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Baseline

Bioavailability of heavy metals in water and sediments from a typical Mediterranean Bay (Málaga Bay, Region of Andalucía, Southern Spain)

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ABSTRACT

Concentrations of heavy metals were measured in sediment and water from Málaga Bay (South Spain). In the later twentieth century, cities such as Málaga, have suffered the impact of mass summer tourism. The ancient industrial activities, and the actual urbanization and coastal development, recreation and tourism, wastewaters treatment facilities, have been sources of marine pollution. In sediments, Ni was the most disturbing metal because Ni concentrations exceeded the effects range low (ERL), concentration at which toxicity could start to be observed in 85% of the samples analyzed. The metal bioavailability decreased in the order: Cd > Ni > Pb > Cu > Cr. In the sea water samples, Cd and Pb were the most disturbing metals because they exceeded the continuous criteria concentration (CCC) of US EPA in a 22.5% and 10.0% of the samples, respectively. Statistical analyses (ANOVA, PCA, CA) were performed.

Málaga was a pioneer city to begin the Industrial Revolution in Spain becoming the first industrial city in country and occupying the second place after Barcelona for years; the city became known as "the chimneys city". In the beginning of the 20th century the economic crisis had its hold all over Spain and especially in Malaga, where the population suffered problems in the agricultural sector due to several natural disasters. This period was also dominated by the political instability throughout the whole country, which culminated with the Spanish civil war from 1936 to 1939. After the civil war, during the dictatorship of General Franco, the economy in Malaga slowly recovered. It was not until the 60s tourist boom, that the economy in Malaga recovered totally. In this decade hotels and tourist resorts were built all over Malaga and Costa del Sol, which still today is one of the most popular destinations with more than 6 million tourists visiting the region every year (Fundación Picasso, 2008). The ancient industrial activities, and the actual urbanization and coastal development, recreation and tourism, wastewaters treatment facilities, have been sources of marine pollution. Estuarine and coastal bays, which are regions of active land-sea interaction, respond sensitively to natural processes and anthropogenic activities (Li et al., 2007; Yu et al., 2010; Okbah et al., 2011). Sediments are the main repository and source of heavy metals in the aquatic environment and play an important role in the transport and storage of potentially hazardous metals (Yan et al., 2010; Gao and Chen, 2012). The distribution of heavy metals in sediment adjacent to populated areas can provide the evidence of the anthropogenic impacts on ecosystems and aid in assessing the risks associated with discharged human waste (Demirak et al., 2006; Balls et al., 1997). Assessment of sediment quality is therefore recognized as a critical step in estimating the risk associated with man-made pollution in aquatic systems. Nonetheless, studies on the water column are also necessary. In this work, concentrations of heavy metals (Cd, Cr, Cu, Ni and Pb) were measured in sediment and water from Bay in the Málaga province (South Spain). Lead is one of the most disturbing metal in the zone due to the ancient industrial activities of the city. Next to a famous beach of the city was located an industrial area (between the mouth of the Guadalhorce river and the port of Málaga). In that area there was a lead foundry called "Los Guindos" since 1923–1979, besides other industries (Rodríguez Marín, 2007; Reina Sánchez, 2009). The fireplaces of this foundry still remain as decorative figures of the promenade "Antonio Banderas".

The determination of the total concentrations of metals in sediments is not sufficient to be able to predict the capacity for mobilization of these elements. The environmental behavior of trace metals is critically dependent on their chemical form, which influences mobility, bioavailability and toxicity to organisms (Bacon and Davidson, 2008; Tuzen et al., 2004; Passos et al., 2010). In this sense, fractionation using sequential extraction schemes has been proposed. The scheme most widely accepted and applied is the three-stage sequential extraction procedure proposed by the European Standards, Measurements and Testing (SM&T) Program, formerly the Community Bureau of Reference (BCR) (Rauret et al., 1999). Based on this scheme, in an earlier work (Alonso Castillo et al., 2011), a new microwave assisted sequential extraction procedure was proposed, which was well compared with BCR procedure. This procedure was employed in the present study for the

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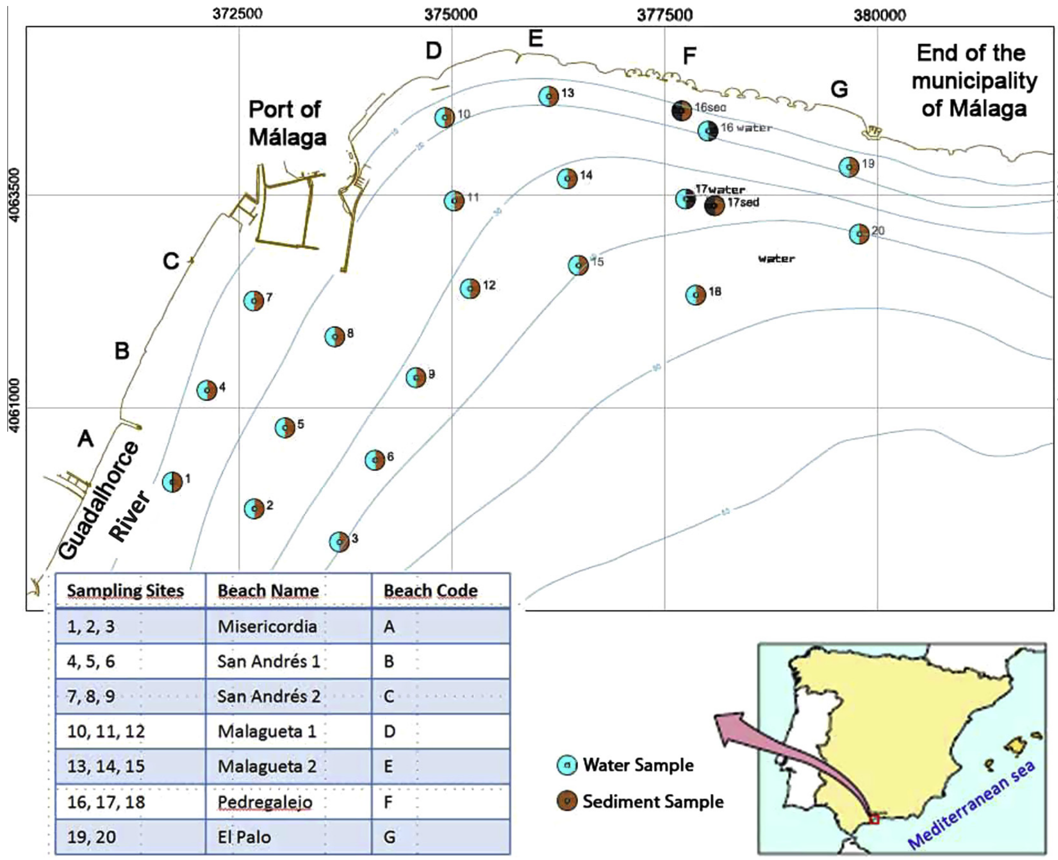

Fig. 1. Location map of sampling sites.

Table 1
Microwave sequential extraction method (sample mass 0.25 g).

Step	Fraction	Reagent	Heating time (s)	Ramping time (min)	MW power (w)	Volume of reagent (mL)
1	Exchangeable (P1)	Acetic acid 0.11 M	120	4.6	300	10
2	Reducible (P2)	Hydroxylammonium chloride 0.5 M pH 1.5	105	6.5	400	10
3	Oxidizable (P3)	Hydrogen peroxide/Acetic acid 5 M	120	4.6	300	2/5

sediment fractionation. Labile (non-residual) fractions of trace elements (sum of the first three fractions) were analyzed because they are more bioavailable than the residual amount (Abdallah, 2007).

The determination of trace elements in sea water is difficult due to the high salinity (approx. 35 g l^{-1}) of the sample matrix; determining the concentration of an analyte in a matrix of major ions that exist at concentrations 10^9–10^{10} times greater is a formidable and difficult analytical task (Lohan et al. 2005). Methods for the determination of trace elements in seawater usually require the inclusion of on-line sample pre-treatment steps, such as matrix separation and analyte pre-concentration, using a closed flow system, which provide best protection against contamination. In the last decade, great interest has been paid to the application and development of flow injection (FI) techniques using inductively coupled plasma mass spectrometry (ICP-MS) as the detection system (Todoli, 2005). In a previous work (Sánchez Trujillo et al., 2012), an on-line FI pre-concentration method for simultaneous determination of heavy metals from natural water samples (sea water, estuarine and river water) by ICP-MS using a chelating resin was developed. This FI-ICP-MS method was applied in the present study for the determination of the trace metals in the sea water samples collected in the Málaga Bay.

Every action involved in modifying the environment has countless repercussions. Scientists seek to understand these complex interactions so that the present condition of the ambient environment can be assessed and measures taken to prevent or minimize

Table 2
Metal concentrations (mg/kg) in sediments from Málaga Bay compared to the sediment quality guidelines (SQGs) for metals in saltwater ecosystems and sediment from other Spanish Mediterranean site (outer Barcelona Harbor).

	Cd	Cr	Cu	Ni	Pb	Ref.
Sediments Málaga Bay	0.021–0.283	4.31–26.0	6.57–21.2	9.48–40.2	7.92–37.1	This work
Sediment outer Barcelona Harbor	0.7–1.1	45–73	64–175	28–32	67–151	Gilbert et al., 2009
SQGs ERL–ERM	1.2–9.6	81–370	34–270	20.9–51.6	46.7–218	Long et al., 1995

ERL: effects range low, concentration at which toxicity could start to be observed.
ERM: effects range median, concentration above which adverse effects might occur.