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The trophic transfer of persistent pollutants (HCB, DDTs, PCBs) within polar marine food webs

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HIGHLIGHTS

- The trophic web in Antarctica was longer but more depleted than the sub-Arctic one.
- The Trophic Magnification Factor was larger in Antarctic than the sub-Arctic areas.
- Biomagnification seems to be less important than bioconcentration.
- PCB residue was mostly made up by congeners with a lower biomagnification potential.
- HCB levels were similar in polar organisms and no biomagnification occurred.

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ABSTRACT

Biomagnification (increase in contaminant concentrations at successively higher levels of trophic web), is a process that can transversally impair biodiversity and human health. Most research shows that biomagnification should be higher at poles with northern sites having a major tendency to biomagnify Persistent Organic Pollutants (POPs) through their marine food webs. We investigated the biomagnification degree into two marine trophic webs combining carbon and nitrogen stable isotopes and POP analyses. We showed that the Antarctic trophic web was more depleted than the sub-Arctic one and the differences highlighted for the basal part could explain the difference in length between them. Concentrations of polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), and *p,p'*-DDE were of the same order of magnitude in the two polar trophic webs, with some values surprisingly higher in the Antarctic than sub-arctic organisms: PCBs ranged (average ± standard deviation) 1.10 ± 0.39 −12.93 ± 7.62, HCB <0.10−7.28 ± 5.32, and *p,p'*-DDE 0.52 ± 0.18−11.36 ± 5.3 ng/g wet weight (wt) in the Antarctic organisms, and 0.53−5.08, <0.10−1.48, and 0.27 ± 0.35−5.46 ± 1.73 ng/g wet wt, respectively, in the sub-Arctic ones. The contribution of tetra- and penta-CBs to the ∑PCBs was 10−65% in the Antarctic species and 15−45% in the Arctic species. The relationships between POPs and trophic levels, and the information obtained by the Trophic Magnification Factor revealed that the Antarctic trophic web had a greater tendency to biomagnify PCBs and *p,p'*-DDE than its sub-Arctic counterpart. POP availability in the environment and specific ecological features may play an important role in the bioaccumulation, and biomagnification is apparently less important than bioconcentration.

1. Introduction

Persistent organic pollutants (POPs) such as hexachlorobenzene (HCB), *p,p'*-DDE (main abiotic and biotic degradation product of the DDT-based pesticide) and polychlorinated biphenyls (PCBs) are some of the most widespread dispersed organohalogenated contaminants (SC, 2004). POPs include several groups of chemicals with similar structures and physical-chemical properties that elicit similar toxic effects (SC, 2004). They have been used extensively worldwide in agricultural (e.g. pesticides), industrial and health applications. All these chemicals are synthetic, ubiquitous, hydrophobic and persistent as their environmental half-life ranges from years to several decades or more. They are semi-volatile and display high chemical and thermal stability, and high resistance to biodegradation. POPs undergo Long Range Atmospheric Transport (LRAT) and deposition in the open sea (Wania and Mackay, 1993;

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Wania, 2003) and can be transported and then detected in polar habitats (e.g. Cincinelli et al., 2009; Corsolini, 2009; Rigét et al., 2010; de Wit et al., 2010; Muir and de Wit, 2010; Pozo et al., in press). The degradation turnover of deposited POPs is very slow in Polar Regions due to several factors including the low temperatures and winter darkness (EPA, 2002; Mangano et al., 2017), which can affect the degradation mechanisms. Ice entraps POPs and releases them into the environment, when it melts, allowing them to enter the trophic webs (TWs), bioaccumulate in the tissues of organisms (being lipophilic, they are stored in the lipid component of tissue) and thereby canalize through food webs by means of biomagnification (Corsolini, 2009; Corsolini et al., 2014). These processes are driven by many physical, chemical, biological and ecological factors. The main POP entrance in trophic webs is through phytoplankton relying on inorganic nutrients in the water mass and the melting of pack ice; phytoplankton is consumed by krill and other zooplankton, predated by fish (including the Antarctic silverfish) and marine birds and mammals through prey-predator relationships. Bioaccumulation is a complex process and, aside from biological and ecological factors, can be affected by local, regional and global mechanisms, POPs being prone to LRAT and to the effects of climate change (their transport and distribution depend on climate conditions, Wania and Mackay, 1993). Determining POP trophic transfer is necessary to better address exposure and risk to the little-known Ross Sea - and generally polar - trophic webs. To investigate it, however we need to fix the trophic position of every species within a food web (Post, 2002) and then assess the POP biomagnification (Fisk et al., 2001).

Stable isotope analysis (SIA) represents a useful tool for gaining information on the structure of trophic webs, prey-predator relationships, and the nature of trophic relationships among levels (Bearhop et al., 1999; Layman et al., 2007; Newsome et al., 2007; Azevedo-Silva et al., 2016). In combination with POP concentration in the organism tissues, we can generate powerful inference on their distribution in organisms, making the study of flows through trophic levels highly informative. Such an approach has produced effective and large amount of information on biomagnification for many food webs (Mangano et al., 2017), in estuarine (e.g. Bodin et al., 2014), temperate (e.g. Corsolini et al., 2007), polar (e.g. Kruse et al., 2015; Reuss et al., 2013) and freshwater (Azevedo-Silva et al., 2016) ecosystems. Overall, most studies revealed that once the trophic position is fixed into a trophic web, most POPs are seen to reach the highest concentrations at upper level (biomagnification) affecting top predators and often generating cases of human health concerns (Bodin et al., 2014).

Polar regions represent sensitive case studies: their trophic webs are characterized by few trophic levels and most of the organisms depend on few key-species. Polar organisms are usually exposed to different levels and patterns of POPs and the evaluation of their concentrations in tissues provides information on the extent of contamination in these remote areas of the globe. The effect of contaminants on polar marine species is further complicated: they have a greater lipid content than temperate or tropical species, which makes them more vulnerable due to the accumulation of persistent, lipophilic, toxic contaminants. Example from the Arctic where POPs can be detected at high-risky levels in top predators, comprise e.g. glaucous gull *Larus hyperboreus* (Verreault et al., 2010), and East Greenland, Svalbard and Hudson Bay polar bears, Alaskan and Northern Norway killer whales, several species of gulls and other seabirds from the Svalbard area, Northern Norway, East Greenland, the Eastern Russian Arctic and/or the Canadian central high Arctic, East Greenland ringed seal and a few populations of arctic char and Greenland shark (Letcher et al., 2010). The exposure threshold of sensitive effects risk for any given organohalogenated contaminant in an Arctic organism was suggested to be 1 ppm level in any target tissue, body compartment or egg as bioindicator of higher risk of a harmful impact on health (Letcher et al., 2010). Such an effect on top predators is seen as the main cause of key-species population decline, able to generate negative impacts on the marine ecosystems (*sensu* Mangano and Sarà, 2017). Thus, it appears crucial to understand the POP transfer mechanisms, as this may increase our ability to preserve the biodiversity and human health (AMAP, 2014).

With this in mind, our main aim was to investigate the POP transfer in two Polar Regions: the Ross Sea in Antarctica and the Icelandic sub-Arctic seawaters. The specific aims were: (i) to investigate the trophic web structure of an Antarctic and a sub-Arctic community by means of SIA, (ii) to assess POP contamination in the organisms from any selected trophic web, (iii) to correlate data from the ecological and ecotoxicological studies and lastly (iv) to assess POP biomagnification in the two polar food webs by providing a correlation between POP concentrations in organisms and their respective trophic positions. To the best of our knowledge, the influence of the organism trophic position on POP biomagnification within a quantified marine food web have not been addressed in the Ross Sea ecosystem. The expectations of this study were to evaluate the basic structure of this polar marine food web (excluding marine birds and mammals) and assess its relationship with the POP biomagnification. Moreover, the comparison with a food web of another extreme cold marine environment, the Icelandic seawaters, would help to assess whether POP concentration was due to the peculiarity of the Antarctic ecosystems, to differences in trophic status, or regional contamination.

2. Material and methods

Study sites and sample collection. The relevant species from the two different polar trophic webs were selected for comparisons upon a systematic review approach (Mangano et al., 2017), and data provided by an open access database (www.fishbase.org).

The studied Antarctic and Arctic species are demersal, bathypelagic, or pelagic (Table S1). Samples were collected from Antarctic and sub-Arctic sites during the 2004–2006 field seasons. Samples were analyzed individually or pooled, depending on the species and sample amount availability; 3–20 individuals per pool were used.

Ross Sea, Antarctica. Vertebrates and invertebrates from coastal food webs (see Table S1 for the list of species collected) were collected in the Antarctic summer (December–January), during campaigns carried out in the Ross Sea, south and west of the Italian "Mario Zucchelli" Scientific Station (74°42′00″S, 164°08′40″E), and the sea depth at the sampling site was 150 m ca. The isobath of 1000 m was used as a limit separating the continental shelf and the open ocean. Samples of *Euphausia sp.* and amphipods were caught by the Plankton Hamburg Net (fishing depth 100–500 m) during an expedition in the Ross Sea onboard of the R/V Italica. The temperature in the shelf waters was around −1.8 °C and salinity was 34 PSU (g/kg) (Fusco et al., 2009) although it was higher in the western sector due to the permanent presence of the Terra Nova Bay polynia (Kurtz and Bromwich, 1983; for more details see: www.morsea.uniparthenope.it).

Iceland, Sub-Arctic region. The study area comprised by many sites off the coasts of South and West Iceland (between 64° and 65° N; and between 21° and 23° W). Depth did not exceed 100 m, salinity was ~35 PSU (g/kg), and seawater temperature ranged from 2° to 9 °C. Further details about physical and chemical features of the Icelandic waters are described in Jakobsson and Stefánsson (1998). Samples were collected during a two-week period in autumn 2004 from landings stored in the fish market of Sandgerdi and Arnarstapi or directly during fishing cruises with the fishing