Available online at www.sciencedirect.com
ScienceDirect
Environmental Pollution 151 (2008) 631–640
ENVIRONMENTAL POLLUTION
www.elsevier.com/locate/envpol

Field validation of a battery of biomarkers to assess sediment quality in Spanish ports

M.L. Martín-Díaz [a,b,*], J. Blasco [b], D. Sales [c], T.A. DelValls [a]

[a] Departamento de Química Física, Facultad de Ciencias del Mar y Ambientales, Polígono Río San Pedro s/n, 11510 Puerto Real, Cádiz, Spain
[b] Consejo Superior de Investigaciones Científicas, Instituto de Ciencias Marinas de Andalucía, Polígono Río San Pedro s/n, 11510 Puerto Real, Cádiz, Spain
[c] Departamento Ciencias Ambientales y Tecnología de los Alimentos, Facultad de Ciencias del Mar y Ambientales, Polígono Río San Pedro s/n, 11510 Puerto Real, Cádiz, Spain

Received 10 August 2006; received in revised form 13 March 2007; accepted 16 March 2007

A battery of biomarkers shows exposure to metals and organic compounds.

Abstract

Two marine invertebrates, the crab *Carcinus maenas* and the clam *Ruditapes philippinarum*, were used as bioindicator species to assess contamination when exposed *in situ* to sediment from different sites from four Spanish ports Cadiz (SW Spain), Huelva (SW Spain), Bilbao (NE Spain) and Pasajes (NE Spain). In an attempt to determine sediments toxicity, a combination of exposure biomarkers was analyzed in both species: metallothionein-like-proteins (MTLPs), ethoxyresorufin *O*-deethylase (EROD), glutathione *S*-transferase activity (GST), glutathione peroxidase (GPX) and glutathione reductase (GR). In parallel, physical and chemical characterization of the different sediments was performed and biological responses related to the contaminants. Significant induction of MTLPs was observed when organisms were exposed to metal contaminated sediments (port of Huelva), and EROD and GPX activities after exposure to sediments containing organic compounds (port of Bilbao and Pasajes). No significant interspecies differences were observed in biomarker responses except for the GST and GR.

Keywords: *Carcinus maenas*; *Ruditapes philippinarum*; Dredged material; Oxidative stress; Metallothionein

1. Introduction

Ecotoxicological data obtained in laboratory studies is often difficult to translate into accurate predictions of possible effects in the field. Since both overestimation and underestimation of effects may occur, laboratory biomarker results are best validated by field research. With respect to sediment, and especially dredged material, observations of a range of parameters in individuals sampled from the field do not necessarily provide relevant information. The transplantation of caged organisms to evaluate dredged material toxicity avoids such drawbacks and allows field assessment to be integrated with laboratory assessment. Prior studies include the analysis of distinct biomarkers in caged mussels transplanted to NW Mediterranean sediment (Munns et al., 2002) as well as in caged crabs and clams exposed to Spanish ports' sediment (Martín-Díaz et al., 2005). Dredged material has been found to have adverse environmental effects, resulting in international treaties and protocols for their proper environmental management. To this end, the Oslo–Paris Convention (OSPAR) and Helsinki Conventions (North Sea, North-East Atlantic, Baltic Sea) proposed guidelines to control the disposal of dredged material. Physical and chemical characteristics of the sediment are treated in these guidelines, together with biological effects. Nevertheless, biological effects are focused on the measurement of acute responses. The use of biomarkers for dredged material assessment is currently under review because of the

* Corresponding author. Departamento de Química Física, Facultad de Ciencias del Mar y Ambientales, Polígono Río San Pedro s/n, 11510 Puerto Real, Cádiz, Spain. Tel.: +34 956 016423; fax: +34 956 016040.
E-mail address: laura.martin@uca.es (M.L. Martín-Díaz).

0269-7491/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.envpol.2007.03.019

inherent capability of detecting early occurrence of various stress conditions within organisms and monitoring temporal progression (or regression) of the disturbance at various levels of biological organization. When assessing exposure to a variety of contaminants in the aquatic environment, biotransformation enzymes and metal-binding proteins, metallothionein-like-proteins (MTLPs), play an important role in organic and metal pollutant contamination respectively.

The present study was undertaken to test the potential impact of distinct contaminants present in dredged material on the crab *Carcinus maenas* and the clam *Ruditapes philippinarum* in four Spanish ports (Fig. 1). Few studies have used multiple biomarkers in more than one species, to determine sublethal effects of contaminants. In an attempt to achieve this main objective, the following were employed: (a) Species with differing feeding styles and distinct physiological characteristics; (b) a battery of exposure biomarkers; and (c) *in situ* assays. The battery of biomarkers was selected in order to examine different defense mechanisms of the organism. The defense mechanisms studied were: metallothionein-like-proteins (MTLPs), proteins for detoxification of metal contamination; mixed function oxidase (EROD), phase I detoxification enzyme; glutathione *S*-transferase (GST) phase II detoxification enzyme; glutathione peroxidase (GPX) and glutathione reductase (GR) antioxidant enzymes. The first of these biomarkers has been reported to be induced by metal exposure, while the remainder are implicated in the detoxification of organic compounds (EROD and GST) as well as the protection of the organism against oxidative stress (GPX and GR).

2. Materials and methods

2.1. General approach

The four Spanish ports chosen (Fig. 1) for the assessment of sediment toxicity were as follows. The Port of the Bay of Cádiz (SW Spain): the bay of

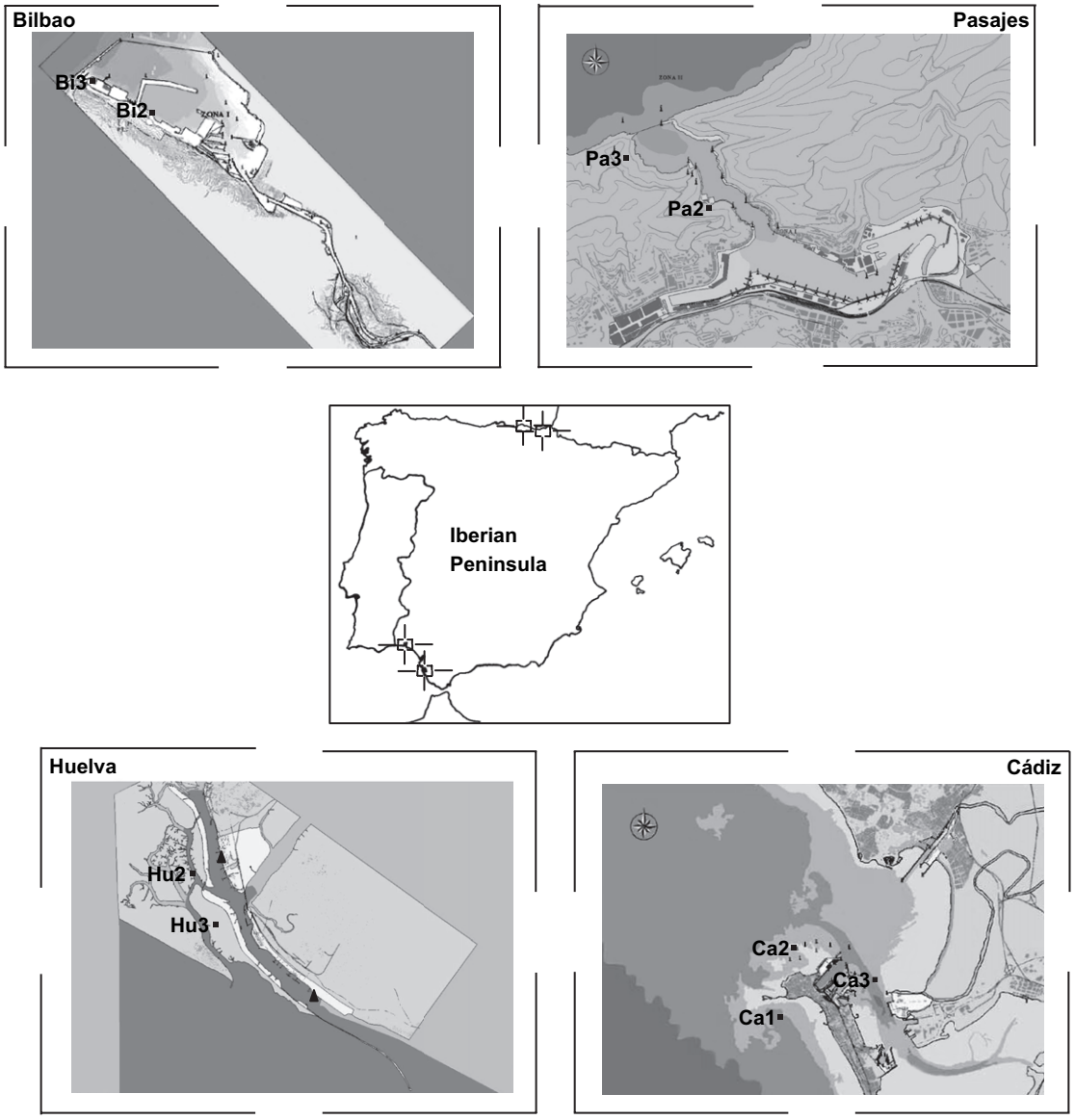

Fig. 1. Localization of sampling points in the Iberian Peninsula.