



^{210}Po and ^{210}Pb trophic transfer within the phytoplankton–zooplankton–anchovy/sardine food web: a case study from the Gulf of Lion (NW Mediterranean Sea)



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ABSTRACT

The transfer of ^{210}Po and ^{210}Pb in the food web of small pelagic fishes (from phytoplankton and zooplankton to anchovy *Engraulis encrasicolus* and sardine *Sardina pilchardus*) is investigated in the Gulf of Lion (GoL). We present original data of ^{210}Po and ^{210}Pb activity concentrations, C and N stable isotope ratios, measured (i) from different size classes of phytoplankton and zooplankton during spring and winter in different environments of the GoL, and (ii) in two fish species. Significant spatial patterns based on ^{210}Po , ^{210}Pb activity concentrations and $^{210}\text{Po}/^{210}\text{Pb}$ ratios in the different plankton size classes are evidenced by hierarchical clustering, both in spring and winter. This variability, also observed for C and N stable isotopes ratios, is connected to local specific pelagic habitats and hydrodynamics. The sampling strategy suggests that ^{210}Po bioaccumulation in the GoL remains at a constant level from the first (dominated by phytoplankton) to the second trophic level (zooplankton), while ^{210}Pb bioaccumulation shows an increase in winter. Based on stable N isotope ratios and ^{210}Po activity concentrations measured in anchovies and sardines, we evidence ^{210}Po bio-magnification along the trophic food web of these two planktivorous pelagic fishes.

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1. Introduction

Lead-210 (^{210}Pb , half-life: 22.4 yrs) and Polonium-210 (^{210}Po , half-life 138 days) are non-conservative natural radionuclides produced from the ^{238}U decay chain whose distribution and behavior in the ocean have been closely investigated to explore (i) marine particle fluxes/exchanges that are essential for contaminant transport and carbon cycling (Bacon et al., 1976, 1985; Moore and Dymond, 1988; Cochran et al., 1990; Radakovitch et al., 1999; Masqué et al., 2002) and (ii) for toxic reasons owing to ^{210}Po accumulation in marine organisms (e.g. Cherry and Shannon, 1974; Heyraud and Cherry, 1979) and health concerns via the radiation dose received by humans through fish and seafood ingestion

(e.g. Carvalho, 1995; Al-Masri et al., 2000). Many inquiries focus on ^{210}Po and ^{210}Pb accumulation in planktonic species at the bottom of the marine food chain that are essential for trapping and removing nutrients and abiotic particles in surface waters (e.g. review of Fowler, 2011) and in fishes (e.g. review of Carvalho, 2011; Stewart et al., 2008). Investigations on bioaccumulation across the food web mostly rely on laboratory experiments (Carvalho and Fowler, 1993, 1994; Stewart et al., 2005; Stewart and Fisher, 2003; Stewart et al., 2008), in particular to discriminate uptake from food ingestion (trophic transfer) and/or water. Zooplankton organisms play a major role in these pelagic food webs by transferring phytoplankton productivity to upper consumer levels like fishes (Saiz et al., 2007; Bănaru et al., 2013a) and allowing contaminants to accumulate from planktonic low-level organisms up to high-level predators in the pelagic food webs (Cossa et al., 2012). Carvalho (2011) notes that both ^{210}Po activity concentrations and $^{210}\text{Po}/^{210}\text{Pb}$ ratio may depend upon the number of trophic levels in

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the food chain, and suggested that enhancement of ^{210}Po activity concentrations is very pronounced in small zooplankton feeding upon bacteria and phytoplankton. However, the amplitude of this enrichment varies widely because of its reliance on numerous parameters such as food type, taxonomic composition, assimilation efficiency or trophic conditions (Fowler, 2011; Jeffree and Szymczak, 2000). Due to such variations, Fowler (2011) concludes in a review that “additional effort is needed to expand the database on ^{210}Po levels in different phytoplankton groups with the corresponding second trophic level zooplankton samples to which they are being compared”. He also underlines that “more detailed ^{210}Po analyses of pelagic organisms within well-defined food chains sampled from the same water mass will help clarify some of the trophic level differences in ^{210}Po noted in previous studies”.

Here we examine the transfer of ^{210}Po and ^{210}Pb in the food webs of small pelagic fishes in the Gulf of Lion (hereafter GoL) as part of the COSTAS ANR-program (Contaminants in the trophic system: phytoplankton, zooplankton, anchovy, sardine). This multidisciplinary program aims at studying organic (PCB and PBDE) and inorganic (trace metals, ^{210}Po and ^{210}Pb) contaminant transfer within the food webs of two dominant planktivorous teleosts, the sardine, *Sardina pilchardus*, and the European anchovy, *Engraulis encrasicolus*, two species that rely entirely on planktonic food resources (Costalago et al., 2012). Stable isotope ratios of carbon and nitrogen have been widely used to analyze marine food webs and determine the trophic level of organisms (Fry and Sherr, 1984; Costalago et al., 2012). They represent also a precious tool to investigate contaminant biomagnification along food webs (Cossa et al., 2012; Harmelin-Vivien et al., 2012). We present ^{210}Po and ^{210}Pb activities as well as C and N stable isotope ratios measured in the GoL from (i) various size classes of phytoplankton and zooplankton in spring and winter and (ii) sardines and anchovies fished during spring.

Our purpose is to (i) investigate seasonal and spatial variability of ^{210}Po and ^{210}Pb activities in plankton in the GoL, (ii) determine ^{210}Po and ^{210}Pb bio-accumulation from phytoplankton to zooplankton trophic levels and (iii) define ^{210}Po bio-magnification from plankton to fishes thus providing a rare opportunity to compare in situ measurements to experimental data.

2. Materials and methods

2.1. Study area

The Gulf of Lion (GoL), in the northwestern Mediterranean Sea, presents complex hydrological dynamic patterns defined by: (i) the cyclonic Northern Current that flows along the continental slope, (ii) a combination of wind-driven processes such as coastal upwelling and dense shelf water formation and (iii) freshwater dynamics associated with the large Rhone River discharge (Millot, 1999). The Rhone River has the largest mean annual discharge ($1700 \text{ m}^3 \text{ s}^{-1}$) in the Western Mediterranean basin. It is responsible for 83% of the suspended particulate matter flux to the French Mediterranean coast (Gairoard et al., 2012) and 50% of the primary production of the GoL (Lochet and Leveau, 1990). The very low tidal range in the Mediterranean allows the Rhone riverine plume to expand westward into the GoL. This plume is particularly evidenced in the first two meters of the water column (Lorthiois et al., 2012). The influence of suspended particulate matter (SPM) from the Rhone River on both surface water and sediment is observed westward all over the gulf area (Durrieu de Madron et al., 2000; Espinasse et al., 2014a).

In the GoL, the diversity of zooplankton communities is generally lower in coastal waters than offshore while its biomass is higher near the coast due to riverine inputs of nutrients

(Champalbert, 1996; Gaudy et al., 2003). Different zooplankton habitats are distinguished based on both biological (species composition, size structure) and physical (depth, salinity, wind, currents) variables (Espinasse et al., 2014a). Phytoplankton and zooplankton communities display conspicuous seasonal variations of composition and structure that are reflected in their related isotopic signatures (Harmelin-Vivien et al., 2008; Bănară et al., 2013a; Espinasse et al., 2014a,b). Phytoplankton spring bloom generally occurs from March to June in the GoL (Alekseenko et al., 2014).

2.2. Sampling and handling

2.2.1. Seawater, SPM and plankton

Seawater, SPM and plankton were sampled in May 2010 and February 2011 onboard RV “L’Europe” in the GoL, at seven sites along an east–west transect (Fig. 1). A chlorophyll-*a* (Chl-*a*) concentration profile was obtained at each sampling site using a CTD probe fitted to a fluorimeter to determine the maximum Chl-*a* concentration depth at which further sampling was performed. Seawater was pumped at Chl-*a* maximum using a Teflon coated pump system and was directly filtered through a $0.45 \mu\text{m}$ pre-weighed cellulose acetate filter in a trace metal dedicated laboratory under laminar flow clean hoods. The Chl-*a* maximum depth was always observed below the river SPM plume near the Rhône River (ST2), suggesting low particle content for samples collected at this location and depth. Filtered seawater was acidified with HCl at pH 2 and kept at 4°C in the dark in acid-cleaned LDPE 1.5 L bottles. Filters were also kept at 4°C for SPM analysis. To obtain a sufficient amount of SPM, 10–15 L of seawater were filtered. Plankton was collected by two means according to particle size: pumping or trawling. Small plankton organisms were sampled by pumping seawater *in-situ* at the Chl-*a* maximum depth with a 8 cm diameter tubing and filtered onboard through $200 \mu\text{m}$, $60 \mu\text{m}$ and $6 \mu\text{m}$ mesh size plankton nets (see Harmelin-Vivien et al., 2008 for more details). Two small plankton size fractions were retained (i.e. $[6–60 \mu\text{m}]$ and $[60–200 \mu\text{m}]$). The trawling system used to get larger plankton organisms ($200 \mu\text{m}$ mesh) was towed at 2–3 knots during 30 min near the Chl-*a* maximum depth. The samples were immediately sieved onboard in our trace metal laboratory through four different filter meshes: $2000 \mu\text{m}$, $1000 \mu\text{m}$, $500 \mu\text{m}$ and $200 \mu\text{m}$. We obtained four large plankton fractions: $[200–500 \mu\text{m}]$, $[500–1000 \mu\text{m}]$, $[1000–2000 \mu\text{m}]$ and $[>2000 \mu\text{m}]$ that were kept in acid pre-cleaned PE tubes and frozen at -18°C onboard the ship. These fractions were then freeze-dried and kept in the dark at room temperature in the laboratory. An aliquot of each plankton fraction was kept apart for stable isotope analysis.

2.2.2. Anchovies and sardines

Anchovies (*E. encrasicolus*) and sardines (*S. pilchardus*) were collected in March 2011 by professional fishermen in two areas of the GoL corresponding to eastern and western zooplankton stations (Fig. 1). Fishes (anchovies $n = 26$ and sardines $n = 8$) were dissected to extract muscles, liver, gonads and the body remains (i.e. skin, head and skeleton). Fishes samples were pooled by area according to species and organs, in order to gather enough material for analyses. All dissected fishes were 10–13 cm long in total length (TL). The time lag of one month between plankton and fish sampling in 2011 (due to the availability of the research vessel) does not modify data interpretation for stable isotope signatures, since the time of integration of prey into fish muscles ranges from 1 to 3 months (Maruyama et al., 2001; Guelinkx et al., 2007). It also do not modify data interpretation for ^{210}Po as its biological half life varied from 40 days in living organisms (ICRP, 1968) to 35 days in phytoplankton (Stewart and Fisher, 2003).

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