Spatial distribution and estuarine sources of dissolved organic matter export to the coastal zone in the Gulf of Cádiz, Spain

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ABSTRACT

Dissolved organic matter (DOM) is a major component of the organic matter transported to the coastal zone by rivers. It controls ecosystem-level processes (e.g. food web) and constitutes an important pathway for nutrients transport from land to coastal waters. We know that estuarine discharges affect the primary production and nutrient composition in the adjacent coastal area. For instance, the current hypernutrification of the Guadalquivir estuary may benefit primary production on adjacent coasts. However, studies on DOM in the Gulf of Cádiz waters are unknown despite its importance in the global ocean functioning. The Gulf of Cádiz is under the estuarine influence of three main estuaries: Guadiana, Tinto-Odiel and Guadalquivir. The present study evaluates the relevance of DOM and the estuarine influence and environmental factors which determine its distribution in the Gulf of Cádiz. Our results suggest that the Gulf of Cádiz water mass is receiving large amounts of dissolved organic transported by the Guadiana and Guadalquivir rivers and much lesser from Tinto-Odiel. Thus, the estuarine influenced area explained the fDOM variability in the Gulf of Cadiz and this variability was shaped by turbidity, water depth and distance from the coast. Within the estuarine ecosystems, salinity and turbidity were the main factors explaining the fDOM variability.

INTRODUCTION

Dissolved organic matter (DOM) influences aquatic food webs and controls the availability of dissolved nutrients and metals (1,2). DOM is also important from regional and global biogeochemical perspectives, as DOM constitutes an important pathway for carbon (C), nitrogen (N), and phosphorus (P) transport from land to sea (Harrison 2005). The quantification of these elements from their sources in the continental shelf has been poorly studied. The Gulf of Cádiz water masses are directly influenced by the three main estuarine systems (Guadiana, Tinto-Odiel and Guadalquivir). Nutrient export to neighbouring coastal waters generates phytoplankton blooms on the shelf (3). In the Guadalquivir estuary 17% and 83% of the estuarine SPM concentration was organic and inorganic matter, respectively (4). However, at present we do not know how fDOM varies through the Gulf of Cádiz and how it is interacting with environmental variables. We hypothesise that fDOM spatial variability in the GC is determined by the rivers influence by transport to costal waters. Advanced sensor technology is widely used in aquatic monitoring and research. We used the YSI EXO2 multiparametric sonde provided by six sensors and an integral pressure transducer. Each sensor measures its parameter via a variety of electrochemical, optical, or physical detection methods. We used the capability of water chemistry sensors embedded in this new sensor platform to document spatial variability in the Gulf of Cádiz. This new sensor platform continuously samples the mouth of the three main estuaries and water column in the Gulf of Cádiz

MATERIALS AND METHODS

Sampling was carried out on board the Ramon Margalef oceanographic vessel during March 2016 (Figure 1). We used a YSI multiparameter sonde (EXO2; Yellow Springs, OH). The EXO2 sonde uses a combination of electrical and optical sensors for specific conductivity, water temperature, pH, dissolved oxygen, turbidity, fluorescent dissolved organic matter (fDOM), chlorophyll-a fluorescence, and phycocyanin fluorescence. Physical parameters of the EXO2 sonde were highly correlated ($R=0.8$, $p<0.01$) with the CTD-ADCP. A multivariate approach to spatial analysis among ecosystems (estuaries *vs.* GC), within ecosystems estuaries and GC (Radials) differences, and depth and coastal influenced area (distance from the main land) differences in the total algae and fDOM was followed using the PRIMER 6.1 (Plymouth Routines in Multivariate

Ecological Research) computer software pack. Multivariate data analysis was carried out by non-metric multidimensional scaling (MDS) ordination with the Euclidian distance similarity. Our physical dataset includes temperature, salinity, dissolved oxygen, turbidity and pH. We used generalised additive models (GAMs) to test the physical factors effects on fDOM.

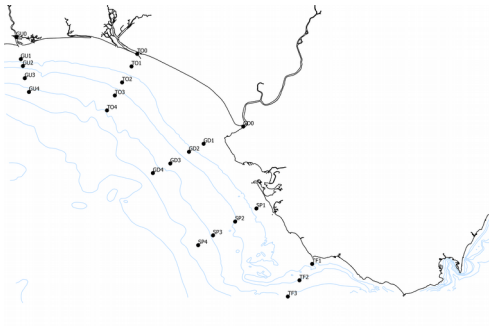

Figure 1. Sampling locations for the different oceanographic cruises. Radials from right to left: TF Trafalgar, SP Sancti Petri, GD Guadalquivir, TO Tinto y Odiel, and GU Guadiana.

RESULTS AND DISCUSSION

We found an expected high dissimilarity among ecosystems in terms of total algae and fDOM concentration (ANOSIM analyses R=0.9, p<0.001). However, among estuarine samples the Tinto-Odiel ones were closer to the Gulf of Cádiz samples (low fDOM values) than the Guadiana and Guadalquivir ones (the highest fDOM values). Among the oceanic samples, the average similarity was low (R=0.49, p<0.001) being this variability explained mainly by the distance from the coastline and the radials (Fig. 2). Most of the differences were found between the station closer to the coastline (Stations 1) and the furthest one (R = 0.6, p< 0.001).

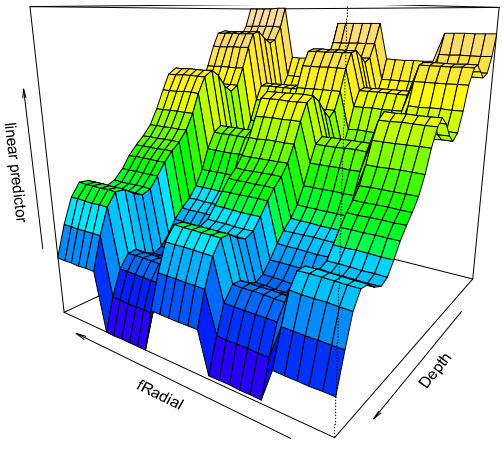

Figure 2. fDOM prediction as a function of depth and the radials of the Gulf of Cádiz salinity. Radials from right to left: TF, SP, GD, TO and GU (see legend in the figure 1).

Nonparametric models (GAM) were fit to the data to estimate the partial effects of the various covariates on fDOM. In the Gulf of Cádiz, we found positive effects of temperature and turbidity in all radials, while depth had a negative effect, reducing fDOM concentration (Fig. 2). In the estuaries, turbidity and salinity were found to have a negative effect (Fig. 3).These results suggest that the estuarine influence from the Guadalquivir and Guadiana estuaries explains the dissolved organic matter variability found in the Gulf of Cádiz. In general, fDOM concentrations are much higher in estuaries than in the open ocean, though concentrations are highly variable (2). Although variations in fDOM are primarily the result of natural processes, human activities such as freshwater discharges and wetland drainage can affect the levels in estuarine systems with carrying out effects on the Gulf of Cádiz. Human transformations of the Tinto-Odiel estuary would explain the high dissimilarity respect to the other two estuaries. These novel observations resulted in high-density, mesoscale spatial data and revealed unknown variability in physical, chemical, and biological factors.

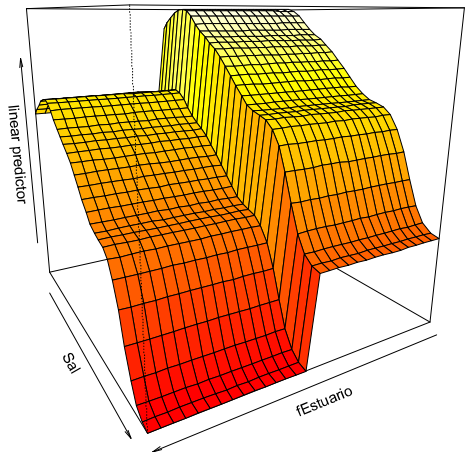

Figure 3. fDOM prediction as a function of salinity in the Guadalquivir (right) and Guadiana (left) estuaries. Tinto-Odiel has not been showed due to the absence of a salinity gradient.

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