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Dissolved organic matter dynamics in Mediterranean lagoons: The relationship between DOC and CDOM

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ABSTRACT

Coastal lagoons are highly vulnerable to climate change-related pressures, such as floods and increasing temperatures, which lead to higher oxygen consumption, anaerobic metabolism and dystrophic events. Although these factors have a significant impact on the carbon cycle, the dynamics of dissolved organic matter (DOM) in these systems have not been extensively investigated. DOM can be analytically determined from the concentration of dissolved organic carbon (DOC) and/or from the spectral properties of chromophoric dissolved organic matter (CDOM), which is the light-absorbing fraction of DOM. In the present study, we investigated the spatio-temporal distribution of surface water trophic variables (Chl *a* and DOC) and CDOM in two Mediterranean lagoon systems, the Oristano Lagoon-Gulf system (OLG) and the Varano Lagoon (VL), in order to provide quantitative information on the dynamics of DOM in these systems. Furthermore, we assessed the value of CDOM-related indices (i.e. absorption coefficients, spectral slopes and Specific UV Absorbance at 254 nm [$SUVA_{254}$]) as tools for describing the dynamics of DOM in coastal lagoons, irrespective of geographical settings, environmental conditions and anthropogenic pressures. In OLG, spatial heterogeneity and compartmentalization, with salinity varying from < 1 (riverine sites) to > 50 (Mistras Lagoon), affected the distribution of DOC and CDOM, with the lowest values on the south side and at sites far from riverine input. In OLG, the highest DOC and CDOM values were found in the sediment pore-water of the organic-rich Cabras Lagoon, where they were nearly double those of the water column. In VL, salinity was homogeneously distributed throughout the lagoon, which indicated a mixing of freshwater with marine waters. DOC and CDOM values were on average lower in VL than in OLG. However, in VL, DOC and CDOM showed strong peaks following a flood (September 2014) and a dystrophic event (July 2015), demonstrating the quick response of the system to environmental perturbation. In OLG, absorption coefficients at 280 nm and 350 nm were slightly negatively correlated with salinity, which indicated the influence of terrigenous inputs at riverine sites. In contrast, in VL, CDOM varied linearly and positively with salinity as a result of the in situ input of organic matter from phytoplankton during the dry season. Segment analysis showed that besides the differences between the two investigated systems, the trophic variables and optical parameters analyzed in the present study shared a common relationship. These results suggest that CDOM indices can be good predictors for the estimation of DOM. Overall, the present study provides insight into the dynamics of DOC and CDOM in little-studied Mediterranean lagoons and demonstrates that the CDOM indices can be a valuable, cost-effective and simple tool for describing the trophic conditions of these systems.

1. Introduction

Dissolved organic matter (DOM) represents a crucial variable in the assessment of the carbon cycle in coastal marine areas and shallow coastal lagoons with high spatial heterogeneity of hydrological conditions. DOM has many ecological implications in aquatic ecosystems and plays a critical role in organic carbon cycling and aquatic biogeochemical processes, as well as interactions with aquatic organisms and

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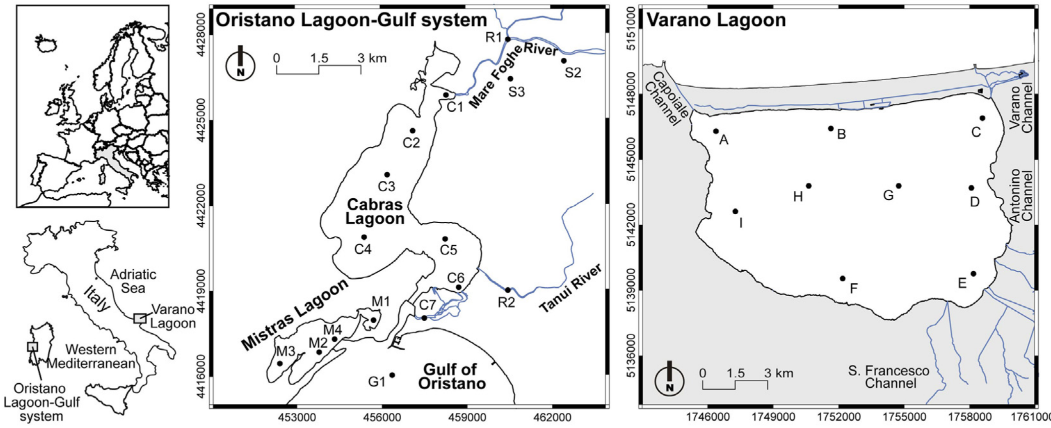

Fig. 1. Study areas and sampling sites in the Oristano Lagoon-Gulf system (western Sardinia) and the Varano Lagoon (Adriatic Sea).

the bioavailability of pollutants (Hopkinson and Vallino, 2005; Watanabe and Kuwae, 2015). Thus, assessment of the chemical composition and dynamics of DOM helps us to understand biogeochemical processes in aquatic environments and its interaction with pollutants in aquatic systems (Melendez-Perez et al., 2016).

Dissolved organic carbon (DOC) accounts for approximately 90% of the organic carbon in the oceans and is therefore an essential part of the global carbon cycle (Hansell et al., 2009). In coastal waters, DOM originates from both in situ biological processes (production and degradation) (Vantrepotte et al., 2007; Maciejewska and Pempkowiak, 2014; Specchiulli et al., 2016a) and transport via river runoff (Kawamura and Kaplan, 1986; Avery et al., 2006; Maie et al., 2014).

DOM concentrations can be assessed from the concentration of DOC and/or from the spectral properties of chromophoric dissolved organic matter (CDOM), the latter representing the light-absorbing fraction of DOM (Hestir et al., 2015). CDOM is responsible for much of the ultraviolet (UV) and visible (VIS) light attenuation in many natural waters (Zepp, 2003; Sasaki et al., 2005) and affects ecosystem functioning (Bidigare et al., 1993; Osburn and Morris, 2003; Guo et al., 2007). Together, DOC concentrations and the spectral properties of CDOM absorption can be used as indicators of DOM content, composition and molecular weight (Helms et al., 2008), and to assess the extent of pollution in sewage (Baker, 2001; Baker and Curry, 2004), rivers (Baker and Inverarity, 2004) and lakes (Wang et al., 2007).

DOM concentrations and CDOM properties in environments subject to anthropogenic impact depend on a complex balance of multiple sources and degradation processes, and the variety of hydrological, biogeochemical and ecological conditions hinders assessment of their dynamics (Yi et al., 2011; Ya et al., 2015). Specifically, coastal lagoons are highly variable systems that are often characterized by eutrophic conditions. The combined effects of high water residence time, poor and often intermittent connectivity with the sea, shallowness and anthropogenic nutrient inputs cause lagoon waters to accumulate organic matter (Magni et al., 2008a; Molinaroli et al., 2009; Tagliapietra et al., 2012). For these reasons, lagoons are expected to be characterized by higher DOC and CDOM levels than those reported for marine waters and estuarine and riverine systems (Amaral et al., 2016; Yang et al., 2013). However, lagoonal systems have not been extensively studied in this regard, and comparison of systems is further complicated by the fact that different absorption coefficients and optical indices are often used in different monitoring programs (Català et al., 2013; Granskog, 2012).

Information on the molecular structure of humic substances is given by spectral slopes ($S_{275-295}$, $S_{350-400}$) and their ratio (S_R), while the aromaticity of the organic matter is indicated by SUVA at a wavelength of 254 nm. Generally, lower S_R and $SUVA_{254}$ indices correspond to a DOM pool with higher average molecular weight and lower aromaticity. Limited studies carried out in coastal lagoons report narrower ranges of spectral slopes and $SUVA_{254}$ than in marine and riverine sites, highlighting the lower variability in molecular weight and aromaticity of lagoon DOM than freshwater and marine DOM (Watanabe and Kuwae, 2015; Ferretto et al., 2017). Importantly, DOC and CDOM measurements are not routinely included in lagoon biogeochemical and ecological studies, indicating the need to increase our knowledge of their dynamics in coastal lagoons.

In the present study, we investigated the dynamics of trophic variables (Chlorophyll *a* [Chl *a*] and DOC) and CDOM in two Mediterranean lagoon systems, the Oristano Lagoon-Gulf system (OLG) and the Varano Lagoon (VL), which are characterized by different physiographic and environmental conditions and different anthropogenic pressures. We aimed to 1) evaluate the spatial distribution of DOC and CDOM in OLG along a salinity gradient ranging from freshwater to hypersaline conditions; 2) compare DOC and CDOM values in OLG and VL; 3) evaluate the spatio-temporal variability of DOC and CDOM in VL following extreme hydrological and ecological events (a flood and a period of hypoxia and dystrophic conditions) occurring at different times during the year; 4) assess the relationships between salinity and DOC/CDOM as a means of identifying the allochthonous/autochthonous sources of DOM; and finally, 5) evaluate if CDOM properties can also be used as a simple and useful indicator of water quality in coastal lagoons, as has been demonstrated for coastal marine systems (Granskog, 2012; Joshi et al., 2017).

2. Materials and methods

2.1. Study areas

2.1.1. The Oristano Lagoon-Gulf system (western Sardinia)

The Oristano Lagoon-Gulf system (OLG) comprises the Gulf of Oristano (150 km^2; maximum depth 24 m) and several shallow water bodies as salt marshes and lagoons that cover an area of ~46 km^2. In the present study, the Cabras Lagoon and its main freshwater tributaries, the Mistras Lagoon and a nearby marine site in the northern sector of the Gulf, were investigated (Fig. 1). The Cabras Lagoon is a shallow water body (22 km^2, z_{mean} = 1.4 m) whose watershed comprises an area of ~430 km^2 and has ~40,000 inhabitants. Most of the freshwater input to the Cabras Lagoon originates upland from the Rio Mare e Foghe, which drains an area of 313 km^2. A minor tributary, Rio Tanui, is located in the lagoon's southern sector (Padedda et al., 2010; Pulina et al., 2011). In the Cabras Lagoon, salinity can vary widely throughout the year from < 5 to > 30 depending on rainfall events (Magni et al., 2005; Pulina et al., 2012). In the late 1990s, artificial barriers were constructed along the "*Scolmatore*" to control the fish catch. The lagoon is now connected to the Gulf of Oristano only via three narrow creeks flowing into a larger canal, which is the "*Scolmatore*" (spillway). The water exchange between the lagoon and the gulf is