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The influence of a metal-enriched mining waste deposit on submarine groundwater discharge to the coastal sea

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ABSTRACT

Submarine groundwater discharge (SGD) was investigated at El Gorguel Bay (Cartagena-La Unión Pb–Zn mining district, Murcia, Spain), a Mediterranean region where mine tailings have been accumulated for decades at the shoreline. At this site, groundwater may become enriched in metals prior to discharge to the coastal sea and may lead to significant releases that can contaminate the coastal environment. The distribution of dissolved metals and Ra isotopes were studied in seawater and groundwater samples collected during the summer season in 2013. Cross-shore gradients of ^{224}Ra in the bay allowed the calculation of a SGD flow of (39 ± 14) 10^3 m^3 day^{-1}. SGD-driven metal fluxes were 47–180 mol day^{-1} km^{-1} for Zn, 0.20–0.60 mol day^{-1} km^{-1} for Pb, 4–32 mol day^{-1} km^{-1} for Fe, 0.8–2.3 mol day^{-1} km^{-1} for Cu and 0.9–2.8 mol day^{-1} km^{-1} for Ni. Compared to other coastal zones not affected by mining activities, SGD-driven metal fluxes were especially significant for dissolved Zn and Pb. The magnitude of these SGD-driven metal fluxes indicates that SGD is a relevant pathway in delivering metals to the coastal environment at El Gorguel Bay. This fact highlights the importance of investigating the role of SGD as a possible source of contamination to the sea in mining districts located in the proximity of the coast.

1. Introduction

Submarine groundwater discharge (SGD) refers to “any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force” (Burnett et al., 2003). SGD is thus composed of two different components, meteoric fresh groundwater flowing towards the sea and seawater recirculated through the sediments, which are mixed in the so-called subterranean estuary (Moore, 1999). The magnitude of SGD can be estimated by using Ra isotopes as geochemical tracers (Moore, 2010). SGD is a carrier of several chemical compounds that can impact the biogeochemistry of coastal environments. The input of dissolved nutrients through SGD plays, for instance, an important role on coastal productivity, leading to eutrophication or harmful algal blooms (Lee et al., 2009). Further, SGD represents a potential source of trace metals to the coastal sea, both in natural (Jeong et al., 2012; Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Windom et al., 2006) and in anthropogenically-modified environments characterized either by the influence of urban wastewater (Beck et al., 2009) or industries (Rahman et al., 2013).

Mining is an anthropogenic activity that can lead to groundwater contamination, mainly due to the interaction of freshwater with the waste materials discarded during separation processes. Thus, mining wastes in coastal environments can significantly influence the SGD composition, especially when tailings are occupying the subterranean estuary. Despite this potential impact, studies evaluating SGD in coastal mining areas have received no attention to date.

The aim of this work is to evaluate how the presence of mine tailings in coastal sediments influences the SGD-driven flux of trace metals in near shore systems. To this end, the highly metal-contaminated area of El Gorguel Bay in the Cartagena-La Unión abandoned Pb–Zn mining district in the eastern coast of the Iberian Peninsula was examined. Mining activities in the area started 2500 years ago and the human impact on the region has had severe environmental consequences. In particular, from 1957 to 1990, waste materials from ore enrichment plants were discharged directly into the sea, resulting in the infilling of two natural bays, Portman and El Gorguel Bays (Manteca et al., 2014;

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Oyarzun et al., 2013). Although many trace metals (e.g., Fe, Cu, Zn, Ni, Co) are essential micronutrients for the planktonic community, at elevated levels these elements can limit algal growth or act as toxic agents in local biological communities (Lafabrie et al., 2013; Morel and Price, 2003; Twining and Baines, 2013). Analyses of red mullets in the Portman area showed that they accumulated the highest concentration of Hg, Pb and As measured in contaminated areas of the Spanish Mediterranean Coast (Martínez-Gómez et al., 2012). These levels of contaminants in organisms may not cause severe health consequences. However, they suggest a need for a more comprehensive study of this mining area. Thus, the identification and quantification of the metal inputs to the coastal sea at El Gorguel Bay is even more relevant considering the presence of an aquaculture farm, located at about 1.5 km from the coastline.

2. Methods

2.1. Study area

Cartagena-La Unión is an abandoned mining district located at the southeast end of the Betic mountain chain, in the region of Murcia (SE Spain). It extends along 25 km of the Western Mediterranean Sea coastline, covering an area of about 50 km^2 (Fig. 1). The ore body consists of a Pb–Zn volcanic massive sulfide deposit, characterized basically by galena, spharelite, pyrite, marcasite, and calchopyrite, with other sulfides and sulfosalts in trace amounts (Navarro-Hervás et al., 2012). In addition, a second association of minerals, dominated by greenalite and magnetite, exists in the district (Oen et al., 1975). A large number of secondary minerals are also present, as the result of strong weathering processes that affected both the host rocks and the primary mineralization (Navarro-Hervás et al., 2012).

The Cartagena-La Unión district is characterized by the presence of a hard-rock aquifer composed mainly of schists, quartzites, phyllites, limestones and marbles, with a thickness ranging between 400 and 800 m. The aquifer is recharged exclusively by rainwater and shows a secondary porosity because of intensive tectonic activity, mining exploitation and, to a lesser extent, karstification processes (Robles-Arenas et al., 2006). The transmissivity of groundwater in the aquifer varies between 7 and 2100 m^2 day^{-1} and the total discharge of fresh groundwater to the coastal sea is estimated to be in the range of 0.5–0.6 hm^3 $year^{-1}$, with a main direction of the flow towards SE (Robles-Arenas, 2007). Climate conditions in the Cartagena-La Unión area are typically Mediterranean, with an annual mean temperature of 18 °C and an annual average rainfall of 250–300 mm , which occurs primarily as strong episodic events concentrated in spring and autumn. This semi-arid climate, together with the topography, favors the development of short ephemeral fast-flowing streams (Conesa et al., 2008).

The Cartagena-La Unión region was already exploited for minerals by the time of the Carthaginians and Romans and became one of the most important mining districts in the south of Spain. The most significant environmental impact from mining in the area took place in the last 50 years of intensive Pb–Zn extraction (1940s–1990). Indeed, two important changes in the mining technology occurred during this period: (1) the switch from underground to open pit operations, and (2) the introduction of froth flotation mineral concentration processes, which commonly produce scrap materials that contain large amounts of pyrite (more than 10%) (Martínez-Sánchez et al., 2008) and minor quantities of other sulfides (Oyarzun et al., 2013). Mining wastes from the flotation process were accumulated in 89 dumps on land and at sea, resulting in the artificial infilling of two Mediterranean bays (El Gorguel and Portman Bays). These waste repositories resulted in one of the most critical cases of contamination in the Mediterranean Sea. These tailings are characterized by high concentrations of Fe, Zn and Pb, with ranges of 160–240, 2.3–11 and 2.3–6.1 mg g^{-1}, respectively (Robles-Arenas et al., 2006).

Our study is focused on El Gorguel Bay, which is located at the end of an ephemeral stream that connects a large dump area with the sea. The mining waste piles have been subjected to erosion for decades during storm events, leading to metal-rich runoff into the adjacent ephemeral stream. This process, together with the anthropogenic accumulation of metal-enriched tailings in the bay (Robles-Arenas et al., 2006), has caused the coastline to aggrade 80–170 m offshore (Fig. 2a). As a consequence, groundwater flowing toward El Gorguel Bay likely moves through mining wastes. The presence of this material in the subterranean estuary, where water from the continent mixes with recirculated seawater, probably results in an elevated flux of metals to near shore seawater via SGD (Fig. 2b).

2.2. Sampling

A survey was conducted during the summer season, on July 23–24th 2013, to quantify SGD and its associated metal fluxes into the bay by means of Ra isotopes. Three transects perpendicular to the shoreline were sampled for surface seawater (Fig. 3a). The two lateral transects consisted of 7 stations located at approximately 0, 100, 200, 300, 400,

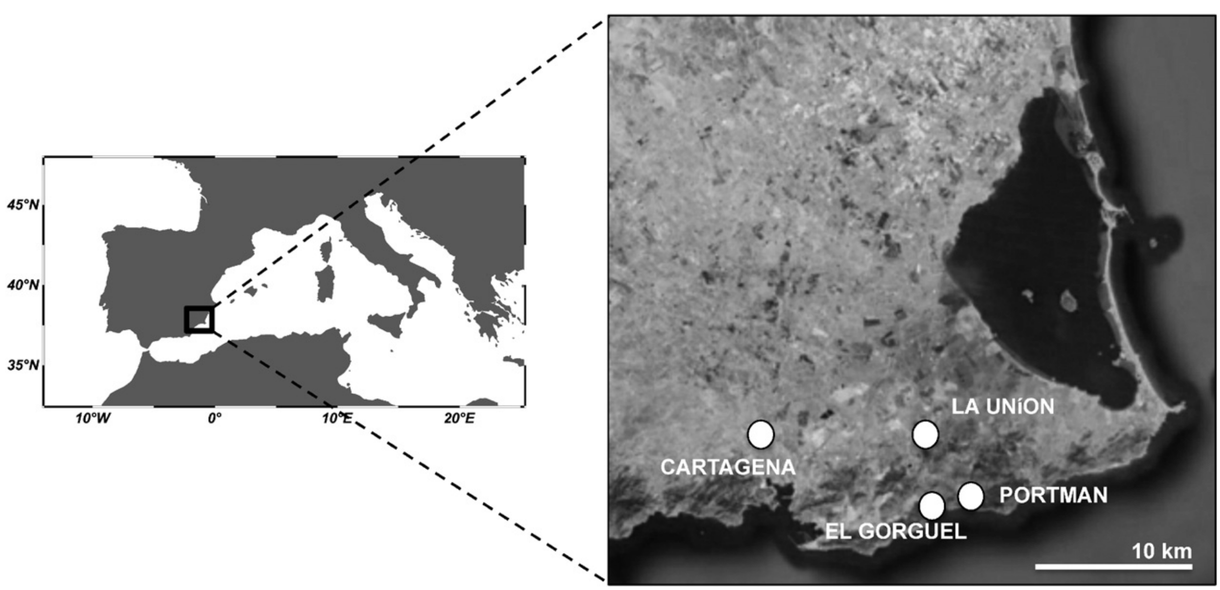

Fig. 1. Location of the study area in the Southeast of the Iberian Peninsula, in the Western Mediterranean coast.