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THE USE OF MOLLUSK SHELLS AS BIOSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WATER

Distribution of minor and trace elements using LA-ICP-MS technique

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Università degli Studi di Ferrara

Terra & Acqua Tech

Ferrara, 20/06/2019

Introduction

Heavy metals in the environment

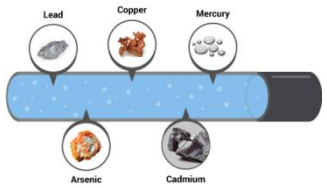
Mining sites

Electroplating

Pigments

Batteries

Plumbing



Water pollution

BIOACCUMULATION of heavy metals in the organism with long persistence time

- Neurological effects
- Kidney desease
- Osteoporosis

WHO Guidelines values*

Cd = 0.003 mg/L

Pb = 0.01 mg/L

Ni = 0.07 mg/L

**Guidelines for Drinking-water Quality* – WHO (2011)

Mollusk shells as bio-adsorbents

40% of all marine aquaculture production is represented by shellfish cultivation*

For 1 Kg of oyster consumed, 370 – 700 g are waste, mainly shells

Disposal

- Soil conditioners
- Calcium supplements
- **Bio-adsorbents**

Bio-indicators

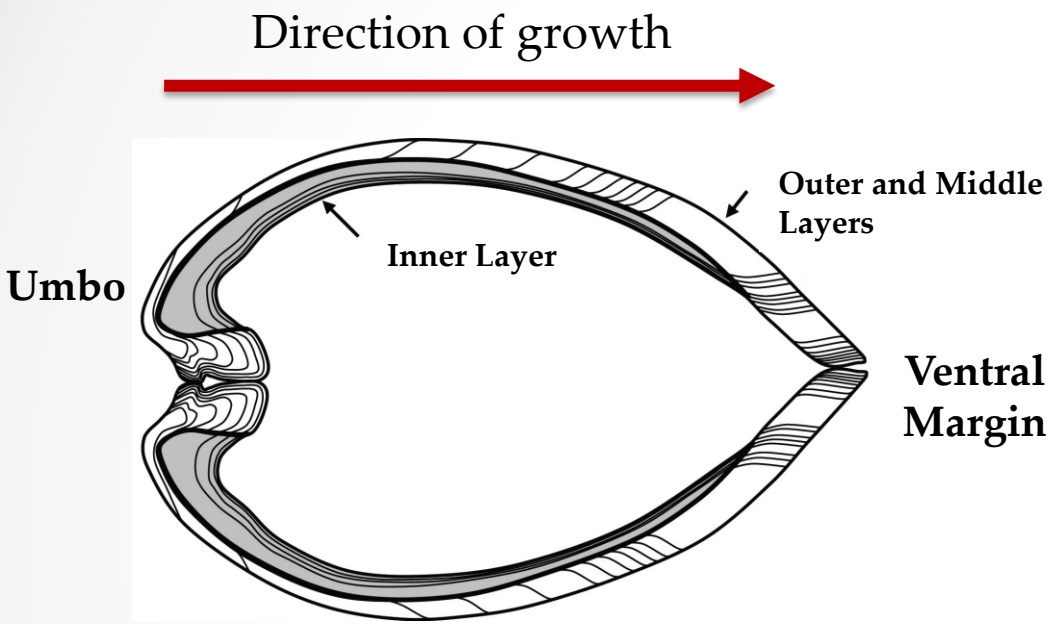
Contact of the shell with polluted environment during the organism growth.

Introduction

Sacca di Goro is a fragile and highly impacted coastal system located along the Adriatic Sea Coast of Italy in the Po River Delta. It receives effluents from the Po River. Due to its position at the sea-land interface, the Sacca di Goro is considered vulnerable. In particular, remediation is a key issue to support local economy and promote water and sediment quality.

Consorzio Pescatori di Goro, with its 566 members is the most important fishing organization on national level for the production and process of shellfish.
Annual turnover of 60000 €
16000 tons per year of clam produced

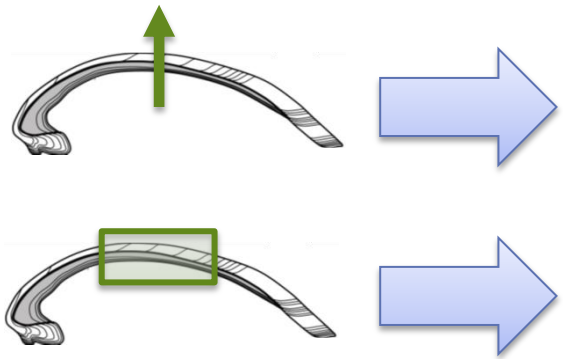
Shell formation



Daily growth with seasonal ring formation

LA-ICP-MS

- Cross section scanning → Diffusion of metals through the different layers
- 2D Imaging → Elemental maps of small sections



Schöne, Bernd R., & Donna M. Surge. 2012. Part N, Revised, Volume 1, Chapter 14: Bivalve sclerochronology and geochemistry. Treatise Online 46:1–24

Experimental



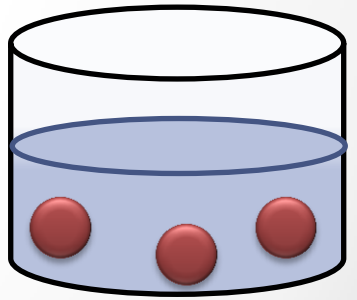
Scallop shells

Oyster shells

- Not treated shells
- Shells treated with cadmium solution 0.1 mg kg^{-1}
- Shells treated with cadmium solution 1 mg kg^{-1}

Batch method:

- Room temperature
- Contact time: 24 h



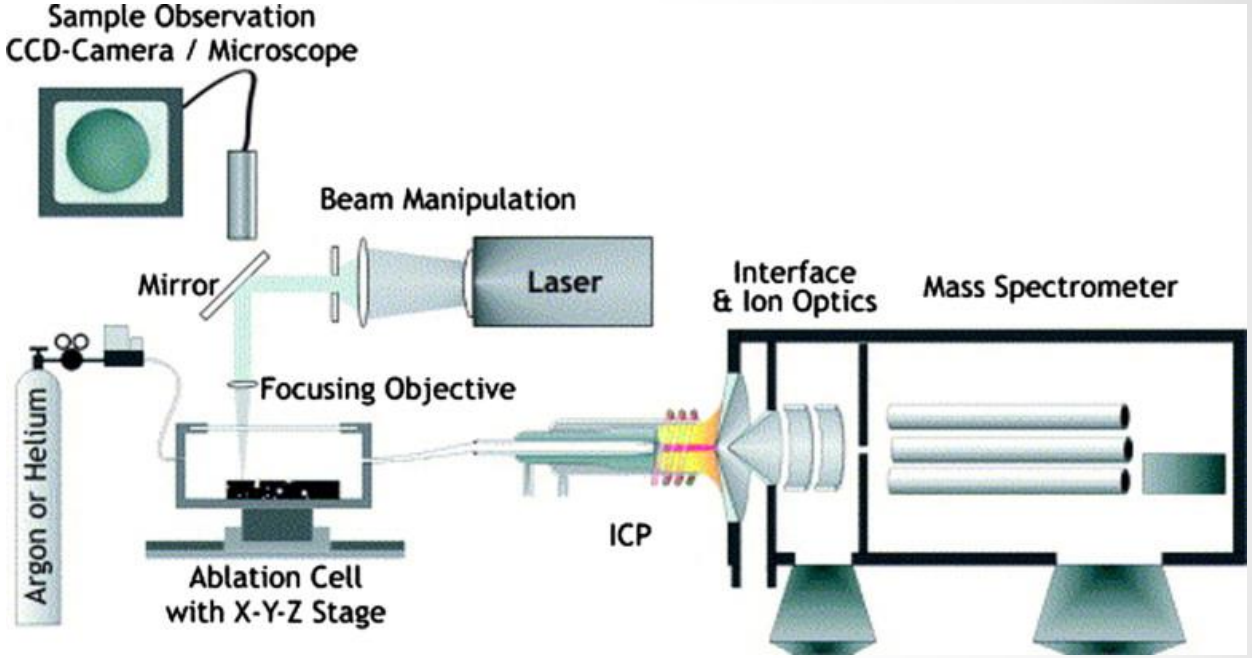
Experimental

- Milled
- Digested in HNO_3 10%
- ICP - MS

Embedding
EpoFix resin

LA-ICPMS

- Line scans
- 2D Imaging



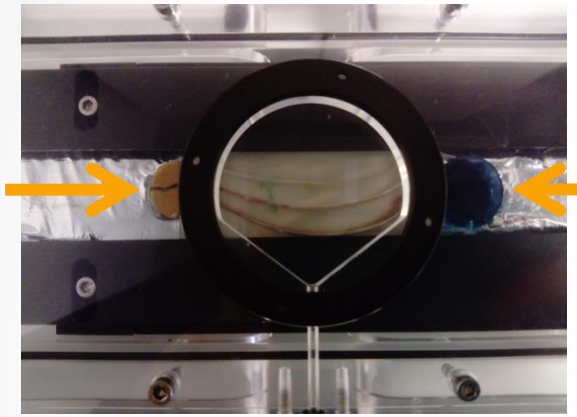
GeoLas C

Argon Fluoride (ArF) excimer laser system operating at a wavelength of 193 nm

LA – ICP – MS
Parameters and Recovery

MACS-3

Recovery



NIST 610

External standard

	Compiled value (µg g^{-1})*	Recovered value (µg g^{-1}) ± RSD(%)	% Recovery
Mg	1756	1859 ± 6.72	105.84
Cr	117	103 ± 5.30	88.21
Mn	536	510 ± 2.60	95.26
Cu	120	110 ± 11.75	92.20
Sr	6760	6797 ± 6.16	100.55
Cd	54.6	47 ± 8.03	87.35
Pb	56.5	56 ± 7.20	99.77

*GeoRem Database

GeoLas C

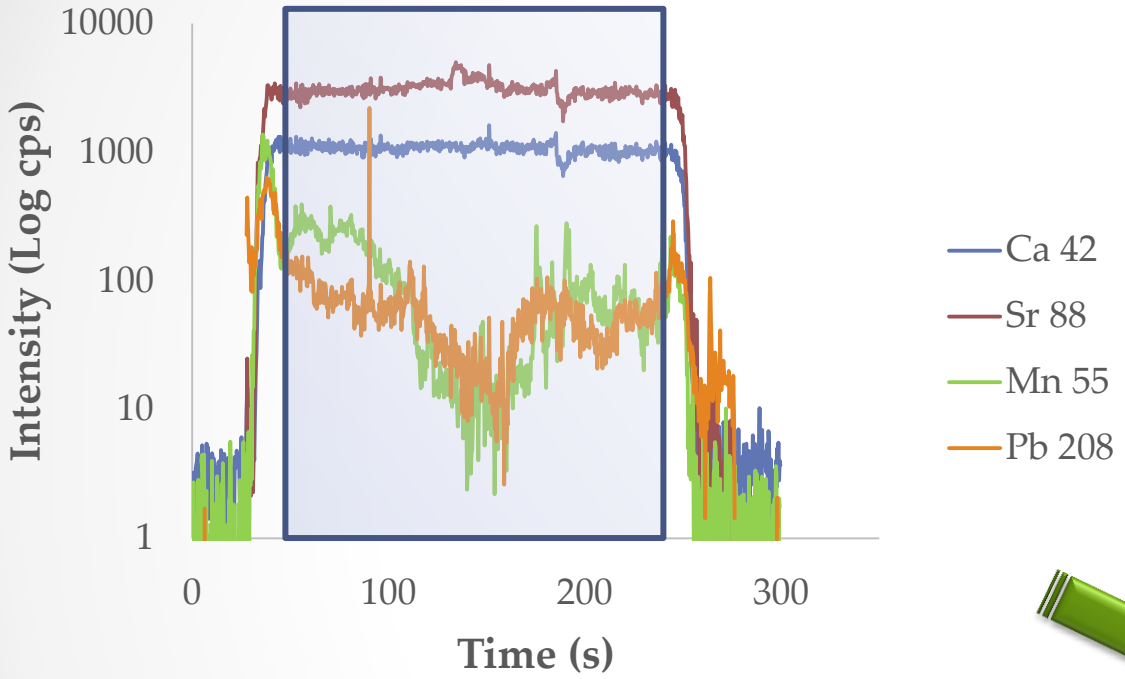
- Spot size: 24 μm
- Scan speed: 3 $\mu m\ s^{-1}$
- HV: 30 kV
- Repetition rate: 10 Hz
- Carrier gas: He (0,6 L min^{-1})

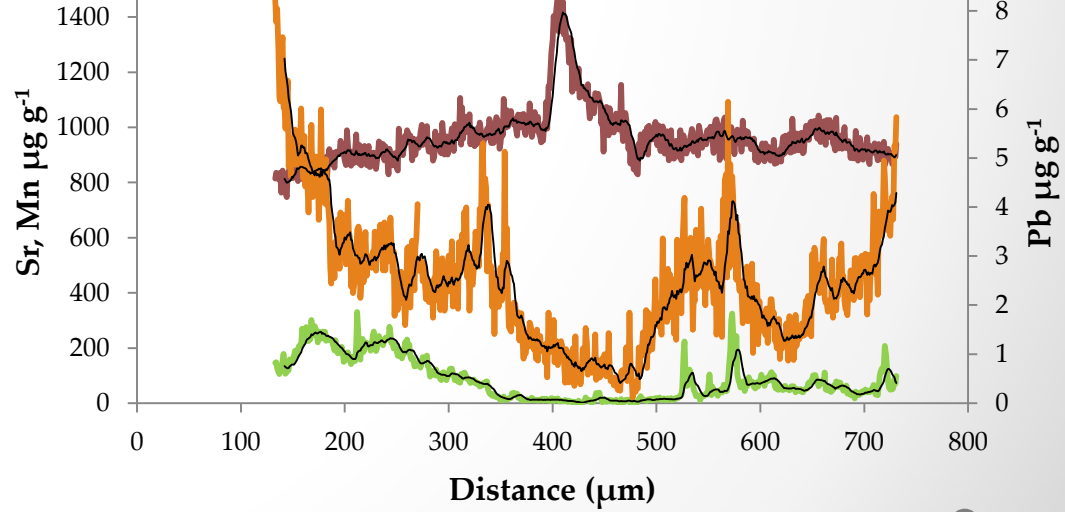
ICP-TOFMS

- RF power: 1550 W
- Sampling depth: 6,8 mm
- Coolant gas (Ar): 16 L min^{-1}
- Auxiliary gas (Ar): 0,8 L min^{-1}
- Nebulizer gas (Ar): 0,82 L min^{-1}

MACS-3 (carbonate pellet) [U.S. Geological Survey, *Box 25046, MS 963, , Denver, CO 80225, USA*]

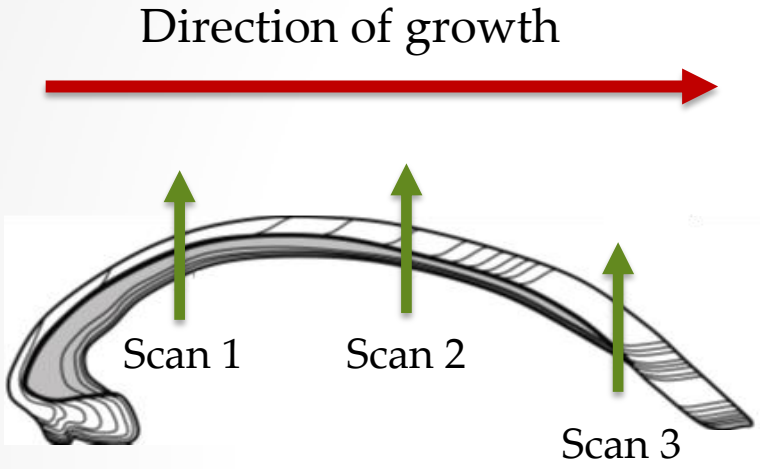
Cross section scanning

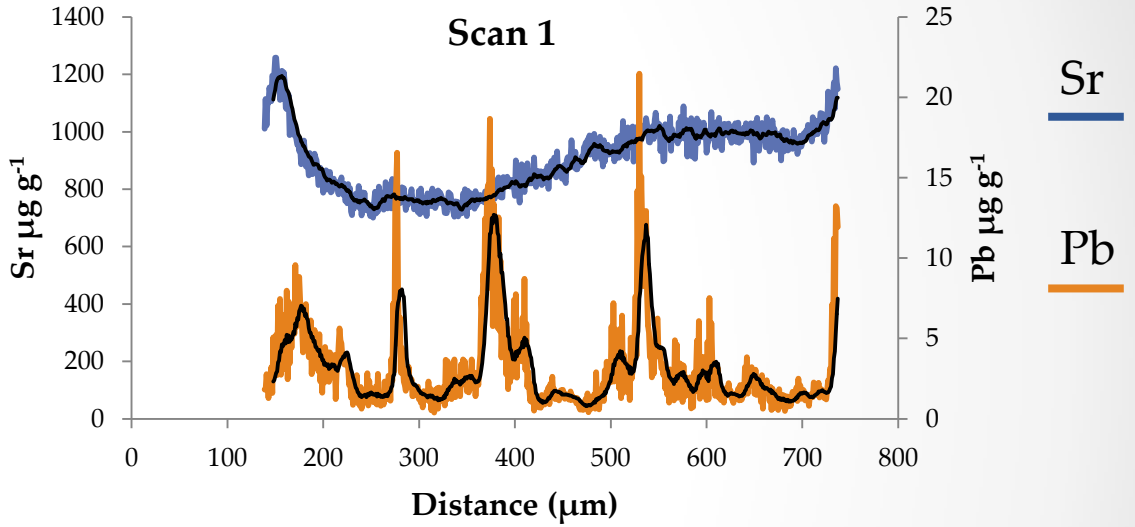


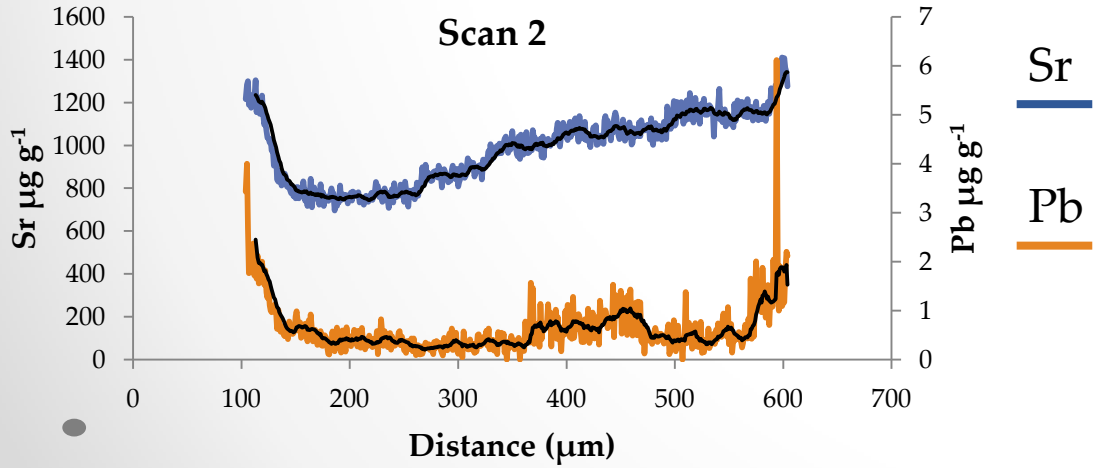


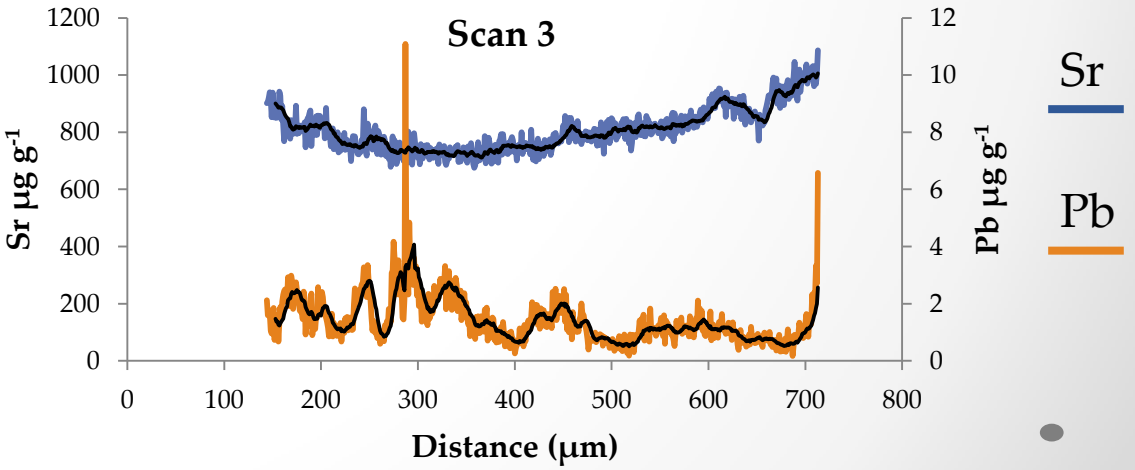
- Point by point evaluation
- Scan speed: Time → Distance

Cross section scanning
Concentration profiles



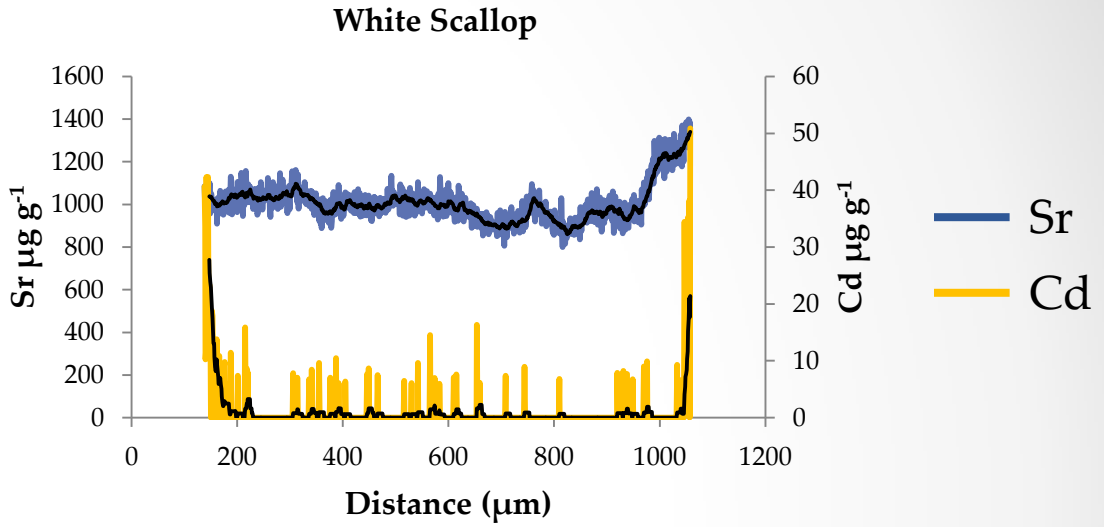


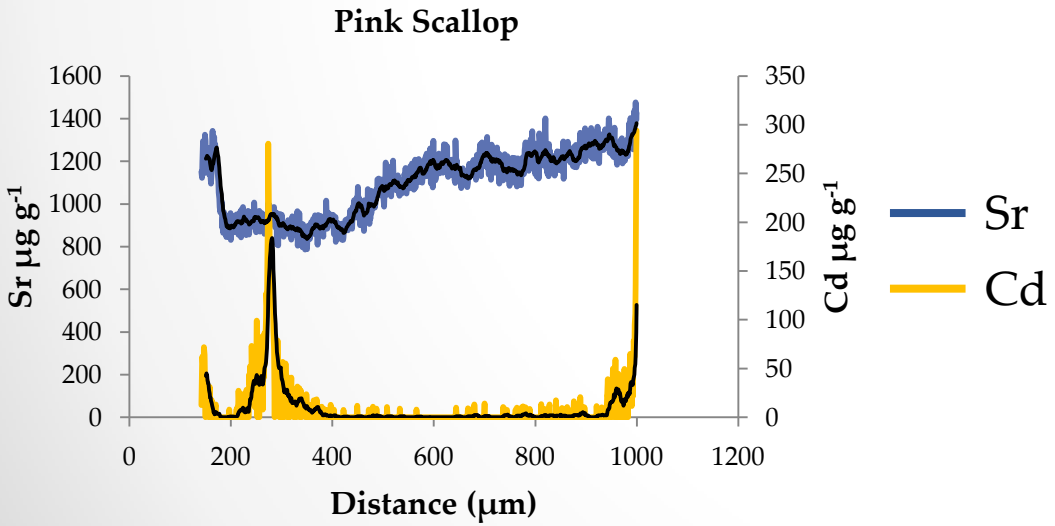


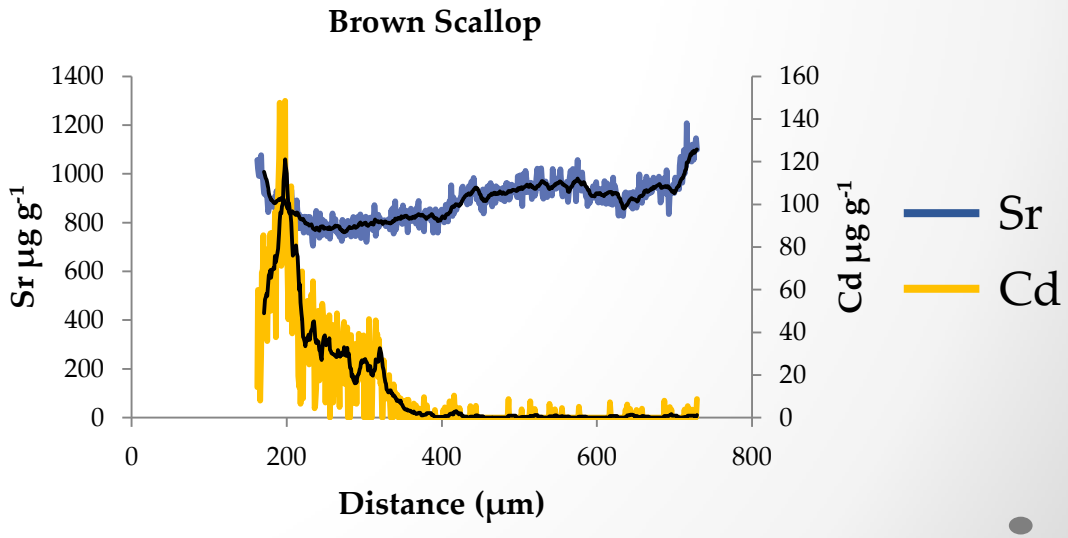


Cross section scanning
Cadmium adsorption

Comparison between scallops with different colours treated with Cd solution 1 ppm



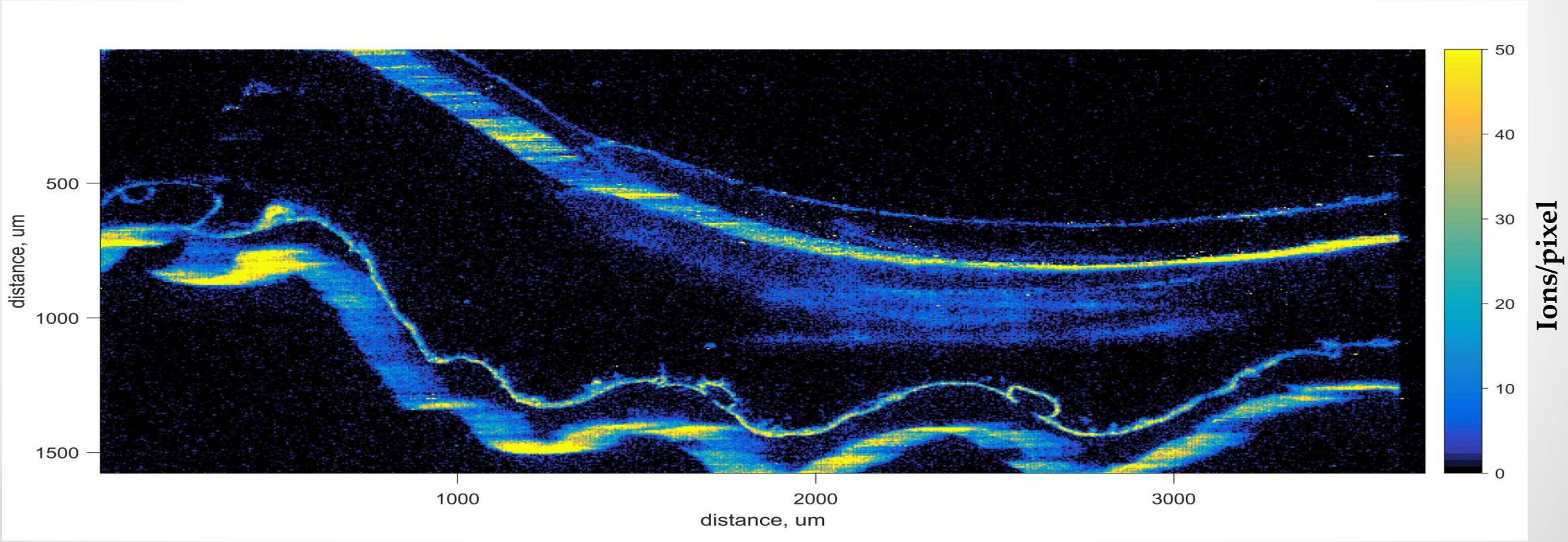




2D Imaging

Scallop shell treated with Cd 1 mg L^{-1}

^{111}Cd

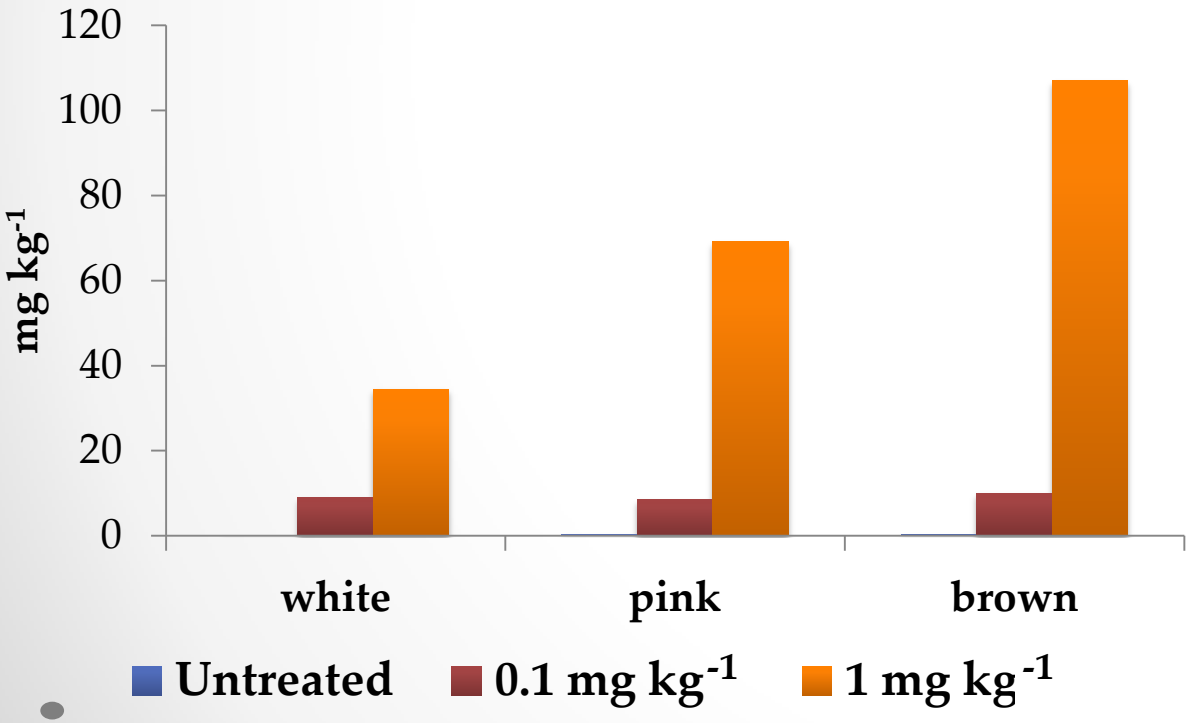


Bulk analyses

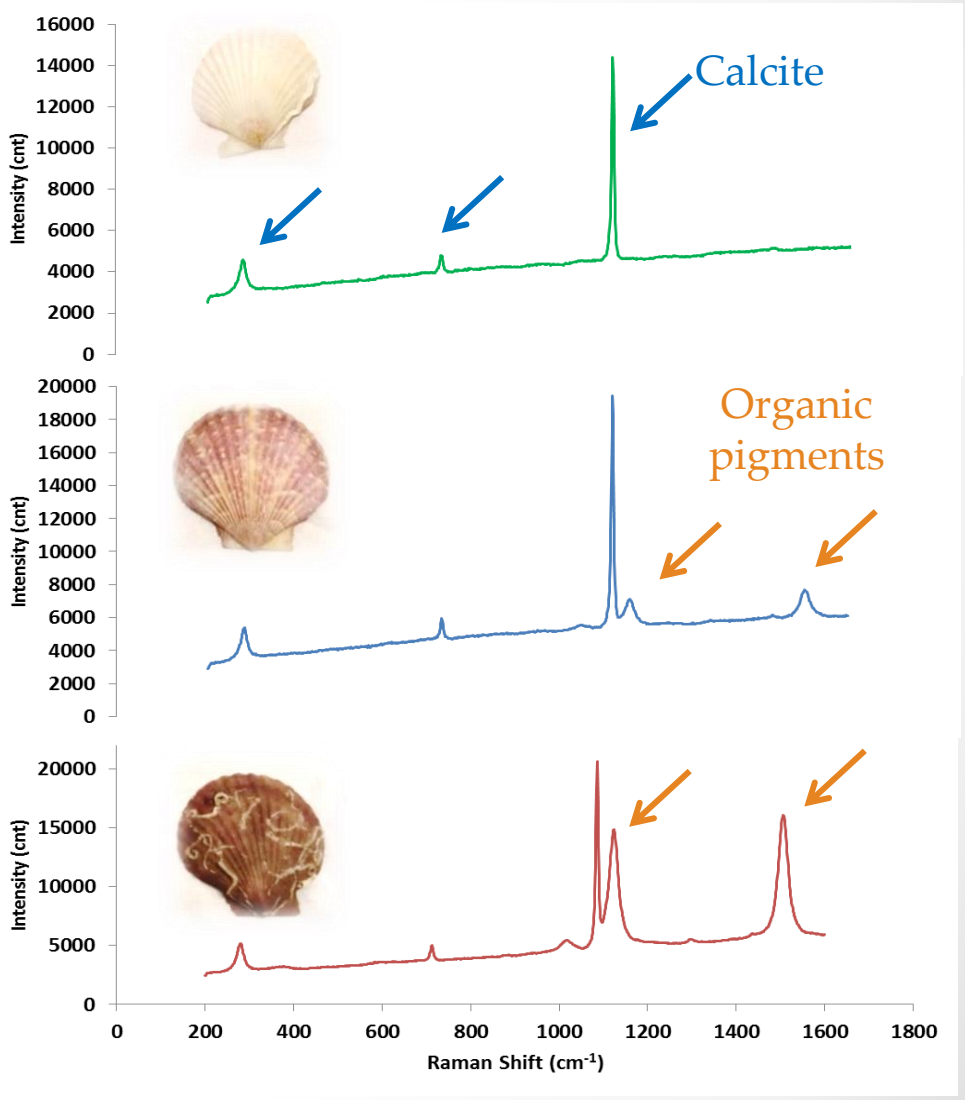
Digested in 10% HNO_3

Solution-based ICPMS

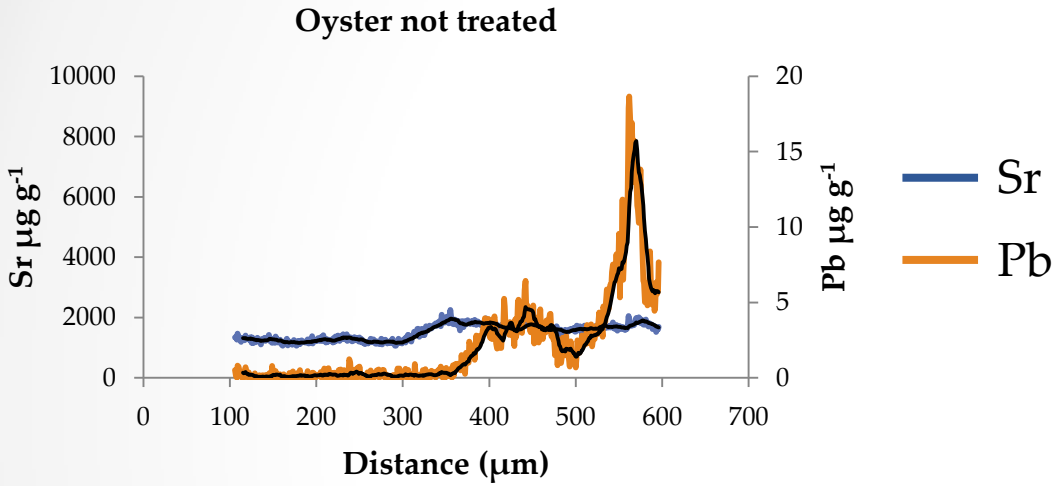
Cd uptake

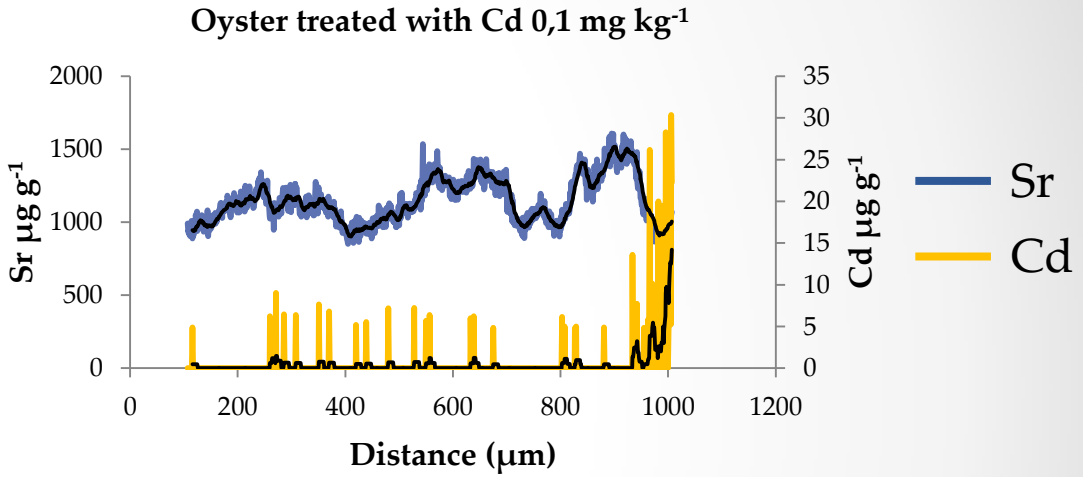


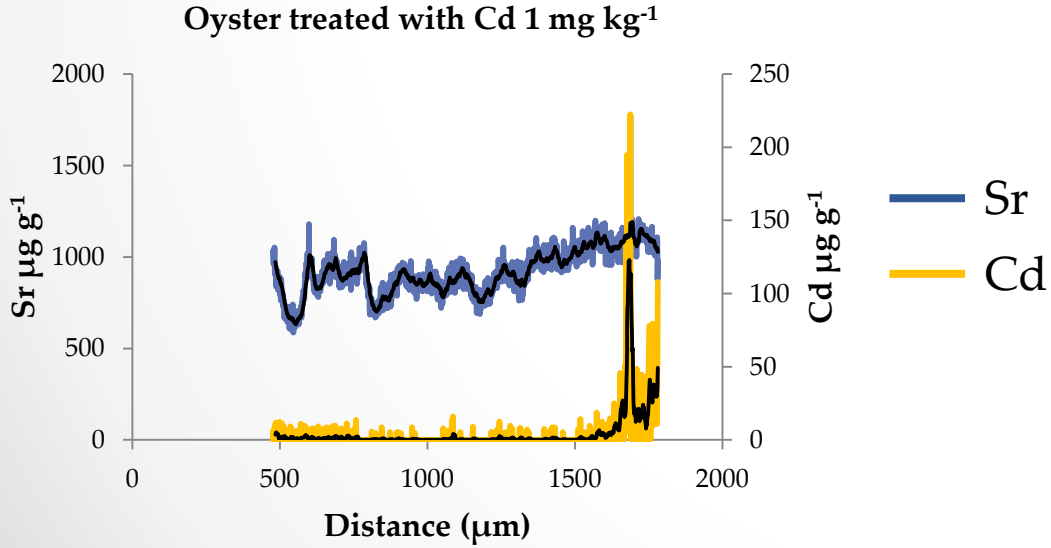
Micro Raman spectra

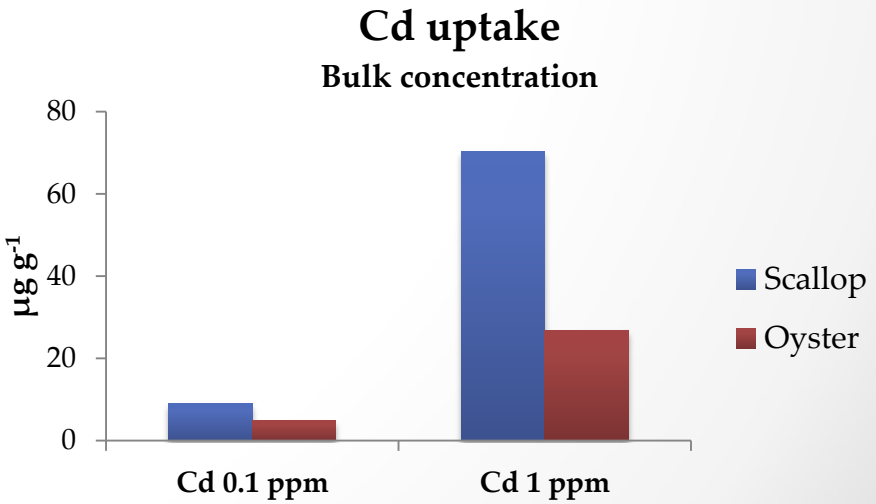


Cross section scanning
Concentration profiles









Conclusions

- LA-ICPMS prove to be a valid technique to evaluate the distribution of trace contaminants through the shell layers;
- Mollusk shells resulted good bio-indicators to evaluate metal contamination of the water environment;
- From the line scans concentration profiles it can be seen that cadmium is localized mainly on the surfaces of the shell, with little diffusion into the inner layers, result confirmed by 2D imaging;
- Brown scallop shells showed higher cadmium adsorption than pink and white ones, the different adsorption behaviour may be due to the presence of pigments in the more colored samples.
- Scallop shells show higher Cd adsorption efficiency than oyster shells.

Thank you for your kind attention