TOXIC AND ESSENTIAL METALS IN *Stenella coeruleoalba*: ASSESSMENT OF MARINE ENVIRONMENTAL POLLUTION AND DOLPHIN HEALTH STATUS

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INTRODUCTION & AIM

Heavy metals are persistent environmental contaminants present in marine ecosystem, assimilated by biota and able to be easily accumulated and biomagnificate in predatory fishes and mammalians, species at the top of the aquatic food chain (*Zhou et al., 2001*). The quality of marine ecosystem is strongly influenced by the anthropogenic activity, responsible of metals release, which significantly affects the health of both marine environment and animal species. Among marine mammalians, striped dolphin (*Stenella coeruleoalba*) is used as sentinel of environmental pollution. Metals accumulation in these marine specie is influenced by several factors, such as habitat, food habits, physio-pathological status of animals, age and sex.
The aim of this study was to determinate the content of metals in tissues of *Stenella coeruleoalba,* the most abundant cetacean present in the Mediterranean Sea, and carry out a comparison among heavy metals and essential elements, expressed as molar ratios, to assess marine environmental pollution and dolphin health status.

MATERIALS and METHOD

Striped dolphins (*Stenella coeruleoalba*) (n=15), stranded along the Sicilian coasts of Mediterranean Sea (**Figure 1**), were collected deaths by the Institute of Experimental Zooprophylaxy of Sicily "A. Mirri", Palermo (Italy). From each dolphins were taken samples of lung, skin, muscle and liver, preserved in PET containers and frozen at −20 °C until to the analysis. All samples were digested with HNO_3 (70%) and H_2O_2 (30%) according to the method of *Naccari et al. 2015,* and submitted to analysis in ICP-MS, for determination of toxic (Hg, Cd, Pb, As) and potentially toxic metals (Ni, Cr), essential micro and macro-elements (Se, Zn, Cu, Fe, Mn and Na, Ca, K, Mg). All analytical parameters of validation method were calculated according to the AOAC 2016. The accuracy was assessed by the analysis of certified materials DOLT-5 (dogfish liver Reference Material for trace metals) from the National Research Council of Canada. Data are expressed as mean ± S.D. of at least three determinations and evaluated by one-way analysis of variance (ANOVA) and student *t*-test (P< 0.05 and P< 0.01). The molar ratios of essential and toxic metals, as described by *Mendez-Fernandez et al. 2014*, were calculated using the atomic masses of each element. In addition, the coefficient of condition (K) was calculated for each samples according to Fulton equation $K = 100 \times W/L^3$, where *W* is weight and *L* is lenght.

Figure 1. Sampling of *Stenella coeruleoalba* form Sicilian coasts of the Mediterranean Sea.

RESULTS & DISCUSSION

The results showed the presence of all metals analyzed, with highest Hg levels statistically significant in all dolphin samples. Considering the essential micro-elements, Fe showed the highest concentrations; the macro-elements were present in significant levels but P was the most abundant in all samples (**Figure 2**). The concentrations of all micro and macro-elements were in normal range for *Stenella spp.* (*Delgado-Suarez et al., 2023*) and predictive of good dolphins health status, confirmed also by the coefficients of condition K with values around or >1 (safety level) in each animals (**Figure 3**). It'was also evaluated the correlation among toxic (Hg, Cd, Pb, As), potentially toxic metals (Cr, Ni) and essential micro-elements (Zn, Se, Cu), espressed as molar ratios. Particlulary, the ratios $^{66}Zn/^{201}Hg$, $^{82}Se/^{201}Hg$, $^{63}Cu/^{201}Hg$ and for $^{66}Zn/^{52}Cr$, $^{82}Se/^{52}Cr$, $^{63}Cu/^{52}Cr$ in all tissues were <1 (value considered as protection index) (**Table 1**), showing that these toxic metals cannot be detoxified by essential metals Se, Zn and Cu, present in enzymatic systems.

Figure 3. Coefficient of condition (K) in striped dolphins (*Stenella coeruleoalba*) samples.

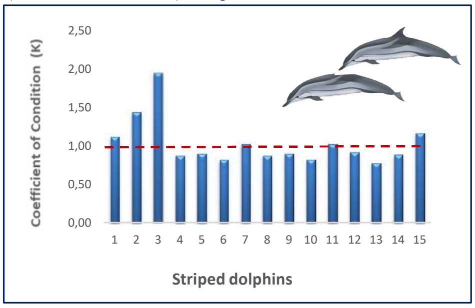
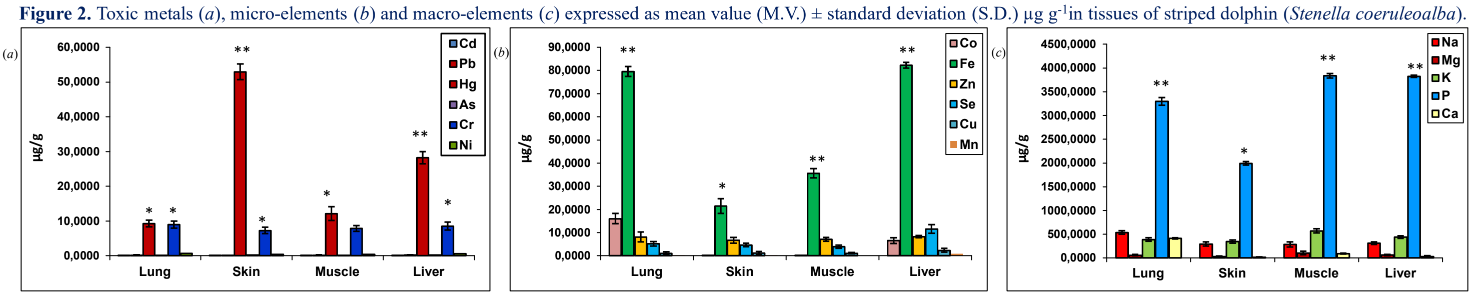


Figure 2. Toxic metals (*a*), micro-elements (*b*) and macro-elements (*c*) expressed as mean value (M.V.) ± standard deviation (S.D.) μg g^{-1}in tissues of striped dolphin (*Stenella coeruleoalba*).



**P< 0.05 ; ** P< 0.01*

CONCLUSION

The presence of toxic metals in tissues of dolphins, mainly correlated to marine environmental and influenced by food habits in living habitat, underlines the key-role of these mammalians to assess marine pollution, found in this study to be relatively low, except for Hg.
The content of micro and macro-elements in all dolphin samples resulted predictive of their health status, as confirmed also by the coefficient of condition K. However, the analysis of molar ratios, usefull to better understand the effects of exposure to these pollutants on organism, showed that the levels of detoxifying essential metals are unable to carry out a protective action against toxic metals Hg and Cr, probably due to deficiency, sequestration or presence of other pollutans.

Table 1: Molar ratios between toxic metals and essential microelements in tissues of common dolphins.

Ratio	LUNG	MUSCLE	LIVER	SKIN
$^{66}Zn/^{201}Hg$	0.19	0.59	0.26	0.13
$^{82}Se/^{201}Hg$	0.12	0.49	0.18	0.10
$^{63}Cu/^{201}Hg$	0.03	0.09	0.07	0.02
$^{66}Zn/^{207}Pb$	32.56	34.52	31.88	39.94
$^{82}Se/^{207}Pb$	20.55	28.80	21.58	32.81
$^{63}Cu/^{207}Pb$	4.38	5.22	9.03	6.97
$^{66}Zn/^{112}Cd$	281.87	95.62	147.95	87.76
$^{82}Se/^{112}Cd$	177.99	79.85	21.46	72.10
$^{63}Cu/^{112}Cd$	37.97	16.69	37.99	47.61
$^{66}Zn/^{75}As$	67.83	44.92	25.12	21.55
$^{82}Se/^{75}As$	42.72	37.48	16.94	17.67
$^{63}Cu/^{75}As$	9.14	6.78	7.11	3.75
$^{66}Zn/^{60}Ni$	45.22	44.18	42.12	14.14
$^{82}Se/^{60}Ni$	28.56	24.25	28.40	9.89
$^{63}Cu/^{60}Ni$	6.09	6.79	11.93	2.46
$^{66}Zn/^{52}Cr$	0.74	0.92	0.97	0.91
$^{82}Se/^{52}Cr$	0.46	0.77	0.65	0.75
$^{63}Cu/^{52}Cr$	0.02	0.14	0.27	0.16

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