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Butyltin contamination in Northern Chilean coast: Is there a potential risk for consumers?

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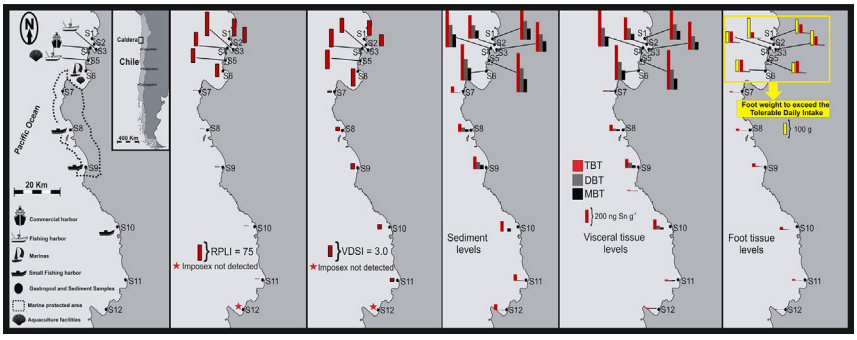
HIGHLIGHTS

- Imposex and TBT levels were analyzed in sediments and edible gastropod tissues.
- High contamination levels and evidences of fresh inputs of TBT were detected.
- TBT contaminated sites were located within "Isla Grande Atacama" marine reserve.
- The ingestion of *Thaisella chocolata* foots from the most contaminated sites is not safe.
- Regulatory actions to protect environment and food safety should be implemented.

GRAPHICAL ABSTRACT



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ABSTRACT

Imposex is the superimposition of non-functional male sex organs in gastropod females. This syndrome is a hormonal imbalance induced by tributyltin (TBT) which have been used in antifouling paints formulation. The present study aimed to perform an integrated environmental assessment of imposex and butyltin (BT) contamination using surface sediments and tissues of *Thaisella chocolata* (an edible gastropod) from northern Chile. The results showed imposex incidence in 11 out of 12 sites. In the most contaminated sites, which are areas under the influence of maritime activities, and also used for fishing and aquaculture, RPLI were over 60 and VDSI over 4 (high incidence of sterile females). Exceptionally high contamination levels and evidences of fresh inputs of tributyltin (TBT) were detected along the studied area. TBT levels above 300 and 90 ng Sn g^{-1}, respectively, were recorded in sediments and edible gastropod tissues of 6 sites. Thus, a daily ingestion of 90 to 173 g of *T. chocolata* foot (4 to 8 organisms) from the most contaminated sites will certainly lead to the consumption of BT exceeding the tolerable daily intake recommended by European Food Safety Authority. It is reasonable to consider that human risk is even higher if daily consumption of additional seafood is considered. Moreover, some contaminated sites were located within the marine reserve "Isla Grande Atacama", indicating that even marine protected areas are under the influence of TBT contamination. These findings suggest that current levels of TBT in the studied area

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are sufficient to induce harmful effects on the environment and constitutes a potential threat to seafood consumers. Thus, national regulatory actions toward environmental protection and food safety of local populations are still mandatory, even after 8 years of the TBT global ban by IMO.

1. Introduction

Tributyltin-based antifouling paints are used since 1960's as protective coatings on hulls of ships and boats (Almeida et al., 2007; Castro et al., 2011). Although they are very effective to prevent and minimize establishment of fouling, these products are highly toxic for non-target species (Laranjeiro et al., 2015; Lopes-dos-Santos et al., 2014). Several studies reported deleterious effects of tributyltin (TBT) on the wildlife, including imposex (imposition of male sexual organs on females) in gastropod species (Blaber, 1970; Castro et al., 2008), immunosuppression in cetaceans (Tanabe, 1999; Choi et al., 2011), obesogenic syndrome in fish (Meador et al., 2011) and shell malformations in bivalves (Alzieu et al., 1986; Alzieu, 2000). In addition, possible human exposure to tributyltin via seafood intake (Cardwell et al., 1999) associated to health risks (as immunosuppression, endocrine disruption, neurotoxic damages, cancer, among others) were also reported (Guerin et al., 2007). Hence, the use of TBT-based antifouling paints was initially regulated by local legislations in Europe (Gipperth, 2009) and later globally banned in 2008, through the convention on the control of harmful antifouling systems on ships (AFS Convention) (IMO, 2016). Furthermore, due to inherent human health risks, the U.S. Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA) has set threshold limits (not exceeding 0.0015% in food composition and 100 ng Sn kg^{-1}, respectively) for the amounts of tin compounds in food (ATSDR, 2005; EFSA-Q-2003-110, 2004).

After TBT restrictions entered into force, its environmental levels as well as imposex incidence (a known biomarker of TBT contamination) begun to decline in many areas worldwide (Castro et al., 2012a, 2012b, 2012c, 2012d; Galante-Oliveira et al., 2011; Guomundsdóttir et al., 2011). However, recent studies have pointed out that present usage of tributyltin is still evident in many South American countries, including Argentina (Del Brio et al., 2016; Laitano et al., 2015; Quintas et al., 2016), Brazil (Artifon et al., 2016; Borges et al., 2013; Petracco et al., 2015; Santos et al., 2016), Central Chile (Batista et al., 2016), Ecuador (Grimón et al., 2016), Peru (Castro and Fillmann, 2012) and Venezuela (Paz-Villarraga et al., 2015). This scenario is, at least partially, caused by the absence of local regulations on the use of TBT-based antifouling paints (Batista et al., 2016). In addition, the gaps of knowledge on TBT contamination and impacts has also helped to hampered the implementation of actions to protect environmental and human health in most of these countries (Castro et al., 2012a, 2012b, 2012c, 2012d).

Chile is particularly susceptible to the environmental impacts produced by the use of antifouling biocides due to the several maritime and harbor activities developed along its 6435 km of coastline (Bravo, 2003). Imposex in marine gastropods (Gooding et al., 1999; Osorio and Huaquin, 2003) and TBT residues (Bravo et al., 2004; Pinochet et al., 2009) in surface sediment samples were previously detected in coastal areas under the influence of harbors and marinas in the central region of Chile. Recently, Batista et al. (2016) have also detected butyltin levels (TBT, dibutyltin (DBT) and monobutyltin (MBT)) in surface sediments and biota tissues and imposex in gastropods (*Acanthina monodon*, *Oliva peruviana* and *Xanthochorus cassidiformis*) from three out of ten regions of the Chilean coast under significant influence of ship and/or boat traffic.

In addition, the Chilean benthic invertebrate fishery (comprising over 60 species of mollusks, crustacean and echinoderms) represents an important food resource, which are consumed by the local population and traded on domestic and international markets (Leiva and Castilla, 2002). In this concern, *Thaisella chocolata* ("Locate") is a gastropod species exploited since 1978 for human consumption, being an important benthic resource caught by artisanal fisheries in northern Chile. Its extraction reached 8244 ton in 1986, but severely declined in subsequent years due to overexploitation (Avendaño et al., 1996). Currently, the "Locate" fisheries are regulated by the Chilean government, which established closed seasons and minimum size of capture (Avendaño et al., 1998). In 2015, the National Service of Fisheries and Aquaculture of Chile reported landings of 492 ton of *T. chocolata* (SERNAPESCA, 2015).

Thaisella chocolata is a good indicator of TBT contamination for the Pacific coast of South America by bioaccumulating butyltin residues and developing imposex (Castro and Fillmann, 2012). However, no studies were performed so far evaluating butyltin (BT) contamination and its potential implications to human health in Chile. Thus, the present study aimed to assess the environmental impacts and potential risk for consumers associated to intake of sea food from exploitation areas of Caldera, Northern Chile. For this, the spatial distribution of imposex in gastropods and butyltins (BT) levels in environmental samples (surface sediments and gastropod tissues) were appraised along a fishing and aquaculture area under different types and intensities of maritime traffic incidence. This assessment shall support the implementation of regulatory actions toward environmental protection and food safety of local populations.

2. Material and methods

2.1. Study area and sampling

The present study was carried out at the region of Caldera city (27°S), Atacama region, Northern Chile (Fig. 1). This region has been promoted as an area of high economic interest, where artisanal fisheries and aquaculture are performed supplying domestic and some international markets (Castillo and Valdés, 2011). Twelve sites (S1 to S12) representing different degrees of human intervention by maritime and/or harbor activities, which are known TBT sources (Mattos and Romero, 2016), were selected for study along 80 km of coast (Table 1).

All selected sites were sampled using a vessel at approximately 500 m from the coast. In each site, a single sample of surface sediments (upper 2 cm) was collected during April 2015 using a stainless steel "Van-veen" dredge. The sediment samples were packed in precleaned aluminum boxes, kept under refrigeration and taken to the laboratory. Simultaneously, at least 30 adult specimens of *T. chocolata* were also caught by SCUBA diving in the subtidal zones from the same 12 sites, totalizing 485 adult specimens along the 12 sites. The organisms were taken to the laboratory for imposex analysis. In the lab, sediment samples were frozen, freeze dried and stored at −20 °C until subsequent analysis.

2.2. Imposex assessment

The gastropods were narcotized with a 3.5% $MgCl_2$ solution (1:1 seawater/distilled water) for 2 h. Shells length (SL) were measured using a digital caliper (0.05 mm) from the apex to the top of the siphonal canal. Soft bodies were removed from the shell using a bench vice and sex determination was based on the presence or absence of sexual accessory glands (capsule, ingesting and albumen). The penis length (PL) were measured with a digital caliper and the presence of vas deferens in females and males were also registered. Imposex parameters were assessed using the following indices: % of imposex in females (I%),