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EVALUATION OF THE USE OF GASTROPOD SHELLS AS BIOINDICATORS OF METAL CONTAMINATION IN RIVERS USING MASS SPECTROMETRY IMAGING TECHNIQUES

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INTRODUCTION

Gastropods are known to be sensitive to metal contamination and to have several characteristics to be a good bioindicator such as sessile, easy to collect and ubiquitous (Amorim *et al.*, 2019; Krupnova *et al.*, 2018; Rainbow, 2002). Up to now, most studies have focused on bivalves and the analysis of total metal concentrations in their soft bodies. Very few have explored their distribution or accumulation in shells. Mollusc shells grow throughout their life by integrating some of the chemical elements present in their environment, including metals. The objectives of this work are:

- 1) Assess the spatial distribution of metals within the shell using mass spectrometry imaging techniques
- 2) Determine how shell concentrations respond to metal chemistry in the environment

For this purpose, mass spectrometry imaging techniques are currently optimized to explore the variability of metals in shells at different spatial scales: Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS - nanoscale) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS - micrometer scale). Both methods are sensitive and provide the elemental (LA-ICP-MS) and molecular (TOF-SIMS) characterization of solids samples (Massonnet & Heeren, 2019; Russo *et al.*, 2002).

MATERIALS AND METHODS

For this purpose, 12 natives *Radix balthica* were collected in spring 2021 at different sites.

- 1) Pilots rivers (outdoor mesocosms) of TotalEnergies (Lacq, France) : water from the Gave de Pau (control).
- 2) Waste Water Treatment Plant (in the effluent, up- and downstream)

At each site, water was sampled (n=3) to be analyzed for their dissolved metal concentrations by ICP-MS, cations, anions and dissolved organic carbon. Also the physicochemical (pH, O₂, conductivity) were collected with a sensor HACH HQ40D.

Shell analysis (n=3 for each site and analysis)

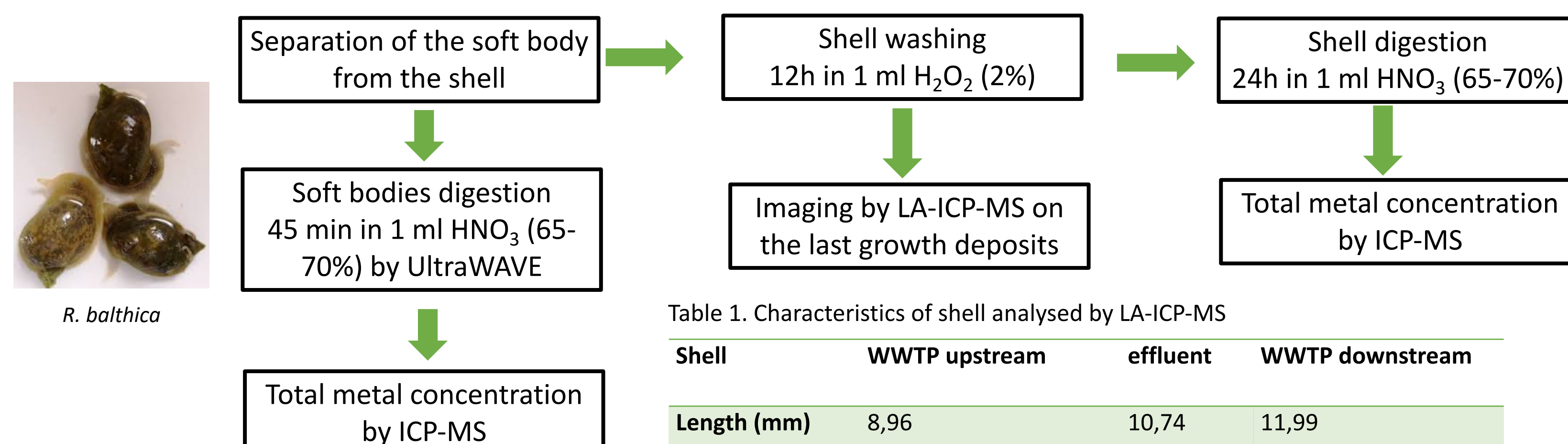


Table 1. Characteristics of shell analysed by LA-ICP-MS

Shell	WWTP upstream	effluent	WWTP downstream
Length (mm)	8,96	10,74	11,99
Width (mm)	6,24	7,43	7,97
Weight (mg)	28,8	43,2	90,6

RESULTS

1) Metals concentration in environment and organisms by ICP-MS

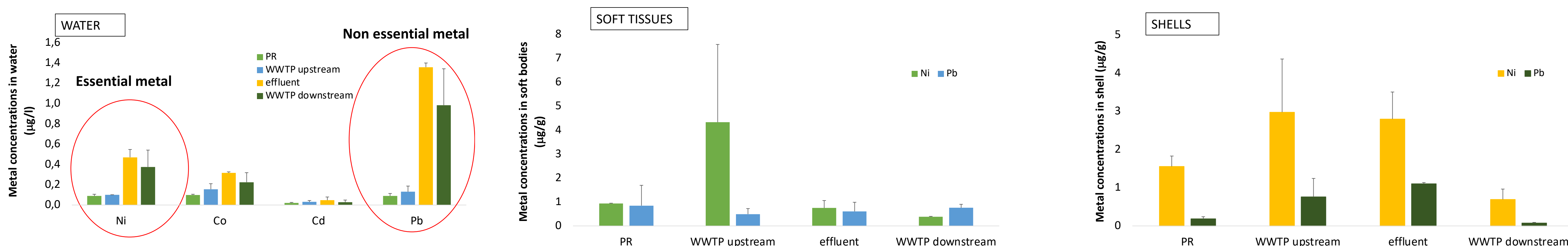


Figure 1. Metal concentrations in water, soft bodies and shells at the different studied sites : pilots rivers (PR) and at WWTP (upstream, effluent, downstream) analysed by ICP-MS.

- Increase in Ni, Co, Cd and Pb concentrations was observed in the effluent as compared to PR and upstream sites
- Ni and Pb were chosen to be studied in the shells by LA-ICP-MS as representative of essential and non-essential metal, respectively.

- Similar Pb concentration were found in the soft tissues of *R. balthica* collected at the 4 sampling sites
- Ni concentrations were higher in WWTP upstream than at the other 3 studied sites
- Comparable concentrations in soft tissues for both metals

- Ni concentrations in shells were similar among studied sites
- Pb concentrations were higher at the upstream site and effluent than at the PR and downstream site
- At all studied sites, higher Ni concentrations than Pb in shells

2) Metal distribution in shell by LA-ICP-MS

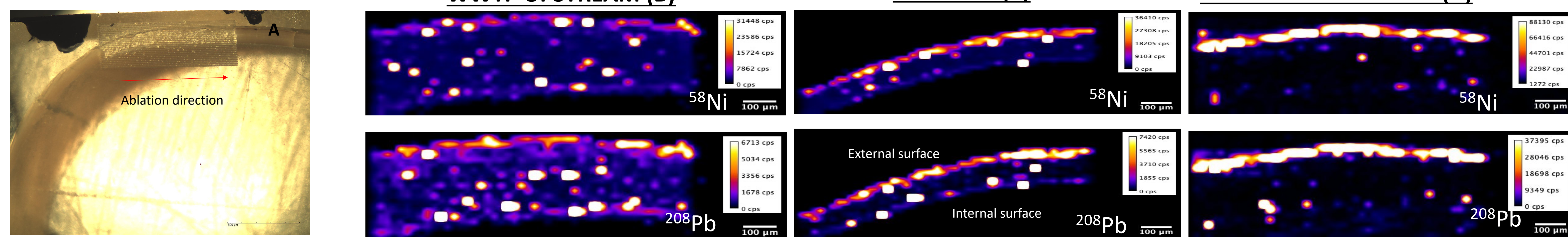


Figure 2. Picture of the ablation of the shell after analysis (A) and imaging obtained by ImageJ for Ni and Pb distribution in the last growth streaks of shell by count per second (cps) at the different studied sites of WWTP (upstream (B), effluent (C), downstream (D)) analysed by LA-ICP-MS

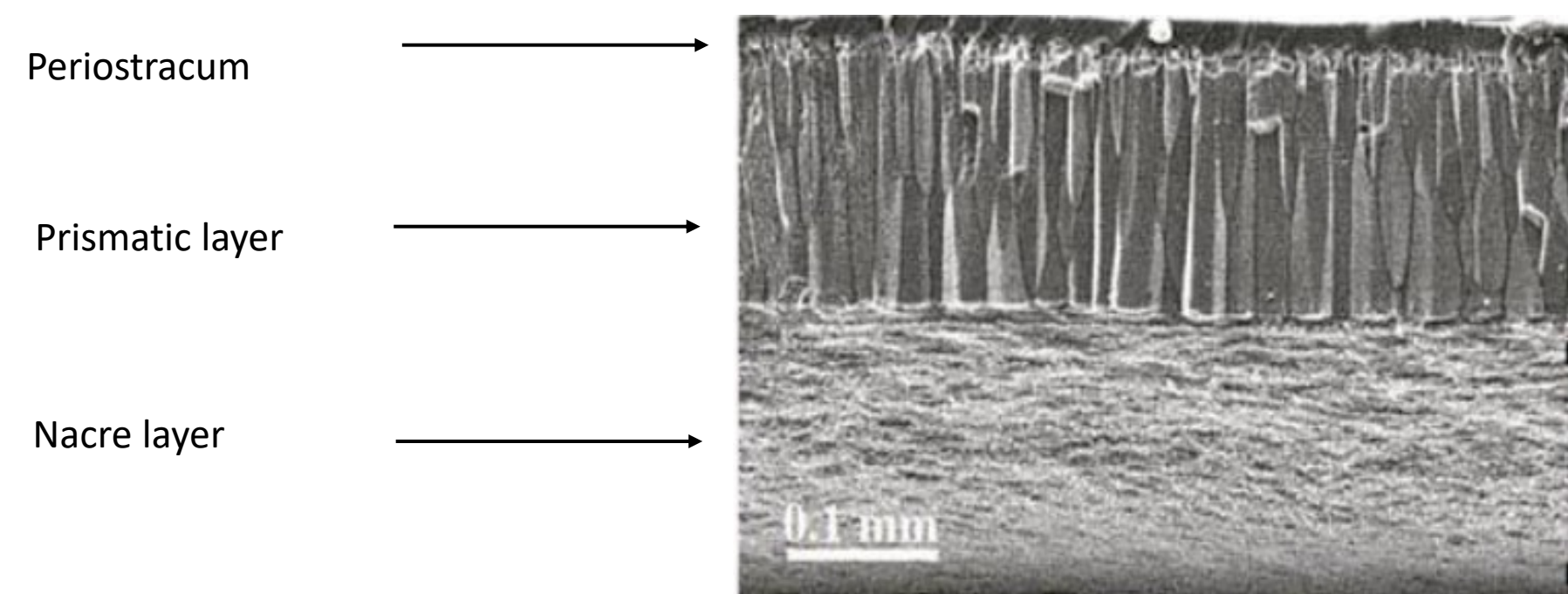


Figure 3. Microstructure of shell mollusc composed of three layers from external to internal : periostracum, prismatic and nacre layer (Checa, 2018)

- Pb and Ni poorly detected in the gastropod shells collected in WWTP upstream and effluent
- Pb and Ni detected mainly at the external surface of the shells in WWTP downstream : larger shell characteristics than at the 2 other studied sites (Table1)

CONCLUSION

- No relation was observed between dissolved metal concentrations in water and metal concentrations in soft bodies and shells: the influence of metal speciation in water, pH and major cations remains to be examined
- Higher concentrations (Fig1) of the essential metal Ni as compared to non essential metal Pb were measured in shell
- Ni and Pb were mainly located at the shell external surface : nature of this layer needs to be determined (further analysis with TOF-SIMS,MEB)

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