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Heavy metal accumulation in surface sediments at the port of Cagliari (Sardinia, western Mediterranean): Environmental assessment using sequential extractions and benthic foraminifera

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ABSTRACT

Superficial sediments were taken at the port of Cagliari (Sardinia, Italy), which includes the oil terminal of one of the largest oil refineries in the Mediterranean. Significant trace metal concentrations were found in the whole port area. Sequential extraction of metals from the different sediment fractions (BCR method) showed a higher risk of remobilisation for Cd, which is mostly bound to the exchangeable fraction. Foraminiferal density and richness of species were variable across the study area. The living assemblages were characterized by low diversity in samples collected close to the port areas. *Ammonia tepida* and bolivinids, which were positively correlated with concentrations of heavy metals and organic matter content, appeared to show tolerance to the environmental disturbance. The sampling sites characterized by the highest values of biotic indices were located far from the port areas and present an epiphytic and epifaunal biocoenosis.

1. Introduction

Ports are usually an important focus of industrial (shipping, loading and unloading, accidental spills) and urban (wastewater emissions) activity, and they are recognised as important locations where inorganic metals and metalloids accumulate in sediments (e.g., Schintu and Degetto, 1999; Adamo et al., 2005; Tessier et al., 2011, Petronio et al., 2012; Mamindy-Pajany et al., 2013). Sediments are known to play an important role as a sink of metals in marine environments, but they can also act as a source of these elements, depending on the physicochemical conditions (Kersten and Forstner, 1986). For this reason, speciation of metals in sediments is focussed on the establishment of metal concentrations that can be extracted under specific environmental conditions (Rao et al., 2008). The anthropogenic pressure on the marine coastal zone makes the identification of ecological indicators important to evaluate the environmental quality and to achieve (or maintain) good environmental status as stated in the Marine Strategy Framework Directive (MSFD, 2008/56/EC). Benthic foraminifera are useful bioindicators in coastal marine environmental research because they are small, abundant, diverse, and include stress-tolerant taxa. For example, *Ammonia tepida* and *Haynesina germanica* have been reported as pollution-tolerant species in coastal and lagoonal environments (e.g., Armynot du Châtelet et al., 2004; Frontalini et al., 2009), whereas *Bolivina*, *Bulimina*, *Epistominella* and *Fursenkoina* have been considered tolerant to organic matter (e.g., Frontalini and Coccioni, 2011). Benthic foraminifera are typically sessile or of limited mobility and are therefore directly influenced by natural or induced stresses in their environment. The response of foraminifera to pollution is considered to be a basic way of assessing the anthropogenic pressure (e.g., Coccioni et al., 2005; Scott et al., 2005; Alve et al., 2009; Martínez-Colón et al., 2009 Armynot du Châtelet and Debenay, 2010; Cosentino et al., 2013). Most of these studies have focussed on the heavy metal concentrations determined by total or partial digestion of the sediments, not considering the different speciation status of the elements. Only very few ongoing studies are dedicated to the availability of heavy metals (e.g., Martins et al., 2011, 2013, 2015).

The sequential extraction schemes are capable of separating non-residual metal complexes from residual metals. Different sequential extraction schemes have been used for the geochemical fractionation study of metals in sediments, starting with the work of Tessier et al. (1979). Owing to the need for standardization and subsequent validation of extraction schemes for sediment analysis, the European Community Bureau of Reference (BCR) introduced in 1993 a new three-step

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sequential extraction (Ure et al., 1993) that has since been modified by Rauret et al. (1999). This BCR sequential extraction method analyses different fractions of metals in the soil: acid-extractable (water soluble, exchangeable, and bound to carbonates), reducible (bound to Fe and Mn oxides), oxidizable (bound to sulphides and organic matter), and residual (e.g. Pueyo et al., 2001). Water-soluble and exchangeable forms are considered readily mobile and available to biota, while metals that are incorporated into the crystalline lattices of clays appear relatively inactive. The other forms (precipitated in carbonates; occluded in Fe, Mn, and Al oxides; or complexed with organic matter) could be considered relatively active or firmly bound depending on the actual combination of physical and chemical properties of the soil or sediment (Kersten, 2007). In terms of bioavailability, various species of metals are more biologically available than others (Nelson and Donkin, 1985; Zimmerman and Weindorf, 2010). However, the prediction of bio-effective or bioavailable concentrations from chemical data is poor (O'Connor and Paul, 2000).

In this paper, an integrated approach based on sequential extractions of metals from sediments and benthic foraminiferal distribution has been utilized to assess pollution in the port of Cagliari (Sardinia, Italy). The port, which occupies a wide portion of the Gulf of Cagliari, is one of the largest in the western Mediterranean, and since the 1960s, it has been exposed to important industrial activities such as oil refining. The main objectives of the study are (1) to quantify and investigate the spatial distribution of trace metals in surface sediments, and (2) to evaluate the response of benthic foraminifera according to the distribution of trace metals in the different phases of the sediments.

2. Materials and methods

2.1. Geological setting

The Gulf of Cagliari (Fig. 1) is placed in the southern end of the Plio-Quaternary Graben of Campidano, where fluvial sedimentation since the Pleistocene has caused favourable conditions for the development of Santa Gilla and Molentargius coastal lagoons separated by the Miocenic hills of Cagliari prevalently formed by rhodalgal limestones. The Holocene La Playa and Poetto sandbars complete the evolution of the coastal margin. The latest Pleistocene-Holocene Cagliari basin is characterized by clayey sand and siliciclastic carbonate sediments. The inner shelf shows geomorphological hollows interpreted as the product of the paleo-river erosion during the Würmian low stand (MIS 4-2) (Ulzega, 1995; Orrù et al., 2004). Inside the Gulf shoreface, sediments are represented prevalently by siliciclastic facies in the eastern part and mixed terrigenous muddy sands in the western part (S. Gilla Lagoon and Pula-Sarroch coastal area). Around the horst of Capo S. Elia, made

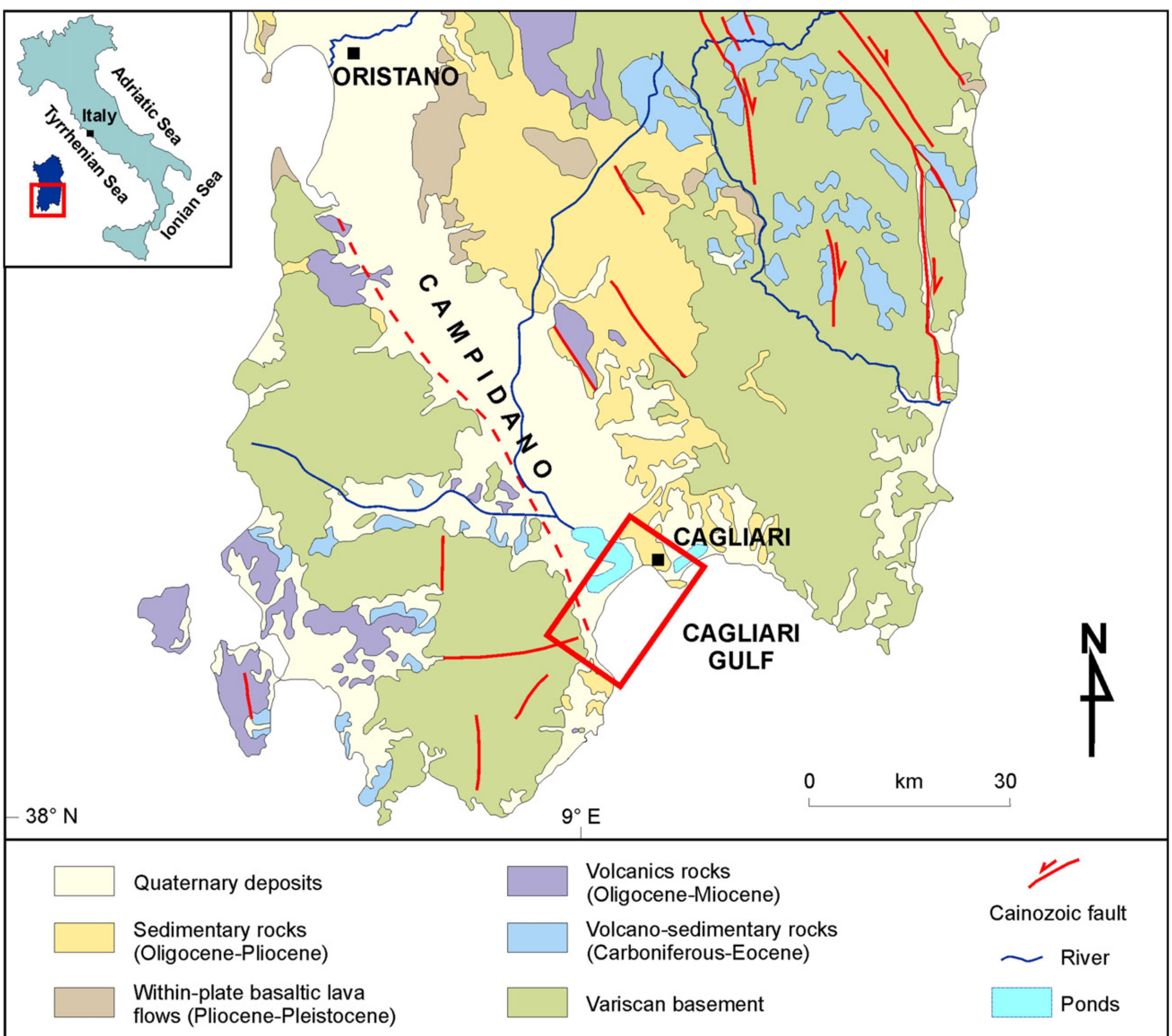

Fig. 1. A sketch map of southern Sardinia (Italy) with the main geological features (from Carmignani et al., 2015, modified).