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Relationship between the lability of sediment-bound metals (Cd, Cu, Zn) and their bioaccumulation in benthic invertebrates

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Abstract

The present study has investigated metal contamination at nine sites (10 sampling stations) from the English Channel to the Mediterranean Sea, including low level and highly contaminated sediments. Both total and labile concentrations of metals were determined in superficial sediments. The influence of different pHs was tested and metal lability at pHs encountered in the gut of invertebrates (the ragworm *Nereis diversicolor*, the blue mussel *Mytilus edulis*, the Japanese oyster *Crassostrea gigas*) was compared with the distribution of metals in various operationally defined geochemical fractions. Cd showed the highest lability and Cu the lowest, whereas Zn lability was intermediate. Metal concentrations were determined in bivalves at six sites and in worms at three sites. Cd in living organisms and labile Cd in sediments increased in proportion over the gradient of contamination. This relationship did not always hold for Cu and Zn and these exceptions are discussed. Even if sediments are not the only source of metal contamination in marine invertebrates, the procedure proposed here to assess metal bioavailability by remobilising sediment-bound metals at physiological pHs, seems a significant improvement of the existing methodologies of risk assessment.

Keywords: sediment-bound metals; lability; bioavailability; bioaccumulation; bivalves; worms

1. Introduction

Quantitatively sediments represent the major compartment for metal storage in aquatic environments (Gagnon and Fisher, 1997). Although the total trace metal concentrations in sediments give a convenient measure of metal pollution, such measures do not necessarily predict the toxicity of these pollutants to aquatic animals (Luoma, 1983; Luoma, 1989; Di Toro et al., 1990; Luoma, 1995). Quantifying the geochemical phases of metals associated with sediments is an important step in predicting the ultimate fate, bioavailability, and toxicity of metals (Salomons and Förstner, 1980; Salomons and Förstner, 1984). Many studies have reported relationships between metal bioavailability and metal partitioning in different geochemical phases (Tessier and Campbell, 1987; Bryan and Langston, 1992; Fan and Wang, 2002).

The ecotoxicological risk posed by a contaminated sediment will depend on metal mobility leading to solution, as well as the ability of living organisms to assimilate metals directly from ingested sedimentary particles. Metal mobility will depend on a variety of processes including chemical (dissolution, desorption, complexation, precipitation and adsorption), biological (degradation, transformation, accumulation, faeces production and filtration) and physical ones (diffusion, phytolysis, aggregation and burying) (Luoma, 1983; Förstner, 1986). For instance, metal ions adsorbed on small grain size particulate matter are often considered to be "bioavailable", whereas metals complexed with organic

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matter or included in amorphous metal oxides through precipitation or coprecipitation are likely to be less bioavailable; metals present in crystalline structures are generally unavailable for uptake (Dicks and Allen, 1983).

In order to assess bioavailability, three major types of methodologies may be implemented: (1) chemical speciation studies designed to assess the degree of degradability (or mobility) of sediment-bound pollutants (2) experimental studies comparing bioaccumulation via water, food and sediment, and (3) in vitro studies mimicking digestive absorption of particle-bound substances. Various extraction schemes have been employed to quantify metal species in sediments and soils (Tessier et al., 1979; Kersten and Förstner, 1989; Amiard, 1992; Li et al., 1995; Stecko and Bendell-Young, 2000). Experimental models of food chains have been designed to determine the retention of metals in aquatic organisms, mainly filter-feeders, according to the environmental source of contamination, namely water, sediment and food (Ettajani et al., 1992, 1996; Lee and Luoma, 1998; Wang and Wong, 2003). Desorption from particles under the conditions prevailing in the digestive tract of aquatic organisms has been quantified as a possible way to predict digestive absorption from particles. Digestive conditions have been simulated using either gut juice (Mayer et al., 1996; Wang et al., 2002; Yan and Wang, 2002; Fen and Wang, 2003) or enzymes tested at pHs which are known to exist in the guts of invertebrates (Amiard et al., 1995; Ettajani and Amiard, 1995; Ettajani et al., 1996).

The objectives of the present study were (1) to examine the relationship between metal lability in sediment and their assimilation in benthic organisms, both deposit-feeders (ragworms *Nereis diversicolor*) and filter-feeders (mussels *Mytilus edulis*, oysters *Crassostrea gigas*); (2) to contrast the differences between metals, namely Cd, Cu, and Zn. The work has focussed on superficial sediments because they are the most easily resuspended (via tides, swell) and thus available to filter-feeding biota. Superficial sediments are also oxic, a characteristic which facilitates desorption. Sediments were collected from nine contaminated and comparatively clean sites in the Channel and the bay of Biscay and in the Thau lagoon, Mediterranean Sea, the metal contamination of which is well documented (Bryan et al., 1985; RNO, 1995, 1998). In the framework of the Microbent programme, special attention has been devoted to the influence of large stocks of filter-feeders on the levels and bioavailability of sediment-bound metals. Thus investigations have been carried out in areas of the Thau lagoon with or without shellfish-farming installations.

2. Materials and methods

2.1. Sediment sampling

The sampling sites are shown in Fig. 1. The intertidal sediments were collected from Boulogne harbour (BL), the Seine estuary (SE), the bay of Bourgneuf (BB), the Gironde estuary (GR), the bay of La Rochelle (LR), the bay of Aiguillon (BA), Fier d'Ars (Ré island) (FA), the Thau lagoon (T4 away from shellfish-farming installations and T5 under these installations) and Restronguet Creek (RC). Sediments were collected on only one occasion at BL, SE, T4, T5 and RC whereas other sites were sampled monthly from spring to fall ($N = 7$ at BB and GR; $N = 8$ at BA, FA and LR).

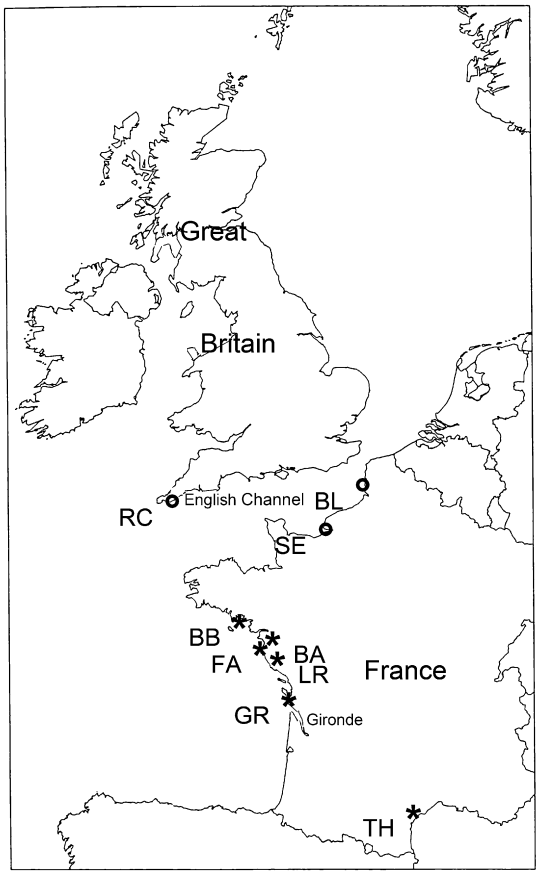

Fig. 1. Map of the sampling sites: ○ collection of sediments and worms; * collection of sediments, oysters and mussels. Boulogne harbour (BL), the Seine estuary (SE), the bay of Bourgneuf (BB), the Gironde estuary (GR), La Rochelle harbour (LR), the bay of Aiguillon (BA), Fier d'Ars (Ré island) (FA), the Thau lagoon (TH: T4 and T5) and Restronguet Creek (RC).

Superficial sediments (<1 cm deep) were scraped using a plastic blade and placed immediately in a plastic box which was filled to the brim to eliminate air. Samples were then transported to the laboratory with icepacks in an isothermic container and centrifuged on their arrival. Sediment samples for desorption tests were stored in the dark at 4 °C, and treated within a week of collection. For metal partitioning, sediments were preserved by freezing. The main characteristics of these sediments are shown in Table 1.

2.2. Desorption tests

All desorption tests were carried out in triplicate. For sediments originating from the Seine estuary, Boulogne harbour and Restronguet Creek, each sample (500 mg) was dispersed into one of a series of buffers at different pHs (20 ml; prepared with 1% acetic acid and adjusted to appropriate pHs by adding suprapure ammonia). For all other sediments, pH 4 only was tested. The samples were shaken gently for 2 h at ambient