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

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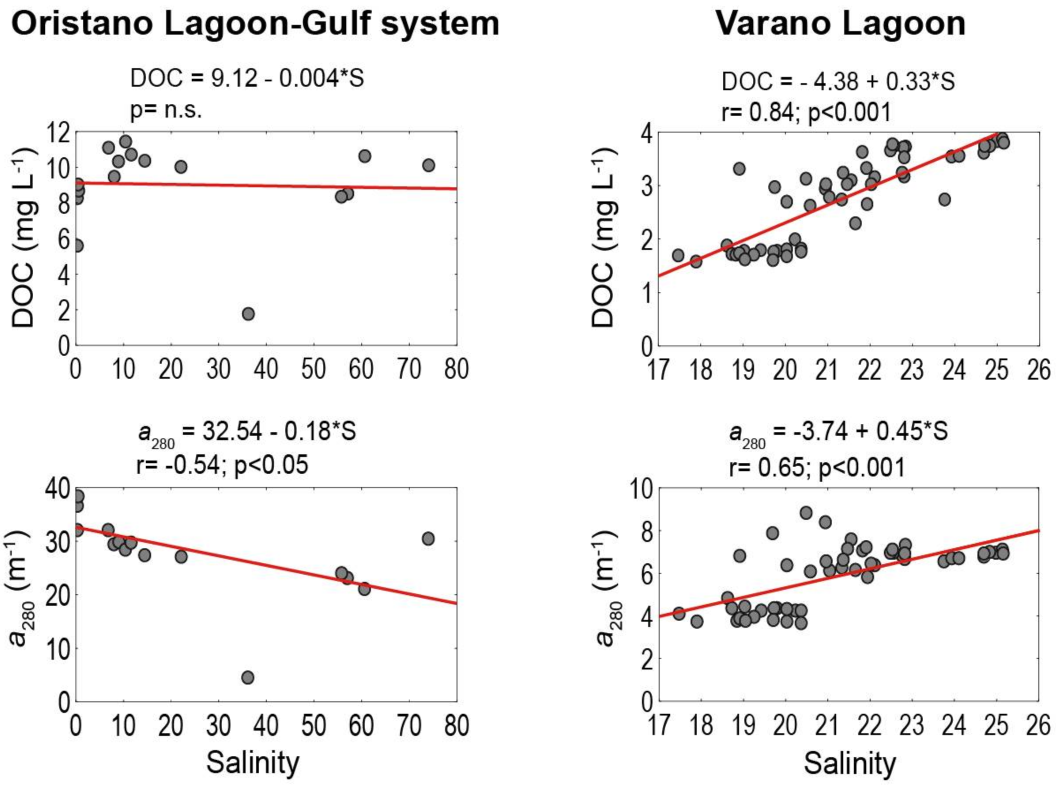

## Highlights

► First *in situ* assessment of DOM and CDOM dynamics in Mediterranean coastal lagoons.

► Spatial compartmentalization controlled DOC and CDOM distribution in the Oristano system.

► Flood and dystrophic events affected DOC and CDOM temporal distribution in the Varano Lagoon.

► DOC and CDOM were highest in the sediment pore-water of the Cabras Lagoon.

► CDOM is a valuable, cost-effective descriptor of the trophic conditions in coastal lagoons.

## 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.

**Keywords**: Carbon cycling; Chromophoric dissolved organic matter; Salinity; Optical indices; Absorption spectra; Coastal lagoons

## 1. Introduction

Dissolved organic matter (DOM) represents a crucial variable in the assessment of the carbon cycle in coastal marine 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 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 et al., 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 et al., 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 thus very limited (Magni et al., 2008a, Satta et al., 2014). Wind-induced currents influence the resuspension and accumulation of fine sediment particles in the lagoon's central sector (De Falco et al., 2004; Magni et al., 2008b). Adjacent to the Cabras Lagoon, the Mistras Lagoon is an artificially semi-enclosed lagoon (4.5 $km^2$, $z_{mean}$< 1 m) with no riverine input and salinity much higher than that in adjacent marine waters, due to strong evaporation in the summer. The Mistras Lagoon was connected to the Cabras Lagoon until the 1970s but now only has an opening to the gulf through its mouth. Both the Cabras and Mistras Lagoons have important fisheries activities (mainly finfish; e.g., Como et al., 2018) and are listed in the Ramsar Convention on Wetlands and subjected to local protection measures.

### 2.1.2. *The Varano Lagoon (southern Adriatic Sea)*

The Varano Lagoon (VL), which is one of the largest brackish systems in the western Mediterranean Sea, is located on the southeastern coast of Italy (65 $km^2$, $z_{mean}$= 3 m). The basin's catchment has a total area of 300 $km^2$. Seawater exchange occurs predominantly through two artificial channels: the Capoiale channel on the western side and the Varano channel on the eastern side of the lagoon (Fig. 1). Two discharge channels, Antonino and S. Francesco, drain freshwater into the southeastern part of the lagoon together with significant loads of nutrients and organic matter from urban and agricultural run-off (Specchiulli et al., 2008; 2010). Other freshwater inputs come from groundwater springs in the southwestern sector of the lagoon. Water renewal times show a fairly uniform pattern; the central and southern sectors are characterized by the highest values (280 days), whereas lower values characterize the area close to the edge and near the connecting channels (Molinaroli et al., 2014). The lagoon hydrodynamics affect sediment grain size, which is mainly represented by mud-silt fractions (>80%) in the central zone and coarser fractions along the edge of the lagoon (Specchiulli et al., 2010; Molinaroli et al., 2014). Generally, VL is considered a meso-trophic/non-polluted environment (Specchiulli et al., 2011) with a high ecological value and important economic activities related to the fishery (e.g., mussel cultivation). At the start of the present study, VL was exposed to strong rainfall which caused flash flooding delivering enormous amounts of water and debris in a very short time. During this flood event, 3963 mm of rainfall was recorded between September 1st and September 6th, with a peak of 240 mm on September 4th (data provided by the "Centro Funzionale" of the Hydrographic and Mareographic Service of Puglia Regional Administration). Subsequently, between the end of July and the beginning of August 2015, a dystrophic event occurred as a major environmental perturbation affecting VL (Cilenti et al., 2017).

### 2.2. *Sampling strategy*

In OLG, we focused on the spatial variations in hydrological and trophic (Chl *a* and DOC) parameters and CDOM properties arising from the presence of heterogeneous environments, including freshwater tributaries, mesohaline (Cabras) and hyperhaline (Mistras) lagoons, and fully marine waters (Gulf of Oristano). In addition, we selected the Cabras Lagoon to determine DOC concentrations and CDOM properties in the sediment pore-water for two reasons. First, we aimed to build on previous studies conducted in the Cabras Lagoon that found organically over-enriched sediments and poor benthic assemblages (e.g., Magni et al., 2005; Como and Magni, 2009), and second, we aimed to provide (for the first time in a Mediterranean lagoon) a comparison of DOC and CDOM in the water column and sediment pore-water. In VL, in addition to assessing the spatial variability of Chl *a*, DOC and CDOM, we aimed to illustrate (for the first time in a Mediterranean lagoon) the temporal dynamics of those components in relation to each other and to the flood (September 2014) and dystrophic event (July 2015) occurring in the period of the present study.

Water samples were collected at 16 sites in OLG in September 2011 and at 9 sites in VL six times between September 2014 and October 2015. In the Cabras Lagoon, sediment samples for the determination of DOC and CDOM in the sediment pore-water were collected at six sampling sites (C1-C6) using a gravity corer. The top 1 cm of the sediment was carefully extruded from the core and kept refrigerated in a cooler-box at 4°C until ready for further treatment in the laboratory. At each site, temperature (T) and salinity (S) were measured *in situ* using a YSI 6600 V2 multi-parametric probe in OLG and an SBE 19Plus (Sea-Bird Electronics, Inc.) probe in VL. Below-surface water samples for Chl *a*, DOC and CDOM measurements were collected with a clean bucket and held at 4 °C until ready for laboratory filtration. All of the containers used in this study were previously acid-washed (10% HCl) and rinsed with Milli-Q water to minimize contamination.

### 2.3 *Laboratory measurements and the calculation of optical indices*

Water samples for Chl *a* analysis were filtered through Whatman GF/F glass fiber filters and extracted with 90% acetone following standard procedures (EPA Methods 445.0, 1997) as detailed in Mariani et al. (2015) and Specchiulli et al. (2016b) for OLG and VL samples, respectively. Sub-samples for DOC and CDOM analysis were filtered through pre-combusted (500 °C for 5 h) GF/F glass fiber filters for OLG and sterile 0.2 µm polyethersulfone (PES) filters using a polyethylene (PE) syringe for VL. A recent study by Nimptsch et al. (2014) showed that calculation of several spectroscopic indices and quantification of optical components is not substantially different between the two types of filters. For the determination of DOC concentrations and CDOM optical properties in the sediment pore-water, part of the fresh sediment sample was centrifuged at 1000×*g*, and the extracted pore-water was immediately filtered on GF/F disposable filters fitted to a 10-mL sterile syringe and transferred into polystyrene test tubes (Magni and Montani, 2006). The filtered water was immediately stored in pre-combusted amber-colored glass bottles at 4°C until the measurements which were completed within one week.

DOC concentrations were measured by high temperature catalytic oxidation using a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany) for OLG (Guo et al., 2011; Hong et al. 2012; Yang et al. 2012) and as non-purgeable organic carbon using a Shimadzu TOC-L CSH series + SSM 5000 for VL. The samples were acidified with 2N HCl and sparged for 8 min (for OLG) and 10 min (for VL) to remove the inorganic carbon before high-temperature catalytic oxidation. From 3 to 5 replicate injections were performed for each sample (CV < 2%), and Milli-Q water was used as the blank. A five-point calibration was conducted with solutions of potassium hydrogen phthalate as standards. Low Carbon Water (LCW) and Consensus Reference Material (CRM) (Hansell Laboratory, University of Miami) were routinely used to check the analytical procedure for the DOC determination. CDOM absorption measurements were conducted using a Techcomp UV-2300 dual beam UV–Vis spectrophotometer with a 5-cm quartz cell for the OLG samples and a dual beam UV-VIS spectrophotometer Shimadzu 2600 Series with a 10-cm quartz cuvette for the VL samples. Absorbance spectra were measured according to Guo et al. (2010) and Specchiulli et al. (2016a) for OLG and VL, respectively. The scanning wavelength range was 250-750 nm, and Milli-Q water was used for the reference. All absorbance values (A) were converted to absorption coefficients ($a_{\mathrm{CDOM}}$, $\mathrm{m}^{-1}$) using expression $a(\lambda) = 2.303 * \mathrm{A}(\lambda)/\mathrm{l}$, where λ is the wavelength and l is the cuvette length in meters. Three indices were derived by absorbance measurements: i) the absorption coefficients at a wavelength of 280 ($a_{280}$) and 350 ($a_{350}$) as a reliable estimation of DOM concentration (Yang et al., 2013; Specchiulli et al., 2016a); ii) $\mathrm{SUVA}_{254}$ ($\mathrm{L\ mg^{-1}\ m^{-1}}$), which was calculated as $\mathrm{SUVA}_{254} = \mathrm{A}_{254}/\mathrm{l}/[\mathrm{DOC}]$, as an indicator of DOM aromaticity (Weishaar et al., 2003); and iii) spectral slope coefficients, which were calculated using a non-linear fit of an exponential function (Granskog et al., 2007) for the absorption spectrum in the ranges of 275-295 nm ($\mathrm{S}_{275\text{-}295}$, $\mathrm{nm}^{-1}$) and over 350-400 nm ($\mathrm{S}_{350\text{-}400}$, $\mathrm{nm}^{-1}$) and the slope ratio ($\mathrm{S_R}$, $\mathrm{S}_{275\text{-}295}/\mathrm{S}_{350\text{-}400}$) as an indicator of CDOM history (e.g., sources and biological and photochemical alterations) (Helms et al., 2008).

### *2.4. Statistical analysis*

To explore the spatial-temporal variability of the hydrological, trophic and optical variables in our study areas, two distinct datasets were considered. The first dataset takes into account measurements from the OLG system to highlight the spatial variability of DOC and CDOM along a salinity gradient ranging between <1 (riverine sites) and >50 (Mistras lagoon). The second dataset concerns the sampling strategy adopted in the VL and based on 6 sampling dates, which include all of the data to illustrate the temporal trend. The significance of the spatial and temporal differences was explored by means of the Kruskal-Wallis Test (Kruskal and Wallis, 1952), which assesses the null hypothesis of no differences between normal distribution and data distribution, returning H (statistics of the test) and p (level of significance). For the OLG system, the dataset was divided into four classes according to the salinity ranges of <1 (riverine sites), 6-22 (Cabras Lagoon), 36 (Oristano Gulf site), and >50 (Mistras Lagoon), whereas for VL, the analysis was based on the entire time-series dataset. The significance of the differences in DOC and CDOM values in water and sediment pore-water and between the two study areas were also tested by the Kruskal-Wallis Test. Spearman rank order was then used to investigate correlations among the physico-chemical, trophic and optical variables in each system and to identify similar anthropogenic sources, whereas scatterplots were used to highlight the linear correlations between trophic/optical variables and salinity. We also tested and quantified relationships between Chl *a*, DOC and CDOM using multiple linear regression. Cluster analysis, based on the Euclidean matrix from the major regions in the OLG system and from the sampling dates in the VL was performed to better assess the usefulness of CDOM as an important factor describing the trophic conditions in different lagoon systems, using group average as cluster mode. Statistical analyses were run after square root and log(x+1) transformation and normalization data by using the STATISTICA 8.0 computer package (StatSoft Inc.) and the Primer-E Software package v6.0 (Plymouth Marine Laboratory, UK).

## Results

### *3.1. Hydrological characteristics and distribution of trophic/optical variables*

### *3.1.1. The Oristano Lagoon–Gulf system (OLG)*

Mean values (when available) for each variable and the significance of the spatial differences among separate areas within OLG are shown in Tables 1 and 2 respectively. Salinity varied widely, from <1 (riverine sites) to >50 (Mistras Lagoon sites). Based on salinity, three major areas were statistically identified, i.e. the riverine, Cabras Lagoon and Mistras Lagoon sites, with a fourth marine site represented by the single station in the Gulf. Temperature also varied significantly across OLG ranging between 22.5°C (R2) and 28.7°C (S3). Although the difference was not significant, the Mistras Lagoon waters were less oxygenated than those of the Cabras Lagoon.

Chl *a* concentrations revealed different trophic conditions among the different areas of OLG, ranging from oligotrophic (1.1 µg $L^{-1}$, Gulf) to eutrophic (25.4 µg $L^{-1,}$ Cabras Lagoon) waters. In addition, mean DOC values differed significantly among areas, with the lowest (1.7 mg $L^{-1}$) and highest (11.1 mg $L^{-1}$) values in the Gulf and the Cabras Lagoon respectively (Fig. 2).

Absorption coefficients at 280 nm ($a_{280}$) and 350 nm ($a_{350}$), which correlated strongly with each other (r = 0.89, $p<0.001$), ranged from 21.1 $m^{-1}$ to 100.1 $m^{-1}$ and from 3.3 $m^{-1}$ to 35.6 $m^{-1}$ respectively. Their distribution followed a persistent north-south gradient with low values at sites far from river input (Fig. 2). Lower mean slope values for $S_{275-295}$ and $S_{350-400}$ were observed at the riverine sites, along with significantly higher values in the Mistras waters and the intermediate values in the Cabras and Gulf sites. The opposite trend was found for $SUVA_{254}$, with riverine sites showing higher aromatic content, generally due to allochthonous humic matter.

DOC and optical properties measured in the pore-water of the surface sediments of Cabras Lagoon showed significantly (H = 9, $p<0.01$) higher values than those found in the water column at the corresponding sites (Fig. 3). The northern sector of the lagoon (site C1) had the highest DOC (22.7 mg $L^{-1}$) and absorption coefficients at both $a_{280}$ (90.5 $m^{-1}$) and $a_{350}$ (47.6 $m^{-1}$). However, the spectral slopes showed lower values in the northern sector, which were mostly affected by riverine inputs. $SUVA_{254}$ was higher at site C1 (2.2 L $mg^{-1}$ $m^{-1}$), where the organic matter is mostly of allochthonous origin, and at sites C4 (2.5 L $mg^{-1}$ $m^{-1}$) and C5 (2.2 L $mg^{-1}$ $m^{-1}$).

### *3.1.2.The Varano Lagoon*

The mean values of all variables and the significance of the spatio-temporal differences among sampling dates and sites for VL are shown in Tables 1 and 2 respectively. Salinity was significantly higher on the last sampling date. However, compared to OLG, salinity was homogeneously distributed throughout the lagoon, indicating a good mixing of freshwater with marine water. Temperature followed a typical seasonal trend and was highest in July ($p<0.001$). More oxygenated waters were observed at the beginning of the study period, oxygen saturation reaching its lowest values in winter ($p<0.001$).

Chl *a* concentrations were highly variable depending on the sampling dates, with the lowest values in January and April 2015 and a peak in July 2015, with a maximum value of 48.5 µg $L^{-1}$ at site G in the central sector of the lagoon (Fig. 4a). DOC values in VL were on average lower than those measured in OLG (H = 28.99, $p<0.001$) (Fig. 2, Table 1). The temporal variation of DOC concentrations in VL was similar to that of Chl *a* except for the last sampling date, with the lowest values in January-April 2015 and the highest in July and October 2015 (Fig. 4a). The highest DOC values (3.87 mg $L^{-1}$) were observed in October 2015 at site E, located in the area that receives constant urban and agricultural runoff. The $a_{280}$ and $a_{350}$ CDOM absorption coefficients were much lower than those measured in OLG (H = 31.77, $p<0.001$), and showed a seasonal trend similar to that observed for Chl *a* and DOC (Fig. 4b). The lowest $a_{280}$ (3.7 $m^{-1}$) and $a_{350}$ (0.7 $m^{-1}$) values were found at site A in April 2015, whereas the highest (8.8 $m^{-1}$ and 2.2 $m^{-1}$, respectively) were observed at site C in September 2014. The $S_{275-295}$ and $S_{350-400}$ slopes were highest in April 2015 and October 2014 ($p<0.001$) (Fig. 4c) respectively, whereas their ratio was lowest (corresponding to the highest molecular weights) in October 2014 ($p<0.01$) (Fig. 4d), which was one month after the flood event. The $SUVA_{254}$ index was lower than in OLG (H = 28.99, $p<0.001$), with relatively high values in January 2015, subsequently decreasing until the end of the sampling period ($p<0.001$) (Fig. 4d; Table 2).

### *3.2 Relationships between salinity and trophic/optical variables*

In OLG, the salinity gradient, from the fresh waters at the riverine sites to the hyper-saline waters in Mistras Lagoon, affected the distribution pattern of several variables (Fig. 5a). Chl *a* decreased (r = -0.52, $p<0.05$) as salinity increased, whereas no correlation was found between DOC and salinity. Although slightly correlated ($p<0.05$), the distribution patterns of both $a_{280}$ and $a_{350}$ along the salinity gradient (r = -0.54 and r = -0.66, respectively) indicated the influence of terrigenous inputs at sites affected by fresh waters. Positive correlations ($p<0.01$) were found for $S_{275-295}$ and $S_R$, which indicated a shift in DOM from high molecular weight (MW) to low molecular weight (MW) with increasing salinity. No correlation was observed with $SUVA_{254}$, which indicated no influence of salinity on the aromatic content of organic matter.

In VL (Fig. 5b), no correlation between salinity and Chl *a* was found, although DOC and CDOM increased with salinity ($p<0.001$). Neither of the slopes was correlated with salinity, indicating that their variation was not affected by marine and/or freshwater inputs. Only $SUVA_{254}$ was significantly ($p<0.001$) and negatively correlated with salinity, which indicated a higher aromatic content of DOM at lower salinity.

### *3.3. Relationships between trophic and optical variables*

Correlation analysis showed that the relationships of Chl *a* and DOC with CDOM properties in OLG were quite different to what they were in VL (Table 3). In OLG, Chl *a* was not correlated with optical variables, whereas DOC was found to be weakly and positively correlated with $S_{350\text{-}400}$ ($r = 0.38$, $p<0.05$). When the data for all of the sampling dates in the VL were combined, Chl *a* and DOC were found to have positive relationships ($p<0.05$) with both $a_{280}$ ($r = 0.77$ and $r = 0.83$, respectively) and $a_{350}$ ($r = 0.79$ and $r = 0.76$, respectively). Indeed, the high mean Chl *a* and DOC concentrations observed in April 2015 were accompanied by high $a_{280}$ and $a_{350}$. In addition, Chl *a* and DOC concentrations increased with the molecular weight of organic matter, as highlighted by the negative relationships between Chl *a* and $S_{275\text{-}295}$ ($r = -0.41$, $p<0.05$) and between DOC and the $S_{275\text{-}295}$ ($r = -0.29$, $p<0.05$). Chlorophyll *a* increased as the aromatic content of organic matter decreased, as shown by its negative correlations with $SUVA_{254}$ ($r = -0.35$, $p<0.05$).

Due to the high temporal and spatial variability of trophic variables and optical properties, multiple linear regression analysis was used to quantify the relationships between dependent (Chl *a* and DOC) and independent (CDOM) variables, all of which were found to predict patterns of Chl *a* and DOC concentrations (Table 4). In OLG, regressions using only optical properties as predictor variables for Chl *a* did not produce significant $\beta$, whereas significant regressions were obtained using salinity, $S_{350\text{-}400}$ and $a_{350}$. Regressions using $a_{280}$, slopes and salinity as predictor variables for the estimation of DOC were more significant, and $R^2$ was slightly higher . In VL, Chl *a* was significantly and negatively associated with both $S_{275\text{-}295}$ ($\beta = -0.39$) and $SUVA_{254}$ ($\beta = -0.37$), but stronger correlations were observed using salinity, both slopes and $a_{350}$ as predictor variables. DOC variability was better described (higher $R^2$) using optical variables (slope ratio and both absorption coefficients) as predictor variables (Table 4).

### *3.4. Cluster analysis*

In OLG, cluster analysis identified three main groups at a resemblance distance of 2.98 (Fig. 6a). Group A included the Cabras Lagoon characterized by the highest DOC and the lowest $SUVA_{254}$ values, group B included the Mistras Lagoon, with the highest optical slopes and $S_R$ values and the lowest $a_{280}$ and $a_{350}$ values, and group C had the riverine sites, with the lowest DOC and the highest CDOM values. In OLG, at a resemblance distance above 4, it was possible to discern two main groups characterized by a large difference in salinity, the first group combining the meso-hyperhaline lagoon sites and the second one combining the riverine sites. In VL, at a resemblance distance of 5 to 6, two main groups were distinguishable (Fig. 6b). The first group included the January 2015 and April 2015 samples, characterized by the lowest Chl *a* and DOC values, and the second group included all the other samples, characterized by higher values for the trophic and optical variables. In contrast, at a resemblance distance of 3.37, three main groups were obtained: group D, including the January 2015 and April 2015 samples, group E, including the September 2014 (flood event) and July 2015 (beginning of the dystrophic event) samples (with the highest Chl *a* and DOC values), and group F, including the October 2014 and October 2015 samples.

## 4. Discussion

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 (Magni et al., 2008c; Tagliapietra et al., 2011; Fabbrocini et al., 2017). Even though these factors have a major impact on the carbon cycle, the dynamics of DOC and CDOM in these systems have not been thoroughly investigated. The present study provides some initial insight into the dynamics of DOM and the relationships between trophic variables (Chl *a* and DOC) and optical properties (CDOM indices) in two Mediterranean lagoon systems characterized by different geographical settings, environmental conditions and anthropogenic pressures. Although several recent studies have focused on the use of CDOM properties (absorption and/or fluorescence) as indicators of the source and dynamics of DOM in transitional waters (Watanabe and Kuwae, 2015; Ya et al., 2015; Yang et al., 2013), few studies have demonstrated the utility of CDOM indices for assessing the environmental quality of these systems (Shanmugam et al., 2016; Ibánhez et al., 2017). This study provides compelling evidence that CDOM can be a valuable indicator for water quality evaluation in lagoon areas, irrespective of their geomorphological and environmental settings.

Coastal lagoons are known to be highly productive and often eutrophic environments (Baran 2000; Viaroli et al., 2008; Tagliapietra et al., 2012). In productive coastal waters, such as estuarine and lagoon systems, turbidity due to CDOM, chlorophyll *a* and non-algal particles is particularly high, and DOM originates mainly from freshwater discharge (up to 75%) rather than autochthonous sources (phytoplankton and other photosynthetic organisms) (Shanmugam et al., 2016). This property makes DOC a key variable in the food web and more specifically in the microbial loop (Ducklow and Carlson, 1992). Consequently, the assessment of its dynamics is important for describing the trophic state of lagoon systems. In the present study, the OLG and VL systems were found to be characterized by different trophic conditions. Marked differences were also observed within the OLG system, with the highest Chl *a*, DOC and CDOM values in the Cabras Lagoon. These results are consistent with the hypertrophic state of the Cabras lagoon throughout the year, with an annual mean Chl *a* of 40 $\mu$g $L^{-1}$ and peaks of > 80 Chl *a* $\mu$g $L^{-1}$ (Padedda et al., 2012). The hypertrophic state is due to the high inputs of organic matter and inorganic phosphorous and nitrogen from domestic discharge and the large catchment area, which is extensively exploited for agricultural activities. As assessed by Padedda et al. (2010), in the Cabras Lagoon, nutrient accumulation prevails over nutrient mobilization, making this ecosystem an ‘autotrophic’ sink and explaining the highest $a_{280}$ values found at the riverine sites. Accordingly, the Cabras Lagoon is characterized by organic-enriched sediments and poor macrobenthic assemblages (Como and Magni, 2009; Magni et al., 2004, 2009), and its degraded condition was confirmed in the present study by the high levels of DOC and CDOM found in the sediment pore-water. These concentrations were about twice as high as those found in the surface water (Table 1), as reported elsewhere for freshwater and marine sediments (Burdige and Komada, 2015; Chen and Hur, 2015) and demonstrated in the present study for the first time in a coastal lagoon.

In OLG, the presence (Cabras Lagoon) or the absence (Mistras Lagoon) of riverine inputs and the overall circulation pattern, which was mainly promoted by the interaction of the Mistral wind with the tide (Magni et al., 2008a; Molinaroli et al., 2009), appeared to be the main factors controlling the observed salinity gradient. The wide salinity range seemed in turn to play a crucial role in regulating the spatial distribution of DOC and CDOM (Fig. 2). Anthropogenic activities (agriculture and urban discharge) and the limited water exchange with the sea (Magni et al., 2005; Como et al., 2007; Pulina et al., 2012) have a strong impact on the trophic level and the quality and quantity of DOM in the Cabras Lagoon. Here, the highest DOC concentrations were found near river mouths (site C1) and in the central part of the Cabras Lagoon (site C4) in the core region of the circulation vortices with the highest water residence time (Magni et al., 2008a; Molinaroli et al., 2009). In contrast, the low DOC values observed at the riverine sites (R1, R2, S2 and S3) are related to the dynamic behaviour of the water streams. Indeed, during transport, anthropogenic DOM can be removed by flocculation, absorption onto suspended sediments, and microbial and photochemical degradation (Raymond and Spencer, 2015). Nevertheless, the relationships between salinity and DOC/CDOM showed that DOC remained relatively constant along the salinity gradient, whereas $a_{280}$ and $SUVA_{254}$ showed non-conservative behaviour, with a slight decrease from the riverine sites and the mesohaline Cabras Lagoon to the hyperhaline Mistras lagoon (Fig. 5a). This incongruity highlights a decoupling between DOC and CDOM, which results from a shift in DOM from terrestrial to planktonic sources, as also found in studies of wetland-influenced rivers (Maie et al., 2014) and estuaries (Dixon et al., 2014). According to the authors of these studies, during the summer period of low discharge, DOM shifts toward a lower molecular weight and becomes more autochthonous in origin, a process that may also be expected to occur in OLG. However, the group with the lowest CDOM and aromatic values (C1-C7 in the Cabras Lagoon) also had the lowest optical slopes, confirming that in OLG sites with low CDOM but high DOC levels, the dissolved organic matter was characterized by autochthonous material of a higher molecular weight.

In VL, DOC and CDOM values were on average lower than those found in OLG, with fewer DOM sources. In VL, water renewal is mainly controlled by sea-lagoon fluxes, with limited freshwater input (less than 1 $m^3$ $s^{-1}$), resulting in a high water residence time (~260 days, Molinaroli et al., 2014). These factors contribute to the limited variation in salinity observed over the sampling period. Major changes in DOC and CDOM occurred in relation to two extreme events, i.e., a flood at the beginning of September 2014 and a period of dystrophic conditions at the end of July 2015. Reflecting the highly dynamic nature of coastal lagoons, VL quickly responded to the external perturbations (Fabbrocini et al., 2017). In the present study, high DOC and CDOM values were detected on the first sampling date, which occurred a week after the flood (Fig. 4a and b). During this event, terrestrially-derived DOM released into the VL was probably responsible for the observed low $S_{275-295}$ and the high ratios of CDOM absorbance to DOC concentrations, consistent with other studies (Chen et al., 2011; Dixon et al., 2014; Guo et al., 2014). In the following months, no rain was reported, while the high water residence time combined with stable meteorological conditions (no wind-induced waves) enhanced sedimentation, leading to a drop in DOC concentrations, as also found in a shallow subtropical estuary in southeast China (Yang et al., 2013). Subsequently, increased temperatures and greater light availability in spring may have enhanced primary production, leading to the development and accumulation of organic matter as a result of the algal bloom. The increased DOC and CDOM absorption coefficients and decreased optical slopes in July were most likely due to autochthonous production and immediate degradation of new DOM, resulting in low molecular weight, consistent with the results obtained by Dixon et al. (2014). VL suffered from a dystrophic event between the end of July and the beginning of August 2015 (Cilenti et al., 2017), when benthic nutrient regeneration, enhanced by high summer temperatures (Magni and Montani, 2006) led to increased organic matter production and trophic conditions. Furthermore, evaporation processes typical of summer, contributed to the rise in DOC concentrations and CDOM levels in more saline waters, as highlighted in Figure 5, explaining the strong positive correlation between DOC and salinity. In addition, the co-occurrence of the DOC and Chl *a* peaks observed in July suggests that the direct *in situ* input of organic carbon from phytoplankton can be significant with respect to terrestrial input, especially during the dry season, due to increased autochthonous productivity (Guo et al., 2011; Specchiulli et al., 2016a). This is in contrast to what is frequently observed in coastal marine areas, where DOM dynamics are dominated by terrigenous inputs (Del Vecchio and Blough, 2004; Fichot and Benner, 2011).

The present study included samples from different geographical and hydrographic settings and contrasting environmental conditions. Although highly variable spatially, the DOC and CDOM values in OLG (particularly the riverine sites and the Cabras Lagoon) were two to three times higher than those obtained in VL, indicating different trophic conditions. This result was consistent with the large differences in phytoplankton biomass between the two systems, as indicated by previous studies (Specchiulli et al., 2008; Padedda et al., 2010; 2012). However, despite these differences, the described spatial and temporal dynamics of the trophic and optical variables showed a constant relationship between DOC and CDOM in both study areas. Our results are consistent with those reported in other coastal areas where organic matter distribution is mainly due to freshwater discharge and/or *in situ* biological processes (Shanmugam et al., 2016). Segment analysis enabled us to quantify these relationships and proved that CDOM indices can be good predictors of DOM. Absorption coefficients at 280 nm and $SUVA_{254}$ are able to provide additional information that leads to a better prediction of DOC concentrations in both systems. The lack of a terrigenous source for DOC in the VL was confirmed by the positive correlation of DOC with $S_R$. As a result, lower $S_R$ values corresponded to higher MW and lower DOC concentrations.

Cluster analysis provided a general framework for evaluating the link between trophic and optical variables in different regions of OLG and different periods in VL (Fig. 6). In OLG, the lagoon sites (Cabras and Mistras) and riverine sites were clearly separated into two main classes, based on the different optical variables (low and high CDOM). At a lower resemblance distance of 2.98, the analysis produced two main clusters, A and B, and a smaller cluster of riverine sites. The two groups A and B were highly eutrophic, with DOM characterized by a relatively low molecular weight (possibly of autochthonous origin), while the freshwater sites were mainly dominated by terrestrial components from riverine discharge, as has also been observed in coastal and estuarine systems (Gardner et al., 2005). The cluster analysis for VL produced three main groups based primarily on different CDOM indices. The lowest trophic conditions in the winter-early spring period were seen in cluster D, which also contained the lowest CDOM, as well as a higher proportion of aromatic organic matter derived from wastewater discharge (Granskog et al., 2007). Cluster E combined the flood (hydrological) and dystrophic (ecological) events, when VL experienced the highest trophic conditions and DOM was characterized by high CDOM and low aromatic content. The observed transition in the properties of DOM reflected a shift from allochthonous to autochthonous sources of DOM (Amaral et al., 2016). The autumn season (October 2014 and October 2015) samples were grouped in cluster F, with intermediate trophic conditions and intermediate optical variables.

A comparison of our results with literature data shows that OLG and VL are characterized by narrower ranges of spectral slopes and SUVA than are generally reported for riverine (Watanabe and Kuwae 2015) and marine (Ferretto et al., 2017) waters. This comparison indicates that lagoon DOM is less variable in terms of molecular weight and aromaticity than either freshwater or marine DOM. Salinity is an indicator of freshwater input (Magni et al., 2002). Generally, a conservative mixing of freshwaters and marine waters produces linear relationships between salinity and DOM properties (Català et al., 2013). Unlike other studies in temperate estuaries (Yamashita et al., 2008; Guo et al., 2011), the assessment of the spatial and temporal dynamics of DOC and related CDOM indices highlighted linear but non-constant relationships with salinity in both study areas. This may be due to major differences between estuaries and lagoons and the distinctive features of the Mediterranean climate, with rainfall mostly restricted to fall and spring, and hence non-continuous runoff (Tagliapietra et al., 2011; 2012). In VL, DOC concentrations and absorption coefficients increased with salinity, as has also been shown in other semi-enclosed systems affected by runoff (Català et al., 2013). During the flood event in VL, the DOM contained more DOC and a higher proportion of aromatic components, which is generally expected in systems affected by riverine discharge (Granskog et al., 2007). However, during the dry season, enhanced evaporation led to increased salinity and a positive relationship between salinity and DOC/CDOM. Thus, we conclude that due to their high sensitivity to changes in salinity, CDOM indices can be considered key variables for tracing the source of DOM in coastal lagoons, which is also suggested by other studies (Yang et al., 2014).

In conclusion, the DOM dynamics investigated in the present study were driven by various physico-chemical and biological factors. In the riverine-dominated OLG system, the levels and composition of DOM were mainly affected by the pronounced spatial heterogeneity and compartmentalization and the salinity gradient, whereas in VL, they seemed to be controlled by *in situ* biological processes such as primary production. In addition, the temporal variability of the trophic variables and the optical properties of water in VL were strongly affected by extreme events (i.e. a flood and a period of dystrophic conditions) that occurred during the study period. Despite the large spatial and temporal variability and the differences between the two studied systems, the DOM dynamics were found to be closely linked to the CDOM indices. Thus, our results demonstrate that the combined study of DOC and CDOM is a useful tool for assessing the dynamics of DOM in coastal transitional ecosystems, irrespective of the differences in geographical settings and environmental conditions. Furthermore, the present study provides further insight into the dynamics of DOC and CDOM in little-studied Mediterranean lagoons. Specifically, it demonstrates that detailed knowledge of the spatial and temporal distribution of CDOM indices in these systems allows us to identify periods and areas within a lagoon that are particularly subject to anthropogenic pressures. Finally, owing to the cost-effectiveness of the CDOM analyses, we conclude that CDOM indices can be a valuable and simple tool for describing the water quality of lagoonal systems.

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**Table 1.** Mean values and standard deviations (SD) of surface water physico-chemical variables, chlorophyll *a*, DOC and optical properties in the Oristano Lagoon–Gulf system (5-7 September 2011) and the Varano Lagoon (6 sampling dates). For symbol explanation, see the text. Sediment pore-water: samples collected in the Cabras Lagoon (stations C1-C6) for the determination of DOC and CDOM; $^{*}$summer mean and SD values of Chl *a* in surface sediment (expressed as μg DWg$^{-1}$) at 3 sites in the Cabras Lagoon (from Foti et al., 2014); $^{**}$summer mean value of Chl *a* in surface water, from the environmental office of Sardinia regional administration; $^{\&}$Annual mean of the first 5 sampling dates (9 Sep 2014-27 Oct 2015).

| Study sites | | T (°C) | S | DO (%) | Chl *a* (μg L$^{-1}$) | DOC (mg L$^{-1}$) | $a_{280}$ (m$^{-1}$) | $a_{350}$ (m$^{-1}$) | $S_{275-295}$ (nm$^{-1}$) | $S_{350-400}$ (nm$^{-1}$) | $S_R$ | $SUVA_{254}$ (L mg$^{-1}$ m$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Oristano Lagoon-Gulf system** | | | | | | | | | | | | |
| Riverine sites (n=4) | mean | 24.5 | 0.4 | 76 | 4.9 | 7.9 | 37.0 | 12.4 | 0.015 | 0.013 | 1.2 | 2.7 |
| | SD | 2.9 | 0.1 | 34 | 6.9 | 1.6 | 3.8 | 1.8 | 0.001 | 0.003 | 0.2 | 0.7 |
| Cabras Lagoon (n=7) | mean | 25.3 | 11.8 | 105 | 16.8 | 10.5 | 29.1 | 6.7 | 0.022 | 0.016 | 1.3 | 1.8 |
| | SD | 0.4 | 5.2 | 12 | 6.1 | 0.7 | 1.7 | 0.6 | 0.001 | 0.001 | 0.1 | 0.1 |
| Sediment pore-water (n=6) | mean | - | - | - | 36$^{*}$ | 16.1 | 59.4 | 25.3 | 0.016 | 0.009 | 1.9 | 2.2 |
| | SD | - | - | - | 32$^{*}$ | 3.6 | 17.1 | 11.8 | 0.002 | 0.002 | 0.4 | 0.2 |
| Oristano Gulf (n=1) | mean | 24.0 | 36.2 | 100 | 1.1 | 1.7 | 4.6 | 1.4 | 0.017 | 0.009 | 1.9 | 1.5 |
| Mistras Lagoon (n=4) | mean | 23.4 | 61.9 | 59 | 1$^{**}$ | 9.4 | 24.7 | 4.8 | 0.026 | 0.018 | 1.4 | 1.8 |
| | SD | 0.9 | 8.4 | 30 | - | 1.1 | 4.1 | 1.2 | 0.002 | 0.001 | 0.0 | 0.2 |
| **Varano Lagoon** | | | | | | | | | | | | |
| 9 Sep 2014 (n=9) | mean | 23.6 | 21.7 | 130 | 17.2 | 3.0 | 7.4 | 1.8 | 0.022 | 0.017 | 1.3 | 1.5 |
| | SD | 0.5 | 1.3 | 16 | 10.9 | 0.4 | 0.9 | 0.2 | 0.001 | 0.002 | 0.2 | 0.2 |
| 17 Oct 2014 (n=9) | mean | 21.8 | 21.0 | 86 | 8.1 | 2.9 | 6.3 | 1.4 | 0.023 | 0.019 | 1.2 | 1.4 |
| | SD | 0.3 | 1.1 | 7 | 3.7 | 0.2 | 0.3 | 0.1 | 0.0004 | 0.001 | 0.0 | 0.1 |
| 29 Jan 2015 (n=9) | mean | 8.4 | 19.6 | 85 | 2.0 | 1.8 | 4.4 | 0.9 | 0.023 | 0.018 | 1.3 | 1.6 |
| | SD | 0.1 | 0.6 | 2 | 1.6 | 0.1 | 0.2 | 0.1 | 0.0003 | 0.001 | 0.0 | 0.1 |
| 14 Apr 2015 (n=9) | mean | 15.5 | 19.1 | 98 | 2.8 | 1.7 | 3.8 | 0.8 | 0.025 | 0.018 | 1.4 | 1.5 |
| | SD | 0.3 | 0.9 | 6 | 0.9 | 0.1 | 0.1 | 0.1 | 0.001 | 0.002 | 0.2 | 0.1 |
| 29 Jul 2015 (n=9) | mean | 30.3 | 22.3 | 102 | 32.2 | 3.5 | 7.0 | 1.6 | 0.023 | 0.017 | 1.3 | 1.3 |
| | SD | 0.5 | 0.5 | 13 | 11.6 | 0.2 | 0.2 | 0.1 | 0.0003 | 0.0004 | 0.0 | 0.1 |
| 27 Oct 2015 (n=9) | mean | 16.2 | 24.7 | 86 | 5.3 | 3.7 | 6.9 | 1.6 | 0.023 | 0.017 | 1.3 | 1.2 |
| | SD | 0.2 | 0.4 | 5 | 1.7 | 0.1 | 0.1 | 0.0 | 0.0003 | 0.001 | 0.1 | 0.0 |
| Annual mean (n=45$^{\&}$) | mean | 19.9 | 20.7 | 100 | 12.5 | 2.6 | 5.8 | 1.3 | 0.023 | 0.018 | 1.3 | 1.5 |
| | SD | 7.6 | 1.5 | 19 | 13.4 | 0.8 | 1.5 | 0.4 | 0.001 | 0.002 | 0.1 | 0.2 |

**Table 2.** Kruskal-Wallis ANOVA by ranks: significant spatial and temporal differences for hydrological, trophic and optical variables observed in the Oristano Lagoon-Gulf system (G1 and sediment pore-water excluded) and the Varano Lagoon.

| | **Oristano Lagoon-Gulf system** | | **Varano Lagoon** | | | |
|---|---|---|---|---|---|---|
| | Site | | Period | | Site | |
| | H | p | H | p | H | p |
| T (°C) | 8.13 | $<0.05$ | 51.55 | $<0.001$ | 0.71 | NS |
| S | 13.32 | $<0.01$ | 42.41 | $<0.001$ | 3.43 | NS |
| DO (%) | 6.59 | NS | 36.16 | $<0.001$ | 4.64 | NS |
| DOC (mg $L^{-1}$) | 10.68 | $<0.05$ | 47.46 | $<0.001$ | 1.39 | NS |
| Chl *a* (µg $L^{-1}$) | 7.14 | NS | 43.07 | $<0.001$ | 2.13 | NS |
| $a_{280}$ ($m^{-1}$) | 7.89 | $<0.05$ | 44.33 | $<0.001$ | 2.02 | NS |
| $a_{350}$ ($m^{-1}$) | 13.43 | $<0.01$ | 48.64 | $<0.001$ | 0.71 | NS |
| $S_{275-295}$ ($nm^{-1}$) | 14.31 | $<0.01$ | 38.25 | $<0.001$ | 5.60 | NS |
| $S_{350-400}$ ($nm^{-1}$) | 9.88 | $<0.05$ | 22.31 | $<0.001$ | 4.36 | NS |
| $S_R$ | 11.68 | $<0.01$ | 18.47 | $<0.01$ | 3.65 | NS |
| $SUVA_{254}$ (L $mg^{-1}$ $m^{-1}$) | 9.64 | $<0.05$ | 38.65 | $<0.001$ | 2.91 | NS |

**Table 3.** Spearman rank order correlations between trophic variables (Chl *a* and DOC) and optical indices ($a_{280}$, $a_{350}$, $S_{275-295}$, $S_{350-400}$, $S_R$ and $SUVA_{254}$) in the Oristano-Lagoon-Gulf system (OLG) and in Varano Lagoon (VL). Significant correlations are shown in bold.

| | $a_{280}$ | $a_{350}$ | $S_{275-295}$ | $S_{350-400}$ | $S_R$ | $SUVA_{254}$ |
|---|---|---|---|---|---|---|
| **OLG** | | | | | | |
| Chl *a* | 0.08 | 0.16 | 0.05 | -0.04 | -0.36 | -0.14 |
| DOC | -0.03 | 0.01 | 0.21 | **0.38** | -0.08 | -0.16 |
| **VL** | | | | | | |
| Chl *a* | **0.77** | **0.79** | **-0.41** | -0.21 | -0.07 | **-0.35** |
| DOC | **0.83** | **0.76** | **-0.29** | **-0.30** | 0.04 | **-0.79** |

**Table 4.** Multiple regression coefficients of determination (adj $R^2$), model probability (p), intercept and probability of ANOVA between dependent trophic variables (Chl *a* and DOC) and independent variables (optical properties) in the surface water of the two studied systems. Significant correlations are shown in bold.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Oristano Lagoon-Gulf system** | | | | | | | |
| Chl *a* | adj $R^2$ | p | $\beta$ S | $\beta\ S_{350-400}$ | $\beta\ a_{350}$ | intercept | ANOVA p |
| | 0.54 | 0.00631 | **-1.1** | **0.46** | **-0.55** | 5.50 | 0.00 |
| DOC | adj $R^2$ | p | $\beta$ S | $\beta\ \mathrm{a}_{280}$ | $\beta\ S_{275-295}$ | intercept | ANOVA p |
| | 0.76 | 0.00012 | **-0.49** | **0.6** | **1.06** | -7.45 | 0.00 |
| DOC | adj $R^2$ | p | $\beta$ S | $\beta\ S_{275-295}$ | $\beta\ SUVA_{254}$ | intercept | ANOVA p |
| | 0.44 | 0.01785 | **-0.83** | **1.08** | -0.01 | -1.98 | 0.00 |
| **Varano Lagoon** | | | | | | | |
| Chl *a* | adj $R^2$ | p | $\beta$ S | $\beta\ S_{275-295}$ | $\beta\ a_{350}$ | intercept | ANOVA p |
| | 0.47 | 0.00060 | **-0.59** | **0.76** | **1.52** | -214.84 | 0.00 |
| DOC | adj $R^2$ | p | $\beta$ S | $\beta\ \mathrm{a}_{280}$ | $\beta\ SUVA_{254}$ | intercept | ANOVA p |
| | 0.99 | 0.00000 | 0.085 | **0.68** | **-0.43** | 2.48 | 0.00 |
| DOC | adj $R^2$ | p | $\beta\ S_R$ | $\beta\ \mathrm{a}_{280}$ | $\beta\ a_{350}$ | intercept | ANOVA p |
| | 0.87 | 0.00000 | **0.22** | **2.74** | **-1.8** | -3.57 | 0.00 |

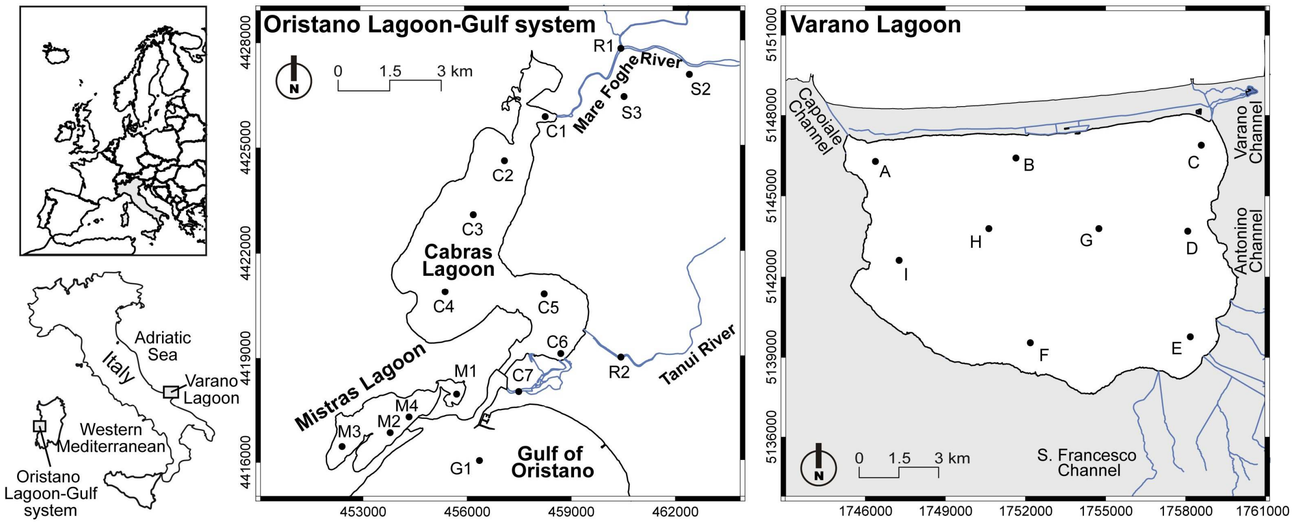


**Figure 1.** Study areas and sampling sites in the Oristano Lagoon-Gulf system (western Sardinia) and the Varano Lagoon (Adriatic Sea).

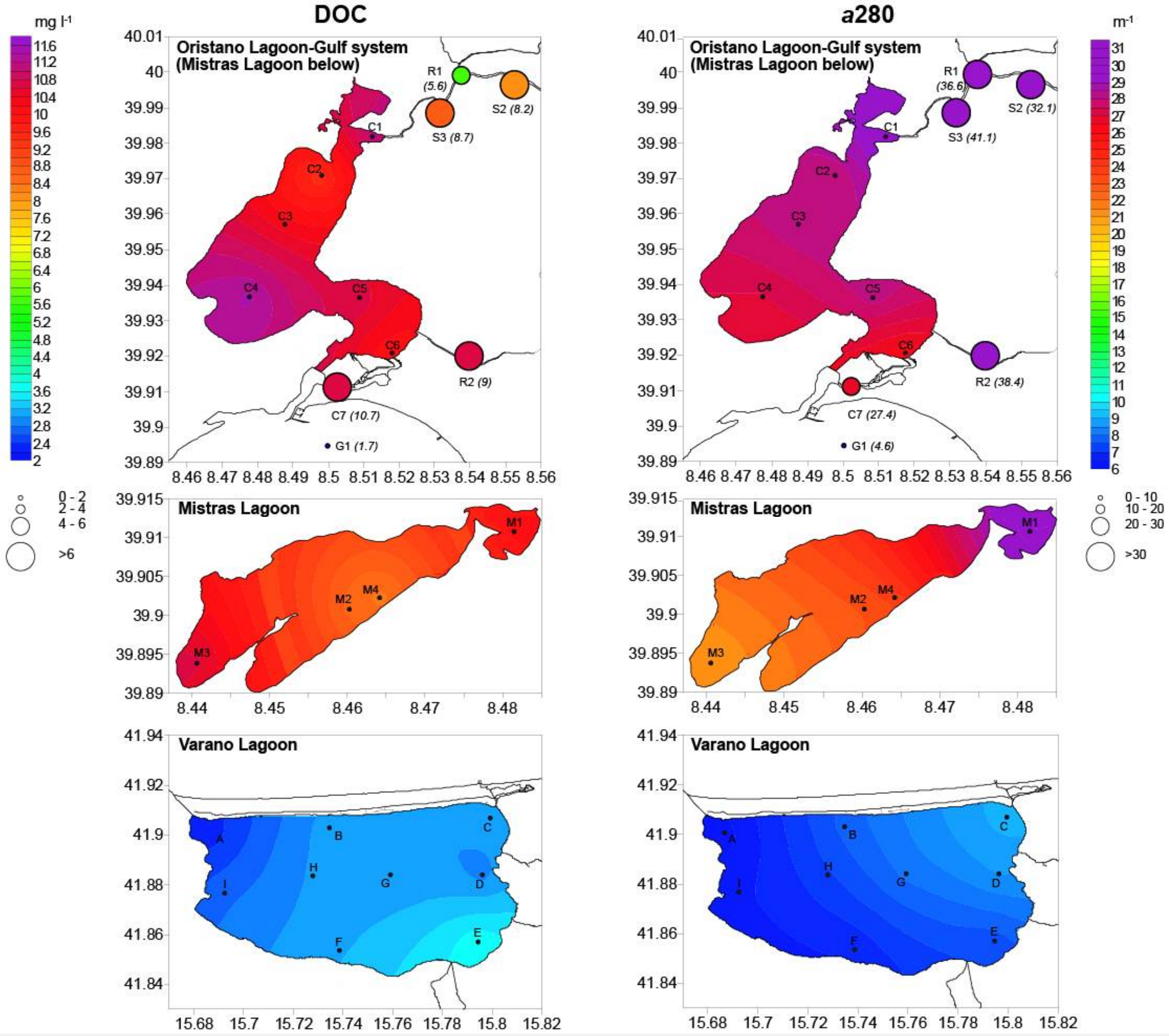


**Figure 2.** Spatial distribution of DOC and absorption coefficients at 280 nm ($a_{280}$) in the surface waters of the Oristano Lagoon-Gulf (OLG) system and the Varano Lagoon (sampling date: 9 September 2014). In OLG, values at the riverine and Gulf sites are also indicated in parentheses.

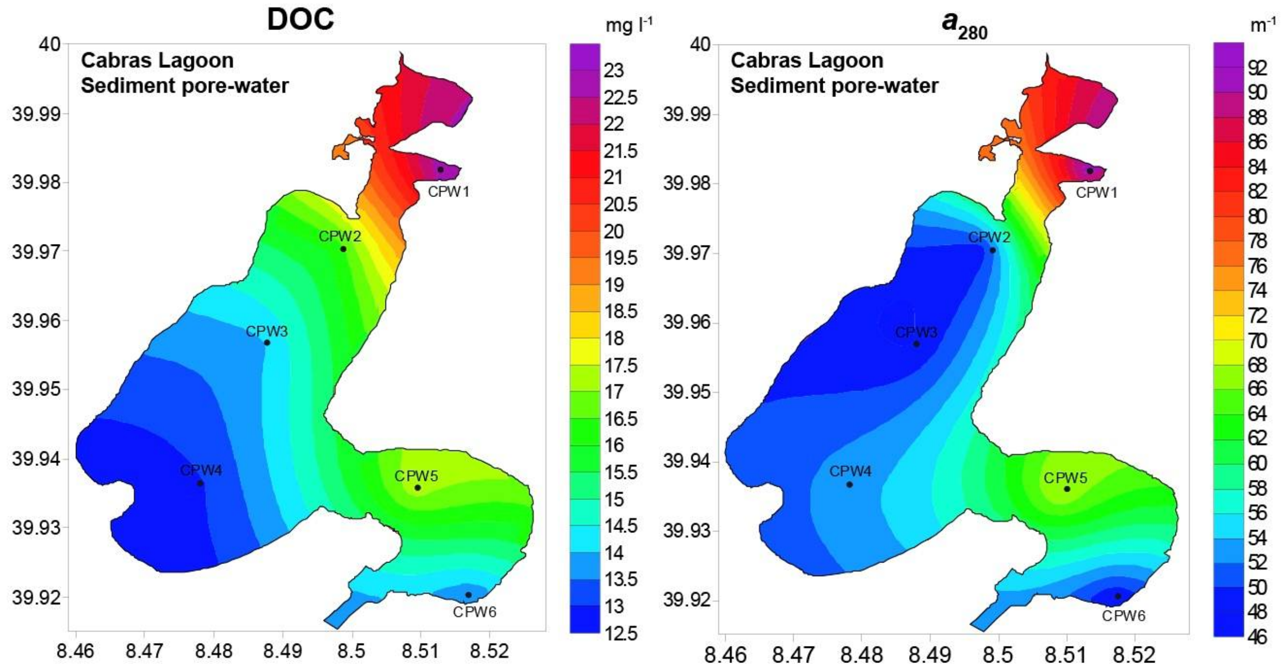


**Figure 3.** Spatial distribution of DOC and absorption coefficients at 280 nm ($a_{280}$) in the sediment pore-water of Cabras Lagoon (note the different scale from Fig. 2).

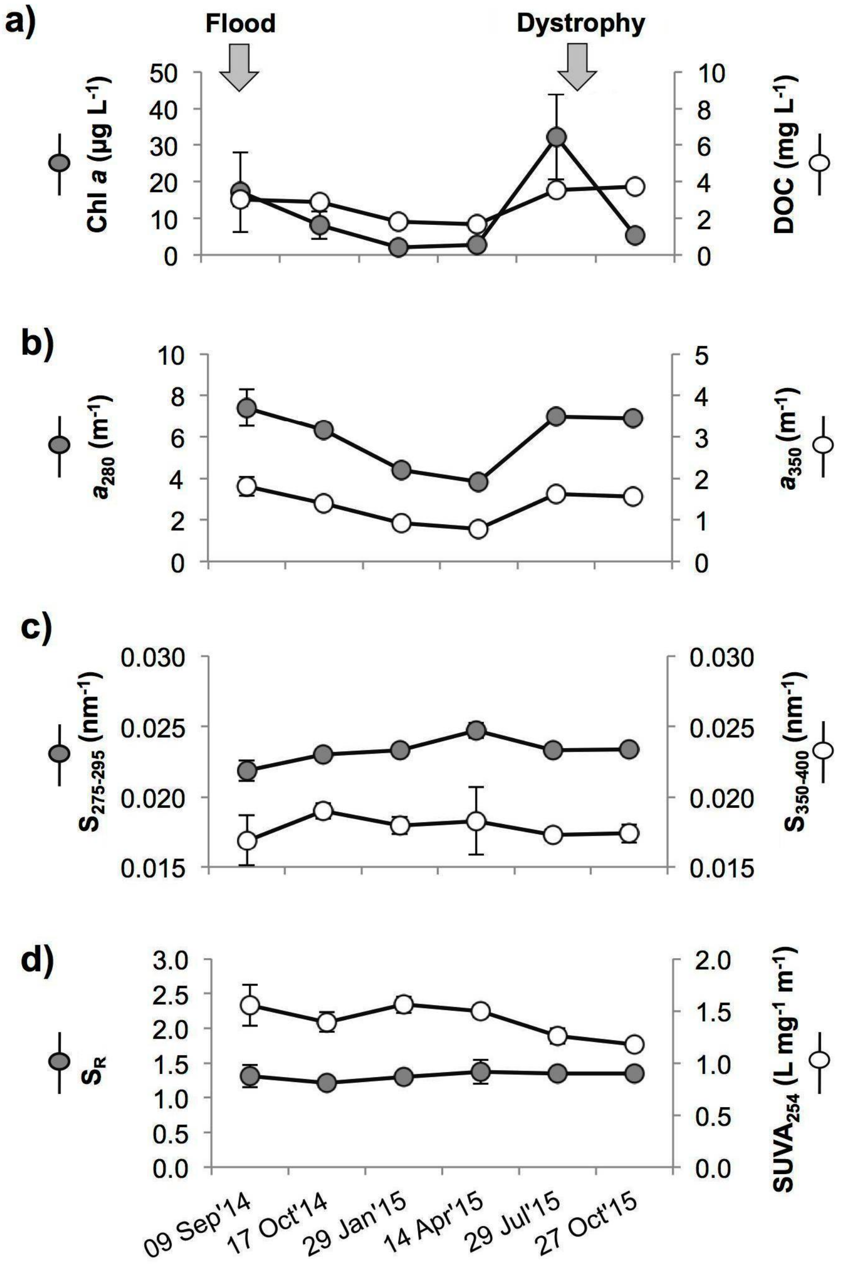


**Figure 4**. Monthly variations (mean ± SD, n = 9) in trophic (Chlorophyll *a* and dissolved organic carbon) and optical variables in the Varano Lagoon: a) chlorophyll *a* (Chl *a*) and dissolved organic carbon (DOC); b) absorption coefficients at 280 nm and 350 nm ($a_{280}$ and $a_{350}$); c) spectral slopes in the ranges 275-295 nm and 350-400 nm ($S_{275-295}$ and $S_{350-400}$), their slope ratio ($S_R$) and organic matter aromaticity ($SUVA_{254}$). The arrows indicate the time of occurrence of the flood and the dystrophic event.

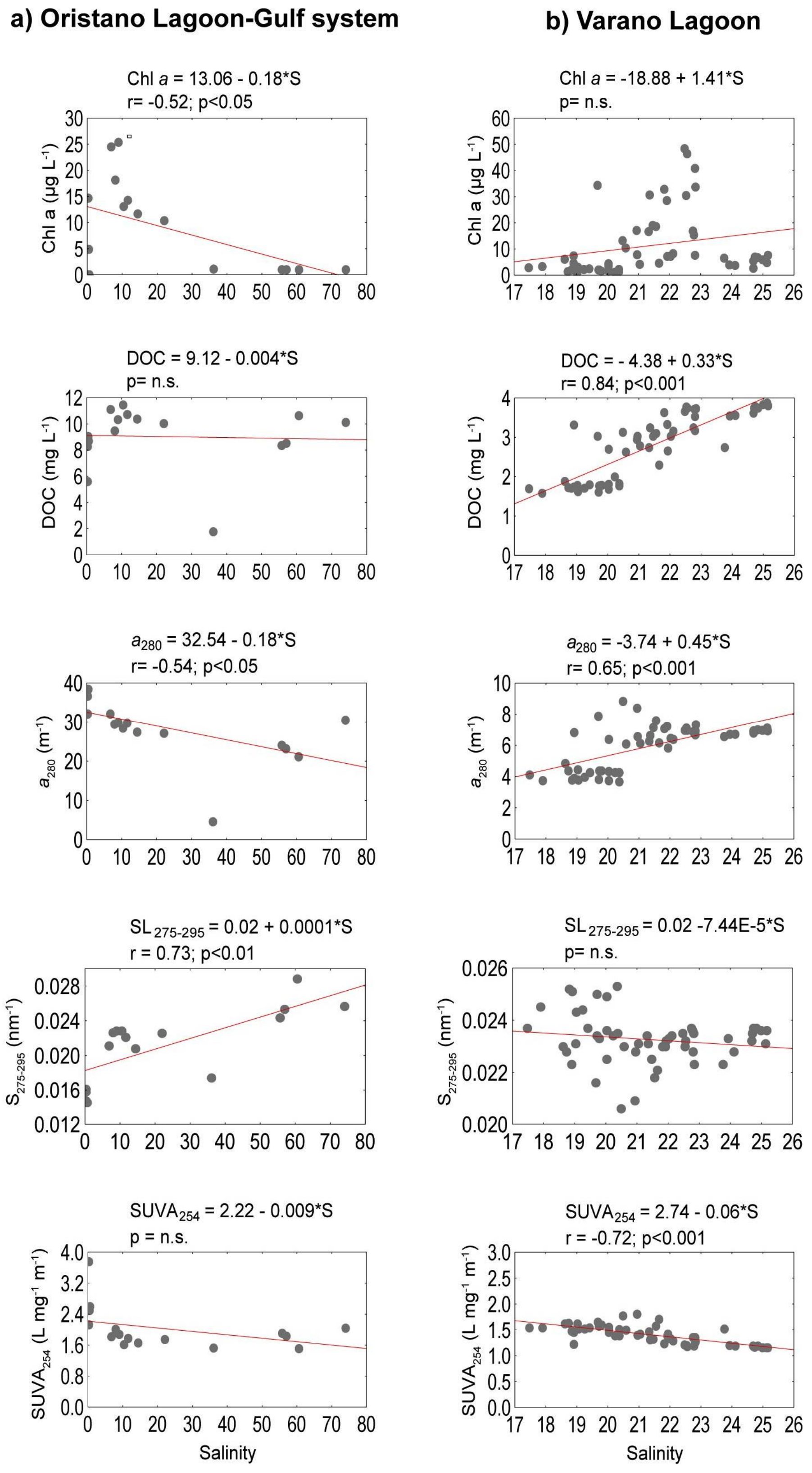
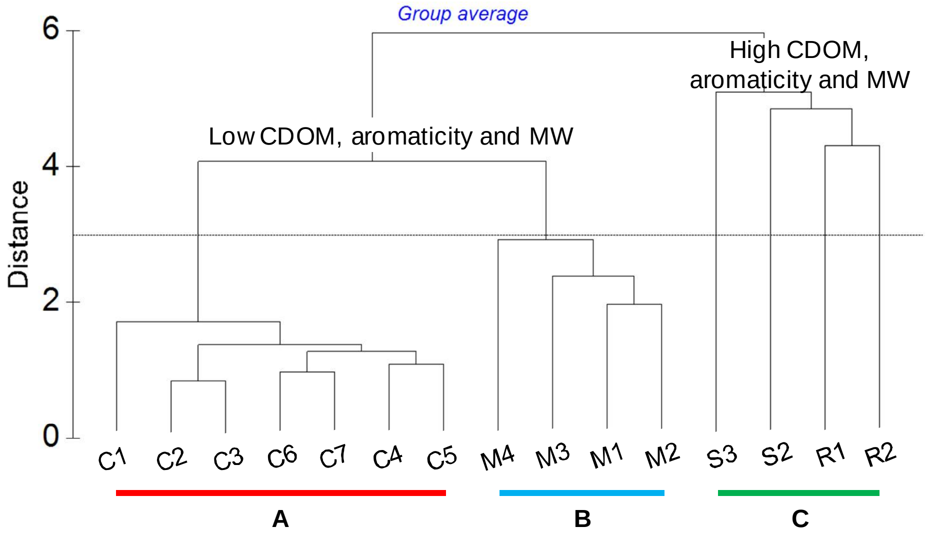


**Figure 5a, b.** Chl *a*, DOC and main optical properties ($a_{280}$, $S_{275\text{-}295}$ and $SUVA_{254}$) plotted against salinity for a) the Oristano Lagoon-Gulf system and b) the Varano Lagoon. S = salinity, n.s. = not significant.

**a) Oristano Lagoon-Gulf system**



**b) Varano Lagoon**

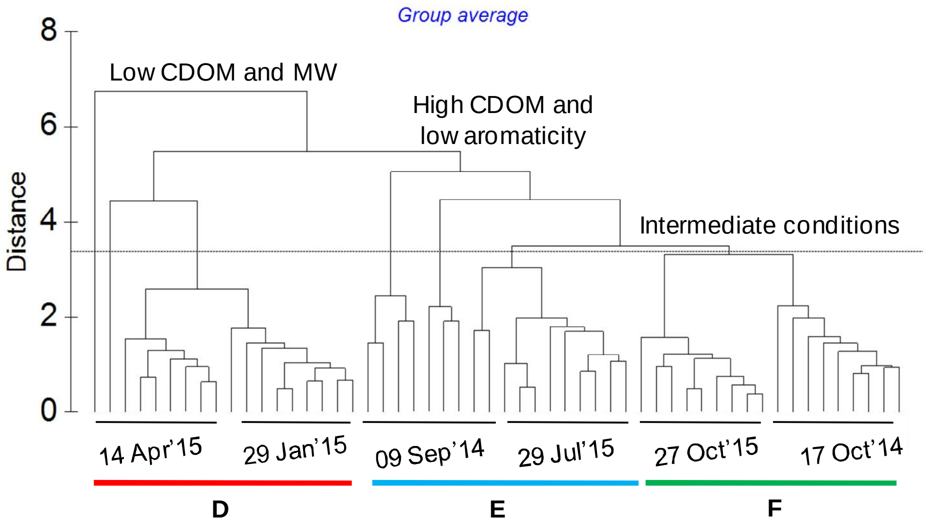


**Figure 6a, b.** Cluster diagram based on trophic (Chlorophyll *a* and dissolved organic carbon) and chromophoric dissolved organic carbon (CDOM) optical variables for a) the Oristano Lagoon-Gulf system (15 sampling sites, G1 and sediment pore-water excluded); and b) the Varano Lagoon (9 sampling sites x 6 sampling dates). MW = molecular weight.