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Concentrations of mercury in tissues of striped dolphins suggest decline of pollution in Mediterranean open waters

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HIGHLIGHTS

- The Mediterranean is a semi-enclosed sea subject to high mercury pollution.
- Monitoring temporal trends of mercury concentration is compulsory.
- Dolphins integrate long-term, large-scale pollution variations in oceanic waters.
- A decline in Mediterranean Hg levels is shown to occur from 1990 to 2009.

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ABSTRACT

The Mediterranean is a semi-enclosed sea subject to high mercury (Hg) pollution from both natural and anthropogenic sources. With the objective of discerning temporal changes in marine Hg pollution in the oceanic waters of the northwestern Mediterranean Sea, we analysed liver and kidney from striped dolphins (*Stenella coeruleoalba*) collected during 2007–2009 and compared them with previous results from a similar sample from 1990–1993. The effect of body length and sex on tissue Hg concentrations was investigated to ensure an unbiased comparison between the periods. The Hg concentrations did not show significant sex-related differences in any tissue or period but were correlated positively with body length. Using body length as a covariate, Hg concentrations in liver and kidney were higher in 1990–1993 than in 2007–2009. This result suggests that measures to reduce emissions in Western European countries have been effective in reducing mercury pollution in Mediterranean open waters.

1. Introduction

Among the trace metals, mercury (Hg) is one of the pollutants of most concern because of its high toxicity, persistence and accumulative behaviour in the environment and biota. Hg pollution in the Mediterranean is particularly relevant because it is a semi-enclosed sea with high natural and anthropogenic inputs of this metal. Natural sources include weathering of the large cinnabar ore deposits found along the bottom (Bacci, 1989), as well as the intense geothermal and volcanic activity of this region (Ferrara et al., 2000). Anthropogenic emissions include current and past intensive mining, fossil fuel combustion, cement production and some specific industries such as chlor-alkali plants. Hg is released into the Mediterranean mostly as a result of atmospheric deposition and river inflow and, to a lesser extent, of point sources (Rajar et al., 2007). However, particulate Hg, which represents approximately 95% of the total Hg carried by rivers, is mainly deposited on the continental shelf relatively near the river mouths, so only a small percentage of the river input reaches open sea waters (Rajar et al., 2007).

The identification of Hg pollution hot spots and potential human health hazards is usually carried out through the monitoring of concentrations in biota. In the case of marine ecosystems, the most common procedure is to analyse bioindicators such as mussels or other shellfish (Carrasco et al., 2008; Benedicto et al., 2011; Guitart et al., 2012), fish (Polak-Juszczak, 2012), or even plants such as seagrass (Lafabrie et al., 2007a,b; Copat et al., 2012). These organisms have the advantage of being abundant and extensively distributed, so they can be readily available to monitoring programs. Hence, these organisms have been employed to assess temporal trends and detect hot spot contamination in nearshore waters, where environmental degradation is likely to be the greatest (Cossa, 1989; Ancora et al., 2004; Fernandes et al., 2008). However, because their distribution is limited to the continental shelf, their coverage is restricted to inshore coastal waters (Zhou et al., 2008).

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Analogous information on oceanic waters is much scarcer given that no suitable indicators are commonly available. Oceanic fish, such as tuna and swordfish, have been found to exhibit elevated Hg concentrations (Storelli et al., 2002a,b; Damiano et al., 2011) that are relatively higher than those of species inhabiting coastal areas, possibly as a result of their higher longevity and trophic levels (Mormede and Davies, 2001). Within this context, mobile (but local) top predators such as dolphins have been proposed as potential indicators for Hg exposure (Augier et al., 2001; Bellante et al., 2011), as has been successfully performed for other groups of environmental pollutants (Aguilar et al., 2002; Aguilar and Borrell, 2005).

The striped dolphin (*Stenella coeruleoalba*) is the most abundant dolphin species in the western Mediterranean Sea, where it mostly inhabits the open waters beyond the continental shelf (Aguilar and Raga, 1993; Forcada and Hammond, 1998). It is known to be exposed through its diet to high levels of pollutants, including trace elements (Monaci et al., 1998) and, as consequence, it has been used to monitor temporal changes in organochlorine compounds in the region (Aguilar and Borrell, 2005; Castrillon et al., 2010).

Consistent with this background, the present study investigates temporal Hg variations in striped dolphin tissues to infer pollution of this metal in the oceanic waters of the northwestern Mediterranean Sea. Thus, we analysed Hg concentrations in the liver and kidneys of individuals collected during 2007–2009 and compared them with previous results from a similar sample from 1990 to 1993. The effect of body length and sex on tissue Hg levels was investigated to ensure an unbiased comparison between periods.

2. Materials and methods

The samples collected for the study were obtained from dolphins stranded in the northern Mediterranean Spanish coasts (Fig. 1). These included twenty-three individuals (8 males and 15 females) stranded during 1990–1993, and thirty (19 males and 11 females) stranded during 2007–2009. After sex and length determination (Table 1), liver and kidney samples were excised, wrapped in a plastic bag and preserved frozen at −25 °C until analyses (see Borrell et al. (2000) for general information).

At the laboratory, a 2 g subsample from each tissue was homogenized; approximately 1 g was oven-dried (40 °C, 72 h) to obtain the percentage of moisture. Another aliquot of approx. 200 mg was oven-digested at 90 °C overnight in an acid solution (H_2O_2/HNO_3, 2:2 ratio) in Teflon vials. Samples were then diluted (1:5) with ultrapure (Milli-Q) water and transferred to plastic tubes to be analysed for mercury (Hg) via Inductively Coupled Plasma Mass (ICP-MS) Spectrometry (Perkin–Elmer Elan 6000). The entire analytical procedure was validated by analysing blanks, replicates and certified reference material (Bovine liver 1577a). Replicates were found to differ below 10%, and the percent recovery was between 90% and 100%. The limit of detection was calculated as three times the standard deviation of the mean of blank determinations. This resulted in a value of 1.02 ng mL^{-1}, far below the concentrations found during the analytical runs. These analyses were performed at the Analytical Services of the University of Barcelona (Centres Científics i Tecnològics de la Universitat de Barcelona, CCT UB). Although the samples were analysed in two separate batches (in 1993 and 2011) the methodology and the calibration curves were similar.

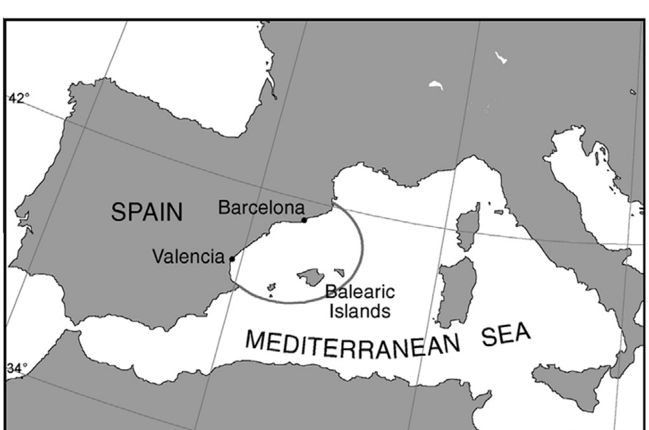

Fig. 1. Sampling sites.

Table 1
Biological information of western Mediterranean striped dolphins from each period.

Period	Sex	*n*	Length (cm)		
			Mean	Range	S.D.
1990–3	F	15	169	81–204	39
	M	8	178	115–212	35
2007–9	F	11	178	91–210	33
	M	19	174	83–224	38

Normality in the distributions of mercury concentrations was tested using the Kolmogorov–Smirnov test. The distribution of mercury concentrations was skewed, and a better fit of the parametric models was obtained by logarithmic transformation of the data. The homogeneity of variances between sample groups was analysed with Levene's test. Analysis of covariance (ANCOVA), with length as the covariate, was used to examine: (i) sex-related differences in Hg accumulation in tissues for each period and (ii) time-related differences in tissue accumulation. All statistical calculations were carried out using the SPSS-15 statistical package.

3. Results

The number of dolphins used for the analyses and their Hg tissue concentration (mean and standard deviation) divided according to sampling period, are depicted in Table 2. The Hg concentrations in both tissues were found to be extremely high, especially in the liver, which is typically the main organ of accumulation (up to ten-fold higher than kidney) (Table 2 and Fig. 2). The highest concentration (2.473 mg kg^{-1} dry weight basis) was found in the liver of a 2 m female stranded in 1990.

Table 2
Statistical information on tissue mercury concentrations (mg kg^{-1} in dry (d.w.) and wet (w.w.) weight basis) in western Mediterranean striped dolphins from each period and results of the comparison between periods.

Hg concentrations		Liver	Kidney
Period 1990–3	*n*	23	23
	Mean (mg kg^{-1} d.w.)	989.03	62.14
	S.D. (mg kg^{-1} d.w.)	804.03	39.23
	Mean (mg kg^{-1} w.w.)	321.43	16.11
	S.D. (mg kg^{-1} w.w.)	261.31	10.17
ANCOVA (within period)	R^2	0.81	0.73
(ln Hg)	*p* length (covariable)	<0.001	<0.001
	p sex (factor)	0.062	0.102
Period 2007–9	*n*	30	30
	Mean (mg kg^{-1} d.w.)	570.70	51.81
	S.D. (mg kg^{-1} d.w.)	606.81	45.19
	Mean (mg kg^{-1} w.w.)	185.48	13.43
	S.D. (mg kg^{-1} w.w.)	197.21	11.72
ANCOVA (within period)	R^2	0.81	0.75
(ln Hg)	*p* length (covariable)	<0.001	<0.001
	p sex (factor)	0.216	0.178
ANCOVA (between periods)	R^2	0.79	0.73
(ln Hg)	*p* length (covariable)	<0.001	<0.001
	p period (factor)	<0.001	<0.05

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