



UNIVERSITÀ DI SIENA 1240

Dipartimento di Scienze fisiche, della Terra e dell'ambiente

Dottorato in Scienze e tecnologie ambientali, geologiche e polari

37° Ciclo

Coordinatore: Prof.ssa Letizia Marsili

EVALUATING THE PRESENCE OF POLLUTANTS IN FOUR ELASMOBRANCH SPECIES CAUGHT IN A MARINE PROTECTED AREA OF THE WESTERN MEDITERRANEAN SEA: IMPACT AND RISK FOR THE ECOSYSTEM AND FOR HUMAN HEALTH

Settore scientifico disciplinare: *BIO/07*

Candidato

Lorenzo Minoia

Università di Siena

Stazione Zoologica Anton Dohrn

Firma digitale del candidato

Tutori

Prof.ssa Letizia Marsili

(Università di Siena)

Dott. Massimiliano Bottaro

(Stazione Zoologica Anton Dohrn)

Anno accademico di conseguimento del titolo di Dottore di ricerca

2023/24

Abstract

The ecology and toxicology of elasmobranchs represent a crucial research field for the conservation of these species and for assessing environmental risks associated with marine pollution. This thesis focuses on analyzing the ecological interactions and toxicological exposures of elasmobranchs in the Mediterranean Sea, with particular attention to demersal species. The main objective of the study is to understand the ecological role of sharks and rays within trophic networks and to evaluate the impact of persistent organic pollutants (POPs), including hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDTs), polychlorinated biphenyls (PCBs), as well as perfluoroalkyl substances (PFAS), on the physiology and behavior of these species. Through a multidisciplinary approach, the trophic position of elasmobranchs was assessed using stable isotope analysis of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$), providing key insights into their diet and position within trophic networks. Spatial and temporal variability in species distribution was also evaluated in relation to environmental factors and anthropogenic pressures, with particular attention to bycatch, one of the main threats to many shark and ray species in the Mediterranean.

A toxicological analysis was conducted to assess elasmobranch exposure to anthropogenic organic contaminants. POPs and PFAS were selected for their environmental persistence, bioaccumulative potential, and known or suspected ecotoxicological effects. Tissue samples collected from various Mediterranean locations were analyzed using advanced mass spectrometry techniques, allowing for the quantification of contaminant loads and comparison across species and habitats. The results highlighted a clear trend of bioaccumulation of these substances in elasmobranch tissues, with possible implications for their physiology and role in marine ecosystems. The methodological approach included advanced chemical analysis techniques for contaminant detection and stable isotope analysis to better understand the trophic dynamics of the studied species. The results showed that the accumulation of POPs and PFAS could have potentially negative effects on elasmobranch health, influencing their growth, reproduction, and disease resistance. Additionally, a correlation was observed between trophic position and contamination levels, with higher trophic level species exhibiting higher concentrations of pollutants, suggesting a potential biomagnification phenomenon, particularly for POPs, along the food chain. PFAS, exhibiting different chemical behaviour, showed more complex accumulation patterns. The collected evidence has important implications for the management and conservation of elasmobranchs in the Mediterranean. The data obtained through this study can inform the

development of targeted mitigation strategies, such as the reinforcement of regulations on organic pollutant emissions and the continuous monitoring of shark and ray populations to assess the risks associated with environmental contamination. Furthermore, the findings emphasize the need to incorporate emerging contaminants, such as PFAS, into marine conservation frameworks to better protect vulnerable species and preserve the functional integrity of marine ecosystems. In conclusion, this thesis highlights the importance of an integrated approach between ecology and toxicology to understand the environmental challenges threatening elasmobranchs in the Mediterranean. The analysis of trophic interactions and the effects of persistent organic pollutants and perfluoroalkyl substances provides fundamental information for developing effective conservation strategies and sustainable management policies. The protection of these species, essential for the stability of marine ecosystems, requires targeted interventions based on solid scientific evidence to counteract increasing anthropogenic pressures and ensure the long-term survival of these marine predators.