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Dissolved organic carbon as potential indicator of global change: A long-term investigation in the northern Adriatic

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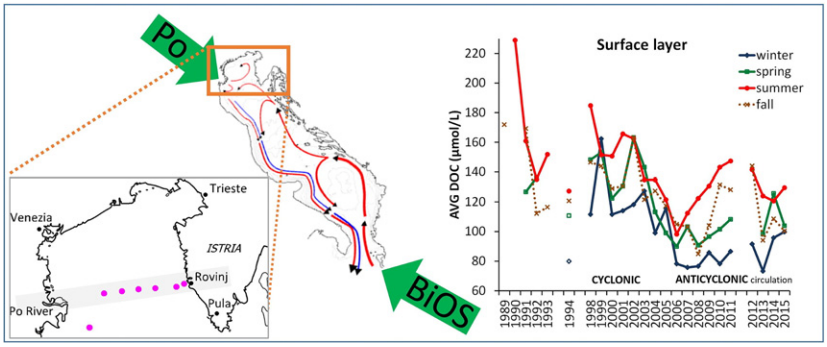
HIGHLIGHTS

- Long-term study of temporal and spatial distribution of DOC in the Adriatic Sea
- The northern Adriatic-periodically eutrophic and oligotrophic system
- DOC content in the northern Adriatic is highly affected by salinity changes.
- DOC variations as a good proxy for the BiOS
- DOC as a potential indicator of climate change

GRAPHICAL ABSTRACT



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ABSTRACT

Dissolved organic carbon (DOC) is an essential component of the biogeochemical marine system, effecting biological and chemical reactions that take place in the sea. DOC represents a dynamic component of the global carbon cycle.

This paper reports 25 years of measurements of DOC content and distribution at seven stations along the transect Po River delta – Rovinj in the northern Adriatic (NA). The results show strong temporal and spatial variability: (1) The highest average DOC concentrations were observed in 1998 and 2002 (143 µmol/L and 137 µmol/L, respectively); (2) The minimum average DOC was recorded in 2006 (88 µmol/L) and (3) The short-term DOC accumulation (up to 203, average 102 µmol/L) for the years 2009 to 2012, was observed during the summer and autumn months followed by unusually low DOC concentrations during the winter and spring. The DOC results from the more recent monitoring at the same stations indicate primarily oligotrophic characteristics of the NA seawater (88 µmol/L).

The results of DOC variability and distribution in the NA appears to be strongly influenced by complex circulation patterns. This paper provides a "link" between the Ionian circulation and the NA ecosystem as a part of the recently identified Adriatic-Ionian Bimodal Oscillating System (BiOS). A good agreement between the BiOS oscillation and other variables related to the DOC concentration, like the NA A and B winter types, the Po River discharge, salinity, chlorophyll *a*, occurrence of hypoxic-anoxic conditions, eutrophication and oligotrophication, suggests that DOC might be a good tool and indicator of global change.

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1. Introduction

Primary photosynthetic production by phytoplankton in surface seawaters is the largest source of organic carbon in marine systems. Dissolved organic carbon (DOC) in the global seas is the Earth's largest reservoir of organic matter (~640 Pg C), comparable to the amount of carbon found in a pool of atmospheric CO_2. It is a significant component of the biogeochemical marine system, now recognized as a possible barometer of the global change (Church et al., 2002; Ducklow, 2002). DOC represents a dynamic component of the global carbon cycle modifying many of the biological and chemical reactions that take place in the sea. It provides nutritional and energy base for micro- and macro-organisms. DOC has major impact on the speciation of many metals by complexation and adsorption processes, and it serves as a precursor for fossil fuels such as petroleum and oil shale.

Improvements in measurement precision, in particular the high-temperature catalytic oxidation method (HTCO), enabled detection of the fine temporal and spatial DOC concentration gradients and their variability. This is important for better understanding of the role of DOC in global changes in the oceans, marginal seas, and coastal areas (Williams et al., 1993; Cauwet, 1994, 1999; Hansell and Carlson, 2001).

The northern Adriatic (NA) is a semi-closed shallow basin with open and coastal waters characteristics, located north-east in the Mediterranean. The mean depth is 33.5 m, total area 118,000 km^2, and volume of 635 m^3. The NA is a dynamic system strongly influenced by anthropogenic pressure and climate changes, now confirmed to be present in the Mediterranean areas (Schiano et al., 2005; Grbec et al., 2009; Giani et al., 2012; Djakovac et al., 2015). Changes in riverine inputs, particularly the Po River discharge with the mean flow rate of 1469 $m^3\ s^{-1}$ (Cozzi and Giani, 2011), advection of the central Adriatic water along the eastern coast, a southerly flow in the coastal zone off Istria, the Istrian Coastal Counter Current (ICCC; Supić et al., 2000), a variable and complex circulation driven by the Adriatic-Ionian Bimodal Oscillating System, BiOS (Gačić et al., 2010, 2014), and intense air-sea interactions were suggested to play a fundamental role in physical and biogeochemical processes in the NA (Zavatarelli et al., 1998; Kraus and Supić, 2011; Djakovac et al., 2012, 2015; Kraus et al., 2016).

The NA is one of the most productive areas of the generally oligotrophic Mediterranean (Fonda Umani et al., 2005, 2007). The annual primary production rates in the NA show strong inter- and intra-annual variability, from 55 to 414 g C $m^{-2}\ yr^{-1}$, measured at the Po delta (Revelante and Gilmartin, 1983; Zoppini et al., 1995; Harding et al., 1999; Sellner and Fonda-Umani, 1999; Fonda Umani et al., 2007). This is often accompanied by the appearance of strong phytoplankton blooms and formation of large gelatinous-mucous aggregates recorded for the NA as far as year 1729 (Vollenweider and Rinaldi, 1995). More recently, this blooming phenomenon occurred rather frequently (1988, 1989, 1991, 1997, 2000–2004) (Iveša et al., 2016), and was often followed by an accumulation of organic matter primarily at the stratification zones characterized by pycnocline (Ciglenečki et al., 2000, 2003; Ćosović and Vojvodić, 2000; Giani et al., 2005).

Significant changes in the NA physical and biological conditions for the past 30 years were reported indicating a process of oligotrophication during the last decade (Mozetič et al., 2010; Djakovac et al., 2012, 2015; Gašparović, 2012; Giani et al., 2012; Colella et al., 2016; Iveša et al., 2016). These observations are consistent with the results of the Intergovernmental Panel on Climate Change, IPCC report (IPCC, 2013), showing that the climate in the Mediterranean region is changing. Significant changes in DOC have been recognized as a possible indicator of long-term biogeochemical- and climate-induced variabilities (Hansell and Carlson, 2015).

Rising atmospheric CO_2 levels and climate change associated with concurrent shifts in temperature, circulation, stratification, nutrient input, oxygen content and ocean acidification could have potentially wide-ranging biological effects (Grbec et al., 2009 and references therein). Changes in temperature and pH could have synergistic negative effects on species composition and growth, survival and development (Noone et al., 2013). Both organisms and ecosystems are changing in response to ocean warming, acidification, and de-oxygenation. That reflects on primary production, and further on organic matter content and composition in the oceans, by changing the ratio between the DOC fraction and the particulate organic carbon (POC) fraction (Wakeham and Lee, 1993).

A comprehensive study of DOC in specific areas of the NA basin and different periods has been conducted since 1989 (Vojvodić and Ćosović, 1996; Pettine et al., 1999, 2001; Giani et al., 2005, 2012). While riverine/estuarine environments were extensively studied with focus on investigation of long-term organic matter (1997–2010) (Wu et al., 2015), similar DOC data are scarce for the marine environment including the NA (Pettine et al., 1999; Berto et al., 2010; Giani et al., 2005; De Vittor et al., 2008). Studies by Giani et al. (2005) and De Vittor et al. (2008, Gulf of Trieste) are the only studies that describe long-term distribution of DOC in the NA, but over a shorter time period. In the Mediterranean Sea, one Dyfamed station in the Ligurian Sea has been studied 3-years (Avril, 2002). Globally, a long-term investigation of organic carbon was carried out at a single ALOHA station (Ducklow et al., 2009), thus not providing information on its spatial pattern that was the aim of this work.

This paper describes the results of 25-years (1989–2015) observations of temporal and spatial distribution of DOC at seven stations along the transect Po River delta – Rovinj in the NA (Fig. 1). The paper examines the complex spatial (horizontal and vertical), as well as temporal (seasonal and annual) DOC distribution with several linear and quadratic random coefficient models to confirm main trends. In a longitudinal analysis, observations (statistical) are made at units, in this case, station-specific sequences of time points, so units are occurring naturally in clusters. The main idea is that observations within a cluster tend to be more similar than observations in general. The observed DOC data were primarily discussed in relation to the recently reported the NA local hydrographic and water circulation conditions (Civitarese et al., 2010; Gačić et al., 2010, 2014; Djakovac et al., 2012, 2015; Kraus and Supić, 2011; Supić et al., 2012; Mihanović et al., 2013, 2015; Janeković et al., 2014; Kraus et al., 2016).

2. Materials and methods

2.1. Sampling

Seawater samples were collected by Niskin samplers in dark 1.3 L bottles. Filtration was performed on-board the cruise vessel mostly within the 4 h after the sample collection. In-line filtration of the samples was performed on glass fibre GF/F filters (Whatman, pore size 0.7 μm) in all-glass filter holders under the pressure < 5 psi. Sub-samples of the filtrate were collected in 20 mL glass vials, preserved with 100 μL of mercury (II)-chloride solution (10 mg/L), closed with Teflon-lined screw caps and stored in the dark until analysis.

Glassware used for the sampling and sample filtration were washed with chromic-sulphuric acid and rinsed well with organic-free Milli-Q water (Millipore) and seawater samples. Glass vials and Whatman GF/F filters were combusted at 450 °C for 4 h.

Continuous monitoring of DOC in the NA started in 1989. Monitoring frequencies and cruise plans varied from year to year (Table 1, Fig. 1): during the first 6 years (1989, 1990, 1991, 1993, 1995, 1997) sampling was done sporadically, mostly in summer (Period I); in year 1994 and during the period 1998–2011 the samples were collected approximately once a month, and more frequently in months characterized with an unusually high organic content and specific biological conditions (Period II). During the last three years (from the summer of 2012 until the end of 2015) the monthly sampling regime was followed, but only at 3 stations (SJ107, SJ101 and SJ108) (Period III), Fig. 1.

Period of 15 years (1994; 1998–2011 - Period II) was chosen for detailed statistical analysis. Seven stations placed on transect Po River