Sources and Transfer of Cu, Hg and Pb into Marine Food Webs using Innovative Tracers (Metal Stable Isotopes, Trophic Markers): Results of a Pilot Study in a French Coastal Area

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Abstract

Copper (Cu), mercury (Hg) and lead (Pb) are elements and contaminants of historical and emerging concerns in coastal environments. Although Cu is considered essential for living organisms, it is bioactive in a narrow range of optimal concentrations. Hg and Pb have no known biological role and are considered toxic towards organisms. Marine consumers incorporate and bioaccumulate these metals mainly through trophic pathways, which are then important to delineate. Since recently, metal stable isotopes are promising to trace origin and processes of the contamination of marine matrices, including biota.

As part of the present study conducted within the SCOTTTI and Pollusols programs, we merged integrated trophic markers (carbon and nitrogen stable isotopes, lipid profiles) and metal stable isotopes to investigate i) the trophic transfer of Cu, Hg and Pb within a model food web of a French human-impacted coastal area (Toulon Bay, NW Mediterranean); and ii) the potential sources of food web contamination. Whenever possible, samples included sediment, suspended organic matter, size fractions of plankton, filter-feeding bivalves (mussels, oysters) and planktivorous fishes, collected at different seasons. Metal- and species-specific patterns throughout the food web were observed, highlighting the role of biological/physiological processes on the observed metal levels and isotope distributions.

Keywords: trace elements; metal isotopes; trophic transfer; food web; NW Mediterranean Sea

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1. Introduction

The Toulon Bay (TB) in the NW Mediterranean Sea has long been documented as an historic site of anthropogenic contamination by trace metals, especially trapped in the sediment (Tessier et al. 2011). The water quality of TB is thus generally considered as poor, and many unknowns persist about the fate and the transfer of this contamination to marine organisms, especially filter-feeding bivalves (mussels, oysters) that are used as bioindicators of the coastal chemical contamination.

Here, we combined different proxies to trace as much as possible i) the trophic sources sustaining consumers in TB (through the analysis of carbon (C) and nitrogen (N) stable isotopes), as the trophic pathways are considered the main pathways for the uptake and incorporation of trace elements by consumers; ii) the potential sources of food web contamination (through the analysis of metal isotopes). Both essential/bioactive (i.e. copper – Cu) and non-essential (i.e. mercury – Hg and lead – Pb) elements were considered and compared.

2. Material and Methods

Samples of sediment, size fractions of plankton (20-60 µm, 60-200 µm, 200-500 µm, >500 µm), transplanted mussels (*Mytilus galloprovincialis*) and oysters (*Crassostrea gigas*), and white seabream juveniles (*Diplodus sargus*) were collected in the inner part of TB (i.e. in the Lazaret Bay) at one or two trimesters of the year 2018: T2 (between April and June) and/or T3 (between July and September).

Freeze-dried and homogenized samples were first analysed for their total Cu, Hg and Pb concentrations, by ICP-Q-MS on acid-digested samples for Cu and Pb, and by AAS on solid samples for Hg. Isotope analyses were then conducted on selected samples and after dedicated sample preparation for each element, by EA-IRMS for C and N isotopes, ICP-Q-MS for Pb isotopes, and MC-ICP-MS for Cu and Hg isotopes. Appropriate certified reference materials were used in analytical series.

3. Results and Discussion

Total Cu, Pb and Hg concentrations differ considerably between food web compartments (**Table 1**), especially Cu concentrations between bivalve species. Mussels are indeed well-documented to regulate this essential metal at a certain concentration, whereas oysters bioaccumulate Cu (Phillips and Yim 1981).

Seasonal variations are also observed, probably resulting from processes such as metal regulation and/or bioaccumulation overtime and/or biomass variations with reproduction, depending on metal and species.

Table 1. Ranges of total Cu, Pb and Hg concentrations (in mg/kg dry mass) in the different compartments.

Trimester	Compartment	[Cu]	[Hg]	[Pb]
T2	Sediment	29	1.34	40
	Plankton	74-133	0.88-1.68	34-48
	Mussels	7.3-8.4	0.55-0.58	4.7-5.9
	Oysters	584	0.42	2.6
	Seabream juv.	2.7-4.6	0.19-0.23	0.42-0.59
T3	Plankton	58-95	0.49-0.92	40-66
	Mussels	4.6	0.46	3.4
	Oysters	1129	0.84	2.6

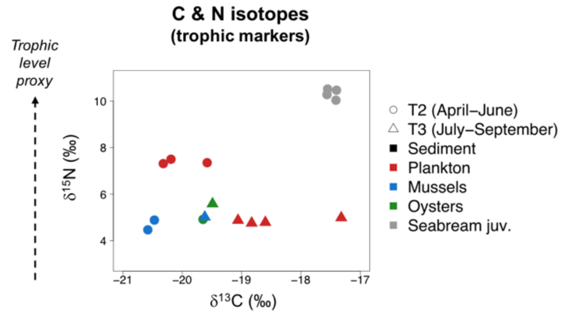

Figure 1: Results of C and N isotopes on selected samples.

Isotope results highlight:
- C & N isotopes (**Figure 1**): mussels and oysters feed on similar trophic sources, which do not correspond to the plankton sampled. Mussels and oysters indeed better assimilate lower size fractions of plankton (>5 µm, but probably <20-60 µm; Troost et al. 2009). Conversely, seabream juveniles actually feed on zooplankton and at higher trophic level than bivalves. These results were confirmed by lipid profiles (here not shown).
- Cu isotopes (**Figure 2**-A): the different signatures of mussels and seabream juveniles relative to sediment, plankton and oysters confirm a considerable Cu isotope fractionation due to the regulation of this essential metal by mussels and seabream juveniles. This should thus be taken into account when using Cu isotopes as potential tracer of Cu contamination.

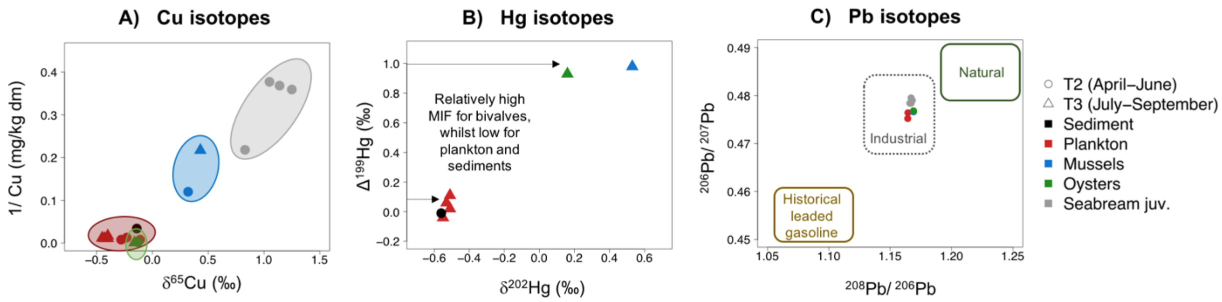

Figure 2. Results of metal isotopes on selected samples; A) Cu isotopes, B) Hg isotopes and C) Pb isotopes.

- Hg isotopes (**Figure 2**-B): signatures of bivalves differed from those of sediment and plankton, suggesting different sources of Hg or different extent of MeHg. The higher mass-independent fractionation (MIF, as revealed by Δ^{199}Hg) in bivalves exhibit a typical signature of marine MeHg, as expected for higher trophic level consumers (Feng et al. 2019).
- Pb isotopes (**Figure 2**-C): all food web compartments showed very similar signatures, corresponding most probably to industrial sources of Pb (Dang et al. 2015). Contrary to Cu, there was thus no evidence of isotope fractionation of this non-essential metal by biota, confirming their potential as tracers of Pb sources in the environment.

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