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TITLE: POPs in free-ranging pilot whales, sperm whales and fin whales from the Mediterranean Sea: Influence of biological and ecological factors

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ABSTRACT:

The pilot whale *Globicephala melas*, the sperm whale *Physeter macrocephalus*, and the fin whale *Balaenoptera physalus* are large cetaceans permanently inhabiting the Mediterranean Sea. These species are subjected to numerous anthropogenic threats such as exposure to high levels of contaminants. Therefore, selected persistent organic pollutants POPs (29 PCBs, 15 organochlorine compounds, 9 PBDEs and 17 PCDD/Fs) were analysed in blubber biopsies of 49 long-finned pilot whales, 61 sperm whales and 70 fin whales sampled in the North Western Mediterranean Sea (NWMS) from 2006 to 2013. Contamination profile and species feeding ecology were then combined through the use of stable isotopes.  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  values and POPs levels were assessed through IR-MS and GC-MS respectively. To assess the toxic potency of the dioxin-like compounds, the TEQ approach was applied.  $\delta^{15}\text{N}$  values were  $12.2 \pm 1.3$ ‰ for sperm whales,  $10.5 \pm 0.7$ ‰ for pilot whales and  $7.7 \pm 0.8$ ‰ in fin whales, positioning sperm whales at higher trophic levels.  $\delta^{13}\text{C}$  of the two odontocetes was similar and amounted to  $-17.3 \pm 0.4$ ‰ for sperm whales and  $-17.8 \pm 0.3$ ‰ for pilot whales; whilst fin whales were more depleted ( $-18.7 \pm 0.4$ ‰). This indicates a partial overlap in toothed-whales feeding habitats, while confirms the differences in feeding behaviour of the mysticete. Pilot whales presented higher concentrations than sperm whales for  $\Sigma\text{PCBs}$  ( $38,666 \pm 25,731$  ng g<sup>-1</sup> lw and  $22,849 \pm 15,566$  ng g<sup>-1</sup> lw respectively),  $\Sigma\text{PBDEs}$  ( $712 \pm 412$  ng g<sup>-1</sup> lw and  $347 \pm 173$  ng g<sup>-1</sup> lw respectively) and  $\Sigma\text{DDTs}$  ( $46,081 \pm 37,506$  ng g<sup>-1</sup> lw and  $37,647 \pm 38,518$  ng g<sup>-1</sup> lw respectively). Fin whales presented the lowest values, in accordance with its trophic position ( $\Sigma\text{PCBs}$ :  $5721 \pm 5180$  ng g<sup>-1</sup> lw,  $\Sigma\text{PBDEs}$ :  $177 \pm 208$  ng g<sup>-1</sup> lw and  $\Sigma\text{DDTs}$ :  $6643 \pm 5549$  ng g<sup>-1</sup> lw). Each species was characterized by large inter-individual variations that are more related to sex than trophic level, with males presenting higher contaminant burden than females. The discriminant analysis (DA) confirmed how DDTs and highly chlorinated PCBs were influential in differentiating the three species. Pollutant concentrations of our species were significantly higher than both their Southern Hemisphere and North Atlantic counterparts, possibly due to the particular Mediterranean geomorphology, which influences pollutants distribution and recycle. Dioxin-like PCBs accounted for over 80% of the total TEQ. This study demonstrated (1) an important exposure to pollutants of Mediterranean cetaceans, often surpassing the estimated threshold toxicity value of 17,000 ng g<sup>-1</sup> lw for blubber in marine mammals; and (2) how the final pollutant burden in these animals is strongly influenced not only by the trophic position but also by numerous other factors such as sex, age, body size and geographical distribution.

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