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Distribution of Cadmium, Copper, Iron, Manganese, Lead, and Zinc in Spinner Dolphins *Stenella longirostris* Stranded in La Paz Lagoon, Southwest Gulf of California

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Stranding of marine mammals has been reported in numerous studies (*e.g.* Law et al., 1992; Marcovecchio et al.,1990; Monaci et al.,1998) but reasons remain unknown. Among odontoceti, spinner dolphins are species with wide distribution and a long life span, these aspects are considered to be important from an ecotoxicological point of view. One possible contribution to the stranding of marine mammals is the ocurrence of high levels of trace metals in their bodies. Trace metals have accumulation preferences that basically depend on the different distribution of specific proteins, the transport of metals on a differential basis to particular organs and the peculiarity of transport through certain cellular barriers (Gaskin, 1982). Liver is among the most appropriate organs for trace metal accumulation studies (Falconer et al., 1983). In this study Cd, Cu, Fe, Mn, Pb and Zn distribution in kidney, liver and muscle of 13 spinner dolphins *Stenella longirostris* (4 females and 9 males) was investigated in order to compare results with data from other stranding events.

MATERIALS AND METHODS

In August 1993, thirty-three spinner dolphins *Stenella longirostris* were found stranded in La Paz Bay, Mexico (Figure 1); 13 specimens were used in this study. La Paz Bay has a north-south axis of 90 km and an average width of 60 km, accounting for an area of *ca* 4500 km^2. The area where dolphins were found stranded has a maximum depth of 6 m and a sandy bottom (Jiménez-Illescas et al., 1997). La Paz city is the largest settlement around La Paz Bay; the city development has changed the coastal ecosystem: the construction of a harbor in Pichilingue, the operation of fuel warehouses, a thermoelectric plant, a mining industry, and facilities related to municipal and tourist services (Urbán-Ramírez and Ramírez-Rodríguez, 1997).

Specimens were measured and weighed *in situ*. Body dissection was

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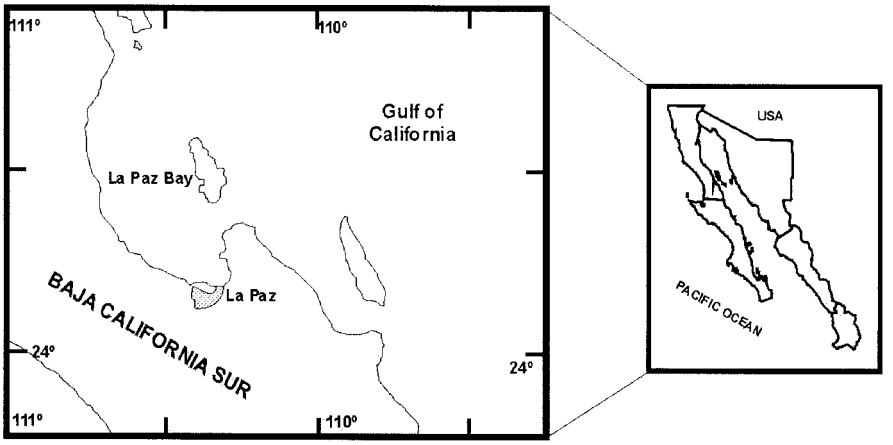

Figure 1. Location of stranding site of spinner dolphins *Stenella longirostris* in the SW Gulf of California in August 1993.

made by using previously washed (Moody and Lindstrom, 1977) utensils.Samples were stored frozen before analysis. Kidney, liver and muscle samples were freeze-dried (Labconco Freeze-dry System) at –49°C and 133 X 10^{-3} mBar (40 h). Dried samples were ground in an automatic agate mortar (Retsch RM100). Powdered samples (0.5 g dry weight) were acid digested (concentrated HNO_3) in a microwave digestion system (CEM-MDS 2000) according to UNEP (1993).

Analysis were performed in an atomic absorption spectrophotometer (AAS) Varian SpectrAA 220. Cu, Fe, Mn and Zn were determined by flame AAS, while Cd and Pb were analyzed by graphite furnace AAS. Analytical control was achieved by using fish tissue MA-B-3/TM reference material (IAEA, 1987). Data were computed in μg g^{-1} on a dry weight basis. Mean lengths and weights for males and females were compared by a Student´s *t*-test. Statistical analysis of data consisted of a one-way ANOVA among mean metal concentrations for kidney, liver and muscle. Statistical analysis were conducted using GraphPad Prism 2.01 (GraphPad Software, San Diego, CA) for Windows.

RESULTS AND DISCUSSION

From biological data on stranded specimens it can be inferred that all specimens were adults (Table 1). In this species newborns are 80 cm in length and reach almost 200 cm when adults (Perrin, 1975). Mean lengths (177 cm for females and 182 cm for males) and mean weights

Table 1. Biometric data of spinner dolphins *Stenella longirostris* from la Paz Bay (SW Gulf of California).

Specimen	Sex	Length (cm)	Weight (kg)
1	Female	178	43.9
2	Female	171	43.1
3	Female	175	39.2
4	Female	184	38.5
5	Male	186	52.6
6	Male	184	55.2
7	Male	167	39.3
8	Male	193	56.6
9	Male	173	38.2
10	Male	185	50.3
11	Male	188	48.7
12	Male	169	35.8
13	Male	183	49.3

Table 2. Average concentration (μg g^{-1} dry weight) of trace metals in selected tissues of spinner dolphins *Stenella longirostris* stranded in La Paz lagoon (SW Gulf of California).

	Essential				Non-essential	
Tissue	Cu	Fe	Mn	Zn	Cd	Pb
Kidney	13.1 ± 4.0	752 ± 192	3.0 ± 0.6	124 ± 27.4	124 ± 60	2.6 ± 2.1
Liver	19.2 ± 4.7	1106 ± 198	10.9 ± 2.8	112 ± 23.3	24.3 ±11.0	3.3 ± 2.3
Muscle	8.2 ± 12	565 ± 67	0.8 ± 0.2	28.6 ± 8.7	1.6 ± 0.9	2.2 ± 1.2

(41.2 kg for females and 47.3 for males) were within the ranges reported for this species in the eastern Pacific (Perrin, 1975). The statistical comparison of mean lengths and mean weights for males and females showed no significant differences ($p<0.05$) for either variable.

Trace metal concentrations in kidney, liver and muscle of stranded dolphins are shown in Table 2. Elements were grouped as essential (Cu, Fe, Mn, Zn) and non-essential (Cd, Pb) metals. With the exception of Zn, essential metals accumulated more in liver, followed by kidney and muscle. The sequence of average essential trace metal concentration was Fe>Zn>Cu>Mn. Average levels of Fe and Mn were significantly higher in liver ($p<0.05$), while average concentration of Zn was significantly higher in kidney ($p<0.05$). Marine mammals have large livers in relation to body size. In this sense Slijper (1962) considered that liver plays a very important part in body metabolism that its size is directly related to metabolic rate; on the basis of the relative weight of the liver,

he concluded that aquatic mammals in general and cetacea in particular have very high metabolic rates. Cu concentrations ranged from 8.2 to 19.2 μg g^{-1} dry weight (Table 2); it has been suggested that in marine mammals homeostatic control of Cu is mediated by metallothioneins (Law et al., 1992) so concentrations are expected to have narrow variations in the different tissues. Fe concentrations ranged from 565 to 1106 μg g^{-1} dry weight. Fe is stored in the liver in a labile form such as ferritin and hemosiderin (Honda et al., 1982). Mn levels ranged from 0.8 to 10.9 μg g^{-1} dry weight (Table 2); this element is an important metal participating in enzimatic systems (*e. g.* piruvate kinase) (Hochachka and Mustafa, 1972). Furness and Rainbow (1990) have mentioned that natural Mn levels in marine mammals are generally below 7 μg g^{-1} wet weight in any tissue; according to the above value and considering a wet content of 70-80%, the values presented here correspond to concentrations in specimens from an environment with low Mn bioavailability. Zn levels ranged from 28.6 to 124 μg g^{-1} dry weight; according to Sanpera *et al.* (1996) this metal is mostly accumulated in liver of marine mammals, but in some species (*Kogia breviceps*, *Delphinapterus leucas*, *Monodon monoceros*, *Ziphius cavirostris*) Zn is more acumulated in the kidney.

Cd was more accumulated in kidney while Pb was more concentrated in liver. Average concentration of Cd was significantly higher in kidney ($p<0.05$). On the average, Cd had higher concentrations than Pb. According to Honda et al. (1983), Cd is an element with no biological function that concentrates primarly in the kidney and then in the liver. In relation to other marine mammals species, Cd concentrations in dolphins are high, it can be ascribed to feedind primarly on squid, in which the Cd concentration is extraordinarily high (Law et al., 1992). Various authors have shown the importance of Cd in the biogeochemical cycles of Baja California waters (e.g. Knauer and Martin, 1981; Segovia-Zavala et al., 1998) found that Cd levels were related with phytoplankton and nutrients in the water column from the coastal upwellings. Consequently for the Gulf of California, upwelling is a feature that might contribute with Cd in dolphin´s environment. The high accumulation of Cd in kidney is probable due to its presence as cadmium-methallotionein (Fujise et al., 1988). As accumulation increases there is a spillage of Cd to other proteins, after which signs of toxicity appear (Underwood, 1977).

Regarding Pb, levels ranged from 2.2 μg g^{-1} in muscle to 3.3 μg g^{-1} in liver (Table 2). Again, liver was the target tissue and concentrations corresponded to values reported in marine mammals from a site with high Pb concentrations in the Liverpool Bay (Law et al., 1992). Considering that species and latitude based differences can account for the resulting trace metal concentration, a comparison was made among livers of some marine mammals. Copper and Zn concentrations were higher in *Tursiops*

Table 3. Comparison of average trace metal concentrations (μg g^{-1} dry weight) in livers of stranded dolphins from different sites.

Species	Cu	Mn	Zn	Cd	Pb	Site	Reference
Stenella coeruleoalba	26.1		140	7.0	<0.2	British Isles	Law et al., 1991
Grampus griseus				32.8	0.5	South Adriatic	Storelli et al., 1999
Tursiops truncatus	23.8		101	0.3	<0.4	South Carolina, USA	Beck et al., 1997
Tursiops gephyreus	303		765	3.1		Coast of Argentina	Marcovecchio et al., 1990
Tursiops truncatus	37.7		263	0.2		Florida, USA	Wood and Van Fleet, 1996
Tursiops truncatus	14.6		117	0.6		French Atlantic coast	Holsbeek et al., 1998
Tursiops truncatus	9.4		54.0	2.35	5.48	South China sea	Parsons and Chan, 2001
Stenella coeruleoalba	22.0		111	4.4		Coast of Italy	Monaci et al., 1998
Delphinus delphis	22.9	12.2	235	10.0		Portuguese coast	Zhou et al., 2001
Delphinus delphis	18		143	5.9		French Atlantic coast	Holsbeek et al., 1998
Stenella longirostris	19.2	10.9	112	76.6	3.3	La Paz, Mexico	This study

gephyreus from the coast of Argentina (Table 3). Cu was an order of magnitude higher in the liver of *T. gephyreus* than in the rest of marine mammals while Zn concentrations were in the same order of magnitude. Literature on Mn levels in marine mammals is scarce, in this study only a report from the Portuguese coast is contrasted with our work, levels were in the same order of magnitude. Cd concentrations were higher in *Stenella longirostris* from La Paz lagoon, Mexico but levels were in the same order of magnitude of those found in livers of *Delphinus delphis* from the Portuguese coast and *Grampus griseus* from the South Adriatic (Table 3). Pb concentrations were higher in *Tursiops truncatus* from the South China sea. Although more information on trace metal concentration and distribution in tissues of marine mammals is necessary, values reported here seem to have no relation with the stranding of *Stenella longirostris* specimens in La Paz lagoon.

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