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Trace metal characterization and fluxes from the Guadiana, Tinto-Odiel and Guadalquivir estuaries to the Gulf of Cadiz

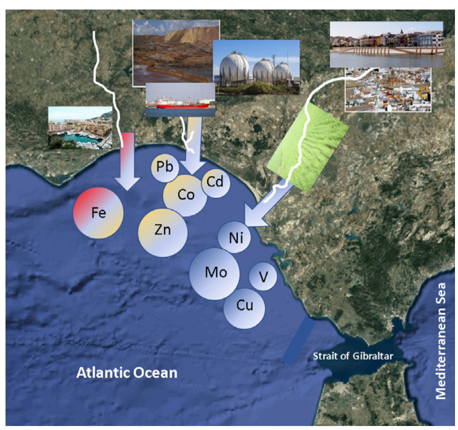
E. González-Ortegón [a,b,*], I. Laiz [c], D. Sánchez-Quiles [a], A. Cobelo-Garcia [d], A. Tovar-Sánchez [a]

[a] Instituto de Ciencias Marinas de Andalucía (ICMAN-CSIC), Campus Universitario Río San Pedro, 11510 Puerto Real, Cádiz, Spain
[b] Campus de Excelencia Internacional del Mar (CEIMAR), Spain
[c] Dept. of Applied Physics, University of Cadiz, Campus Universitario Río San Pedro, 11510 Puerto Real, Cádiz, Spain
[d] Instituto de Investigaciones Marinas (IIM-CSIC), Vigo, Spain

HIGHLIGHTS

- High metal concentrations in the Tinto-Odiel estuary by historical mining activities
- Metal concentrations in Guadiana and Guadalquivir mostly due to urban-agricultural uses
- High fluxes of Ni (73%) and Cu (19%) from the Guadalquivir river to the GoC shelf
- Metal pattern over continental shelf largely determined by the Guadalquivir fluxes
- Net transport of trace metals from Guadalquivir river to the Mediterranean Sea

GRAPHICAL ABSTRACT



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ABSTRACT

Metals transported into the coastal zone by the South Iberian rivers are key to understand the biogeochemical cycles and distribution of trace elements in the Gulf of Cadiz (GoC hereinafter) and the exchange with the Mediterranean Sea. Previous studies carried out in the 80s have suggested that metal enrichment in the Alboran Sea (Western Mediterranean) is related with fluvial inputs from acid mine drainage from the Tinto and Odiel rivers. The present study evaluates the contribution of dissolved trace metal concentrations (i.e. Cd, Co, Cu, Fe, Mo, Ni, Pb, V, Zn) from the three main rivers discharging into the GoC (i.e. Guadiana, Tinto-Odiel and Guadalquivir rivers). Our results show that the metal composition of water discharged from each river is impacted by the activities developed in the course of the rivers, which clearly influence the GoC coastal surface waters composition. Metal fluxes from the Guadalquivir river are quantitatively higher than those from the Tinto-Odiel (e.g. up to 73% and 19% higher for Ni and Cu, respectively). Although the metal concentrations spatial distributions in the GoC are dominated by the circulation pattern between the Atlantic and the Mediterranean Sea, the concentrations within the GoC continental shelf could be explained by a greater contribution from the Guadalquivir estuary (e.g. 80.5%, 54.6%, 56.5% and 56.6% for Ni, Cu, Mo, and V respectively).

* Corresponding author at: Instituto de Ciencias Marinas de Andalucía (CSIC), Campus Universitario Río San Pedro, 11519 Puerto Real, Cádiz, Spain.
E-mail address: quique.gonzalez@icman.csic.es (E. González-Ortegón).

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1. Introduction

Understanding linkages between basin characteristics (e.g. bedrock lithology), anthropogenic activities (e.g. land uses of river basin or mining) and river flow (dam discharges and rainfall) is key in developing spatial models of trace metals in a temperate continental shelf as the Gulf of Cadiz (GoC). The GoC surface water enters the Mediterranean Sea (Sánchez-Leal et al., 2017) through the north Atlantic inflow in the Gibraltar Strait, affecting the water masses composition. In fact, enrichments of Cu, Ni and Cd in the Mediterranean Sea have been associated to the Atlantic Ocean inflow (Migon, 2005; Boyle et al., 1985).

The GoC basin receives freshwater inputs from three main rivers, i.e., Guadiana, Tinto-Odiel and Guadalquivir, that significantly increase the concentrations of metals (Martin and Whitfield, 1983; Viers et al., 2009), and dissolved organic matter (González-Ortegón et al., 2018) in their adjacent coastal waters. Thus, for example, the concentrations of Zn, Cu and Cd in the GoC continental shelf waters were reported to be much higher than in other coastal areas (van Geen et al., 1991).

There are multiple sources and processes, such as river inflow, groundwater, aerosol deposition, anthropogenic activities, biological recycling, remineralization, sediment resuspension, etc., that complicate the metal sources identification and contribution in a water mass. Overall, river discharge is the major source of metals introduced to continental shelf waters (Viers et al., 2009; Olías et al., 2006) and hence, the transport of most chemicals depends on the precipitation regime in the river basin, with a few exceptions in some areas (e.g. V, Cd by coastal upwelling process) (Monteiro et al., 2015; Santos-Echeandía et al., 2009). In the case of the GoC continental shelf, the concentration of trace metals could indicate the existence of a direct input through freshwater fluxes in the wet period. Considering that the three main rivers that discharge over the GoC continental shelf are regulated by dams, freshwater discharges and terrestrial inputs of organic matter into each of the estuaries directly depend on the damming control (Elbaz-Poulichet et al., 2001; González-Ortegón et al., 2015; Vasconcelos et al., 2007).

Despite the fact that metal levels in the Mediterranean Sea are directly influenced by the GoC shelf waters (van Geen et al., 1988) and that any variation of their concentrations in the GoC could influence the Western Mediterranean functioning, few environmental studies on trace metals have considered a complete spatial sampling design in the GoC between the potential sources (estuaries) and the surrounding waters along the continental shelf (Elbaz-Poulichet et al., 2001). At present, the contribution of each estuarine ecosystem as a source of metals into the GoC is unknown.

The objective of this study is to characterize the metal composition (Fe, Ni, Co, Cu, Mo, Cd and Pb) within the above mentioned estuaries and to evaluate the contribution of each river to the GoC trace metal load. We hypothesize that the spatial variability of metal concentration within the GoC continental shelf is mainly determined by the land uses of each river basin, the basin characteristics (bedrock lithology) (e.g. sulphide deposits) and river fluxes. Water management regulation in these river basins usually causes a decrease in the freshwater input to the estuaries and an increase in the residence time of suspended matter (González-Ortegón et al., 2010). The study of the levels and distribution of metal concentrations within the main estuaries and coastal water masses of the GoC in a wet and dry month should bring updated knowledge about the biogeochemical cycles of metals in the GoC.

2. Material and methods

2.1. Study area

The GoC (southwest Spain) is a semi-enclosed basin whose oceanographic dynamics are mainly controlled by the exchanges between the environmental sub-basins: the Mediterranean and Atlantic basins and the coastal system (Sánchez-Leal et al., 2017). The three most important rivers discharging into the GoC continental shelf are the Guadiana, Tinto-Odiel and Guadalquivir (Fig. 1). The freshwater inflow to the Guadiana, Tinto-Odiel and Guadalquivir estuaries, located in a semiarid environment, are totally regulated by dams. The Guadiana and Guadalquivir estuaries, with a higher freshwater inflow (>2000 hm^3 $year^{-1}$) than the Tinto-Odiel (100–473 hm^3 $year^{-1}$) (Elbaz-Poulichet et al., 2001), are well-mixed and tidally dominated systems (Fortunato and Oliveira, 2004; Díez-Minguito et al., 2012), with a longitudinal salinity gradient that shows both long-term (seasonal and inter-annual) and short-term (tidal and dam management-related) displacements along the river course. According to Galvão et al. (2012), during the Alqueva Dam construction and filling from 1999 to 2003, fluvial discharge was below 10 m^3 s^{-1}, while the summer river flow increased to 10–15 m^3 s^{-1} during 2004 and 2005, and reached 20–25 m^3 s^{-1} during 2007 and 2008 before decreasing again to below 10 m^3 s^{-1} during 2008 and 2009. In the Guadalquivir estuary, occasionally, during the passage of Atlantic storms, freshwater discharges from the dam may be >400 m^3 s^{-1} and the estuaries becomes fluvially-dominated (Díez-Minguito et al., 2012).

At the latitude of the GoC, the climate is characterized as having a short, mild winter when most of the annual rainfall occurs, and warm, dry summers (Cánovas et al., 2007). Freshwater inflow into the interior of these estuaries from these rivers revealed significant seasonal and annual variations (Fig. S1). In this study, the effect of season (winter and summer) was included to take into account climatic variations within the studied year, although the freshwater inflow to these three estuaries could be totally regulated by dams in 2016.

The estuary of the Odiel and Tinto rivers, also known as the Ria of Huelva, extends along the southwestern coastal margin of the Guadalquivir sedimentary basin (Carro et al., 2019). Historically, the Tinto and Odiel rivers drained the world's largest sulphide deposit, being one of the oldest exploited regions in the world (mined for the last 4500 years) (Nelson and Lamothe, 1993; Olías and Nieto, 2015). Natural changes to these sulphide deposits, in conjunction with mining activity has led to the secular pollution of the Odiel and Tinto rivers, whose waters now contain very high concentrations of heavy metals and have extremely low pH values—<3 (Grande et al., 2000). The combination of acidic waters from mines, industrial effluents, and seawater has played a decisive role in the development of the chemical composition of the water in the estuary (Carro et al., 2019). Investigations carried out in the 80s and 90s in the Tinto-Odiel estuary concluded that it acts as a source of certain metals (i.e. Cu, Zn and Cd) to the GoC (van Geen et al., 1991; Elbaz-Poulichet et al., 2001; van Geen and Boyle, 1990; Braungardt et al., 2007). With very high concentrations of dissolved metals and metalloids and low pH values, discharges from the Tinto and Odiel rivers were suggested to seasonally affect the surface entry of metals into the Mediterranean through the Strait of Gibraltar (Elbaz-Poulichet et al., 2001).

The Guadiana is a rockbound estuary with a longitudinal salinity gradient (Garel and Ferreira, 2013). The pollution impact of acidic mine drainage by leachate seeps into the fluvial system from a small number of active mines (see Delgado et al., 2009 for details). Moreover, the potential occurrence of pollutants related to harbor activities within the estuarine area (Gomez-Ariza et al., 1998) and to tourism developments in the mouth of the estuary which increases the population during summer time, could contribute to the contamination of water in the estuarine area. Finally, the irrigation of intensive crops (e.g. strawberry crops) in lands adjacent to the estuary will also exert a significant increase of nutrients, pesticides and fertilizers in its water (Ménanteau et al., 2005).

The Guadalquivir estuary shows a salinity gradient and a high load of sediment which significantly increases the water turbidity (González-Ortegón et al., 2015). Differences about the water transparency in estuaries could affect the cycling and remineralization rates (Ciutat and