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

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Running head: Trace metals in the estuaries of the Gulf of Cadiz

Keywords

RIVERINE INPUTS, BIOGEOCHEMICAL CYCLES, METAL, GIBRALTAR STRAIT, POLLUTION, LAND USES

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).

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 et al., 1983; Viers et al., 2009), and dissolved organic matter (González-Ortegón et al., 2018) in their adjacent coastal waters. Thus, for example, the concentraitions 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; Olias 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 characterise 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 (Figure 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 hm3 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 greater than 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 (Figure 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; Olias 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—less than 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 harbour 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 Boudon, 2003). In the lower Guadalquivir basin, there was a significant transformation of its marshlands into irrigated agricultural lands during the 20th century (mainly rice fields, tomatoes and cotton cultivations) with a high demand of freshwater for irrigation (e.g. for 35.000 Ha of rice fields) (del Moral Ituarte, 1991). Thus, the Guadalquivir river catchments, with intensive agriculture and large populations, have an increased nutrient load input in their waters (González-Ortegón and Drake, 2012). Even though the Guadalquivir basin presents historic mines (Turner et al., 2008), metal contamination was not detected in its estuary despite the Aznalcollar toxic spill into two of its lower tributaries in 1998 (Tornero et al., 2011; 2014).

2.2. Sampling and metal analysis

Coastal water

Water samples in the GoC were collected during 3rd-8th March 2016 (wet season) and 20th-24th June 2016 (dry season) on board the Ramon Margalef R.V. and the Ángeles Alvariño R.V., respectively. One surface water sample (1-5 m depth) for trace metals analysis (Cd, Co, Cu, Fe, Mo, Ni, Pb, V, Zn) was collected using a teflon towfish system (e.g. Tovar-Sánchez, 2012) deployed from the research vessel during 10 minutes at each station. This towfish is a bracket connected to a plastic hose which pumps water samples into the boat. Seawater was pumped into a class- 100 HEPA laminar flow hood through acid- cleaned Teflon tubing coupled to C-flex tubing using a teflon diaphragm pump (Sandpiper Cole-Palmer), filtered online through an acid-washed 0.22 µm polypropylene Calyx capsule filter, and collected into acid- washed 500 mL LDPE bottles. Samples were acidified on board to pH <2 with ultrapure grade HCl (Merck), and stored for at least 1 month before extraction.

Estuaries

Samples in the estuaries were collected on 24th-25th February 2016 (Guadalquivir and Tinto-Odiel) and 17th March 2016 (Guadiana) (wet season), and on 5th -9th July 2016 (dry season). 24 h sampling stations were located in the middle of each estuary in order to evaluate the water composition discharge during a daily tidal cycle: Guadiana (Lat. 37.1989 N, Long -7.4095 W), Tinto and Odiel (Lat. 37.13271 N; Long. -6.8426 W) and Guadalquivir (Lat. 36.7923 N; Long. -6.35623 W) (GU0, TO0 and GD0, respectively, in Figure 1). Surface seawater (1 m depth) for trace metals analysis and inorganic nutrients (PO_4^{3-}, NH_4^+, NO_3^-, NO_2^-) was sampled each hour for a period of 6 h (during the wet season) and 12 h (dry season) using a peristaltic pump with acid-cleaned Teflon tubing coupled to a C-flex tubing (for the Cole-Parmer peristaltic pump head), filtered through an acid-cleaned polypropylene cartridge filter (0.22 µm; MSI, Calyx®), and collected in a 0.5 L low-density polyethylene bottle for metals and in 15 mL PE tubes for inorganic nutrients. Thus, a total of 6 and 12 samples were collected in the wet and dry seasons, respectively. Samples for trace metals were acidified on the lab to a pH <2 with ultrapure grade HCl (Merck) in a class- 100 HEPA laminar flow hood and stored for at least 1 month before extraction. Samples for nutrients were frozen for subsequent analysis at the laboratory.

Metals were pre-concentrated by the APDC/DDDC organic extraction method (Bruland et al., 1979), and analyzed by ICP-MS (PerkinElmer ELAN DRC-e). The accuracy of the pre-concentration method and analysis for each campaign was established using Nearshore Seawater Reference Material for Trace Metals (CASS 4, NRC-CNRC) with a range of recoveries from

92% for Co to 106% for Cd. Concentrations of dissolved nutrients, phosphate, nitrite and nitrate were determined with an autoanalyzer (Skalar San^{++} System) using colorimetric techniques (Murphy and Riley, 1962; Grasshoff and Kremling, 1983). The accuracy of the analysis was established using Coastal Seawater Reference Material for Nutrients (MOOS-1, NRC-CNRC), resulting in 98 %, 96%, and 94 %, for PO_4^{3-}, NO_3^- and NO_2^-, respectively.

Riverine fluxes of dissolved metals were calculated by multiplying the concentration value by the corresponding river discharge on each of the surveys. Freshwater discharges were obtained from the Regional River Authorities. Freshwater discharges from the Alcalá del Río dam (110 km upstream the mouth of Guadiana river) were obtained from the *Confederación Hidrográfica del Guadalquivir* database (http://www.juntadeandalucia.es/agenciadelagua/saih/DatosHistoricos.aspx). Discharge values recorded at the Pulo do Lobo gauging station (60 km upstream the mouth of Guadiana river) were retrieved from the *Sistema National de Informação de Recursos Hídricos* database (http://snirh.inag.pt/). Data for the Tinto-Odiel estuary were provided by the Spanish Ministry of Rural and Marine Environments (https://www.mapama.gob.es/es/) for the period 1st January 1993 until 7th December 2005, when the gauging station stopped measuring. Hence, data for this estuary were estimated by doing correlations with the Guadalquivir data. We used the Guadalquivir data to avoid underestimating the reconstructed Tinto-Odiel discharges because the Guadalquivir discharge rates were higher than those of the Guadiana river for the studied period. Thus, the Guadiana and Guadalquivir data were measured, and the Tinto-Odiel data were interpolated (Figure S1). In the Tinto-Odiel estuary for the two sampling months (February and July), the salinity was high (seawater) along the full water column during the studied tidal periods. In this case, the volume of flow is less than 6 $m^3\ s^{-1}$ according to Borrego (et al., 2002).

2.3 Data Analysis

The ANOSIM permutation global test (R), a non-parametric method for multivariate analysis of variance, was used to assess statistically significant differences of metal concentrations between estuaries and campaigns. In order to do this, a dissimilarity matrix based on the Euclidian distance for trace metal concentration data was calculated on log transformed and normalized variables using the PRIMER 6.1 (Plymouth Routines in Multivariate Ecological Research) computer software package (Clarke and Warwick, 1994). Pearson correlations (r) were used to determine the relationship between the concentration of each metal and the physical parameters; the latter included oceanographic data (salinity, temperature, turbidity, and oxygen concentration) measured *in situ* using a CTD (Conductivity, Temperature, Depth) probe within the GoC continental shelf, and data from a multiparameter sonde (salinity and temperature) in the estuaries. Statistical procedures were performed using the corrplot package (Wei et al., 2013) in R version 3.4.0 (R Development Core Team, 2017) to display graphically the correlation matrices. Linear regressions of metal concentrations were plotted using the package ggplot2 in R.

Linear regression models were applied to evaluate differences in each metal concentration (univariate data) among campaigns and estuaries using the multcomp and the sandwich package in R (Herberich et al., 2010). A robust statistical test for unbalanced dataset and heterogeneous variance that allows making post hoc comparisons between different campaigns and estuaries was used.

In order to obtain the metals concentration spatial distribution, the sampled concentrations were gridded using the data-Interpolating Variational Analysis (DIVA) (Troupin et al., 2010). This method takes into account the coastlines and bottom topography, hence, being the most suitable one to spatially interpolate physical, chemical and biological oceanographic variables. Moreover, DIVA also generates error maps to help interpret the gridded fields which are especially useful when the data coverage is sparse.

3. Results and Discussion

Understanding the short-term consequences of Mediterranean rivers' streamflow (mostly determined by seasonal climatic conditions and demand of fresh water to irrigate cultivation fields) is necessary for the assessment of the trace metals spatial distribution on the GoC continental shelf. This study highlights the importance of the basin characteristics, river flows and season in the dispersion of pollutants, and the exporting role of the GoC towards neighbouring seas. The Guadalquivir estuary seems to supply an important metal enrichment to the GoC continental shelf that can be transported onto the Mediterranean Sea.

3.1 Dissolved Metal composition of estuarine waters

Metal composition differed significantly in the three estuaries ($R = 0.84$, $p \leq 0.01$) and between the studied months ($R = 0.5$, $p \leq 0.01$) (Figure 2). The Tinto-Odiel estuary registered a greater number of metals with higher concentrations, especially in February (Table 1 and Supplementary Table S1). A comparison of the data from these three estuaries with data reported from elsewhere indicates that the highest concentrations of metals in the Tinto-Odiel were significantly higher than in other estuaries worldwide (Table 2). For instance, Co, Cu and Mo showed the maximum concentrations in the Tinto-Odiel (30.7 nM, 172.2 nM and 121.9 nM, respectively) and Mo in the Guadalquivir estuary (114.7 nM) with a similar order of magnitude than in other ports and estuaries worldwide. Although the ports are probably one of the most polluted areas in the world, the fact the Tinto-Odiel estuarine zone is a site of major industrial activity (Elbaz-Poulichet et al.,

2001) suggest this system shows similarities to other ports worldwide (Table 2). Since these rivers flow through different materials of the Iberian Pyrite Belt (one of the most important metal bearing areas in the world), they are enriched in trace metals, especially the Tinto-Odiel (Olias and Nieto, 2015) and Guadiana river (Delgado et al., 2009; Saez et al., 1999). The highest average concentrations of Co (14.4 ± 11.9 nM), Cd (3.6 ± 2.5 nM), Pb (3.0 ± 0.7 nM), and Zn (445.8 ± 300.3 nM) were measured in the Tinto-Odiel estuary; Ni, Mo and Cu in the Guadalquivir (18.1 ± 7.0 nM, 104.3 ± 11.2 nM, 43.7 ± 11.3 nM, respectively) and Tinto-Odiel estuaries (11.9 ± 6.8 nM, 117.6 ± 2.7, 103.9 ± 56.7 nM, respectively). The highest concentrations of Fe where found in the Tinto-Odiel (492.4 ± 220.8 nM) and Guadiana (334.5 ± 358.1 nM) estuaries (Figure 2 and Table1). On the contrary, Vanadium showed a similar concentration among the three estuaries (Guadiana: 19.8 ± 4.3 nM, Tinto-Odiel: 17.0 ±4.9 nM and Guadalquivir: 19.8 ± 6.6 nM).

The correlation matrix of metal concentration, nutrients and tidal height (TH) highlighted a different performance in the three estuaries: whilst water discharged from the Tinto-Odiel river is clearly affected by historical mining activities (Nelson and Lamothe, 1993; Olías and Nieto, 2015) with a metal signal characterized by high positive correlations among most metals (Cu, Cd, Ni and Co) and poor correlations with N (Figure 3), the Guadiana and Guadalquivir rivers seem to be more affected by urban and agricultural uses. Waters in the Guadiana and Guadalquivir estuaries showed a positive correlation between N and the concentrations of Cu, Cd and Ni; also, these concentrations were negatively related to the tidal height, suggesting a riverine metal input. However, in the case of Guadalquivir, the high concentrations of P (0.9 ± 0.4 µM) and N (47.5 ± 33.8 µM) (Figure S4), highly correlated among them (r=0.9, p<0.01), with an order of magnitude higher than the other two estuaries in the case of N, and the significant correlation with the Ni, Cu and Cd concentrations (r=0.80, 0.68 and 0.54, p<0.01) suggests an influence of the intense agriculture in the river water, as previously stated (Mendiguchía et al., 2007). As reported in other estuaries (Peierls et al., 1991), the Guadalquivir river, with a wide agricultural extension (e.g. rice fields), keeps high nutrients concentrations along the years due to cropland runoff (González-Ortegón and Drake, 2012). The historical use of inorganic fertilizers and pesticides (fungicides and herbicides) in the rice fields could explain a surplus of Cu and Ni in the estuarine water (Gimeno-García et al., 1996; He et al., 2005; Spencer and Greene, 1981). In fact, recent studies indicate that the maximum concentrations of Cu and Ni along the Guadalquivir river basin are located in the agricultural area (Mendiguchía et al., 2007). Phosphorous concentration is also significantly high in the Tinto-Odiel estuary (0.9 ± 0.5 µM); however, it did not show any relation with N, which suggests that the origin is different than in the Guadalquivir river. In Spain, the production of H_3PO_4 was restricted to a large fertilizer industrial complex situated in the lower Tinto-Odiel river basin (Pérez-López et al., 2010) which produced large volumes of phosphogypsum waste adjacent to the estuary and discharged fluids into it (Davis et al., 2000). The contributions of the phosphate plant in the region was increasing the concentration of P and also polluting with Cd, Co, Cu and Zn impurities in its entire estuarine portion (Gimeno-García et al., 1996; Davis et al., 2000). Despite the fact that the production of phosphoric acid in this factory ended in 2010, and that restoration actions were carried out for some disposal modules of the phosphogypsum stack, recent studies to assess the efficiency of the restoration measures found yet high potential of contamination of the stack, including those zones that were supposedly restored (Pérez-López et al., 2016, 2018). Overall, the results of this study match well with a recent one (Hanebuth et al., 2018: see table 1) where they recompile information of the mouth of these three estuaries based on sediment cores. That is, the modern sediment close to the Guadiana river estuary shows a comparably low degree of contamination, that off the Guadalquivir estuary is moderately polluted, twice as high as in the Guadiana area, and that off the Tinto-Odiel estuarine system is heavily contaminated.

The distribution of metal concentrations showed a gradual pattern with the tidal flux in in the three estuaries, with the exception of Mo and V (Figure 3 and Supplementary Figure S2). For example, Cu and Ni showed a gradually decrease of their concentrations between the low tide and the succeeding high tide (i.e. from the landward to the seaward waters). This pattern was stronger in the Tinto-Odiel estuary than in the Guadiana and Guadalquivir estuaries for Cd, Cu and Ni (Figure 3 and Supplementary Figure S2), reflecting the high levels of riverine metal input into the Tinto-Odiel estuary. However, in the Guadiana estuary, an inverse pattern (a concentration increase between the low and high tide) was found in July for Pb, Fe and Zn (Figure 3 and Supplementary Figure S2: positive correlation with tidal height). When comparing July with February (Table 1), the former showed higher levels of water-dissolved Fe and a relative increase of Pb and Zn at the outer (i.e., seaward) waters (Figure 2 and Table 1). The lower sector of the Guadiana river basin hosts soils with elevated Pb mostly related to the occurrence of sulphide-rich ore deposits, volcanic sedimentary formations and mining (Batista et al., 2013). Due to the ore formation, these host rocks are in fact, at least in part, the source of these metals that may be concentrated in certain areas (Relvas et al., 2006) which could explain the high levels of Pb between the Guadiana and Tinto-Odiel estuaries (Hanebuth et al., 2018). However, Pb and Zn represent two of the most hazardous heavy metals found in industrial wastewater and modern marine sediments (Khan et al., 2017). The fact that the peak of these metals occurred in summer could be explained by a population increase during the summer season in the mouth of the estuary (e.g. Isla Cristina), which is a highly touristic area (Ménanteau et al., 2005; Delgado et al., 2011). In any case, these river-estuaries are sources to the adjacent continental shelf waters of the GoC and, hence, the surface ocean metal content is affected by the dominant freshwater fluxes from these estuarine sources.

3.2 Metal rivers contribution and spatial-temporal distribution in the GoC

Elevated surface metal concentrations in differentregions of the GoC were affected by the flux and metal composition of each estuary, particularly during the wet season (Figure 4 and 5). The correlation matrix in the GoC showed a seasonal effect, where a higher number of metals were highly correlated in the wet season compared to the dry one (Figure 6). The concentrations of Cd, Pb and Ni showed high and significant negative correlations with salinity (-0.83, -0.77 and -0.74, $p<0.01$) and temperature (-0.88, -0.88 and -0.88, $p<0.01$), and positive correlations with turbidity (0.88, 0.79 and 0.89, $p<0.01$) during the wet season (Figure 6 and Supplementary Figure S3). With respect to the spatial distribution along the GoC continental shelf (Figure 5), clear differences were observed both among metals for the same season, and between the wet (March 2016) and dry (July 2016) season for the same metal. For example, Cd, Co and Cu (and Pb and Ni in the wet season) showed higher concentrations near the estuaries (sources) and along a narrow coastal fringe (between the Bay of Cadiz and the Tinto-Odiel estuary), with overall larger values during the wet season (except Co). Other metals like Mo and V did not show a clear spatial pattern in both seasons. In most cases, the main source seemed to be the Guadalquivir river. Other metals like Pb and Zn seemed to originate at the Tinto-Odiel estuary or the Bay of

Cadiz, the latter probably linked to the activities at the Cadiz harbor. Metal concentrations in the continental shelf of the GoC (Figure 5) are mostly related to freshwater inputs (rainfall and discharges) which have been accumulated between autumn-spring (wet season). By contrast, during summer, the generally lower freshwater discharges tend to decrease the metal concentrations in the adjacent continental shelf.

This spatial distribution might be also related with the surface circulation on the GoC continental shelf which is mainly parallel to the coastline (Sánchez et al., 2006). Considering that the surface circulation within the GoC inner shelf flows mainly southeastward, i.e., toward the Strait of Gibraltar, but that it frequently reverses to flow northwestward (~40% of the time) (Garel et al., 2016), the metals discharged onto the continental shelf by the studied rivers are subject to be transported either onto the Mediterranean Sea or even northwards along the western Portuguese coast. For instance, the Coastal Counter Current could be increasing the concentration of Zn on the surface sediments along the coastal fringe between the mouths of the Guadalquivir and the Tinto-Odiel estuaries (Hanebouth et al., 2008) originating at the Guadalquivir estuary. This is probably related to larger freshwater discharge events, which in this region mainly take place during spring (González-Ortegón et al., 2015), with some exceptions. In this sense, the Guadalquivir river discharges usually increase from late spring to early summer during droughts to irrigate the large cultivation fields in the region (González-Ortegón and Drake, 2012).

Although it has been demonstrated that the Tinto-Odiel used to discharge high concentrations of metals into the GoC (Leblanc et al., 1995; van Geen et al., 1997), the contribution of the other two main rivers had not been evaluated. Our results show that, despite the fact that metal concentrations are generally higher in the Tinto-Odiel river , with a few exceptions (e.g. Ni in the

Guadalquivir river), the greater average flow rate of the Guadalquivir river, together with the also elevated concentration of dissolved metals, makes the latter the major input of dissolved metals to the GoC. It must be pointed out that, during the 90s and early 2000s, the Tinto-Odiel average discharge rate, although always lower than that of the Guadalquivir, was about 20 m^3 s^{-1}, with peak values between 500-2700 m^3 s^{-1} (not shown) and that, from 2003 onwards, the average discharge rate dropped to about 5 m^3 s^{-1}, with peaks around 28 - 270 m^3 s^{-1}. During the last year of available measurements (2005), the maximum (average) discharge rate had dramatically decreased to 6.8 (0.23) m^3 s^{-1}. In fact, the metal concentration within the Tinto-Odiel estuary remains in it and increases under low flow rate, and therefore does not export as much pollution as for example other estuaries (González et al., 2007; Olias et al., 2006).

Thus, considering the water fluxes in the estuaries of the Guadiana (21.47 m^{3}s^{-1} in March and 12.85 m^{3}s^{-1} in July), Tinto-Odiel (7.52 m^{3}s^{-1} in February and 6.38 m^{3}s^{-1} in July) and Guadalquivir (25.51 m^{3}s^{-1} in February and 29.41 m^{3}s^{-1} in July) rivers, the highest fluxes of Ni (491±234 μmols^{-1}), Cu (1115 ± 290 μmols^{-1}), Mo (2660±290 μmols^{-1}) and V (502±191 μmols^{-1}) were obtained for the Guadalquivir river. With respect to the Tinto-Odiel river, the fluxes of Pb (19.2 ± 4.7 μmols^{-1}), Zn (3353 ± 2259 μmol s^{-1}), Co (108 ± 90 μmol s^{-1}) and Cd (27.5 ± 19.4 μmol s^{-1}) showed the highest contributions, ranging from 48-66%. Although, in the Guadalquivir estuary the fluxes of Pb (5.32 ± 0.76 μmols^{-1}), Zn (1457 ±164 μmol s^{-1}), Co (39.9 ± 9.7 μmol s^{-1}) and Cd (14.0 ±1.3 μmol s^{-1}) had lower contributions to the GoC (21-36%), these were not less significant. These data could support the global importance of these two rivers (i.e., Guadalquivir and Tinto-Odiel) in the transport of metals to the GoC and the enrichment of the Atlantic inflow into the Mediterranean through the Strait of Gibraltar. The contribution of the Guadiana and Tinto-Odiel was only higher for Fe (4298 ± 4601 µmol s^{-1} and 3144 ± 1410 µmol s^{-1}, respectively). Thus, variations in the estuarine inputs to the adjacent continental shelf are largely determined by the freshwater flux and not only by the metal concentration.

4. Conclusions

The trace metals composition and fluxes of the three estuaries discharging to the GoC continental shelf (Guadiana, Tinto-Odiel and Guadalquivir) were characterized. Metal concentrations in the Tinto-Odiel estuary are clearly affected by historical mining activities, in the Guadiana by urban and mining activities (Delgado et al., 2009), and in the Guadalquivir by urban and agricultural uses (Mendiguchía et al., 2007). Variations in the estuarine inputs to the adjacent continental shelf of the GoC are largely determined by the freshwater fluxes from the Guadalquivir river (especially for the input of Ni and Cu) and, to a lesser extent, by the Tinto-Odiel and Guadiana rivers. During the dry season (i.e. summer with low river discharge conditions and low metal fluxes), the enlarged anthropogenic activities within the Guadiana estuarine area (such as touristic and harbor activities) could represent a greater proportion of the total inputs of Fe, Pb and Zn to the adjacent continental shelf waters.

The fluxes evaluated in this study provide a first estimate of the dissolved metals discharge from the three main estuaries to the GoC. The spatial pattern of metal concentrations over the GoC continental shelf is explained by high contributions from the Guadalquivir river and, to a lesser extent, by the Tinto-Odiel river. This, together with the oceanographic dynamics over the GoC continental shelf, point to an unexpectedly important contribution and net transport of trace metals from the Guadalquivir river basin to the Mediterranean Sea.

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Conflict of Interest

None declared

Figure legends

Figure 1. Map of the Gulf of Cadiz showing the location of the sampling sites and some geographical features mentioned in the text. GU0, TO0 and GD0 refer to the three estuaries (Guadiana, Tinto-Odiel and Guadalquivir, respectively). The remaining points indicate the sampling locations for the different oceanographic cruises carried out within the GoC continental shelf.

Figure 2. Boxplot of metal concentrations (log-transformed, nM) at each estuary and studied month. Middle line = median; upper edge = 75th percentile; lower edge = 25th percentile; lines = variability outside the quartiles. The letters on top of each boxplot indicate whether there are significant differences (max-t test: $p < 0.001$) between two or more boxplots (i.e., letters are different) or not (same letter). "Wet" corresponds to the sampling date, i.e., February 2016 for the Tinto-Odiel and Guadalquivir estuaries, and March 2016 for the Guadiana estuary. "Dry" corresponds to the sampling date of July 2016.

Figure 3. Plots of the Pearson's correlations between metal species and physical variables, including tidal height, for each estuary. Only significant correlations ($p < 0.01$) between metal concentration, nutrients and tidal height (TH) are depicted with colours, with the sign of the correlations represented by red and blue for negative and positive correlations, respectively.

Figure 4. Boxplot of metal fluxes (log-transformed, µmol s-1) at each estuary and studied month. Middle line = median; upper edge = 75th percentile; lower edge = 25th percentile; lines = variability outside the quartiles. The letters on top of each boxplot indicate whether there are

significant differences (max-t test: $p < 0.001$) between two or more boxplots (i.e., letters are different) or not (same letter).

Figure 5. Metals concentration spatial distribution for each studied month as obtained with DIVA (Data-Interpolating Variational Analysis) in March and July 2016 (Wet and dry seasons, respectively). Red asterisks indicate the sampling locations. The 50, 100, 200, 500, and 1000 m isobaths are shown.

Figure 6. Plots of the Pearson's correlations between metal species and physical variables from the GoC in a wet (March) and dry (June) month. Only the significant correlations, as based on the 99% credible intervals excluding zero, have been plotted. The sign of the correlations is represented by colours (red and blue for negative and positive correlations, respectively).

Table 1. Average concentration and flux ± standard deviation of metals measured in February and July 2016 of the Guadalquivir, Guadiana and Tinto-Odiel estuaries. Units of metal concentration in nM and flux in pmol seg-1

Estuary	Month	Fe	Ni	Co	Cu	Mo	Cd	Pb	Zn	V
Concentration										
Guadalquivir	February	5.93±2.41	18.20±7.03	1.00±0.12	43.73±11.35	104.33±11.23	0.55±11.23	0.21±0.03	57.13±6.44	19.68±7.51
	July	6.72±3.51	16.72±7.99	1.36±0.33	29.27±7.02	85.07±5.67	0.29±5.67	0.16±0.04	22.93±2.20	19.99±6.48
Guadiana	February	5.69±1.56	5.20±0.37	0.83±0.07	11.12±1.87	88.16±8.04	0.30±8.04	0.04±0.01	10.86±0.95	19.52±5.71
	July	334.53±358.11	3.85±0.82	1.16±0.37	11.15±3.97	80.87±7.05	0.16±7.05	0.29±0.28	15.63±3.75	19.97±3.81
Tinto-Odiel	February	4.75±1.08	11.98±6.87	14.45±11.95	103.98±56.73	117.70±2.75	3.67±2.75	0.66±0.03	445.85±300.36	12.95±6.11
	July	492.42±220.89	4.05±0.92	3.57±1.47	83.45±26.45	81.17±12.28	1.45±12.28	3.00±0.73	144.10±54.18	18.74±3.46
Flux										
Guadalquivir	February	151.20±61.60	464.19±179.30	25.46±3.03	1115.57±289.50	2661.23±286.47	14.04±1.29	5.33±0.77	1457.39±164.32	502.02±191.46
	July	197.50±103.16	491.79±234.96	39.94±9.69	860.66±206.34	2501.75±166.81	8.51±2.21	4.63±1.20	674.43±64.62	587.83±190.57
Guadiana	February	122.27±33.47	111.69±7.89	17.92±1.46	238.83±40.09	1893.19±172.71	6.34±0.54	0.80±0.18	233.16±20.44	419.16±122.55
	July	4298.64±4601.64	49.42±10.58	14.96±4.76	143.24±51.00	1039.22±90.54	2.05±0.36	3.78±3.57	200.86±48.17	256.58±48.95
Tinto-	Febr	35.70±8.	90.08±5	108.69	782.05±	885.24±	27.58±	5.00±	3353.39±	97.38±4

Odiel	uary	10	1.68	±89.91	426.65	20.68	19.45	0.25	2259.07	5.99
	July	3144.65±1410.66	25.87±5.87	22.80±9.41	532.95±168.92	518.39±78.42	9.24±5.88	19.16±4.66	920.23±346.02	119.70±22.09

Location	Cd	Co	Cu	Fe	Mo	Ni	Pb	V	Zn	Reference
Torres Strait and Gulf of Papua	0.01-0.26		0.57-15.52			16.02-78.38				Apte and Day, 1998
New South Wales coast, Australia	0-0.02		0-0.49			0-3.07	0.04		0-0.34	Apte and Batley, 1998
Archelos estuary, Greece			10.7	2023.28		0-22.49	1.11		0-44.96	Dassenakis et al., 1997
Weser estuary, Germany	1.42		31.47	3.58		34.08	265.44			Turner et al., 1992
Six estuaries, Texas, USA			1.57-20.46	17.91-268.58			0.27-0.65		4.59-185.04	Benoit et al., 1994; Morse et al., 1993
Tweed estuary, UK	0.09-0.29		7.71-73.96						6.58-29.06	Laslett, 1995
Humber estuary,UK	0.44-1.96		11.8-56.65						55.05-229.39	Laslett, 1995
Humber estuary, UK	0.44-4		28.33-158.94			42.6-204.46			45.88-313.5	Comber et al., 1995
Mersey estuary, UK	0.09-0.98		12.59-77.9			34.08-178.91			99.4-428.2	Comber et al., 1995
Scheldt estuary, Netherlands	0.09-0.27		4.72-34.94						9.18-351.74	Zwolsman et al., 1997
Tay estuary, Scotland	0.02-1.07		7.08-29.9			3.92-15.33			6.12-122.34	Owens and Balls, 1997
Bristol Channel, Uk	3.56-83.62		9.44-84.98			3.41-51.12	1.69-62.74		41.29-672.89	Abdullah and Royle, 1974
Poole Harbour, Uk	2.67-373.63		3.15-440.63						15.29-10307.39	Rainbow, 1990
Derwent estuary, Australia									1	Coughanowr et al., 2015
N Australian coast and estuaries	0.01-0.31	0.09-1.15	2.33-16.37	1.43-610.56		1.98-9.41	0.01-0.27		0.15-7.62	Munksgaard and Parry, 2001
Gironde estuary, France	0.44-3.56									Elbaz-Poulichet et al., 1987
Gironde estuary, France	0.09									Chiffoleau et al., 1994
Seine estuary, France	0.7	1	10			20	1		50	Jouanneau et al., 1990
Loire river, France	0.21						0.4			Boutier et al., 1993
Scheldt estuary, NL			13.5	61			48	7		van den Berg et al., 1987
Elbe, Germany	0.09-2.14		7.87-110.16				193.05-1930.5			Mart et al., 1985
Humber, UK	0.44-1.96		11.8-56.65			15.33-107.34	0.11-2.99		55.05-229.39	Laslett, 1995
Tees, UK	0.13-0.86		7.71-157.37			3.58-17.04	0.26-3.96		10.71-214.1	Laslett, 1995
Wear, UK	0.12-0.52		5.19-22.03			5.11-49.41	0.28-2.65		7.65-114.7	Laslett, 1995
Tyne, UK	0.1-1.16		4.72-25.18			4.77-47.71	0.28-5.31		9.18-382.32	Laslett, 1995
Tweed, UK	0.06-0.29		7.71-73.96			3.92-13.8	0.19-0.82		6.58-29.06	Laslett, 1995
Mersey, UK	0.08-0.54		20.46-51.93			13.63-160.16	0.15-4.25		22.94-259.98	Laslett, 1995
Morecambe Bay, UK	0.08-0.44		9.13-29.9			6.82-1380.13	0.13-1.25		21.41-113.17	Laslett, 1995
Port Jackson, Australia	8.9		47.212-62.95	393.912-1378.69	83.392-104.23	17.04	4.832-9.65	58.892-137.42	137.642-581.13	Jahan and Strezov, 2017
Port Botany, Australia			15.742-141.63	268.582-9507.61	104.232-135.5	17.04	4.832-33.78	78.522-196.31	61.172-382.32	Jahan and Strezov, 2017

Port Kembla, Australia			62.95	143.242-644.58	93.812-135.5		4.83	58.892-78.52		Jahan and Strezov, 2017
Port Newcastle, Australia			78.68	143.242-3419.87	62.542-104.23		4.83	78.522-98.15	152.932-305.86	Jahan and Strezov, 2017
Port Yamba, Australia		16.97	629.47	286.482-4834.38	83.392-104.23		24.13	58.892-157.05	168.222-535.25	Jahan and Strezov, 2017
Port Eden, Australia	8.92-62.27	33.94		1683.08	83.392-104.23	153.35	4.83	78.522-98.15	15.292-443.49	Jahan and Strezov, 2017
Guadalquivir estuary, Spain	0.19-0.60	0.83-1.75	20.6-60.1	2.60-13.1	74.8-115	7.85-29.8	0.10-0.25	12.3-31.8	20.2-64.3	This study
Gudiana estuary, Spain	0.13-0.33	0.72-2.16	7.12-17.8	3.35-974	67.2-97.4	2.57-5.62	0.03-0.78	12.5-29.0	9.01-21.1	This study
Tinto-Odiel estuary, Spain	0.6-7.19	1.92-30.7	50.4-172	3.02-919	47.8-122	2.20-21.2	0.63-3.98	7.50-23.1	92.4-845	This study

Table 2 Range of dissolved metal concentrations (nM) in surface waters from estuaries and coastal ports elsewhere (min-max).

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

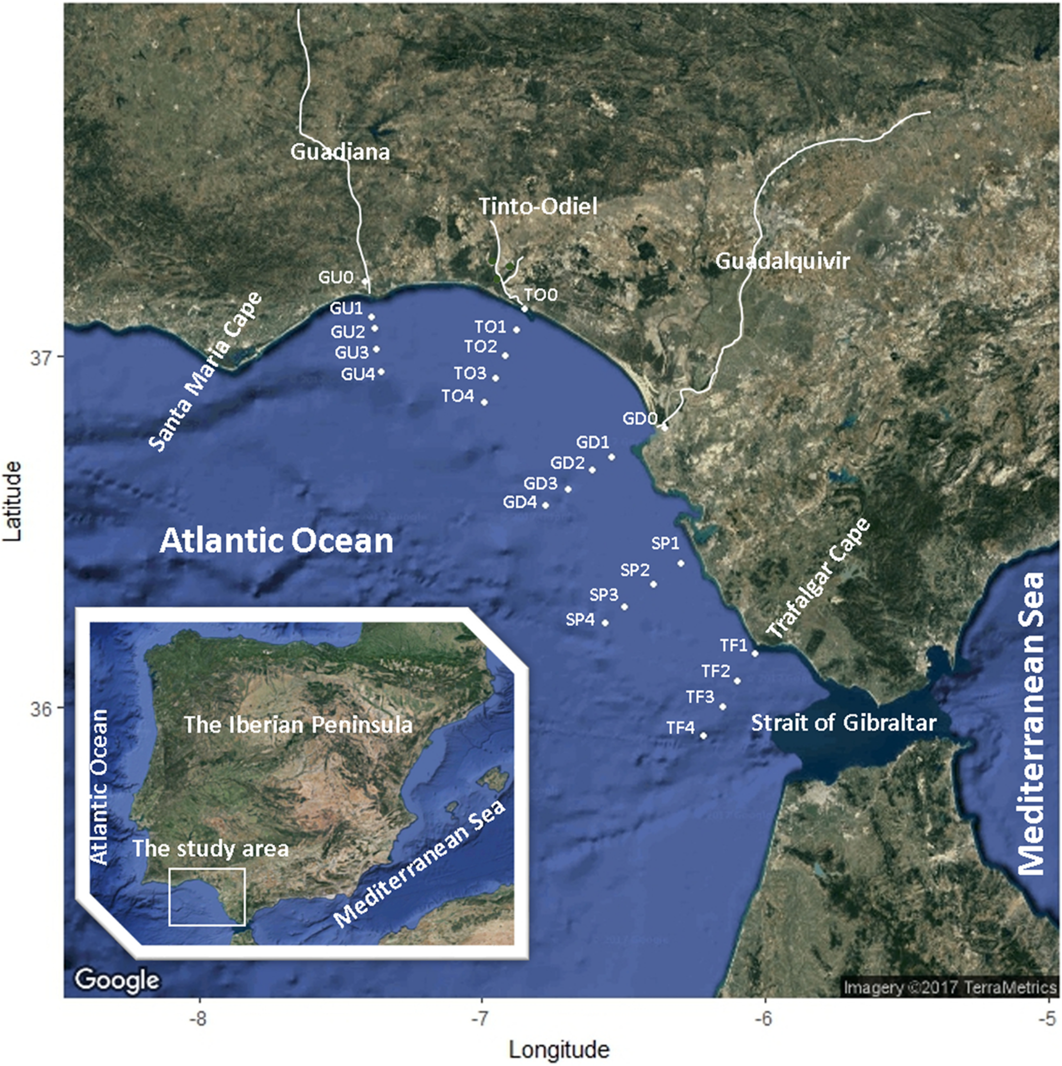
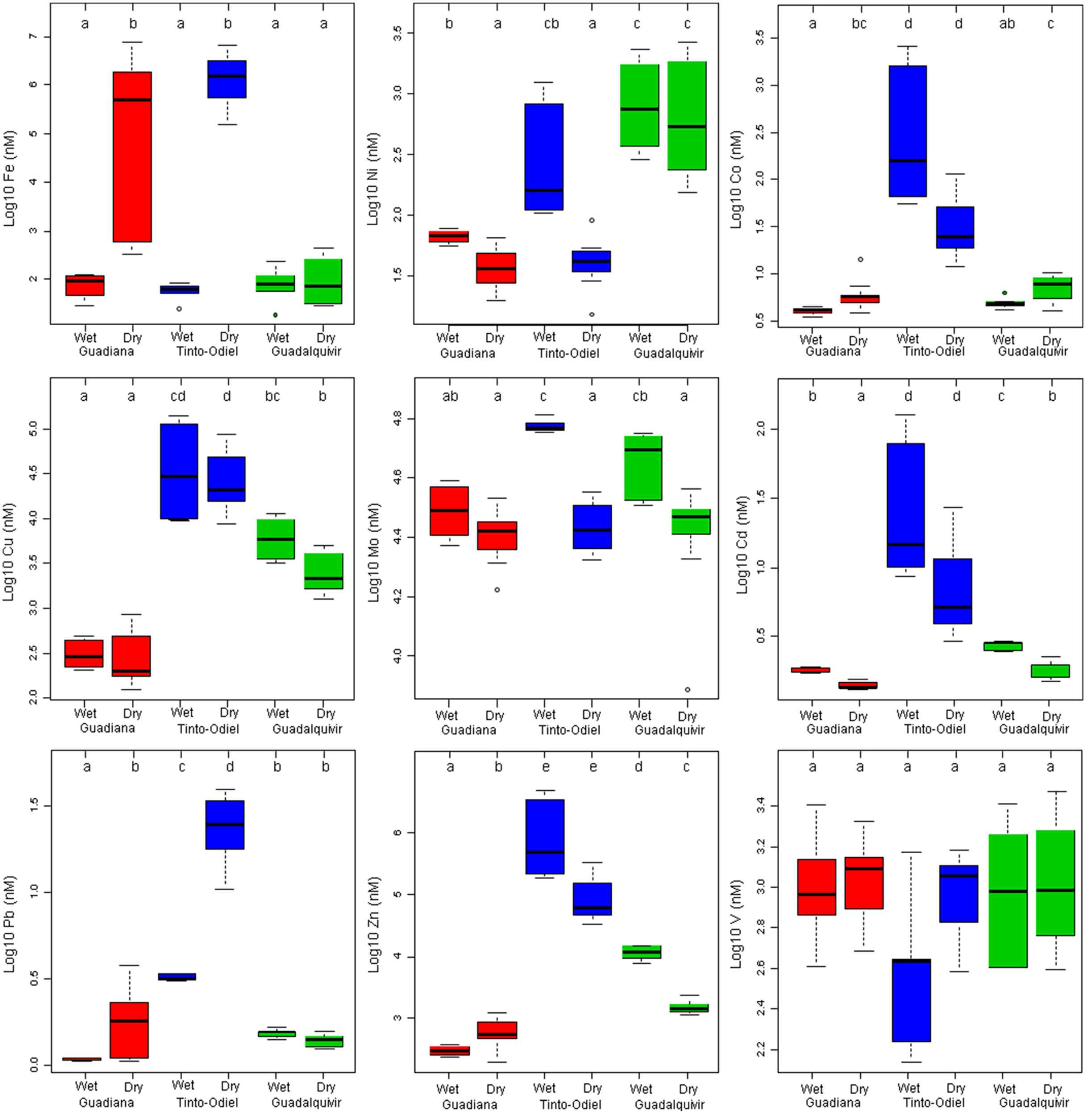
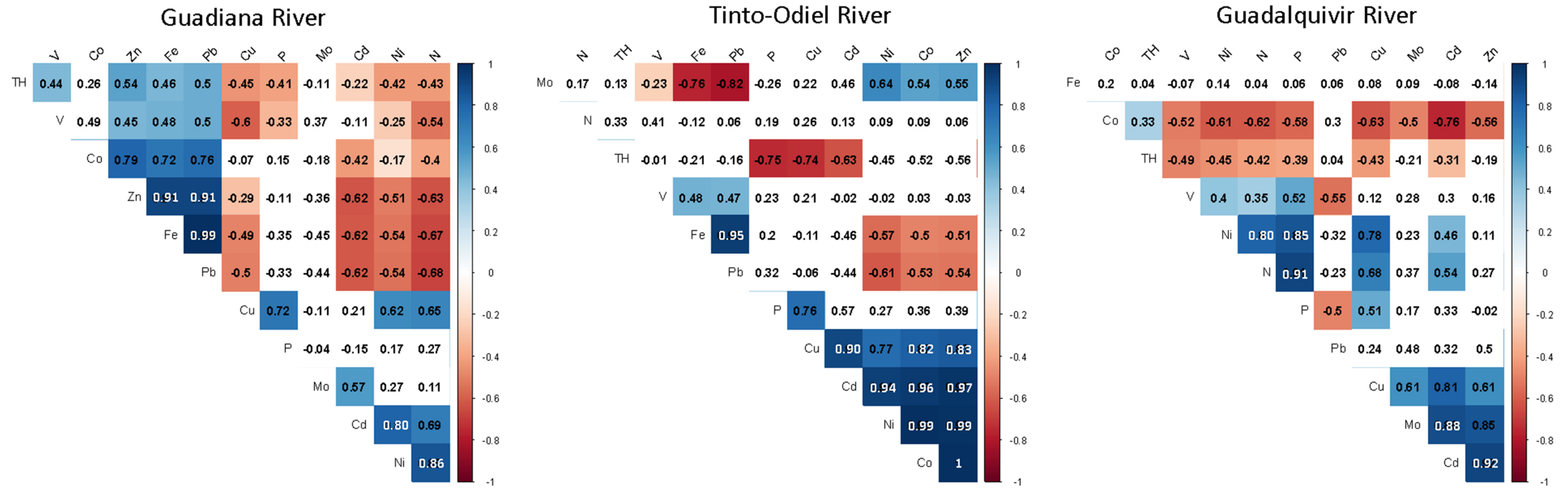

Guadiana
Tinto-Odiel
Guadalquivir
GU0
GU1
GU2
GU3
GU4
TO0
TO1
TO2
TO3
TO4
GD0
GD1
GD2
GD3
GD4
SP1
SP2
SP3
SP4
TF1
TF2
TF3
TF4
Santa Maria Cape
Trafalgar Cape
Atlantic Ocean
Strait of Gibraltar
Mediterranean Sea
The Iberian Peninsula
The study area
Atlantic Ocean
Mediterranean Sea
Google
Imagery ©2017 TerraMetrics
37
36
Latitude
-8
-7
-6
-5
Longitude

Figure 1



Log10 Fe (nM)
2
3
4
5
6
7
a b a b a a
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Ni (nM)
1.5
2.0
2.5
3.0
3.5
b a cb a c c
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Co (nM)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
a bc d d ab c
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Cu (nM)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
a a cd d bc b
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Mo (nM)
4.0
4.2
4.4
4.6
4.8
ab a c a cb a
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Cd (nM)
0.5
1.0
1.5
2.0
b a d d c b
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Pb (nM)
0.0
0.5
1.0
1.5
a b c d b b
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 Zn (nM)
3
4
5
6
a b e e d c
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir
Log10 V (nM)
2.2
2.4
2.6
2.8
3.0
3.2
3.4
a a a a a a
Wet Dry Wet Dry Wet Dry
Guadiana Tinto-Odiel Guadalquivir

Figure 2



Guadiana River

	V	Co	Zn	Fe	Pb	Cu	P	Mo	Cd	Ni	N
TH	0.44	0.26	0.54	0.46	0.5	-0.45	-0.41	-0.11	-0.22	-0.42	-0.43
V		0.49	0.45	0.48	0.5	-0.6	-0.33	0.37	-0.11	-0.25	-0.54
Co			0.79	0.72	0.76	-0.07	0.15	-0.18	-0.42	-0.17	-0.4
Zn				0.91	0.91	-0.29	-0.11	-0.36	-0.62	-0.51	-0.63
Fe					0.99	-0.49	-0.35	-0.45	-0.62	-0.54	-0.67
Pb						-0.5	-0.33	-0.44	-0.62	-0.54	-0.68
Cu							0.72	-0.11	0.21	0.62	0.65
P								-0.04	-0.15	0.17	0.27
Mo									0.57	0.27	0.11
Cd										0.80	0.69
Ni											0.86

Tinto-Odiel River

	N	TH	V	Fe	Pb	P	Cu	Cd	Ni	Co	Zn
Mo	0.17	0.13	-0.23	-0.76	-0.82	-0.26	0.22	0.46	0.64	0.54	0.55
N		0.33	0.41	-0.12	0.06	0.19	0.26	0.13	0.09	0.09	0.06
TH			-0.01	-0.21	-0.16	-0.75	-0.74	-0.63	-0.45	-0.52	-0.56
V				0.48	0.47	0.23	0.21	-0.02	-0.02	0.03	-0.03
Fe					0.95	0.2	-0.11	-0.46	-0.57	-0.5	-0.51
Pb						0.32	-0.06	-0.44	-0.61	-0.53	-0.54
P							0.76	0.57	0.27	0.36	0.39
Cu								0.90	0.77	0.82	0.83
Cd									0.94	0.96	0.97
Ni										0.99	0.99
Co											1

Guadalquivir River

	Co	TH	V	Ni	N	P	Pb	Cu	Mo	Cd	Zn
Fe	0.2	0.04	-0.07	0.14	0.04	0.06	0.06	0.08	0.09	-0.08	-0.14
Co		0.33	-0.52	-0.61	-0.62	-0.58	0.3	-0.63	-0.5	-0.76	-0.56
TH			-0.49	-0.45	-0.42	-0.39	0.04	-0.43	-0.21	-0.31	-0.19
V				0.4	0.35	0.52	-0.55	0.12	0.28	0.3	0.16
Ni					0.80	0.85	-0.32	0.78	0.23	0.46	0.11
N						0.91	-0.23	0.68	0.37	0.54	0.27
P							-0.5	0.51	0.17	0.33	-0.02
Pb								0.24	0.48	0.32	0.5
Cu									0.61	0.81	0.61
Mo										0.88	0.85
Cd											0.92

Figure 3

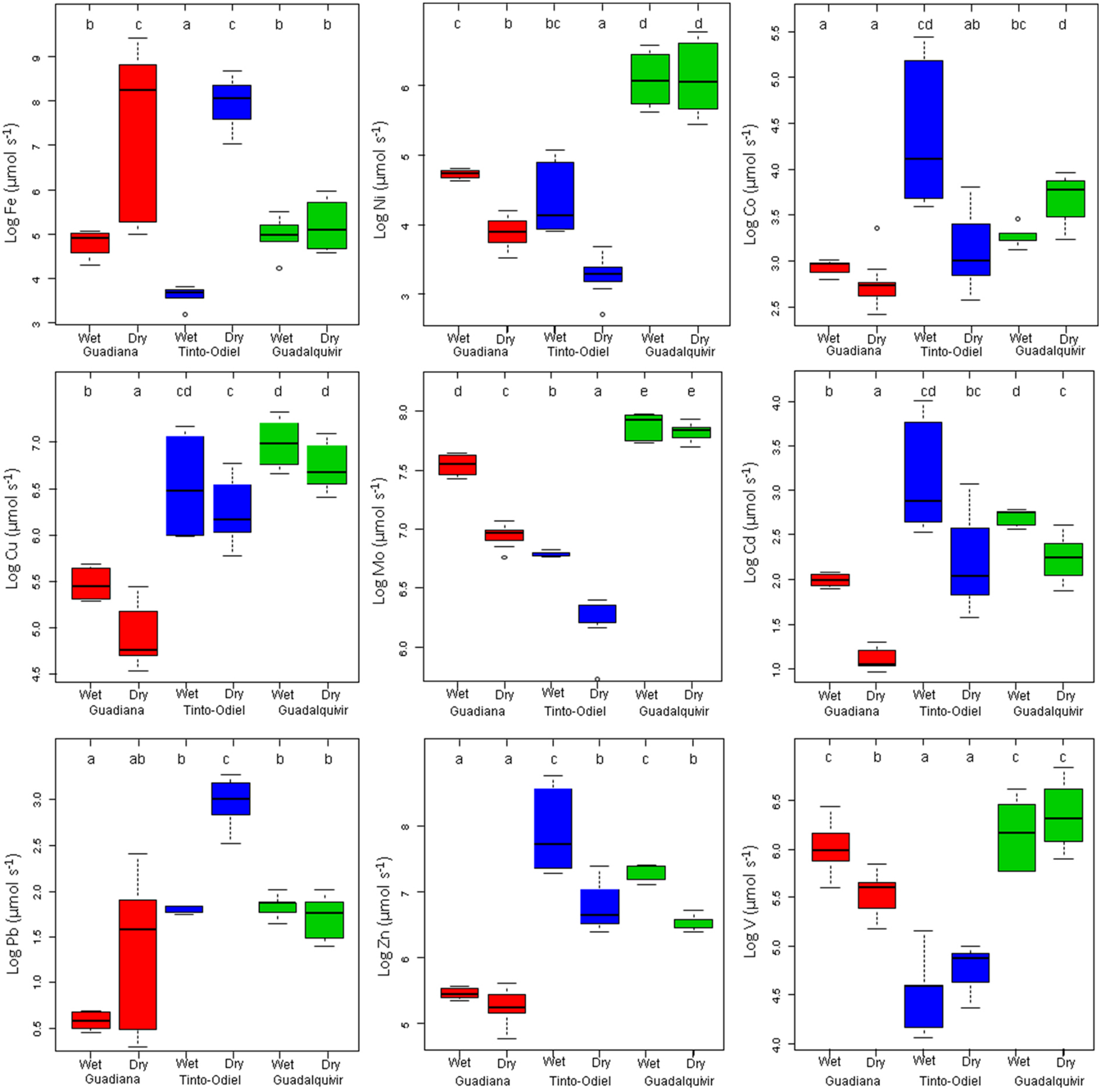

b c a c b b
Log Fe (µmol s-1)
3 4 5 6 7 8 9
c b bc a d d
Log Ni (µmol s-1)
3 4 5 6
a a cd ab bc d
Log Co (µmol s-1)
2.5 3.0 3.5 4.0 4.5 5.0 5.5
b a cd c d d
Log Cu (µmol s-1)
4.5 5.0 5.5 6.0 6.5 7.0
d c b a e e
Log Mo (µmol s-1)
6.0 6.5 7.0 7.5 8.0
b a cd bc d c
Log Cd (µmol s-1)
1.0 1.5 2.0 2.5 3.0 3.5 4.0
a ab b c b b
Log Pb (µmol s-1)
0.5 1.0 1.5 2.0 2.5 3.0
a a c b c b
Log Zn (µmol s-1)
5 6 7 8
c b a a c c
Log V (µmol s-1)
4.0 4.5 5.0 5.5 6.0 6.5
Wet Dry Wet Dry Wet Dry
Guadiana
Tinto-Odiel
Guadalquivir

Figure 4

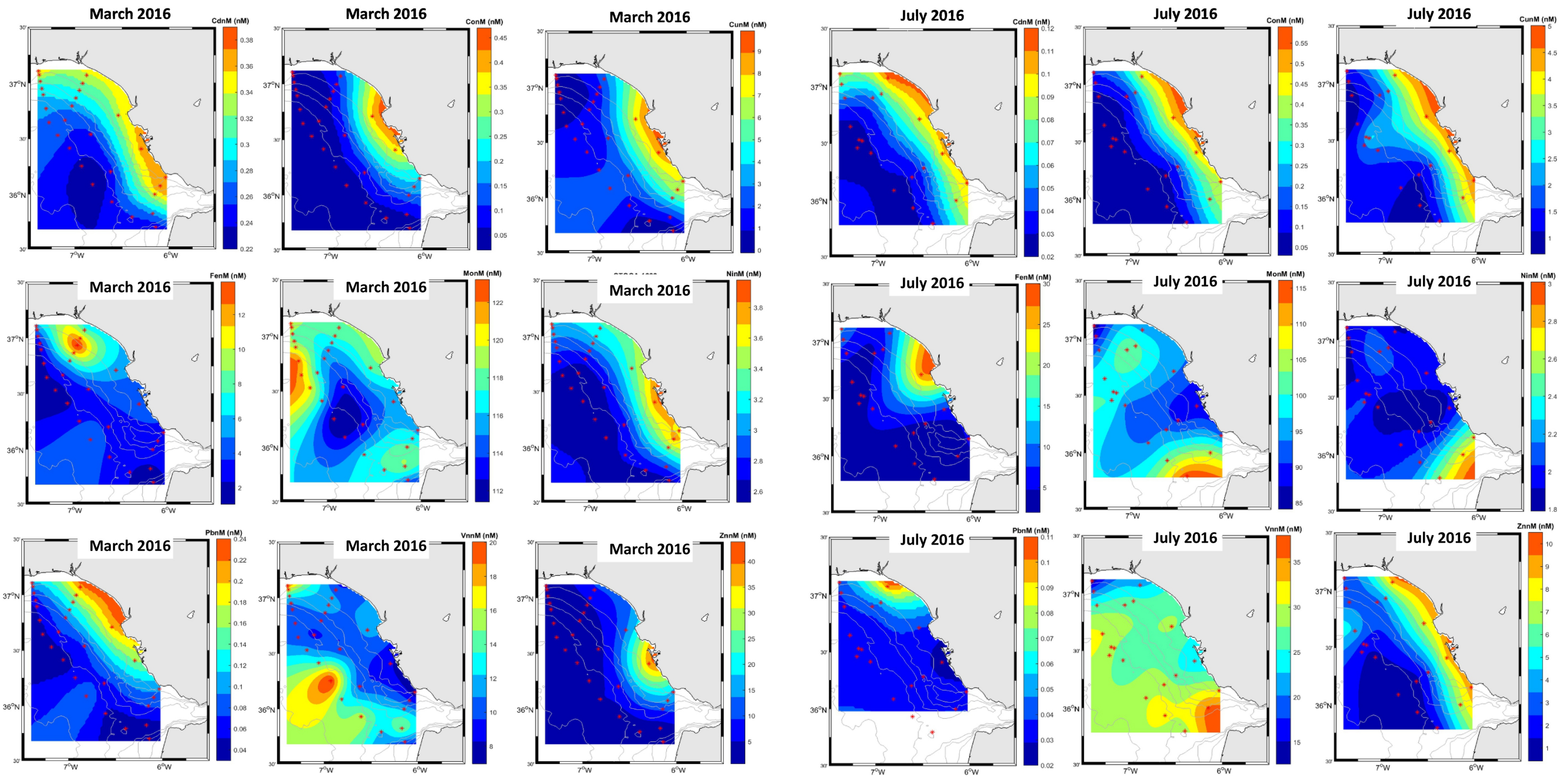

March 2016
CdnM (nM)
March 2016
ConM (nM)
March 2016
CunM (nM)
July 2016
CdnM (nM)
July 2016
ConM (nM)
July 2016
CunM (nM)
March 2016
FenM (nM)
March 2016
MonM (nM)
March 2016
NinM (nM)
July 2016
FenM (nM)
July 2016
MonM (nM)
July 2016
NinM (nM)
March 2016
PbnM (nM)
March 2016
VnnM (nM)
March 2016
ZnnM (nM)
July 2016
PbnM (nM)
July 2016
VnnM (nM)
July 2016
ZnnM (nM)
37°N
36°N
7°W
6°W

Figure 5

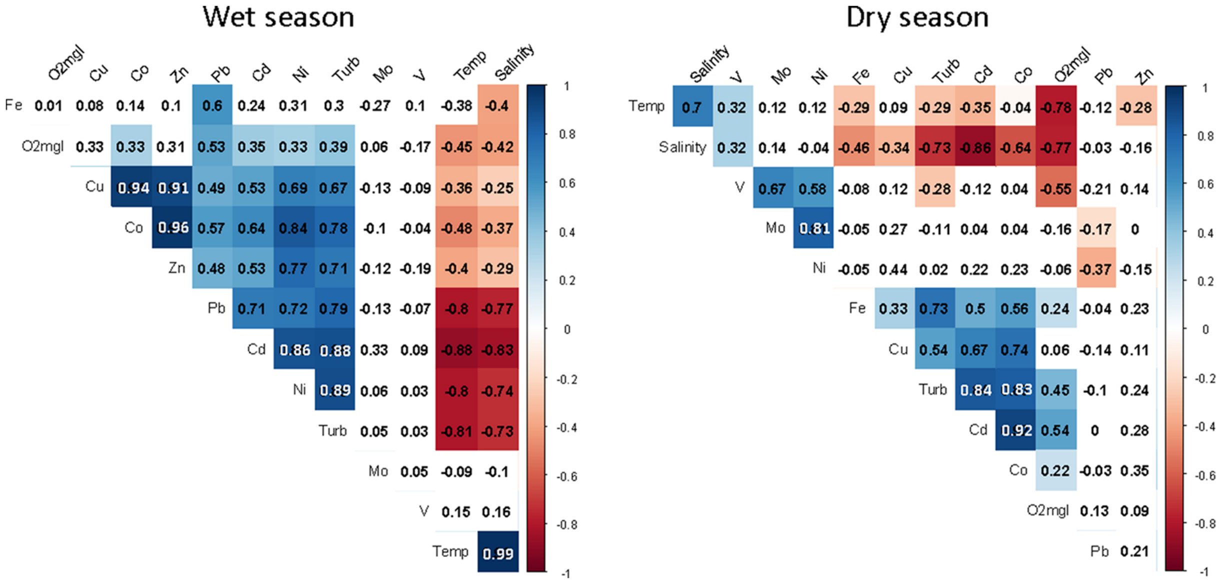

Wet season
O2mgl Cu Co Zn Pb Cd Ni Turb Mo V Temp Salinity
Fe 0.01 0.08 0.14 0.1 0.6 0.24 0.31 0.3 -0.27 0.1 -0.38 -0.4
O2mgl 0.33 0.33 0.31 0.53 0.35 0.33 0.39 0.06 -0.17 -0.45 -0.42
Cu 0.94 0.91 0.49 0.53 0.69 0.67 -0.13 -0.09 -0.36 -0.25
Co 0.96 0.57 0.64 0.84 0.78 -0.1 -0.04 -0.48 -0.37
Zn 0.48 0.53 0.77 0.71 -0.12 -0.19 -0.4 -0.29
Pb 0.71 0.72 0.79 -0.13 -0.07 -0.8 -0.77
Cd 0.86 0.88 0.33 0.09 -0.88 -0.83
Ni 0.89 0.06 0.03 -0.8 -0.74
Turb 0.05 0.03 -0.81 -0.73
Mo 0.05 -0.09 -0.1
V 0.15 0.16
Temp 0.99
1 0.8 0.6 0.4 0.2 0 -0.2 -0.4 -0.6 -0.8 -1
Dry season
Salinity V Mo Ni Fe Cu Turb Cd Co O2mgl Pb Zn
Temp 0.7 0.32 0.12 0.12 -0.29 0.09 -0.29 -0.35 -0.04 -0.78 -0.12 -0.28
Salinity 0.32 0.14 -0.04 -0.46 -0.34 -0.73 -0.86 -0.64 -0.77 -0.03 -0.16
V 0.67 0.58 -0.08 0.12 -0.28 -0.12 0.04 -0.55 -0.21 0.14
Mo 0.81 -0.05 0.27 -0.11 0.04 0.04 -0.16 -0.17 0
Ni -0.05 0.44 0.02 0.22 0.23 -0.06 -0.37 -0.15
Fe 0.33 0.73 0.5 0.56 0.24 -0.04 0.23
Cu 0.54 0.67 0.74 0.06 -0.14 0.11
Turb 0.84 0.83 0.45 -0.1 0.24
Cd 0.92 0.54 0 0.28
Co 0.22 -0.03 0.35
O2mgl 0.13 0.09
Pb 0.21
1 0.8 0.6 0.4 0.2 0 -0.2 -0.4 -0.6 -0.8 -1

Figure 6