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Fingerprint of persistent organic pollutants in tissues of Antarctic notothenioid fish

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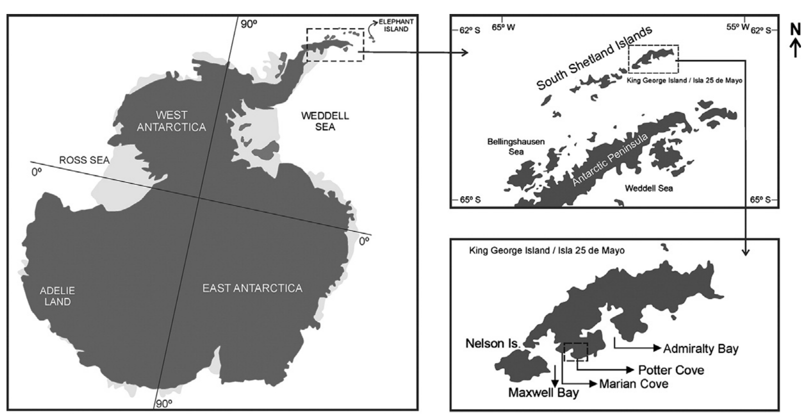
HIGHLIGHTS

- POPs levels and tissue distribution in Antarctic notothenioid fish
- *Trematomus newnesi*, *Notothenia coriiceps* and *Notothenia rossii* analyzed for POPs
- This is the first report on POPs levels in the Antarctic notothenioid *Trematomus newnesi*.
- Gonads and gills of analyzed specimens presented the highest levels of studied POPs.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and metabolites, polybrominated diphenyl ethers (PBDEs), and hexachlorocyclohexane (HCH) were analyzed in three Antarctic notothenioids fish species: *Trematomus newnesi* (TRN), *Notothenia coriiceps* (NOC) and *Notothenia rossii* (NOR). The contribution of each POP-family to the total load was as follows: ΣPCB (40%) > ΣDDT (27%) > ΣPBDEs (23%) > ΣHCH (10%). Among the 23 PCB congeners analyzed, *penta*-CBs homologues were the prevalent group, followed by *hexa*-CBs and *hepta*-CBs. DDT and its metabolites presented the following trend: *p,p′*-DDT > *p,p′*-DDE ~ *p,p′*-DDD. PBDE profile was dominated by BDE-47 and BDE-99 congeners, followed by BDE-100 > BDE-28 > BDE-154, BDE-153. Among HCHs, the γ-HCH isomer was detected in all samples, constituting 69% total HCH load, while α-HCH and β-HCH contributions were 15% and 16%, respectively.

The levels of POPs reported here suggest that NOR and NOC are more susceptible to accumulate the analyzed contaminants than TRN, a species not previously analyzed for POPs.

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Distribution of POPs among different tissues of the three species (muscle, liver, gonads, and gills) was also investigated. Considering lipid weight, the general pattern of POPs distribution in tissues indicated that while gonads showed higher levels of PCBs, DDTs and HCH, the most significant PBDE concentrations were recorded in gills. Also, a comparative analysis of POPs concentration in fish samples from Antarctic area was included.

1. Introduction

Although the human presence in Antarctica is low, with relatively little impact of wastewater and solid waste, the anthropogenic effect on the ecosystem has increased progressively, mainly through the commercial fishery of living resources such as finfish and krill (Ainley and Pauly, 2014; Kock, 1992). Contamination with persistent organic pollutants (POPs) was documented in the region since 1960s (Sladen et al., 1966; Tatton and Ruzicka, 1967). Due to their physicochemical properties and low decomposition rate, POPs like polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) are transported over long distances and/or widely dispersed into the environment after released. Transport of POPs can be accomplished through atmospheric and/or water flows as a gas phase and/or associated to particulate matter. Previous reports demonstrated that POPs associated with organic particles are transported by sedimentation from the pelagic zone to the sea-bed (Wania and Daly, 2002).

Cold condensation and global fractionation were proposed as the main mechanisms whereby POPs reach polar locations (Wania and Mackay, 1996). In this way, the more volatile POPs, such as HCH and low-PCBs reach polar regions in a higher rate than the less volatiles ones (highly halogenated PCBs, PBDEs and DDT) (Paasivirta et al., 1999). The combination of environmental conditions and physicochemical properties of POPs makes Antarctica to be a sink for such type of compounds (Wania and Mackay, 1996). Cold-adapted species present a slower metabolism, resulting in a slowdown of biological processes including growth and reproduction (Bargagli, 2005). This adaptation to cold environments can affect the fish's ability to detoxify or remove pollutants from its body which, added to the storage of lipids as an energy source, favor the bioaccumulation of hydrophobic chemicals during the Antarctic fish lifespan (Goutte et al., 2013). These factors also have significant influence on POPs biomagnification within the Antarctic food webs (Corsolini et al., 2006).

Antarctic fish constitute an important link of marine Antarctic food webs because they prey on a variety of benthic, epibenthic and planktonic organisms and are preyed by squids, other fish, penguins, flying sea birds, seals and whales (Barrera-Oro, 2002). Among fish, the suborder Notothenioidei is an endemic coastal demersal group, which includes six dominant families in terms of diversity (35%) and biomass (Kock and Kellermann, 1991). Based on their feeding strategies and their relevance to the marine environment under analysis (Barrera-Oro, 2003), three different species of the family Nototheniidae, *Trematomus newnesi* (TRN), *Notothenia coriiceps* (NOC) and *Notothenia rossii* (NOR), were selected for the present study. TRN is found in the permanent and seasonal packed-ice zones around Antarctica and adjacent islands. It is a benthos and plankton feeder, with benthic and benthopelagic habits (Eastman and Barrera Oro, 2010). NOC inhabits different areas of the same ichthyofaunistic subregion in the Atlantic Ocean sector, Southern Indian Ocean sector and High Antarctic Zone (Barrera-Oro, 2002). This fish species is euriphagous and changes its diet seasonally according to prey availability. It is a benthos feeder, with benthic and epibenthic habits. NOR inhabits the Scotia Arc, the western Antarctic Peninsula and circum-Antarctic waters of sub-Antarctic islands (Barrera-Oro, 2002). It is a benthos and plankton feeder and is characterized by offshore–inshore migrations in its life cycle. During its juvenile stage, NOR feeds on benthos, epibenthos, plankton and nekton (Casaux et al., 1990). It migrates then offshore to join the adult population, and feeds primarily on krill (*Euphausia superba*) and fish (Barrera-Oro, 2002; Casaux et al., 1990).

It is know that POPs and metabolites present different degradation rates, as well as accumulation patterns among tissues, depending on their chemical structures and/or the metabolic system involved (Cipro et al., 2010; Ondarza et al., 2011; Tanabe et al., 1997). However, contaminants tissues distribution pattern not only are conditioned by the physicochemical properties of POPs and its major metabolites, but also by the biology and ecology of fish (Mormede and Davies, 2003; Storelli et al., 2009). Considering the feeding habits of the fish studied in this work, NOR and TRN species, both ephibentic and semipelagic water column feeders, it is possible to hypothesize that POPs and major metabolites should have a comparable pattern of accumulation in these two species. Furthermore, this accumulation pattern would likely be different in NOC, a mainly benthos feeder with a wide trophic spectrum. Although the number of NOC samples is low, our expected results could be taken as indicative.

In the present work the occurrence, distribution and isomeric profiles of target POPs, including PCBs, PBDEs, HCH, and DDT, and main metabolites, were investigated in three Antarctic notothenioid species: TRN, NOC and NOR. Additionally, distribution of the mentioned contaminants in tissues such as muscle, liver, gonads, and gills was evaluated to find target organs. This is the first report about these POPs groups and metabolites in TRN specimens.

2. Materials and methods

2.1. Reagents and materials

The following compounds were included in the analysis: 23 PCB congeners (*penta*-CB: 99, 101, 105, 118; *hexa*-CB: 128, 138, 146, 149, 151, 153, 156; *hepta*-CB: 170, 171, 174, 177, 180, 183, 187; *octa*-CB: 194, 195, 199; *nona*-CB:206; *deca*-CB: 209), 7 PBDE congeners (nos: 28, 47, 99, 100, 153, 154, 183), HCH isomers (α-, β-, γ-), and DDT and metabolites (*p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *p,p′*-DDT). Abbreviations are expressed as follows: ΣPCB as the sum of the 23 congeners, ΣDDT as the sum of the 4 compounds, ΣPBDEs as the sum of the 7 congeners and ΣHCH as the sum of the 3 isomers.

Individual PCB, HCH and DDT standards were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). PBDE standard mixtures were purchased from Wellington Laboratories (Guelph, Ontario, Canada). General reagents, such as acetone, n-hexane, dichloromethane (DCM), isooctane (all pesticide grade), and sulfuric acid (analytical grade) were purchased from Merck (Darmstadt, Germany). Silica gel 60 (63–230 mesh) and anhydrous Na_2SO_4 (Merck, Germany) were pre-washed with hexane aliquots and dried afterward. Before use, silica gel and Na_2SO_4 were heated at 150 °C for 24 h. Extraction thimbles were pre-extracted (1 h) with the solvent-extraction mixture used for the samples and dried at 100 °C for 1 h.

2.2. Collection, preservation of samples, and biometric determinations

Specimens of TRN (n = 21), NOC (n = 2), and NOR (n = 8) were collected during summer campaigns from year 2008 to 2011 at Potter Cove, King George Island/Isla 25 de Mayo, South Shetland Islands, close to the Scientific Station Carlini – formerly Jubany Station – (62°14′ S; 58°40′ W). Trammel nets (length 25, 35 and 50 m; width 1.5 m; inner mesh 2.5 cm; outer mesh 12 cm) were set for 6–96 h at