Distribution and transport of dissolved trace metals in the Gulf of Cádiz, Spain

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ABSTRACT

The Gulf of Cadiz plays a key role in the exchanges of biogeochemical fluxes between the Mediterranean Sea and the Atlantic Ocean through the Strait of Gibraltar. Oceanographers have carried out many investigations in the Gulf of Cádiz on water mass circulation and mass balance of nutrients and carbon. However, despite its importance in the global ocean functioning, studies on trace metals in the waters of the Golf of Cádiz and the Strait of Gibraltar are very scarce, and for more than two decades ago, nonexistent.Here we show the result of dissolved trace metal composition (i.e. Ag, Cd, Co, Cu, Fe, Mo, Ni, Pb and Zn) in surface waters of the Gulf of Cádiz and Mediterranean Sea obtained from 5 oceanographic campaigns. Our results indicate that the surface water mass of the Gulf is receiving large amounts of trace metals transported by the different rivers that flow into the Gulf of Cadiz. Thus, dissolved trace metals in these waters were highly variable with the highest ranges measured for Co (0.06 – 3.1 nM), Fe (0.6 – 392 nM) and Pb (0.04 – 512 nM).

INTRODUCTION

The Gulf of Cádiz is a semi-enclosed basin whose oceanographic dynamics is controlled by the exchanges between the environmental sub-basins: the Mediterranean and Atlantic basins, the coastal system, the atmosphere and the seafloor.The water masses of the Gulf of Cádiz are directly influenced by the Iberian pyrite belt (one of the largest sulfide deposits in the world), receiving large amounts of trace metals transported by the different rivers that run through the belt and flow into the Gulf of Cadiz [1-4].Trace metals play a critical role in the ocean functioning. Some metals, e.g.V, Cr, Mn, Fe, Co, Ni, Cu, Zn or Mo, despite of being present in organisms at trace concentrations, are considered essential for life if ambient concentrations do not exceed a threshold value for toxicity [5]. On the other hand, the presence of some trace metals at high concentrations such as As, Hg, or Pb can damage ecosystem health. Thus, the distribution of trace metals has the potential to enhance or limit primary productivity in some regions of the world ocean. Despite their importance, we do not have a good understanding of the global distribution and cycling of trace metals in many ocean areas. Here, we collected surface water samples during 5 oceanographic cruises carry out during 2014 – 2015 in the Gulf of Cadiz and Mediterranean Sea providing an opportunity to further advance the study of both, the distribution of trace elements in surface waters of Gulf and their flux to the Mediterranean Sea.

MATERIALS AND METHODS

Sampling was carried out on board different oceanographic vessels, during October and December 2014, and during Marc, Septemeber and November 2015 (Figure 1).Samples for trace metals were collected using a teflon tow-fish sampling system deployed at approximately 2 m depth utilizing established trace metal-clean techniques.After sample collection, seawater was filtered on board through acid-washed 0.2 µm filter cartridges and acidified using Optima grade HCl to a pH<2.Dissolved samples (<0.2 µm) were double bagged in polyethylene bags and shipped to the trace metal cleanlaboratories, where they were preconcentrated by anorganic extraction procedure using the APDC/DDDC ligand technique [6]. Levels of metals were quantified by ICP-MS. To evaluatethe accuracy of our analytical procedures, a certified seawater reference material (SRM) (CASS-5) was preconcentratedand analyzed with the samples.

RESULTS AND DISCUSSION

Dissolved metal (Ag, Cd, Co, Cu, Fe, Mo, Ni, Pb and Zn) concentrations measured in surface waters during our study varied broadly with geographic locations. The highest concentrations of most of the metals were measured in areas under the influence of the rivers discharge (e.g. Ag: 11.3 pM, Cd: 0.3 nM, Co: 2.1 nM, Cu: 13.3 nM, Fe: 88.6 nM, Mo: 121.1 nM, Ni: 70.8 nM and Zn: 49.5 nM under the influence of the Guadalquivir river during December

2014). On the other hand the lowest concentrations were measured in offshore waters (e.g. Ag: <1 pM, Cd: 0.17nM, Co: 60 pM, Cu: 1.9nM, Fe: 0.6nM, Mo: 105.5nM, Ni: 2.3nM and Zn: 1.1nM).The mean surface current alongshore and cross-shore velocities were calculated by using the measured top current velocity in the field between stations. Thus, the horizontal advective fluxes of metals can be estimated by multiplying each velocity component by the different metal concentrations.

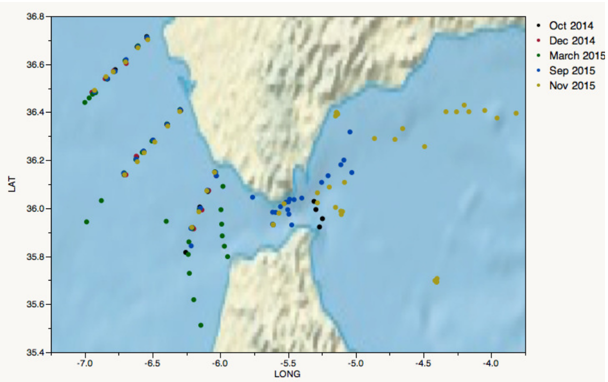

Figure 1. Sampling locations for the different oceanographic cruises

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