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Biotic and environmental stress induces nitration and changes in structure and function of the sea urchin major yolk protein toposome

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The major yolk protein toposome plays crucial roles during gametogenesis and development of sea urchins. We previously found that nitration of toposome increases in the gonads of a *Paracentrotus lividus* population living in a marine protected area affected by toxic blooms of *Ostreospsis* cf. *ovata*, compared to control populations. This modification is associated with ovatoxin accumulation, high levels of nitric oxide in the gonads, and a remarkable impairment of progeny development. However, nothing is known about the environmental-mediated-regulation of the structure and biological function of toposome. Here, we characterize through wide-ranging biochemical and structural analyses the nitrated toposome of sea urchins exposed to the bloom, and subsequently detoxified. The increased number of nitrated tyrosines in toposome of sea urchins collected during algal bloom induced structural changes and improvement of the Ca^{2+}-binding affinity of the protein. After 3 months' detoxification, ovatoxin was undetectable, and the number of nitric oxide-modified tyrosines was reduced. However, the nitration of specific residues was irreversible and occurred also in embryos treated with metals, used as a proxy of environmental pollutants. The structural and functional changes of toposome caused by nitration under adverse environmental conditions may be related to the defective development of sea urchins' progeny.

The ability of organisms to adapt to changing environmental conditions depends, among other factors, on the life history of their parents and on the environmental factors they have experienced in their early life stages. Indeed, environmental factors can either positively or negatively influence the reproductive fitness of parents and this can determine if the offspring lives or dies, especially if it develops in a stressful environment[1]. This phenomenon of non-genetic inheritance is often referred to as trans-generational plasticity and can involve the transfer between generations of processes such as hormonal changes, nutritional provisioning or epigenetics[2].

Most marine organisms, including echinoderms, are broadcast spawners lacking parental care and releasing their gametes into the seawater for external fertilization[3]. Maternal provisioning is critical for the survival of the offspring of such organisms, especially to guarantee sufficient energy reserves to sustain embryos/larvae until they reach an autonomous developmental stage for external food supply[4]. Because of their sensitivity to the surrounding environment, planktonic embryos and larvae have been extensively used as model organisms in ecotoxicological studies[5–8]. Sea urchins are ubiquitous in the marine benthic environment, where they graze on macroalgal assemblages, and their associated epiphytes, and act as keystone species in confined ecosystems. Their life cycle involves short-lived embryonic and larval stages which metamorphosize into juveniles, and then to mature long-lived adults[3]. The larval stage is a critical phase, as the recruitment success is primarily determined by the survival of the embryos and larvae in the environment they experience[3]. Protective molecular strategies have evolved to allow eggs and early embryos to survive in response to environmental pollutants and marine

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