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Mercury and selenium status of bottlenose dolphins (*Tursiops truncatus*): A study in stranded animals on the Canary Islands

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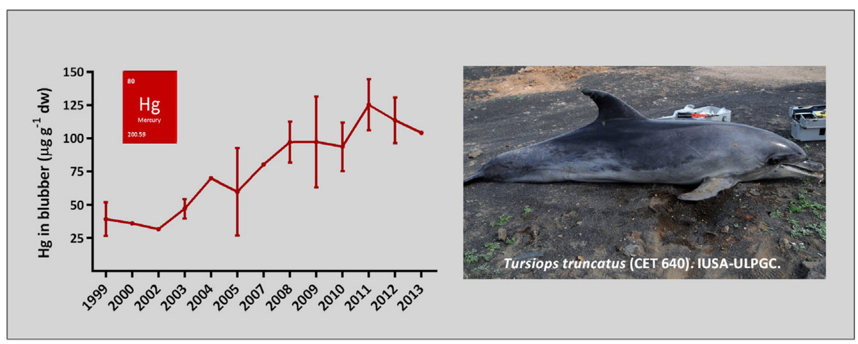
HIGHLIGHTS

- Hg and Se in bottlenose dolphins stranded on the Canary Islands from 1997 to 2013
- Upward temporal trend of Hg concentration during the study period
- The youngest and oldest animals appear to be of greater toxicological concern
- Some dolphins have Hg levels within the threshold established for hepatic damage
- First report of Se/Hg molar ratio in cetaceans stranded along the Canary coasts

GRAPHICAL ABSTRACT



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ABSTRACT

The mercury (Hg) level in the marine environment has tripled in recent decades, becoming a great concern because of its high toxic potential. This study reports Hg and selenium (Se) status, and the first Se/Hg molar ratio assessment in bottlenose dolphins (*Tursiops truncatus*) inhabiting the waters of the Canary Islands. Total Hg and Se concentrations were determined in the blubber and liver collected from 30 specimens stranded along the coasts of the archipelago from 1997 to 2013. The median values for total Hg in the blubber and liver were 80.83 and 223.77 μg g^{-1} dry weight (dw), and the median levels for Se in both tissues were 7.29 and 68.63 μg g^{-1} dw, respectively. Hg concentrations in the liver were lower than 100 μg g^{-1} wet weight (ww), comparable to those obtained in bottlenose dolphins from the North Sea, the Western Atlantic Ocean and several locations in the Pacific Ocean. The Mediterranean Sea and South of Australia are the most contaminated areas for both elements in this cetacean species. In addition, it must be stressed that the levels of Hg and Se in the liver showed an increasing trend with the age of the animals. As expected, a strong positive correlation between Hg and Se was observed ($r_s = 0.960$). Surprisingly, both younger and older specimens had a Se/Hg molar ratio different from 1, suggesting that these individuals may be at greater toxicological risk for high concentrations of both elements or a deficiency of Se without a protective action against Hg toxicity.

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1. Introduction

Mercury (Hg) is a natural element that is a ubiquitous environmental contaminant. It is distributed around the world by atmospheric transportation. The sources of Hg contamination can be both natural (e.g., degassing of the earth's crust, volcanic activities and forest fires) and anthropogenic (e.g., mining, chlorine industry, coal-burning power plants, cement and metallurgical industries, paper mills, agricultural pesticides, or medical waste incineration) (Van de Merwe et al., 2010). Natural inputs might be highly relevant in certain areas (Andre et al., 1991), but industrial activities might increase the exposure to this toxic element (AMAP, 2011; Magos and Clarkson, 2006), and recently published data even suggested that the amount of Hg in water has almost tripled compared to the pre-industrial period (Lamborg et al., 2014). Hg in its inorganic form is moderately toxic, but once in the aquatic environment, it is quickly transformed into methylmercury (MeHg), a highly toxic form of Hg of most concern to the health of humans and biota. MeHg is strongly neurotoxic (Clarkson and Magos, 2006), harmful to the kidneys, lungs, the thyroid gland, and the immune system (Das et al., 2008; De Guise et al., 1995); it is also teratogenic (Crespo-Lopez et al., 2009) and carcinogenic (Vos et al., 2003; Vos et al., 2000). In the marine environment, MeHg accumulates and biomagnifies along the food chain (Seixas et al., 2014) representing a serious threat, especially to top predators such as humans (Visnjevec et al., 2014) or cetaceans, which are exposed to this metal mainly via the diet (Bennett et al., 2001; Storelli et al., 2005).

It is well known that the toxic potential of Hg is suppressed in the presence of sufficient amounts of selenium (Se) (Parizek and Ostadalova, 1967). This effect has been shown in studies in a variety of species, including marine mammals (Cuvin-Aralar and Furness, 1991; Frodello et al., 2000; Gui et al., 2014; Sakamoto et al., 2013) exposed to these elements for a long time, even before the industrial period (Holsbeek et al., 1998). Thus, several mechanisms for resistance to the adverse effects of Hg have been proposed. On the one hand, Se can easily combined with various forms of Hg to yield complexes with lower toxicity, such as methylmercury selenide (MeHg-Se), methylmercury selenocysteinate (MeHg-Sec), or mercury selenide, tiemannite (HgSe), which is considered the last step in Hg detoxification (Palmisano et al., 1995). These compounds also contribute to the mobilization of mercury from the most vulnerable targets (such as kidney or nervous system tissues) to other less sensitive bodily regions, such as muscle. Furthermore, Se competes with Hg for its various biological targets, which also contributes to lowering the potential toxicity of Hg (Khan and Wang, 2009). Therefore, the Se/Hg molar ratio has been widely used (McHuron et al., 2014; Mendez-Fernandez et al., 2014; Squadrone et al., 2015; Vos et al., 2003), and many authors have established that Se, in a molar ratio of 1:1 or above with Hg, protects against the toxic effects of this metal (Ganther et al., 1972; Ralston and Raymond, 2013; Ralston et al., 2007; Ralston and Raymond, 2010; Sormo et al., 2011; Squadrone et al., 2015). However, paradoxically, this protective action can be harmful to the body because complex formation also results in the sequestration of both elements, causing them to become biologically unavailable (Martoja and Berry, 1980). Se is a well-known essential element with multiple biological functions, such as its critical participation in reproduction, the metabolism of thyroid hormones or DNA synthesis, in addition to its important antioxidant role (anticarcinogenic activity), among other functions (Schwarz and Foltz, 1957; Taylor et al., 2009; Zhang et al., 2014). Therefore, the presence of high levels of Hg could lead to Se deficiency, which could even cause the death in extreme cases (Chen, 2012; Sunde, 2006). Thus, the toxicological effects might be due to both MeHg toxicity and the induced Se deficiency (Zhang et al., 2014). However, Se levels have increased dramatically in many marine areas, presenting an environmental toxicity problem (Lavery et al., 2008). Se pollution probably occurs as a result of anthropogenic activities such as coal burning, smelting, ceramic and glass manufacturing, or copper refining (Van de Merwe et al., 2010). Therefore, to evaluate the health status of the ecosystems, the simultaneous study of Hg and Se and the relationship between them is of great interest, particularly in those species usually considered as sentinels for environmental pollution.

Because of its large size, longevity, and high position within the food chain, many authors have proposed the cetaceans as good sentinels for ocean health. Species with a worldwide distribution such as the bottlenose dolphin (*Tursiops truncatus*), are usually employed to assess global pollution and regional variations (Wilson et al., 2012). Therefore, this species has been selected for the present study because previous reports indicate that bottlenose dolphins clearly reflect the contamination of the waters of the Canary Islands (Eastern Atlantic Ocean) due to their proximity to likely anthropogenic sources (Garcia-Alvarez et al., 2014a; Garcia-Alvarez et al., 2014b). Moreover, these cetaceans have been extensively studied, allowing comparison of the results of this research with other marine areas around the world, to obtain more comprehensive approach to pollution observations.

Bottlenose dolphins inhabit the Canary Islands as local resident populations that show inter-island movements within the archipelago (Tobeña et al., 2014). This species faces a high exposure to organic pollutants (Garcia-Alvarez et al., 2014a; Garcia-Alvarez et al., 2014b) and is considered a valuable biomarker of the health status of the marine ecosystems. A high concentration of contaminants has also been reported in humans from this archipelago (Luzardo et al., 2012; Luzardo et al., 2009) and in other marine animals from the Canary Islands waters (Camacho et al., 2014) and other nearby areas (Camacho et al., 2013). Although there is a previous research concerning a few inorganic pollutants in 12 bottlenose dolphins stranded on the canary coasts (Carballo et al., 2004), there is a need of more recent and comprehensive data from this marine region.

The major goal of this study was to investigate the levels, relationship and toxicity of Hg and Se in bottlenose dolphins, through the direct measurement of these toxic elements in blubber and liver of animals stranded on the Canary Islands; thus, extending the knowledge on the contamination status of this cetacean species, which is frequently used as sentinel of the pollution of seas and oceans.

2. Materials and methods

2.1. Study area

The Canary archipelago is located in the Eastern North Atlantic Ocean near Europe and North Africa. These islands are a protected territory with 12 marine Special Areas of Conservation (SACs) because of the presence of bottlenose dolphins, species listed in Annex II and IV in the European Habitats Directive (EC., 1992).

However, as mentioned above, a lack of data exists concerning toxic metals and other inorganic pollutants from cetaceans inhabiting this marine region.

2.2. Sample collection

Over a period from 1997 to 2013, 29 each of blubber and liver samples were collected from 30 bottlenose dolphins stranded on the Canary Islands coasts. According to the literature, Hg and Se were found to accumulate in both tissues, reaching the highest levels in the liver (Beck et al., 1997). Besides, these tissues have been selected to be in accordance with previous studies of contaminants in stranded dolphins from this archipelago (Garcia-Alvarez et al., 2014a). The blubber is considered as a main target for pollutant assessment, in order to possible future comparisons with biopsy samples from live cetacean. On the other hand, the liver tissue was also selected because pattern distribution of metals is tissue specific, being the mercury mostly concentrated in the liver (Das et al., 2003).

Tissue sampling and the state of decomposition of the stranded specimens were determined by adapting the Geraci and Lounsbury