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Invited Feature Barnacles as biomonitors of metal contamination in coastal waters

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ABSTRACT

The use of barnacles as biomonitors of metal contamination in coastal waters worldwide is reviewed as a critique compilation of the reported studies and presents resume-tables of available data for future reference. The barnacle body reflects both short and long-term metal level environmental variations and the metal bioaccumulation occurs mainly in their granules (relatively inactive pools). The barnacle body is considered as good biomonitoring material and different barnacle species could bioaccumulate metal concentration ranges of 40–153,000 µg/g of Zn, 20–22,230 µg/g de Fe, 1.5–21,800 µg/g of Cu, 5.9 -4742 µg/g of Mn, 0.1-1000 µg/g of Pb, 0.7-330 µg/g of Cd, 0.4-99 µg/g of Ni and 0.2-49 µg/g of Cr. However, as the plates ('shells') of barnacle exoskeletons can be affected by metal levels in coastal waters, mainly in their composition and morphology, they are not considered good biomonitoring material. Despite this, the use of a specific barnacle species or group of species in a specific region must firstly be carefully validated and the interpretation of the contaminant bioaccumulation levels should involve specific environmental variations of the region, physiological parameters of the barnacle species and the relationship between the potential toxicity of the contaminant for the environment and their significance for the barnacle species. Barnacles, particularly a widespread cosmopolitan species such as Amphibalanus amphitrite, have a great potential as biomonitors of anthropogenic contamination in coastal waters and have been used worldwide, including Europe (United Kingdom, Turkey, Poland, Croatia, Spain and Portugal), Asia (India and China), Oceania (Australia), North America (Florida, Massachusetts and Mexico) and South America (Brazil). The use of barnacle species as biomonitors of metal contamination in coastal waters is considered an important and valuable tool to evaluate and predict the ecological quality of an ecosystem.

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1. Introdution

Anthropogenic contaminants reach coastal waters through rivers or directly from untreated discharges or atmospheric deposition. The quality of the sea water, sediments and biota should be frequently monitored and often involves using organisms as biomonitors (Morillo and Usero, 2008). According to Barbaro et al. (1978), biomonitor species should present the following main characteristics:

- (1) sessile or restricted mobility;
- (2) ubiquitous and sufficiently abundant in the sampling area;
- (3) available in all seasons;
- (4) ease of sampling;

- (5) predisposition for a consistent uptake of contaminants;
- (6) high capacity to accumulate contaminants above environment levels;
- (7) predisposition to retain contaminants for a sufficient time after reduction in the environment.

Later, Blackmore (1998) completed the definition of biomonitors as species capable of accumulate trace contaminants in their tissues, responding to the contaminant bioavailable fraction, which includes the dissolved and particulate phases that present the highest ecotoxicological potential. The accumulated concentrations in a biomonitor represent the total time-integrated exposure of the organism to all sources of bioavailable forms of the contaminant (Rainbow et al., 2002). Thus, comparisons between different sites involve recent contamination of the biomonitor, allowing both spatial and temporal variation studies (Rainbow et al., 2002). Although, the use of a single biomonitor does not represent the ecological behavior of all local biota, extrapolation of the

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conclusions from that site to a regional extension are usually considered of some value, by highlighting local bioavailability of the contaminant in at least some compartments of the habitat (Barber and Trefry, 1981). However, a more complete approach is achieved by using a range of different biomonitors, because the presence of a unique cosmopolitan species through all coastal waters is extremely rare and the use of a suite of biomonitors can cover all the different habitat compartments and therefore potential routes of contaminants uptake to local flora and fauna (e.g. solution, seston, sediment, etc.) (Páez-Osuna et al., 1999; Rainbow et al., 2002). Various organisms have been used as biomonitors to assess contaminant bioavailability in coastal waters worldwide: macroalgae, oysters, mussels, clams and barnacles (Ruelas-Inzunza and Páez-Osuna, 1998). Barnacles are present in different types of locations, with different degrees of pollution, so this group of organisms may be considered ideal for contaminants biomonitoring programmes (Ruelas-Inzunza and Páez-Osuna, 1998). Indeed, barnacles normally satisfy all the main characteristics proposed by Barbaro et al. (1978).

Metals are particularly toxic and have low or no degradation rates in the environment, so biomonitoring of these contaminants is considered an important tool for assessing the degree of contamination in coastal waters (Morillo et al., 2002).

This work reviews data on the use of barnacles as biomonitors of metal availabilities in coastal waters.

2. Barnacles as biomonitors of metal contamination in coastal waters

Most of the studies dealing with the kinetics of contaminants in barnacles are done by the analysis of the amount of the xenobiotic in the soft tissues of the invertebrate. Nevertheless, some work has been done on the potential accumulation of metals in the shell plates.

It should be stated that in this review, the authors used the terms of barnacle "soft tissues" as referring to entire barnacle body (head: cirripides or feeding legs and mouth; thorax and vestigial abdomen: muscles, stomach, intestine, mantle cavity, cement gland, ovaries, eggs and penis) and barnacle "hard tissues" as referring to their shell plates.

Much of the literature quoted in this review refers to species of the genus *Balanus*. The taxonomy of this genus has recently been revised by Pitombo (2004) with many of these *Balanus* species being reassigned to new genera, many of which were previously subgenera of the very large genus *Balanus*. In order to act as a consistent starting point for future research, this review uses the new generic names throughout, even though the original paper quoted would not have used these names.

Specific names remain unchanged, except in the case of *Balanus* uliginosus, which is synonymous with the previously described *Balanus kondakovi*. The species concerned are *Amphibalanus amphitrite*, *Amphibalanus eburneus*, *Amphibalanus improvisus*, *Fistulobalanus dentivarians*, *Fistulobalanus kondakovi*, *Megabalanus coccopoma*, *Perforatus perforatus*, and *Semibalanus balanoides*. *Balanus trigonus* remains as a species of *Balanus*.

2.1. Metal accumulation in the soft tissues

The first reported study using barnacles regarding the toxic and poisoning effects of anti-fouling agents was published by Bray (1919) who concluded that the more effective paints produced leachates highly toxic to the nauplius larva of a barnacle. After this study, various chemical means of measuring the loss of toxicity from paint films were tested, but only later, Clarke (1947) extensively studied poisoning and recovery in barnacles and mussels. The results obtained with the barnacles *Semibalanus balanoides* and *Amphibalanus eburneus* (Table 1) concluded that a long exposure to high concentrations of Cu could kill the barnacle larvae (Clarke, 1947) whereas moderate concentrations of Cu retarded and prevented the development of the calcareous base needed for the barnacle attachment. Thus, the early metamorphose-stage of the barnacles appeared to be the most vulnerable to Cu poisoning present in anti-fouling agents.

Alexander and Rowland (1966) measured Zn in soft tissues of *Amphibalanus amphitrite* and *Pollicipes polymerus* collected from La Jolla and from Columbia (USA) coastal shores. The Zn-65 specific activities (65 Zn: total Zn ratio) can be used to estimate biological transport of Zn and obtain Zn background levels through the coastal waters. This study showed that body tissues of *A. amphitrite* and *P. polymerus* accumulated 910 µg Zn/g (dry wt.) and 2090 µg Zn/g (dry wt.), respectively, and suggested that in future works barnacles can be used for the estimation of metal levels in marine coastal waters (Table 1).

Ireland (1974) measured Cu, Mn, Pb and Zn in soft tissues of *Semibalanus balanoides* collected from the Cardigan Bay (Wales, UK) and found seasonal and spatial variation in metal concentrations, possibly as a result of environmental changes in the river flow rates and in the phytoplankton productivity (Table 1). Walker et al. (1975) introduced the use of barnacles as potential biomonitor organisms of trace metals contamination in coastal waters. Walker et al. (1975) used *S. balanoides, Elminius modestus* and *Lepas anatifera* to study Zn contamination in coastal waters of North Wales (UK). This work revealed that barnacles accumulated Zn in their soft tissues, mainly in granules of the mid-gut, in levels which directly reflected the concentrations of the coastal environment (Table 1).

Stenner and Nickless (1975) measured Cu, Pb and Zn in *Amphibalanus amphitrite, Balanus perforates* and *Chthamalus stellatus* collected from the Rio Tinto estuary (Huelva, Spain) and from the Atlantic coast of Portugal. In this study, much higher barnacle soft tissues concentrations of Cu, Pb and Zn were found in the Rio Tinto estuary than in the Portuguese coast, where barnacle metal concentrations have low natural levels (Table 1).

The use of *Amphibalanus amphitrite* as a potential biomonitor was studied in the North Adriatic Lagoons and the authors concluded that it has a high uptake capacity to retain Cu, F and Pb, reflecting the proportion of these metals in the water (Barbaro et al., 1978). The bioaccumulation of Cr and Hg in the barnacles was detectable but low (Table 1). This study clearly demonstrated that *A. amphitrite* has two important properties to be a suitable biomonitor of metal contamination: (1) it has a strong predisposition to uptake and retain metals and (2) accumulates metals above environmental levels (Barbaro et al., 1978).

Barber and Trefry (1981) showed that barnacles, particularly *Amphibalanus eburneus*, satisfy the characteristics mentioned by Barbaro et al. (1978) to be considered a good biomonitor: (1) is sessile in the adult stage; (2) is a dominant Cirripidea in coastal waters of Eau Gallie Harbor and Indian River Lagoon (Florida); (3) it can be found in all seasons; (4) is easily collected from surfaces; (5) presents consistent uptake of Cu and Zn above environmental levels and (6) is tolerant to low salinities (Table 1). Thus, *A. eburneus* was considered a sensitive biomonitor of Cu and Zn contamination in these coastal waters. Anil and Wagh (1988) collected *Amphibalanus amphitrite* from the Zuari Estuary in west coast of India and showed that *A. amphitrite* could accumulate 865 μ g Cu/g and 1937 μ g Zn/g in its soft tissues, when the coastal waters only presented 1–11 μ g Cu/L and 13–46 μ g Zn/L (Table 1).

Rainbow (1985) made a laboratory experiment with *Elminius modestus* and showed that this barnacle could accumulate Cd, Cu and Zn in its soft tissues. Later, Rainbow (1987) showed that *Amphibalanus improvisus* from Thames estuary (United Kingdom)

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