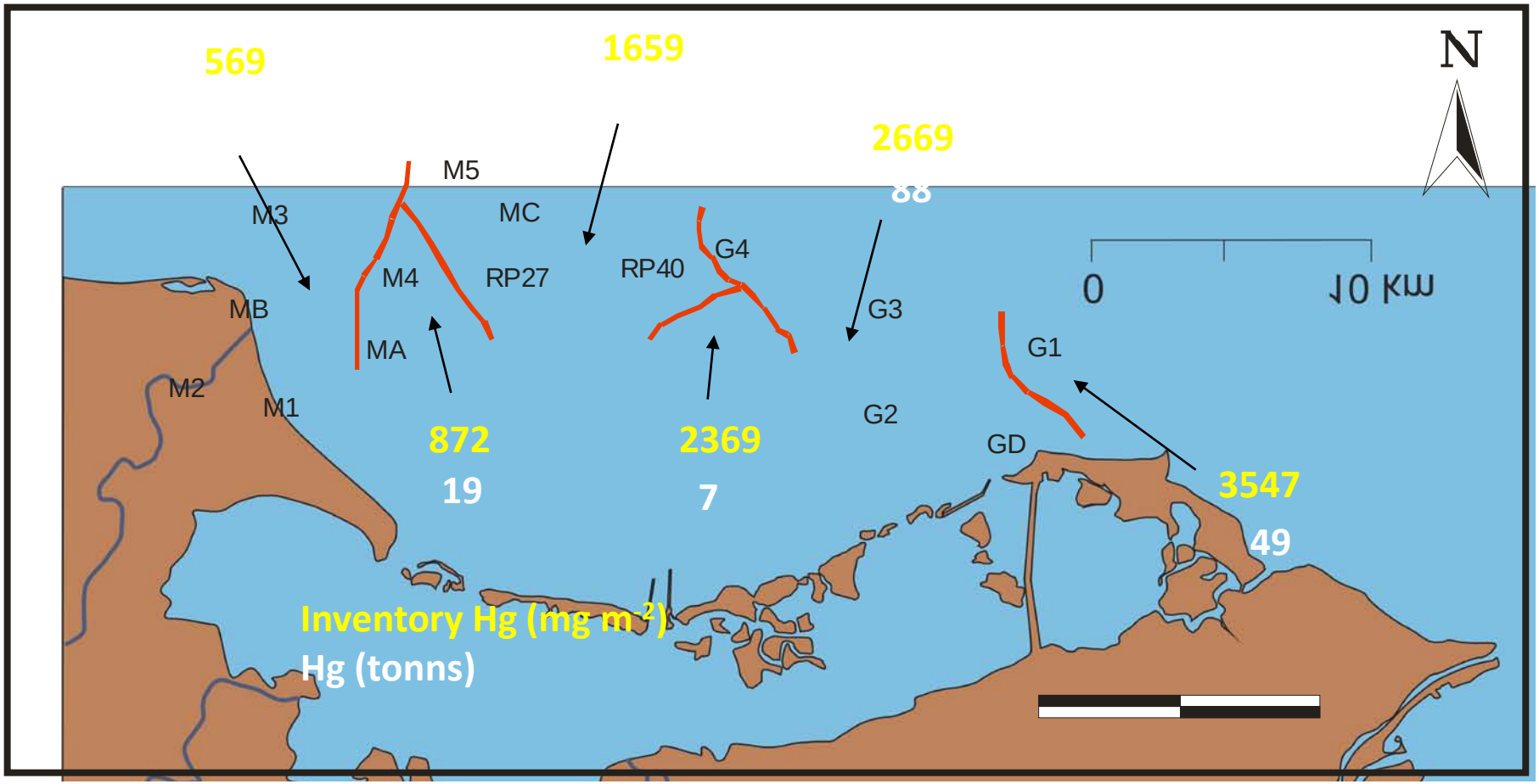
A preliminary rough estimation (by defect) of the ammount of Hg "entrapped" in the bottom sediments of the Lagoon accounts for about 250 tonnes!



Idrijca (tributary of the Isonzo River) 2029 tonns
Žibret & Gosar (2006)

Gulf of Trieste 900 tonns
Covelli et al. (2006)

Results overview: benthic fluxes

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To estimate daily fluxes of Hg species at the sediment-water interface, 2 benthic chambers were simultaneously deployed for each experimental site (MB and MC).

autumn (October 2008)
winter (March 2009)
summer (July 2009).

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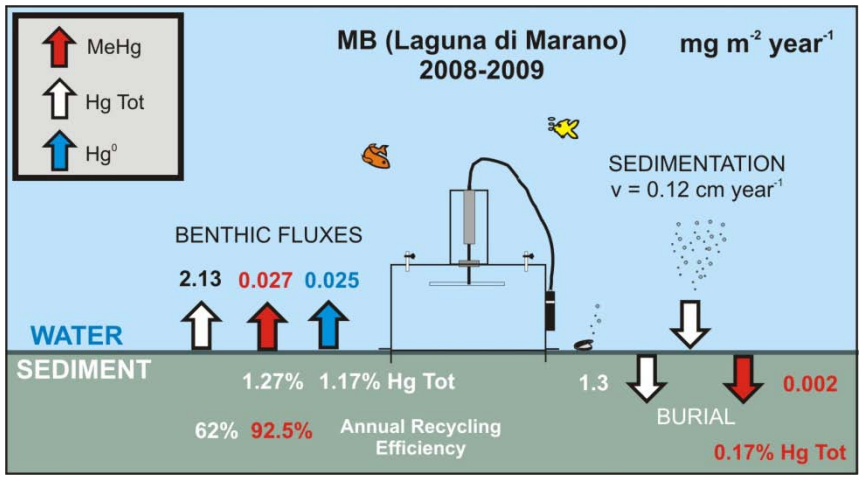
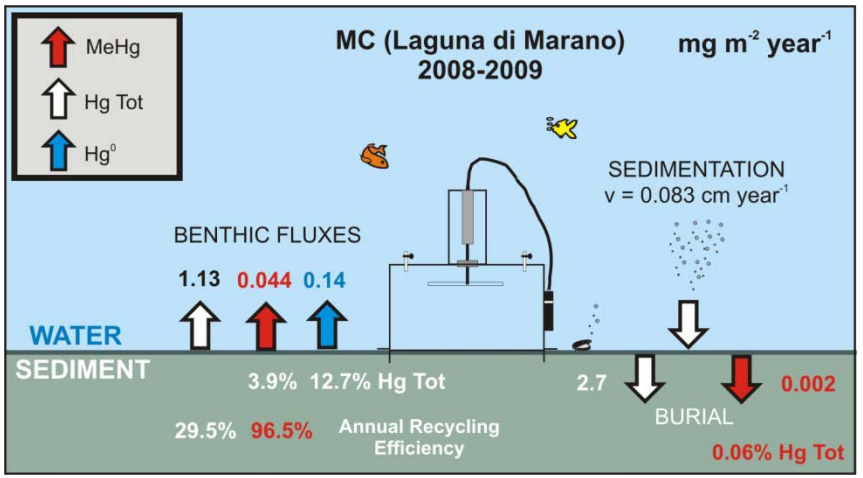
A yearly budget for THg, MeHg and DGM (Hg^0)



$Hg_{sed} \approx 1.4\ \mu g\ g^{-1}$



$Hg_{sed} \approx 4.3\ \mu g\ g^{-1}$

1. Results suggest that **both experimental sites (MB and MC)** are **very active** in **recycling Hg** from the sediment to the water column.
2. **Hg reduction** seems to be an **important process in this environment**, with DGM fluxes which are similar or higher than MeHg fluxes.
3. **MeHg release**, which pose the higher risk for potential bioaccumulation in clams, **is mostly present in MC (in front of the industrial source)**.

Results overview: methylation/demethylation and microbiology

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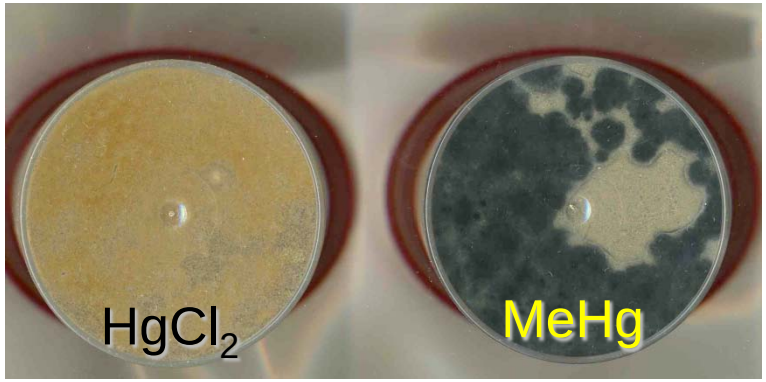
1. The microbial community is formed (up to 70% of the total) by **Hg-resistant** and **Hg-tolerant bacteria**.
2. Radiotracer experiments confirmed **active Hg methylation by sulfate-reducing bacteria (SRB),** under anaerobic conditions.



3. Using classic microbiological assays, it was possible to isolate **non-SRB** that **methylate Hg under aerobic conditions**, using nitrates and sugars as metabolic substrates.
4. On the other hand, SRB are also active demethylators and, in the Lagoon, **demethylation rates were more rapid than any ever reported** using tracer methodology.
5. **Quick sulfate-reduction rates in MB and MC**, compared to GD (Grado sector), could lead to inorganic Hg removal, reducing its bioavailable fraction and preventing bacterial methylation, thus suggesting that the **Marano sites** are better **suited for clam farming**.

Dredging of lagoon channels

clam harvesting
by the “Marano dredge”

SEDIMENT RESUSPENSION

River flood

Storm events

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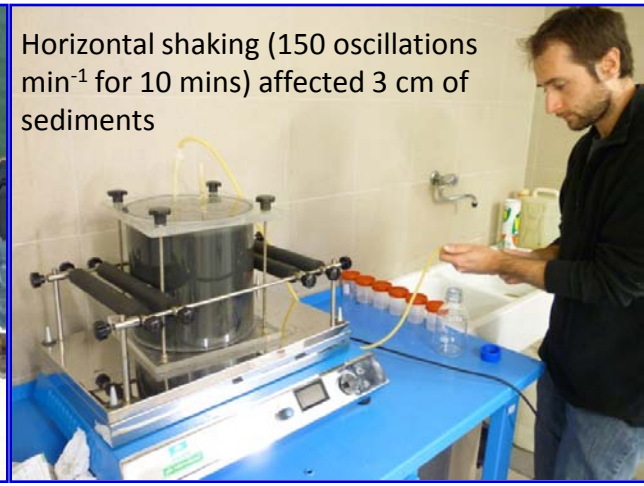
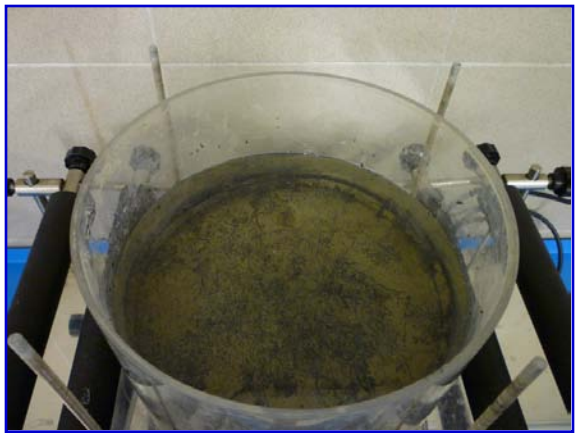
A mechanical re-suspension of bottom sediments from a Grado Lagoon channel simulated the effects of dredging operations and potential remobilization of Hg



Sampling from inside the chamber at t=0, 0.5, 1, 2, 4 and 17 hours after re-suspension. Samples were centrifuged at 3820 rpm for 10 minutes to make particles settle; the resulting dissolved phase was filtered at 0.45 µm.



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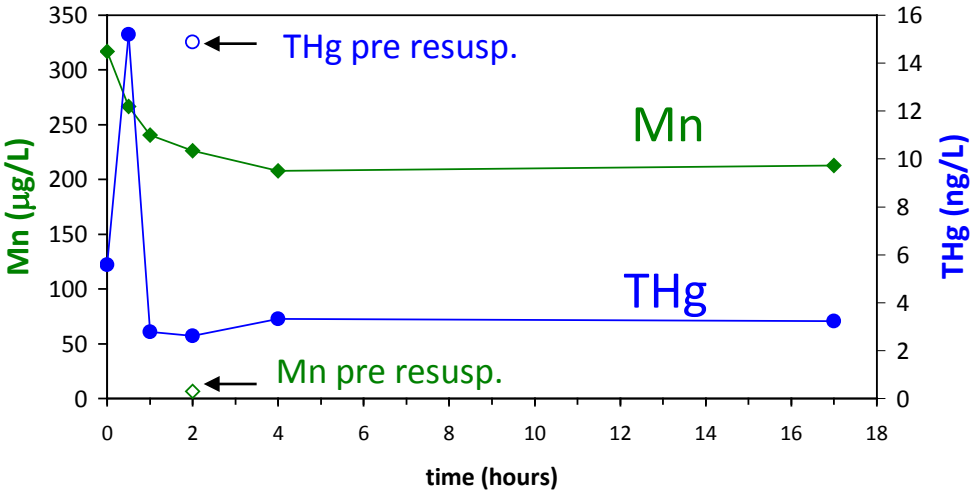
Release, tranformation and risedimentation of Hg

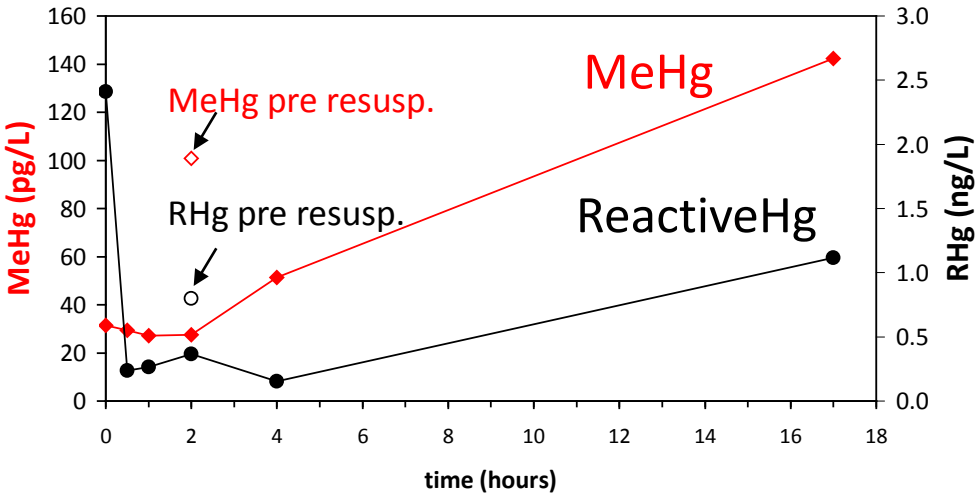
In this short term experiment, the combined effect of adsorption on resuspended particles and the formation of oxyhydroxides results in THg scavenging from the water column.

MeHg seems to be remobilized (produced?) after resuspension and risedimentation but at later stage. *Remobilization of organic matter favouring methylation?*

Mesocosm experiments, partially reflect real environmental conditions, thus results should be verified during dredging operations.

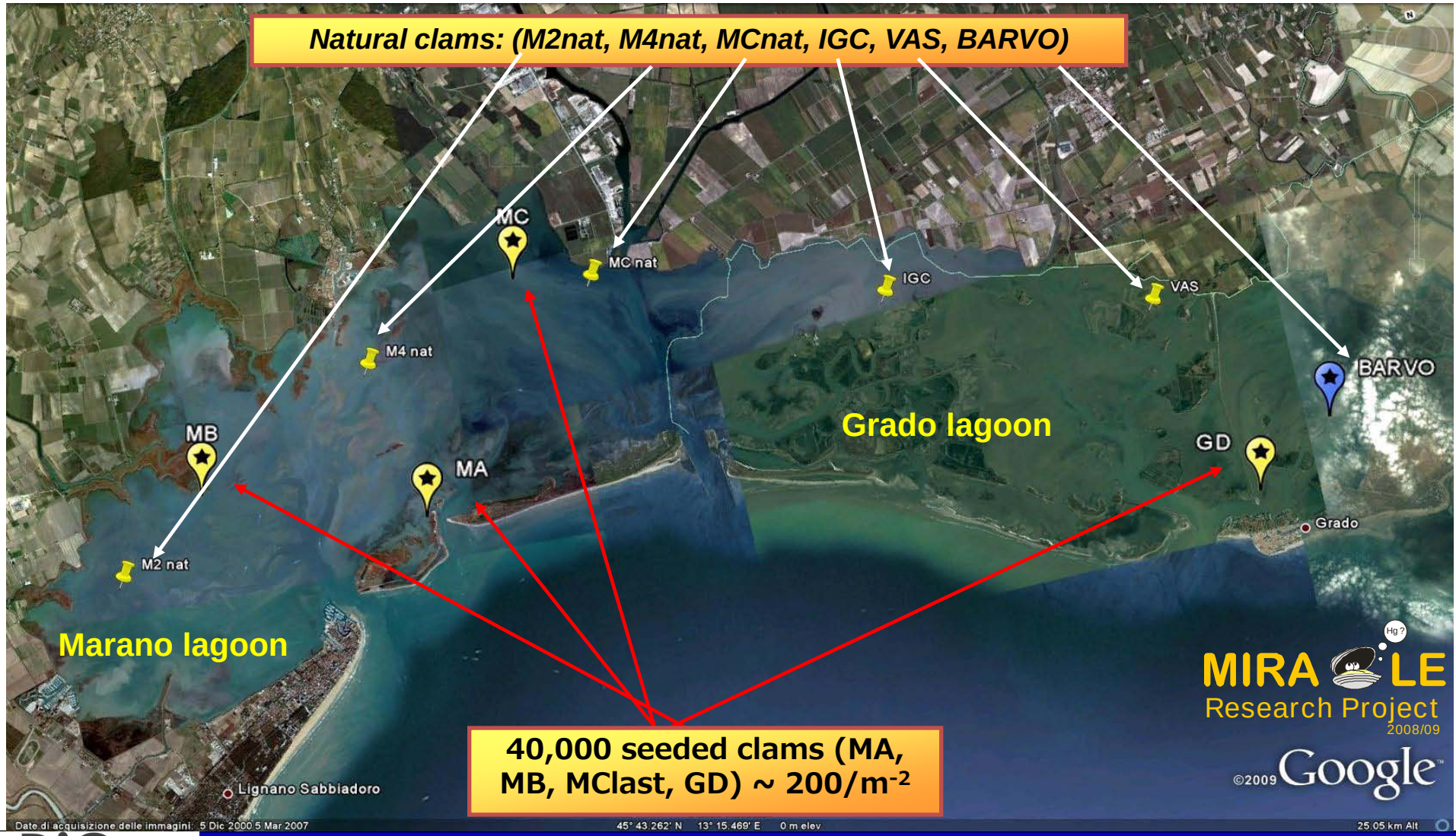
3,000,000 m³ of sediments are estimated to be dredged from the lagoon channels in the near future!





Results overview: Hg bioaccumulation in clams

Manila clams (*Tapes philippinarum*) were seeded in 4 selected sites to verify bioaccumulation of Hg with growth (15 months) up to exceed the limit size (28 mm) for commercialization.



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Manila clams (*Tapes philippinarum*) to be seeded were provided by the local clam farming of Marano village

clams collection every 45 days

Analyses

- biometrics (n=30)
- Hg
- Metil-Hg

Aussa-Corno River mouth - MC site

Stella River mouth - MB site

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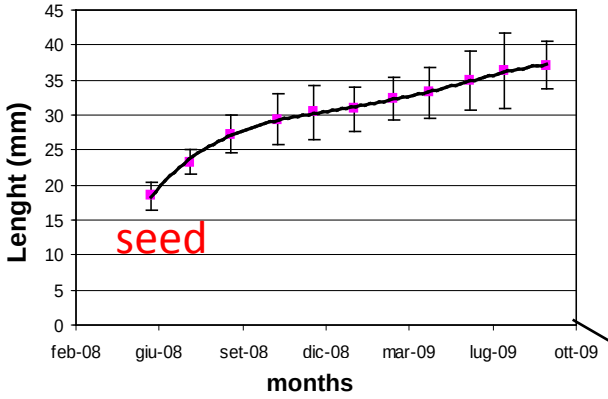
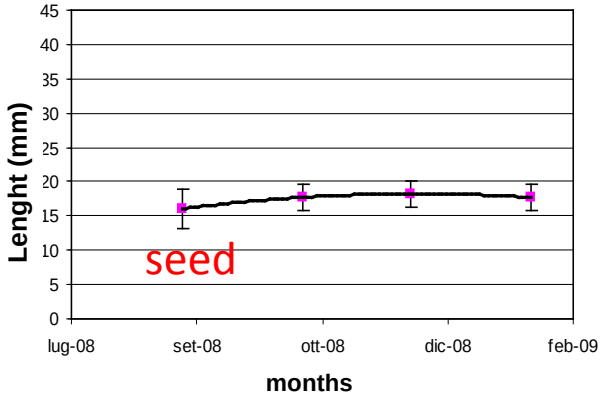
Manila clam growth rate

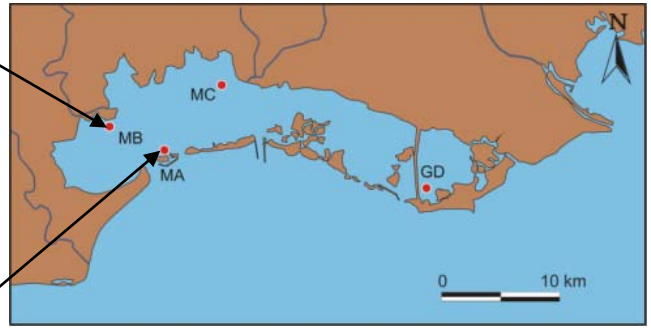
MB



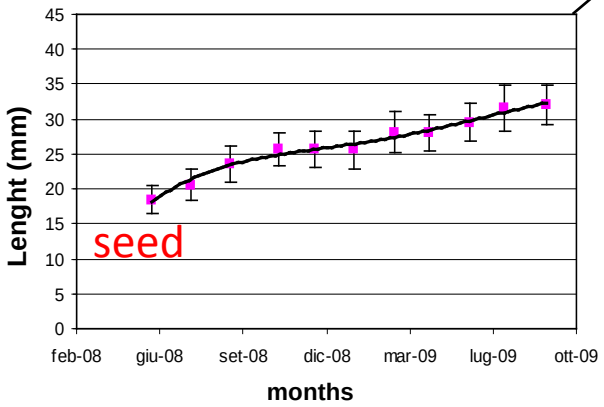
Among the 4 experimental sites, only **MA** and **MB** gave positive results. The second one also showed a very quick growth rate.

MClast



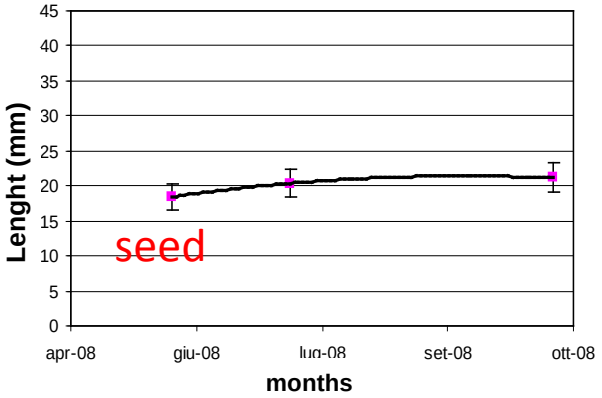


MA



Environmental factors (ex. predators) inhibited clam survival in MC and GD sites thus preventing data collection after some months.

GD



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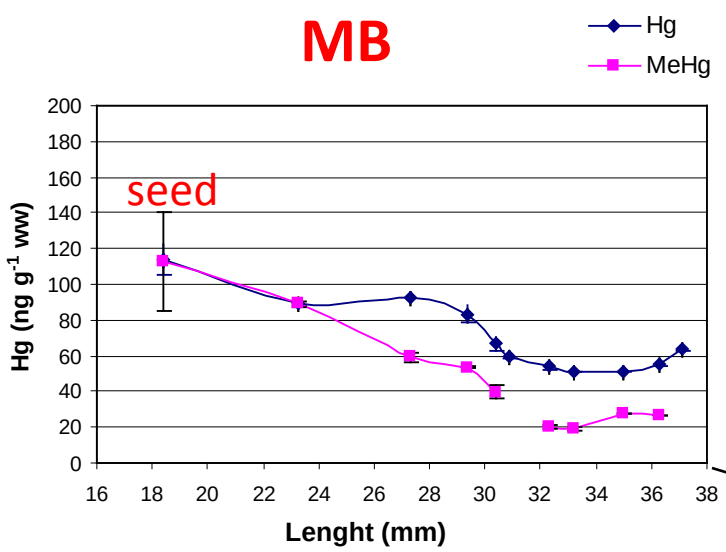
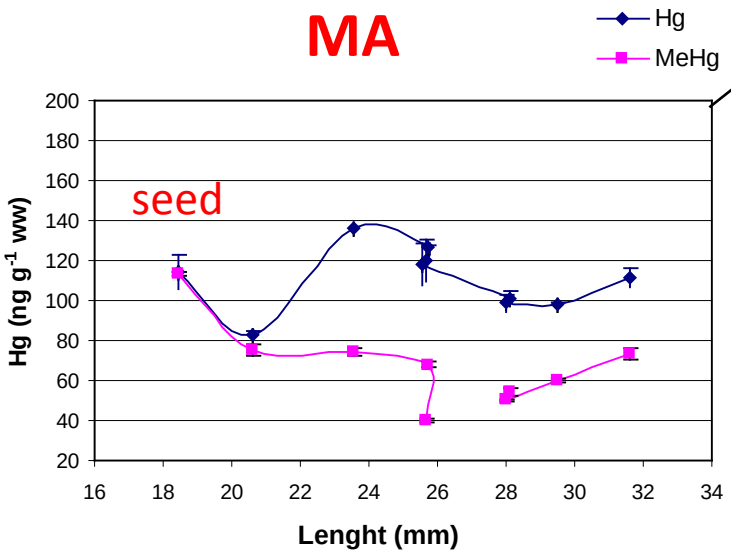
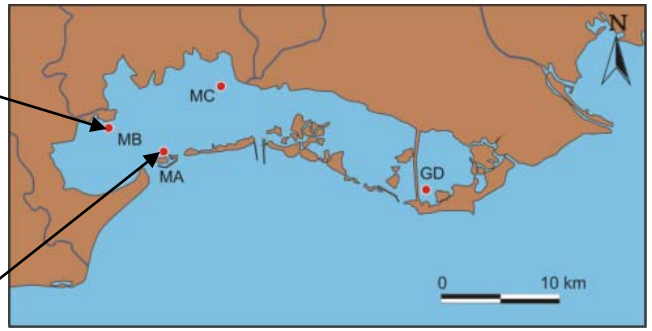




Hg content in clams was always lower than the 500 ng g^{-1} w.w. limit for commercialization.

As clams grew bigger in size, their Hg and MeHg concentration decreased, and they were lower than in the starting seeded pool.



Dilution of Hg species in clams?
Or presence of Hg-resistant bacterial strains, which are capable of active detoxification, forming colonies on the clams soft tissues (siphons, in particular)?

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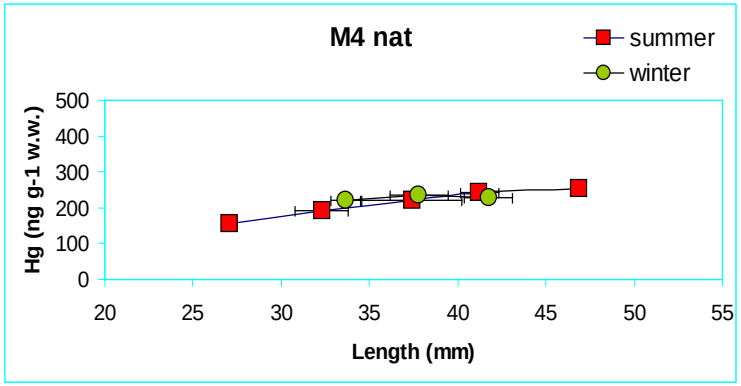
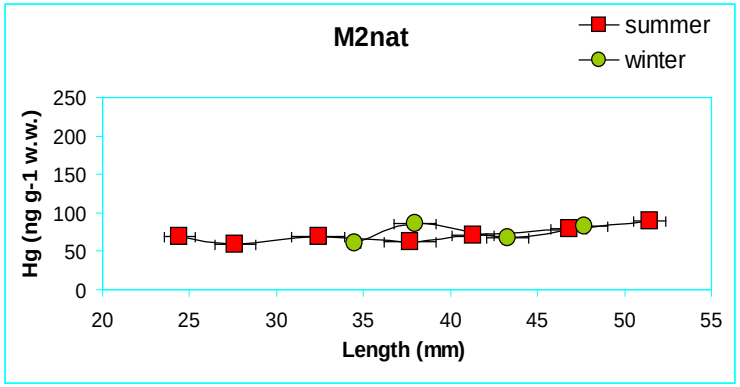
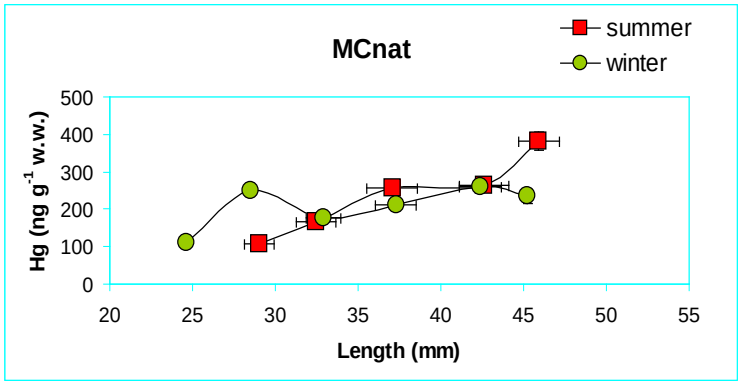
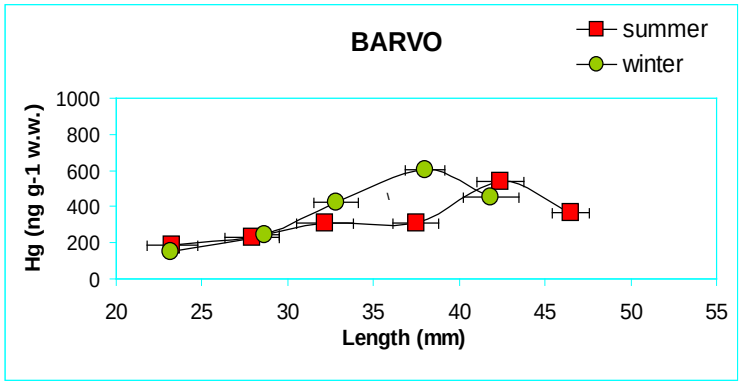
Sampling of natural populations of clams was performed by hand or by dredge in 6 selected sites, in summer and winter.

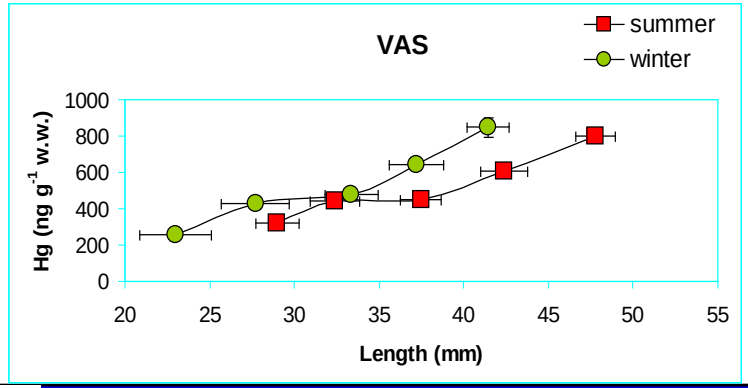
Hg contents in natural Manila clams tend to increase with size, exceeding the limit of 500 ng g^{-1} (w.w.) for individual clam sizes > 35mm only in the Grado Lagoon

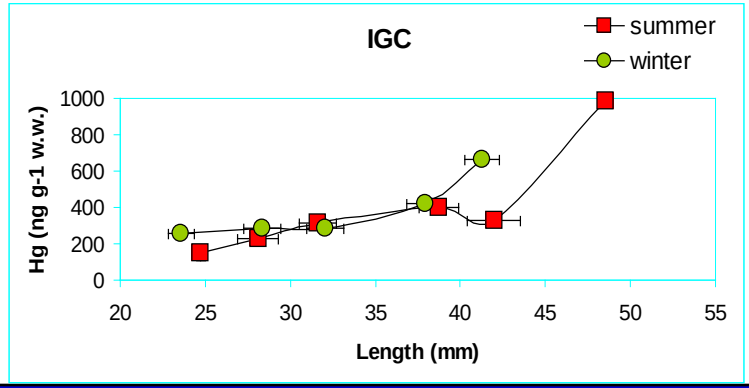












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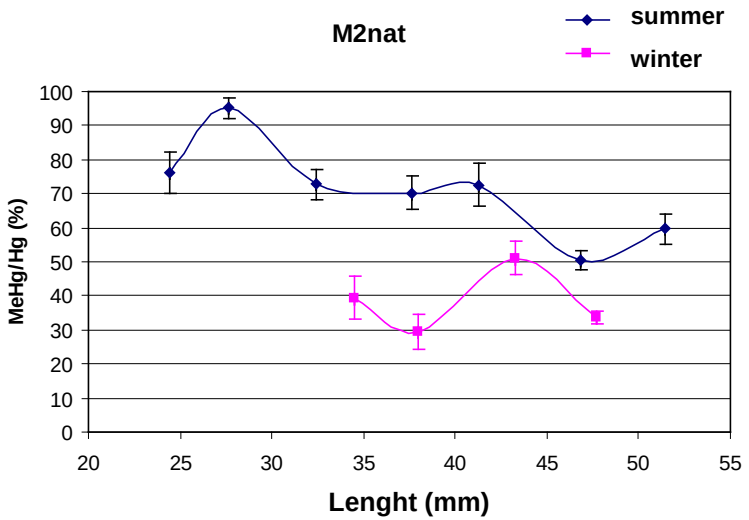
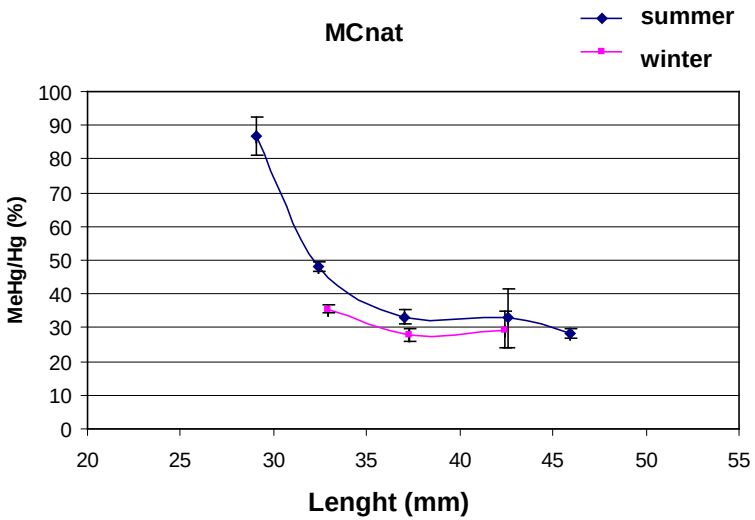
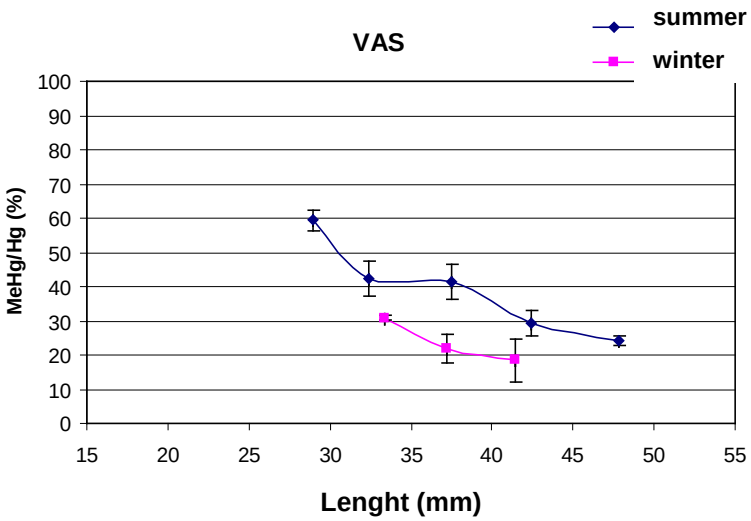
Percentage of MeHg on total Hg content in natural clams decreased with size

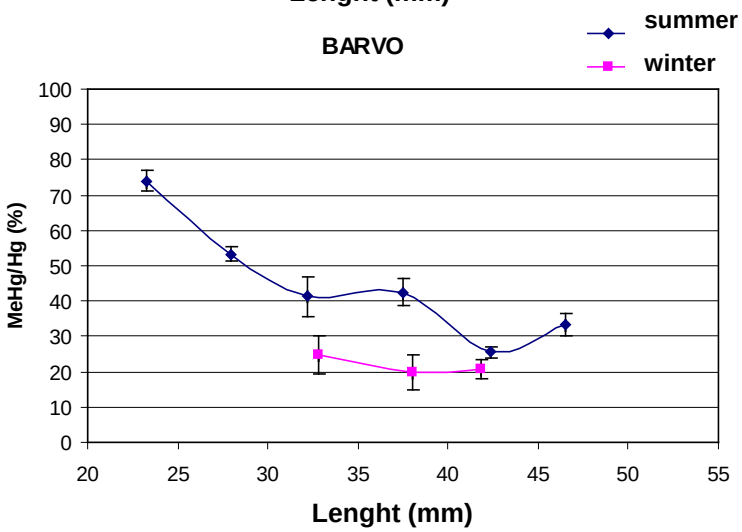
MeHg: mean 28-187 ng g^{-1}
max 35-194 ng g^{-1}





MARANO





GRADO

Any risk if clams are consumed?

Provisional tolerable weekly intake (PTWI)

FAO/WHO Expert Committee On Food Additives

- Hg: 5 μg kg^{-1} body weight/week
- MeHg: 1.6 μg kg^{-1} body weight/week

Daily intake of clams:

1) Best case Scenario: 11 g*
2) Worst Case Scenario: 30 g**

* an average from *Fung et al.* (2004) *Env Poll* and *Whyte et al.* (2009) STOTEN

** estimated from *Boscolo et al.* (2007) *Food Chem Tox* for the Venice Lagoon and comparable to *Ferrara & Funari* (1999) *Rep Sanitary Institute*

Daily intake of Hg and MeHg by consuming natural clams from the Lagoon: 2 groups of consumers are considered (BEST and WORST SCENARIO)

Date	SITE	BCS (Best Case Scenario) groups Daily intake of 11 g				WCS (Worst Case Scenario) groups Daily intake of 30 g			
		Hg mean (µg/day)	Hg max (µg/day)	MeHg mean (µg/day)	MeHg max (µg/day)	Hg mean (µg/day)	Hg max (µg/day)	MeHg mean (µg/day)	MeHg max (µg/day)
29/07 2008	IGC	4	10			11	28		
	VAS	6	9	2	2	17	26	6	6
	MC Nat	2	4	1	1	6	10	3	3
	M2 Nat	1	1	1	1	2	3	2	2
	M4 Nat	2	3			5	7		
09/03 2009	IGC	5	7			13	19		
	VAS	7	12	2	2	20	34	4	5
	MC Nat	2	3	1	1	7	8	2	2
	M2 Nat	1	1			2	2	1	1
	M4 Nat	2	2			6	6		
	BARVO	5	8	1	1	14	22	3	4
21/07 2009	BARVO	3	6	1	2	9	15	4	4

Tolerant level of daily intake for an adult of 70 kg is 50 µg/day for total mercury (THg) and 16 µg/day for metilmercury (MeHg).

Final Remarks

1. The Miracle Research Project represents an informed knowledge base for the drafting of best practice guidelines for clam farming management in a Hg contaminated environment.
2. Despite very high Hg contamination levels, seeded clams, in association with the bacterial community, are able to grow and their Hg accumulation does not exceed the concentration limit for commercialization.
3. It has be hypothesized that other areas of the Lagoon, particularly in the Marano sector, which are currently unused or prohibited for clam farming, could be suitable for clam farming.

Thank you for your attention !

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