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Organic matter in the northern Adriatic Sea: long-term trends, variability and drivers

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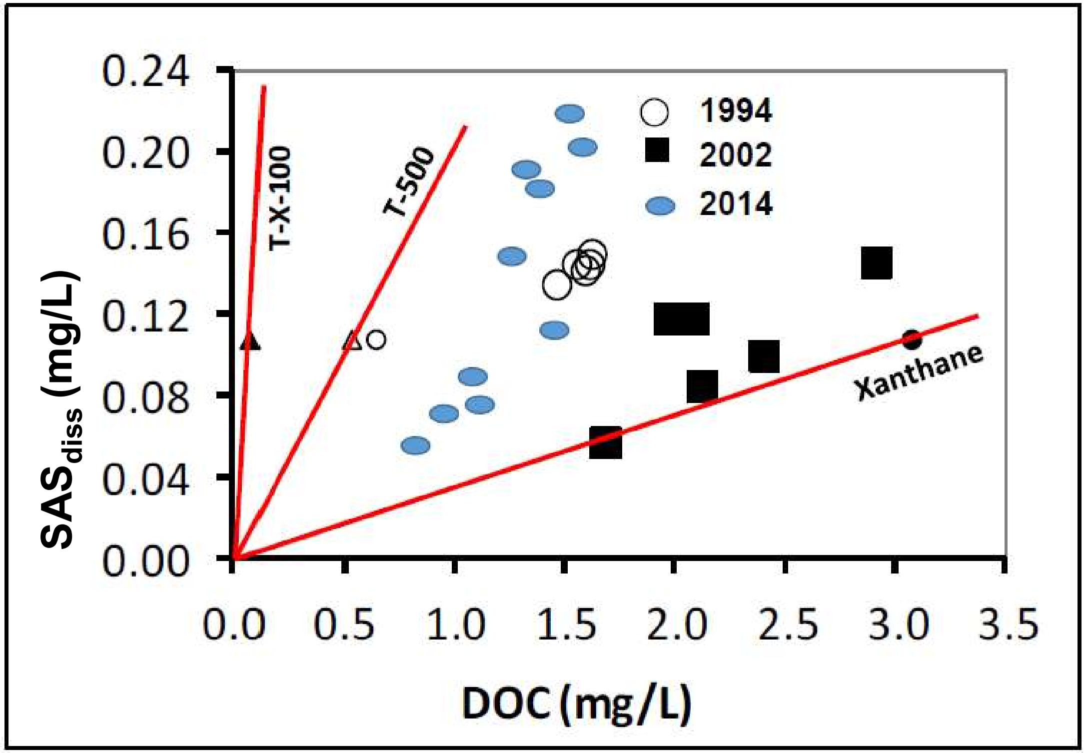
Abstract

The paper presents a unique time series of organic matter content (dissolved organic carbon, DOC, and its surface active fraction, SAS) collected in the northern Adriatic along the Po-Rovinj transect between 1998 and 2017. The data were collected on a monthly or a bimonthly basis. Seasonal variance of organic matter content does not exceed 30% of the total variance, while the DOC and the SAS trends are significantly negative and positive, respectively, over the whole transect. The organic matter content, however, exhibits pronounced interannual and decadal changes, with periods of high and low carbon content and evident changes in reactivity regarding to the SAS type content. The changes indicate altering episodes between eutrophication and oligotrophication, embedded to the overall oligotrophication trend in the considered period. Both series were correlated to the potential local and regional yearly-averaged drivers in both atmosphere and sea. For the DOC, the largest correlations (significant at 99%) are obtained with the Po River discharges, at the phase lag of -1 to -2 years. For the SAS, the largest correlations (significant at 99%) are obtained with the Adriatic-Ionian Bimodal Oscillating System index (BiOS index), at the phase lag of -3 to -4 years. Correlations between the organic matter content and the hemispheric or the regional patterns (North Atlantic Oscillation, East Atlantic/West Russia, East Atlantic, Scandinavian, and Mediterranean Oscillation) are much lower and only sparsely correlated at some phase lags. The same was found for the other local drivers (precipitation and net heat flux). Our analysis highlights the importance of the remote processes, like the BiOS, that weren't previously considered to shape the biogeochemical properties of such shallow coastal regions highly impacted by the freshwater load.

Keywords: DOC, surface active substances, north Adriatic, long-term trends, BiOS, long-term drivers

***Graphical Abstract**



Model substances taken as representatives for hydrophobic and hydrophilic SAS: T-X-100; Polysacharides Dextrane T-500 and Xanthane

Changes in organic matter reactivity (hydrophobicity) in the surface seawater of stations 107 and 108 (Po river – Rovinj profile) in the northern Adriatic.

***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Highlights

- long-term study of temporal and spatial distribution of OM in the Adriatic Sea
- altering episodes of eutrophication and oligotrophication in the northern Adriatic
- seawater OM as a complex mixture of organic material with surface active properties
- decreasing DOC and increasing SAS trend in the northern Adriatic over last 30 years
- NAd OM quality and quantity as a consequence of variable Po water discharge and BiOS
- DOC and SAS as a potential indicator of climate changes

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Keywords: DOC, surface active substances, north Adriatic, long-term trends, BiOS, long-term drivers

1. Introduction

Long-term environmental data collected over the prescribed areas in freshwater, estuarine, and marine ecosystems are a prerequisite for assessing complex dynamics of organisms and ecosystems, particularly as they respond to both anthropogenic pressures and climate phenomena. Modern monitoring techniques (like gliders, Argo profiling floats) prevail in recent decades, as allowing for better temporal and spatial coverage of the acquired data, while frequently being less costly in comparison to the data acquired by a research vessel. Yet, problem is an inconsistency of these data with the data collected through classical campaigns, often leading to an inhomogeneity in a long time series. These long-term environmental series are a prerequisite for a plausible assessment of the changes in the era of climate change, including the role of interannual to decadal variability, which can be substantial in the Adriatic Sea. Long-term environmental data collected in the northern Adriatic (NAd) – 200 km x 200 km wide northernmost Mediterranean shelf with depths up to 60 m (Fig. 1) – indeed showed the variability and allowed for an assessment of the biogeochemistry and ecosystem functioning over the long term (Plavšić, 2004; Mozetič et al., 2010; Ivančić et al., 2010; Kraus and Supić, 2011; Marić et al., 2012; Giani et al., 2012; Djakovac et al., 2015; Iveša et al., 2016; Dautović et al., 2017). This also includes monitoring of organic matter, which was initiated in the late 1980s (Dautović et al., 2017).

The organic matter (OM) data include dissolved organic carbon (DOC) and its surface active substances (SAS). In the seawater, the OM is a complex mixture of organic substances (proteins, carbohydrates, lipids, humic and fulvic material), which possess different surface active properties (SAS). These substances can either be dissolved, particulated or colloidally dispersed in the water column. Filtration through 0.7 μm separates particulate fraction from the dissolved and colloidal one. The OM with surface active properties (SAS) is also distributed between the dissolved and particulate fraction (Gašparović, 2012; Ciglenečki et al., 2018).

As a measurable elemental organic carbon content of dissolved OM (Fillela, 2009), the DOC is generally defined as a compound that can pass through a 0.45 μm or 0.7 μm filter. The SAS is reported as an important part of the phytoplankton exudates (Žutić et al., 1981; Ćosović and Vojvodić, 1998; Ciglenečki et al., 2018), and it includes a variety of organic substances (proteins, polysachaarides, lipids and humic type substances). These substances contain hydrophobic (e.g. fatty acid chains, aromatic rings, or hydrocarbons) and hydrophilic functional groups (e.g. NH_2, COOH, OH, or SH) that enable the SAS accumulation at a different marine interfaces (seawater interacts with the atmosphere, living and nonliving dispersed and particulate material, with the sediment, at chemocline in the stratified water column). By adsorption and solubilization, the SAS influences physico-chemical properties and the structure of the natural interfaces, and in this way moderate transfer processes between different phases. Accumulation of the SAS in the sea-surface microlayer generates marine boundary layer of aerosols and lowers the air-sea transfer of CO_2 and other climate relevant gases (Tsai and Liu, 2003; Sabbaghzaden et al., 2017; Wurl et al. 2017, and references therein). On the other side, by adsorption processes, the SAS influences trace metal and other organic matter bioavailability and their fate in natural waters (Plavšić et al., 2009, 2011; Tercier-Waeber et al., 2012).

Organic matter reactivity in the sea is directly related to its hydrophobic and hydrophilic properties, being a consequence of biological activities, mainly of the phytoplankton (Vojvodić and Ćosović, 1996). Yet, the phytoplankton activities are known to be influenced by the local and remote ocean dynamics, of which the Adriatic-Ionian Bimodal Oscillating System (BiOS) and the Po River discharges are qualitatively related to them (Kraus and Supić, 2011; Marić et al. 2012, 2013; Kraus et al., 2016; Dautović et al., 2017).

The BiOS is represented by the circulation regime and related sea level anomaly in the northern Ionian Sea, where the change between cyclonic and anticyclonic circulation regimes is driven by the dense water formation in the Adriatic and the Aegean basins (Gačić et al., 2010, 2014; Mihanović et al., 2015; Reale et al., 2017). In the situation of the cyclonic BiOS regime, very saline, warm and ultraoligotrophic waters from the Eastern Mediterranean are advected into the Adriatic Sea, while anticyclonic BiOS regime transports less saline and nutrient-richer western Mediterranean waters into the Adriatic (Civitarese et al., 2010; Vilibić et al., 2012). The BiOS regimes have periods from 5 to 10 years, being the dominant drivers of the Adriatic quasi-decadal thermohaline and biogeochemical variations (Buljan and Zore-Armanda, 1976; Batistić et al., 2014; Mihanović et al., 2015; Vilibić et al., 2019). The variations were already noticed in 1950s in a form of salinity changes in the Adriatic (Buljan, 1953). Recent studies found the connection between the BiOS and the bivalve growth in coastal regions of middle and northern Adriatic (Peharda et al., 2016, 2018). Still, correlations between the BiOS and the organic matter are not established – which is the exact aim of this paper – although qualitative matching has already been found (Dautović et al., 2017). These recent findings are contrasting the classical picture developed in the 1980s and later, which is stating that the biogeochemical properties of NAd are almost exclusively influenced by the local forcing, such as a quite large freshwater load coming from the northern Adriatic rivers (Franco and Michelato, 1992).

To quantify the importance of local, remote, global or regional drivers to the OM content variability in the NAd, we performed lagged correlation analyses between the different potential drivers (local river discharges, precipitation, net heat flux, the BiOS index, various indices of hemispheric processes – North Atlantic Oscillation (NAO), East Atlantic pattern (EA), East Atlantic/West Russia pattern (EA/WR), Scandinavian pattern (SCAND), Mediterranean Oscillation (MO)) and the OM measured along the prescribed stations over the Po-Rovinj transect between 1998 and 2017. Hemispheric processes are known to affect temperature and precipitation in the central Mediterranean (Quadrelli et al., 2001; Brandimarte et al., 2011; Matić et al., 2019), which in turn may influence nutrient load and primary production in a coastal area. Section 2 introduces long-term measurements of the OM content, environmental drivers and the methodology. Interannual variability, seasonal signal and trends of the OM content are described in Section 3, continued by the correlation analyses between the OM content and the environmental drivers. Discussion and conclusions are provided in Section 4.

2. Materials and methods

Seawater samples used for the OM content analyses (DOC and SAS) were collected in the NAd along the transect situated between Po River delta and Rovinj (Fig. 1) from 1998 to 2017. Some samples were taken previously, since 1989, yet with much lower resolution, thus were not used in this study. The samples were regularly collected at six stations (SJ108, SJ101, SJ103, SJ105, SJ107 and RV001) at standard oceanographic depths (0, 5, 10, 20 and 2 m above the bottom) by Niskin bottles, once every month or two months during the most of the investigated period. After 2011, samples at RV001 were collected sparsely, and from the summer of 2012 until the end of 2017) the monthly sampling regime was followed, but only at 3 stations (SJ107, SJ101 and SJ108) which were found to be representative for the studied transect (Dautović et al., 2017). Altogether, between 1998 and 2017, there were 220, 226, 186, 191, 233 and 160 samplings at stations SJ108, SJ101, SJ103, SJ105, SJ107 and RV001, respectively.

Sampling and samples for the DOC analyses were treated following the method described in Dautović et al. (2017). DOC concentrations were determined using the sensitive High-Temperature Catalytic Oxidation (HTCO) method at 680 ^{o}C (Shimadzu carbon analysers, TOC 500 and TOC-VCPH – 5000).

For determination and characterization of the SAS, the electrochemical method a.c. voltammetry was used (Ćosović and Vojvodić, 1982, 1998; Ciglenečki et al. 2018). Methodology was based on the measurements of the SAS adsorption effects at the surface of the hanging mercury drop as a working electrode, in the seawater sample and 0.55 M NaCl as the model electrolyte. We used selected adsorption potential conditions (-0.6 V by Ag/AgCl electrode) and adsorption time (15-120 s) with stirring. Changes of the working electrode double layer, reflected on the capacitance current, are approximately proportional to all (dissolved and particulated) SAS in the solution. By filtration through a Whatman GF/F filter (0.7 µm pore size), total SAS (SAS_T, non-filtered) from the original sample is separated into particulate and dissolved fractions (SAS_{diss}, filtered). Content of SAS is expressed in the equivalents of the selected model organic matter substance of Triton-X-100, which is proved to be a good representative of the most reactive part of SAS in natural waters (Ćosović and Vojvodić, 1982, 1998; Orlović-Leko et al., 2016; Ciglenečki et al., 2018).

For correlation analysis with the OM content, different local and remote drivers have been used, averaged over a year: (i) net heat flux (NHF) and total precipitation (TP), both taken from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalysis (www.ecmwf.int) and averaged over the NAd (north of the Pula-Rimini line), (ii) freshwater discharges of the largest NAd river, Po River (PO), at station Pontelagoscuro (44.89° N, 11.61° E), (iii) NAO, EA, EA/WR and SCAND indices, all available at the National Oceanic and Atmospheric Administration (NOAA) Climate Prediction Center website (https://www.cpc.ncep.noaa.gov), (iv) the MO index, defined as the air pressure difference between Algiers, 36.4°N, 3.1°E, and Cairo, 30.1°N, 31.4°E (Palutikof et al., 1996), taken from the University of East Anglia Climate Research Unit website (https://crudata.uea.ac.uk/cru/data/moi), and (v) the BiOS index, defined as the mean absolute dynamic topography (ADT) difference between the rectangles at the perimeter of the northern Ionian gyre (39.25-39.75°N, 18.25-19.75°E) and at its center (38.0-38.5°N, 18.5-19.0°E). The position of the rectangles are defined following the studies given by Gačić et al. (2014) and Peharda et al. (2018). The ADT fields are a product of AVISO+ database, available since 1993, with 1/8° resolution (http://marine.copernicus.eu). Positive BiOS index indicates cyclonic circulation of the northern Ionian Sea and advection of saline and ultraoligotrophic waters from the Eastern Mediterranean to the Adriatic, whilst negative BiOS index stands for the anticyclonic circulation of the northern Ionian Sea and advection of less saline Western Mediterranean waters to the Adriatic.

Prior to the analysis, seasonal signal is removed from all series by fitting annual (12 months) and semi-annual (6 months) cosine functions, separately for each variable (DOC, SAS), station and depth and for each driver. Such an approach removes the effect of uneven seasonal sampling to the annual mean value. The procedure is based on a general harmonic regression model (Chatfield, 2004; Wilks, 2011), and has been frequently used in various analyses of the Adriatic thermohaline data due to the time series discontinuousness. To minimize the effects of data undersampling, the series without seasonal signal were averaged on the annual basis. Testing of the trend significance was done by the Mann-Kendall nonparametric test. Linear correlations have been estimated between the OM variables and the potential drivers that were preceding the OM up to 5 years (phase lags from 0 to -5 years).

3. Results

3.1. Seasonal cycle and variance

Time series of the DOC and the SAS (dissolved - SAS_{diss}, total - SAS_T) content in the surface water layer (0.5 m) of the NAd (Fig. 2) exhibit a substantial change between the different intervals within the investigated period. The first part of the investigated period (1998-2004) is characterized by much higher DOC values compared to the other periods, in particular during wintertime. These years are matching a substantial occurrence of mucilaginous aggregates in the

NAd, extending up to a several kilometers in length of gelatinous layers (Precali et al., 2005). After 2004, the NAd region is predominantly reflecting oligotrophic conditions during the whole year. The only DOC increase was found between 2010 and 2012, in summer and autumn. Yet, these years are characterized by a low DOC during winter and spring. Average DOC values and range differ significantly in the oligotrophic period 2005-2017 (1.166 mg/L, 0.769-3.093 mg/L) compared to the more eutrophic years 1998-2004 (1.524 mg/L, 0.920-7.160 mg/L).

In terms of a seasonal distribution, the DOC is accumulated during the spring, reaches its maximum in the summer and reduces its concentration during autumn and winter. In terms of a spatial distribution, the DOC content decreases from the west towards the east of the Po-Rovinj transect, and decreases with depth (Fig. 3). The maximum of all variables is reached at the surface at station SJ108, where the DOC, SAS_{diss} and SAS_T reach 1.5 mg/L, 0.12 mg/L and 0.15 mg/L, respectively. The minimum is found near the bottom of the eastern side of the transect (station RV001), as low as 1.1 mg/L, 0.07 mg/L and 0.07 mg/L for the DOC, SAS_{diss} and SAS_T values, respectively. The DOC seasonal cycle is the most prominent in the surface layer (Fig. 4), where DOC accumulation occurs during the summer period and DOC depletion during the winter time.

There is a similarity between the DOC and the SAS_T behavior, which has a similar seasonal cycle with maximum reaching in summer. Yet, the SAS_T values are less pronounced in the late 1990s and early 2000s, with spring, summer and autumn values being higher just in the 1998-2000 period (Fig. 2). Winter SAS_T values are not showing a substantial change through the whole investigated period, being low in the first period when the DOC is reflecting more eutrophicated conditions (1998-2004). Low values in the first period are documented also for the SAS_{diss}

values, with an increase in time during the investigated period, in all seasons. Still, the SAS_{diss} values reach the maximum in summer, while being the lowest during winter.

It seems that all investigated OM variables (DOC, SAS_T, SAS_{diss}) have higher seasonality in the surface layer, in which the seasonal variance is reaching 30% of the total variance (Fig. 4). Yet, for the DOC, such seasonality is restricted to the very surface, while the SAS_T and the SAS_{diss} have similar seasonality in the first 10 m of the water column. Near the bottom, seasonal changes in the DOC are almost negligible, less than 10%, while seasonality in the SAS_T and the SAS_{diss} are a bit higher, about 10-20%, although much lower than for the surface layer.

3.2. Trends

Trends of organic matter parameters in the considered period (Fig. 5) are largely influenced by the change of the NAd eutrophication, which occurred in the mid-2000s. The DOC trends are strongly and significantly negative at all stations and all depths, with maximum values reaching -0.5 mg/L over 10 years in the subsurface layer in the middle of the transect. The trends are slightly lower in the rest of the transect, mostly around -0.3 mg/L to -0.4 mg/L over 10 years.

On the other hand, the positive trends are documented for the SAS_{diss} values, being significant at all stations and depths, with values mostly between 0.02 mg/L and 0.03 mg/L over 10 years, while reaching 0.04 mg/L over 10 years at coastal parts of the transect (stations RV001 and SJ108). Differently, the SAS_T trends are mostly insignificant, aside from bottom layer at some stations, where they are mildly but significantly positive, with trends less than 0.015 mg/L over 10 years.

3.3. Correlations with the environmental drivers

There are two environmental drivers that are reflecting strong and consistent correlations to the OM variables. The strongest correlations for the DOC are found with the Po River discharge (PO) at both sides of the transect and throughout the whole column (Figs. 6 and 7). The most significant correlations, surpassing 99% significance level, are found for phase lags of -1 and -2 years in the eastern section of the transect ($r=0.85$, $p<0.001$ and $r=0.77$, $p=0.001$, phase lag of -1 year at RV001 at 0 m and 30 m, respectively), while correlations are the strongest at the phase lag of -2 years for station off the Po River delta ($r=0.73$, $p<0.001$ and $r=0.63$, $p=0.004$, phase lag of -2 years at SJ101 at 0 m and 30 m, respectively). It is interesting that no significant correlations between the PO and the DOC were found at the 0 phase lag (except at RV001 at 30 m), although it is known that the Po River is rapidly affecting the NAd thermohaline properties, with the phase lag between discharges and salinity up to a year (Supić and Vilibić, 2006). The nutrient load by the northern Adriatic rivers are setting the conditions for the primary production in a subsequent year or two, as being the strongest only in spring and summer (Kovač et al., 2018), also found to affect the SAS with a phase lag (Gašparović et al., 2011).

Still, no significant correlations have been found between the PO and the SAS_T or the SAS_{diss} for any phase lag or depth, for both stations. This might be a consequence of yearly data averaging, and therefore losing the capability to capture the real processes that are occurring on a daily or a weekly timescale (e.g. phytoplankton bloom, Gačić et al., 2002).

However, quite significant correlations have been found between the SAS_T and the BiOS index at both sides of the transect (Figs. 8 and 9), much higher at the western section of the transect, at station SJ101 situated in front of the Po River, where the ocean variability is much larger (Franco and Michelato, 1992). The largest correlations are found at a phase lags of -3 to -5 years ($r=-0.72$, p<0.001 and r=-0.63, p=0.004, phase lag of -3 years at SJ101 at 0 m and 30 m, respectively). The correlations are somewhat lower at RV001 (r=-0.62, p=0.018 and r=-0.51, p=0.061, phase lag of -4 years at RV001 at 0 m and 30 m, respectively). Interestingly, such a significant correlation has been found between the salinity along the NAd transect and the BiOS index, with maximum correlations at phase lags between -2 and -4 years (Vilibić et al., 2019b).

Sporadic significant correlations may be found between the BiOS index and the DOC, revealing the change in relationship with the phase lag, positive at the phase lag of 0 years and negative at the phase lag of -5 years. As it is not feasible that the BiOS may affect the NAd DOC immediately – i.e. it takes a year for the water masses to travel from the northern Ionian Sea to the NAd (Mihanović et al., 2015), while maximum correlations between the BiOS index and the NAd salinity is found at the phase lags of -2 to -4 years (Vilibić et al., 2019b) – our hypothesis is that the real effect of the BiOS on the DOC is occurring at the phase lag of -5 years. Namely, negative BiOS index that resembles anticyclonic circulation in the northern Ionian Sea with advection of nutrient-richer waters from the Western Mediterranean, is expected to increase the primary production in the NAd, and therefore the increase of DOC values, sometimes after the arrival of these waters to the NAd.

In regard to the other environmental drivers, the correlations are mostly insignificant (not shown). In particular, local drivers, TP and NHF, show no correlations significant at 95% for any phase lag and OM variable (not shown). The only exception is NHF-SAS_T correlation at the phase lag of 0 years, r=0.46, p=0.046 at SJ101 at 30 m). The same applies to the hemispheric processes, where the EA/WR and the SCAND indices are not coherently correlated with the organic matter variables, although some sporadic significant correlations are documented. Yet, the NAO index shows systematic negative correlations with the SAS_{diss} and the SAS_T at the phase lag of – 2 years (the maximum is attained with the SAS_{diss} at SJ101 at 30 m, r=-0.64, p=0.003), which might be related to the NAO influence on the precipitation in the Alpine region (Brugnara and Maugeri, 2019), being the major source of the Po River waters. EA shows significant correlations with the SAS_T at the phase lag of -3 years, higher at the western section of the transect (SJ101, r=-0.64, p=0.003 and r=-0.65, p=0.003 at 0 and 30 m, respectively). For the MO index, coherent correlations over most of the stations and depths are found with the DOC at the phase lag of -1 year in the eastern section of the transect (RV001, r=-0.69, p=0.007 and r=-0.57, p=0.033 at 0 and 30 m, respectively) and at the phase lag of -2 years in the western section of the transect (SJ101, r=-0.50, p=0.031 and r=-0.61, p=0.006 at 0 and 30 m, respectively). These correlations might resemble the input of nutrients, in particularly of phosphorus, due to the dust coming from the northern Africa (Herbert et al., 2018; Richon et al., 2018; Kanakidou et al., 2019), as the index is primarily describing northward vs. southward flow over the Adriatic (Palutikof et al., 1996), which includes meridional transport of the Sahara dust.

4. Discussion and conclusions

There are several issues to be discussed related to the data used in our analyses. The first is eventual undersampling of both thermohaline and OM content data. Both data are taken in a single moment of time and at a certain position in space, while the relevant processes occur on a daily timescale, e.g. the dense water formation and the cooling of the water column is occurring over a few days during extensive cooling driven by the severe bora wind outbreaks (Bergamasco et al., 1999; Janeković et al., 2014; Ličer et al., 2016). For that reason, the samples can differ for a few ^oC in temperature over a few days. This also applies for the warm part of the year, when an extensive spring heating may strongly increase the sea surface temperature over a week. The western section of the transect may exhibit a rapid change of surface salinity, as the Po River plume can move a lot during a few days (Kourafalou, 1999). The same can be applied for the OM content data, which may be influenced by the timescales of both physical and biological processes. Biological processes, relevant to our analyses may evolve rapidly, like phytoplankton blooms in the NAd, the most eutrophicated region in the Adriatic (Franco and Michelato, 1992). All these reasons may affect the performed statistics and the trend analyses, in particular the correlation analyses as they were performed with the drivers that are averaged over a larger timescale, in our case a year. For that, we estimated the correlations between the potential drivers and the DOC and the SAS in a more robust way, by "taking out" the processes from the data that are known to dominate in the NAd, such as seasonal changes. Additional averaging on a yearly scale made our analyses more competent. Still, with averaging, one is not able to properly capture and document the trends and the correlations for the processes that are occurring on a short time scale, which may affect the analyzed OM data. For proper quantification at the process scale, different approaches should be used, which was not the objective of this paper.

We found high inter-annual and decadal variability of the analyzed OM variables (DOC and SAS), being reflected in the reported oligotrophication of the area, especially after 2000 (Solidoro 2009; Djakovac et al., 2012; Giani et al., 2012). Precisely, the DOC concentration is decreasing in the whole studied period (Dautović et al., 2017), with maximum trend of 5 mg/L over 100 years in the subsurface region. However, the SAS, in particular its dissolved fraction, shows an increasing trend. This implies a certain change in the OM quality, visible by recording more hydrophobic, i.e. reactive OM. It is interesting that the SAS_T concentrations in the bottom layer show mildly, but significantly positive trend, which is in accordance with earlier observation of Gašparović (2012) for the stations SJ101 and SJ107 in the 1998-2010 period. These results were explained as a direct consequence of an oligotrophication in the surface layer, when phytoplankton (as the main producer of the SAS) moves in deeper layers where more nutrients coming from the remineralization processes are available for primary production. Our long-term results underline the importance of the remineralization in supplying the nutrients for primary production.

Increased concentrations of the DOC and the SAS were found in the surface layer, especially during the 2002, when the DOC ranged between 1,020-3,250 mg/L in individual samples (1,695 mg/L in average) and the SAS_{diss} was recorded up to 0,215 mg/L in individual samples (0,112 mg/L in average). For comparison, the lowest DOC average value of 1,056 mg/L was recorded in 2006, while the average SAS_{diss} was 0,092 mg/L. It is a consequence of the ratio between the particulate and the dissolved OM fractions, which is changing during the phytoplankton bloom (Ciglenečki et al., 2018, and references therein). Usually particulate fraction is dominating at the beginning of the bloom, while contribution of the dissolved substances is prevailing later (Yoshimura et al., 2009; Gašparović, 2012). The $SAS_{T,}$ as a fraction which contains both particulate and dissolved SAS, represent the most reactive part of the OM, and is usually correlated with the particulate organic carbon (POC) presence. For example, during the diatom bloom (*C. closterium*), hydrophobic material is predominantly associated with the particulate fraction in average (Ciglenečki et. al., 2018). The SAS_T, especially its particulate part, is very important in adsorption and aggregation processes such as formation of sea-surface microlayer (Sabbaghzaden et al., 2017; Wurl et al. 2017), where they significantly influence the air-sea climate active gasses transfer. The SAS have an important role in aggregation processes, such as formation of micro- and macro-agregates, i.e. mucilages (Ciglenečki et al. 2003), which were frequently found in the NAd in the strong eutrophication period recorded between 1998 and 2004 (Precali et al., 2005; Degobbis et al., 2005; Djakovac et al., 2012; Giani et al., 2005, 2012).

The analysis of a long-term data indicates that the content and properties of the OM in the NAd vary on a spatial (station position) and temporal scale (months, seasons, years), depending on the local impact of the freshwater input, mainly of the Po River, and on the remote impact of the water inflow entering the Adriatic Sea from the Mediterranean, controlled by the BiOS (Dautović et al., 2017). OM in the seawater originate from several sources, including excretion carried out by the plants and animals, bacterial decomposition, autolysis of dead organisms, inputs by rivers, effluents, and from the atmosphere. Primary photosynthetic production by the phytoplankton in the surface waters is the largest source of organic carbon in marine systems (marine SAS are mainly derived from phytoplankton, Žutić et al., 1981; Gašparović and Ćosović, 2001; Croot et al., 2007). Therefore, the SAS in the NAd is highly dependent on the phytoplankton activities (Gašparović and Ćosović, 2001). As expected, the highest DOC and SAS values in the NAd were measured in the surface layer, with the largest variability and with a declining trend from west to east, or from surface to bottom.

The correlation studies show that the DOC is significantly (99%) correlated with the Po River discharges, but at the phase lag of -1 to -2 years, while for the SAS the largest correlations (significant at 99%) are obtained with the BiOS index, with the phase lag of -3 to -4 years. So far, the Po River discharge was considered as the main nutrient supply in the NAd which controls the primary production (Viličić et al., 2009). Nonetheless, the Po River is also representing a significant source of the NAd OM (165-218 uM, 1995-2007, Cozzi and Giani, 2011). However, no significant correlation between the nutrients and the Chl *a,* as well as between the SAS and the Chl *a* was found (Gašparović et al., 2011), which was explained with a time delay among the nutrient uptake, phytoplankton reproduction (Chl *a* increase) and the OM excretion. Opposite to this, significant correlation was found between the SAS, DOC and decreasing salinity (Gašparović et al., 2011; Dautović et al., 2017), which can be considered as an indication of nutrient inputs, the latter consumed at the time of the sampling and/or measurements. In line with this and our study, Kraus et al. (2016) also showed that the phytoplankton abundance in the NAd depends on the forcing of the previous 1-12 months of surface fluxes and/or the Po River discharge rates. The main hypothesis is that the bioproduction is affected by the circulation patterns and by the intensity of the Po river discharge. Circulation patterns in the NAd consist of several gyres (cyclonic/anticyclonic) that are changing their position and extent seasonally and yearly (Supić et al., 2012). These gyres act as a "hot spots" filled with different quality of waters with lower salinity, which further influence different prokaryotic activities, and subsequently accumulation of nutrients and organic matter (Orlić et al., 2013).

On top of this, the correlations between the BiOS index and SAS_T indicate that the BiOS might be a significant driver of the interannual variability of some OM variables, as it was found for the NAd salinity (Vilibić et al., 2019b). However, the phase lag at which the maximum correlations are achieved for the OM are -3 to -5 years, while the documented phase lag for the salinity is -2 to -4 years (Vilibić et al., 2019b). Correlations are higher at the western section of the NAd, more influenced by an interplay between freshened waters of Po River and saline waters advected from the southeast. As the phase lags between the SAS_T and the BiOS index is about a year larger than the phase lags between the salinity and the BiOS index, our results are supporting the major finding by Vilibić et al. (2019b), who documented that the Po River discharge is the major driver of thermohaline changes up to a year. Differently, biogeochemical processes need some time to cause a change in the OM variables, thus the Po River discharge is strongly influencing the biogeochemical variables (the DOC in our case) in the subsequent two years. On the other hand, the BiOS was found to be the dominant driver of the thermohaline changes in the NAd at a multi-year time scale (phase lag of -2 to -4 years, Vilibić et al., 2019b), while the biogeochemical properties (SAS_T) are driven by the BiOS for a year more, proving that an interplay between advection of either ultraoligotrophic saline Eastern Mediterranean waters or nutrient-richer less saline Western Mediterranean waters into the Adriatic is affecting the Adriatic oceanographic properties up to the NAd.

A weak correlation is obtained between the OM variables and the total precipitation, even though it is known that wet atmospheric deposition could be an important source of the DOC (Iavorivska et al., 2019). A significant increase in dissolved inorganic nitrogen (DIN) and orthophosphates (PO4) was reported in the 2007-2016 period, implying that the phosphorus-limiting conditions, typical for the NAd (Giani et al., 2012), seem to be attenuated, and that the observed phosphorus levels cannot be explained by the respective concentrations measured in the Po River waters (Toti et al., 2019). Such results suggest the presence of other phosphorus sources, possibly related to the intensity of heavy rainfall (Toti et al., 2019), and possible aerosol dust coming from the northern Africa (Richon et al., 2018).

In the NAd, the freshwater flow reduction was identified as the cause of both changes in phytoplankton composition, and the reduction of total abundance during the 1986–2017 period (Aubry et al., 2012; Cabrini et al., 2012). Recently, in the same region, a re-increase of the Po River outflow observed during the 2007–2016 was followed by a reduction of coccolithophorid and by an increase in phytoflagellate biomass (Totti et al., 2019). The same paper reported that the spring community (2007–2016) markedly differed from that of the 1988–2002 period, for the more relevant contribution of the dinoflagellates, with intensive blooms of *Noctiluca scintillans*.

Since dinoflagellates are known as an important producer of more hydrophobic SAS (Vojvodić and Ćosović, 1996), such findings are an important support for the observed increasing SAS trend in our study. Similar changes in primary production and related processes are also reported for the semi-enclosed Toulon Bay (NW Mediterranean Sea), as a result of changes in rainfall rates, temperature, salinity and regional convection events (wintering deep mixing) (Serranito et al., 2019).

Our results are supportive to previously reported long-term ecological studies in the NAd, in which significant modifications of the environmental conditions were discussed as a consequence of a climatic fluctuations and changes in the anthropogenic pressure (Djakovac et al., 2012; Giani et al., 2012; Marić et al., 2012). The main confirmed environmental changes are: (i) a warming of surface waters (Vilibić et al., 2019a); (ii) a marked freshwater outflow decrease during the 2000s (Cozzi et al., 2012; Djakovac et al., 2012) due to the reduction of precipitation that caused an surface salinity increase at that time; (iii) a decrease in frequency of Istrian Coastal Counter-current (ICCC, Supić et al., 2000) after the 2000; (iv) an increased river loads of nitrogen, coupled with a phosphorus load decrease (Cozzi and Giani, 2011) due to the enforcements of law of the environmental protection in Italy (Sfriso et al., 2019); (v) an increased DIN/PO4 ratio in the sea water due to the reduction of riverine total phosphorus and to the nitrogen uptake limitation (Cozzi and Giani, 2011). All these changes and variability are either directly or indirectly linked to the OM composition and concentrations. Consequently, a phytoplankton biomass reduction was observed in the NAd (Aubry et al., 2012; Mozetić et al., 2010), as well as the community shifts toward the small size species (Marić et al., 2012) that can produce different OMs. It is known that the composition of the phytoplankton community in the euphotic zone largely determines the quantity and quality of the OM that sinks to a greater depths (Herndel and

Reinthaler, 2013), and which further dictates microbial diversity and activity with a direct implication on an organic carbon fate (Korlević et al., 2016; Čanković et al., 2017). Also, differences in the composition and concentration of the OM in the particulate and the dissolved phase may be reflected in the physiology and life strategy of particle-associated versus free-living microbes in the ocean (Herndel and Reinthaler, 2013).

The results of this long-term study clearly show how an interplay between different physical, chemical and biological, local and remote processes controls the OM accumulation and biogeochemical fate in the NAd marine system. The findings from this study are contrasting the classical picture of the NAd developed in the 1980s and later, when it has been considered that the NAd is almost exclusively influenced by the local forcing, of which quite large freshwater load by the NAd rivers (Franco and Michelato, 1992) – in particular of the Po River (Raicich, 1996) - is found to be the most important forcing. Changes in the Po River discharge rates presumably occur as a result of a global changes and trends in the NAd precipitation catchment area (Blöschl et al., 2017). Yet, understanding the influence of a more complex circulation regimes in the NAd, like those controlled by the BiOS, is a challenge for a future research studies. For now, it is evident that the different nutrient supply due to the changes affected by the water column stratification and by the water circulation, promotes shifts in phytoplankton community composition and its activity (Pulina et al., 2016), which further affects the quality and quantity of the organic matter, as well as the microbial diversity and activity. This greatly affects the organic matter accumulation and the cycle in the NAd on different timescales.

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Figure captions

Figure 1. Map of the sampling area in the northern Adriatic. Sampling stations along the transect Po River delta – Rovinj are: SJ108 (44°45’24’’N, 12°45’0’’E); SJ101 (44°59’53’’N, 12°49’48’’E); SJ103 (45°1’0’’N, 12°59’35’’E); SJ105 (45°1’59’’N, 13°9’18’’E); SJ107 (45°2’52’’N, 13°19’0’’E) and RV001 (45°4’48’’N, 13°36’36’’E).

Figure 2. Time series of seasonal DOC, SAS_T and SAS_{diss} values averaged over the northern Adriatic transect in the surface layer (0.5 m).

Figure 3. Mean DOC, SAS_T and SAS_{diss} values over the northern Adriatic transect. The values are computed on the series with annual and semiannual cycles removed.

Figure 4. Ratio between seasonal and total variance of DOC, SAS_T and SAS_{diss} over the northern Adriatic transect.

Figure 5. DOC, SAS_T and SAS_{diss} trends over the northern Adriatic transect. The trends are computed on the series with annual and semiannual cycles removed. Full circles are denoting the values which are significant at 95% level.

Figure 6. Pearson’s correlation coefficients between yearly averaged DOC, SAS_T and SAS_{diss} measured at RV001 at 0 m and 30 m, and the PO for phase lags between 0 and -5 years. Light

red, red and violet denote correlation values which are significant at 90%, 95% and 99%, respectively.

Figure 7. As in Fig. 6, but for station SJ101.

Figure 8. Pearson's correlation coefficient between yearly averaged DOC, SAS_T and SAS_{diss} measured at RV001 at 0 m and 30 m, and the BiOS index for phase lags between 0 and -5 years. Light red, red and violet denote correlation values which are significant at 90%, 95% and 99%, respectively.

Figure 9. As in Fig. 8, but for station SJ101.

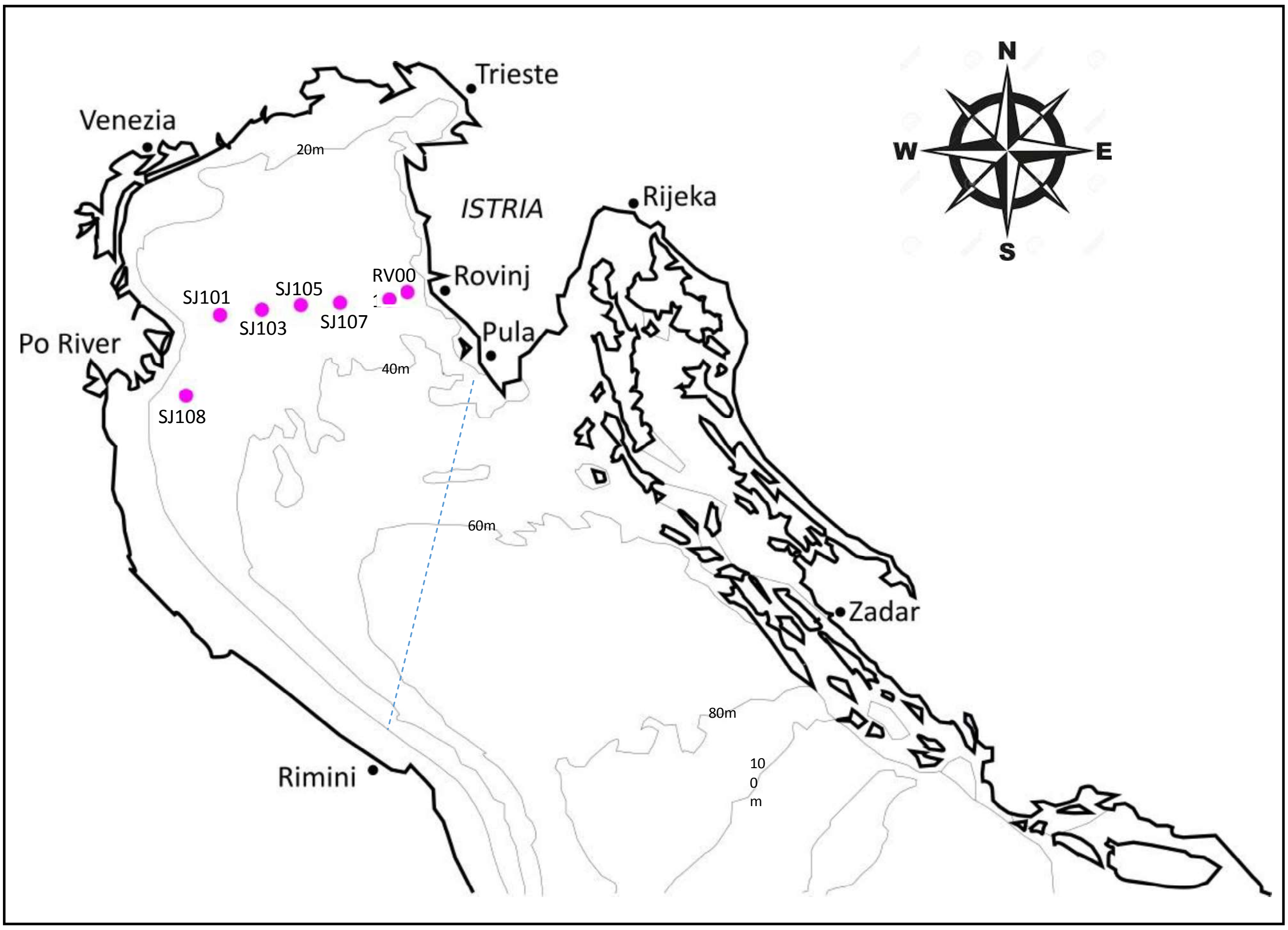
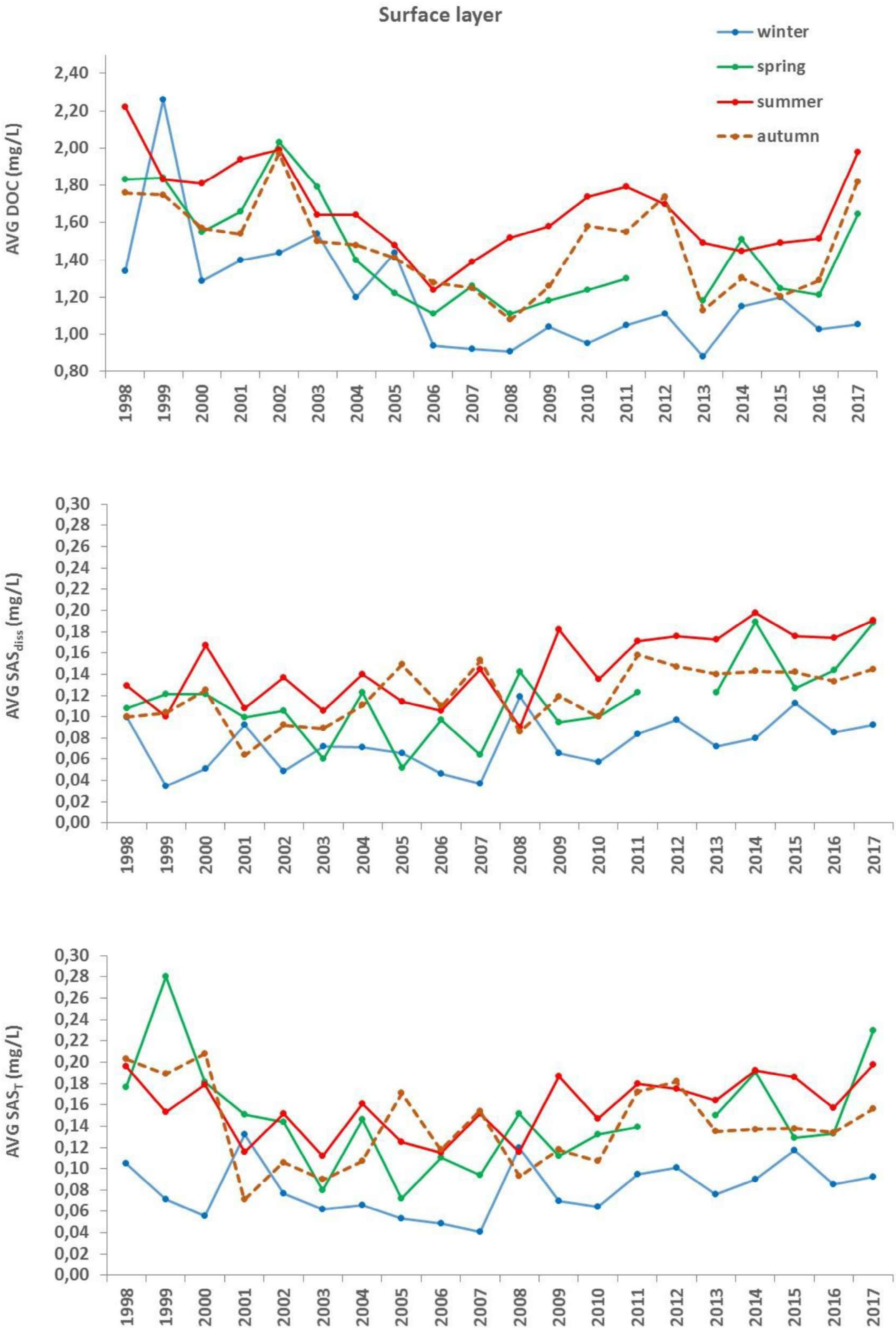

N
W
E
S
Trieste
Venezia
20m
ISTRIA
Rijeka
Rovinj
RV00
SJ101
SJ105
SJ103
SJ107
Pula
Po River
40m
SJ108
60m
Zadar
80m
Rimini
10
0
m

Figure 1.



Surface layer
winter
spring
summer
autumn
AVG DOC (mg/L)
AVG SAS$_{diss}$ (mg/L)
AVG SAS$_T$ (mg/L)

Figure 2

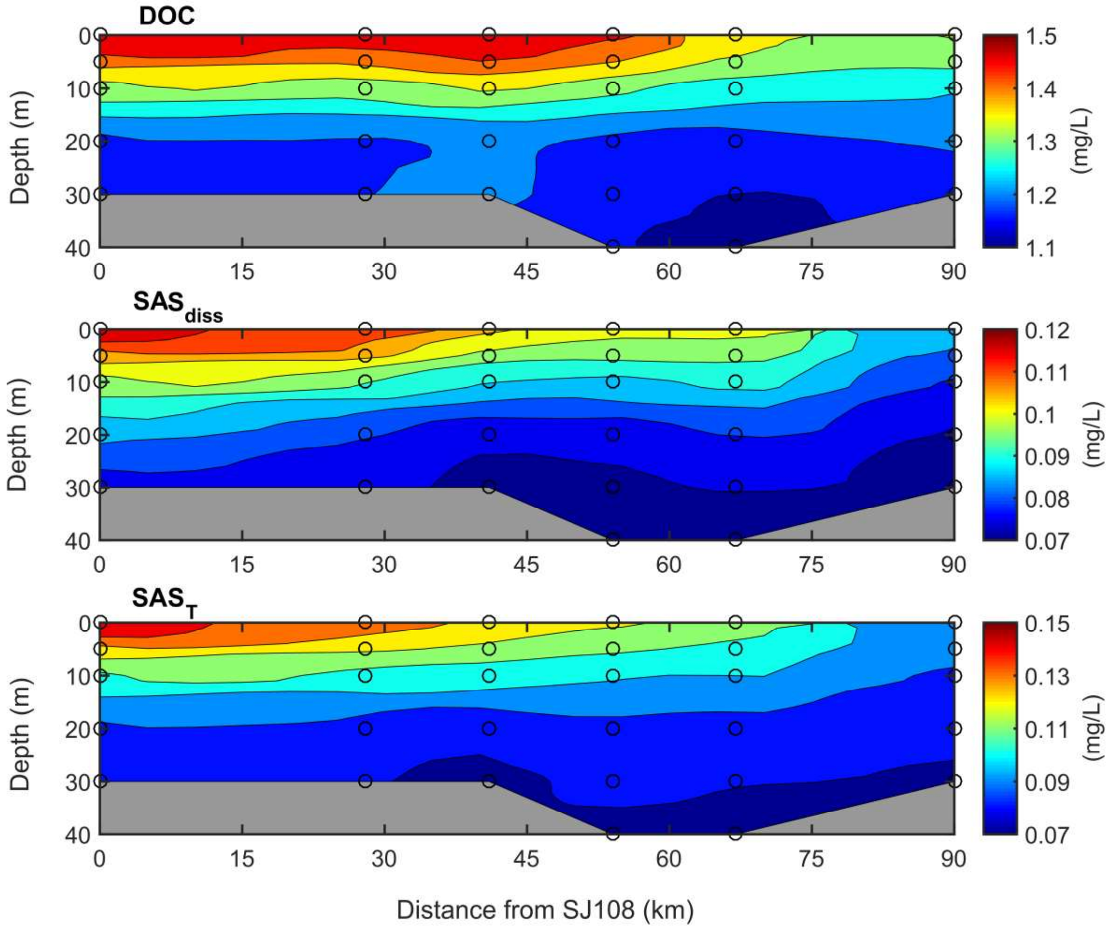

DOC
Depth (m)
(mg/L)
1.5
1.4
1.3
1.2
1.1
SAS$_{diss}$
Depth (m)
(mg/L)
0.12
0.11
0.1
0.09
0.08
0.07
SAS$_T$
Depth (m)
(mg/L)
0.15
0.13
0.11
0.09
0.07
0
10
20
30
40
0
15
30
45
60
75
90
Distance from SJ108 (km)

Figure 3.

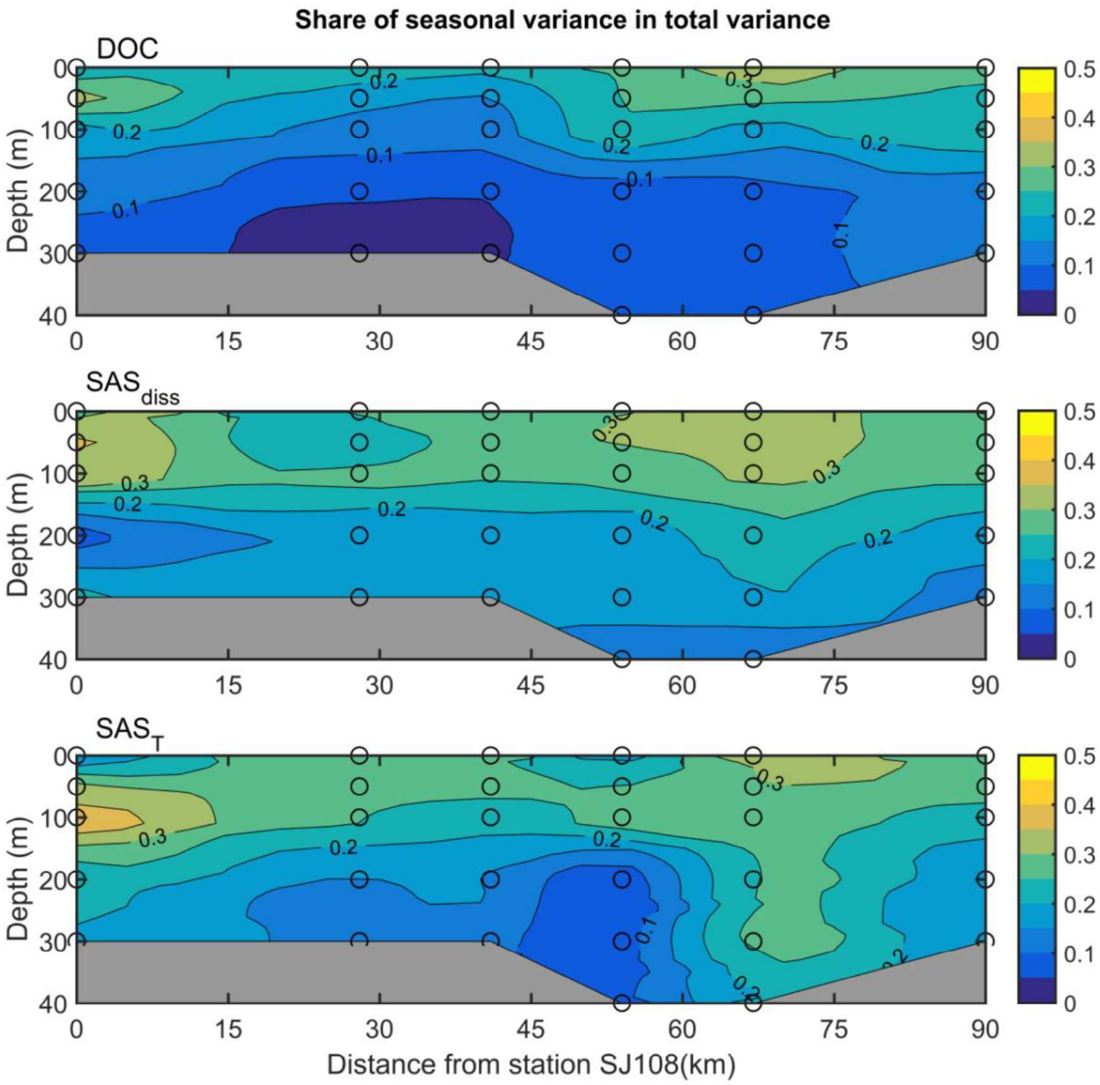

Share of seasonal variance in total variance
DOC
SAS$_{diss}$
SAS$_T$
Depth (m)
Distance from station SJ108(km)

Figure 4

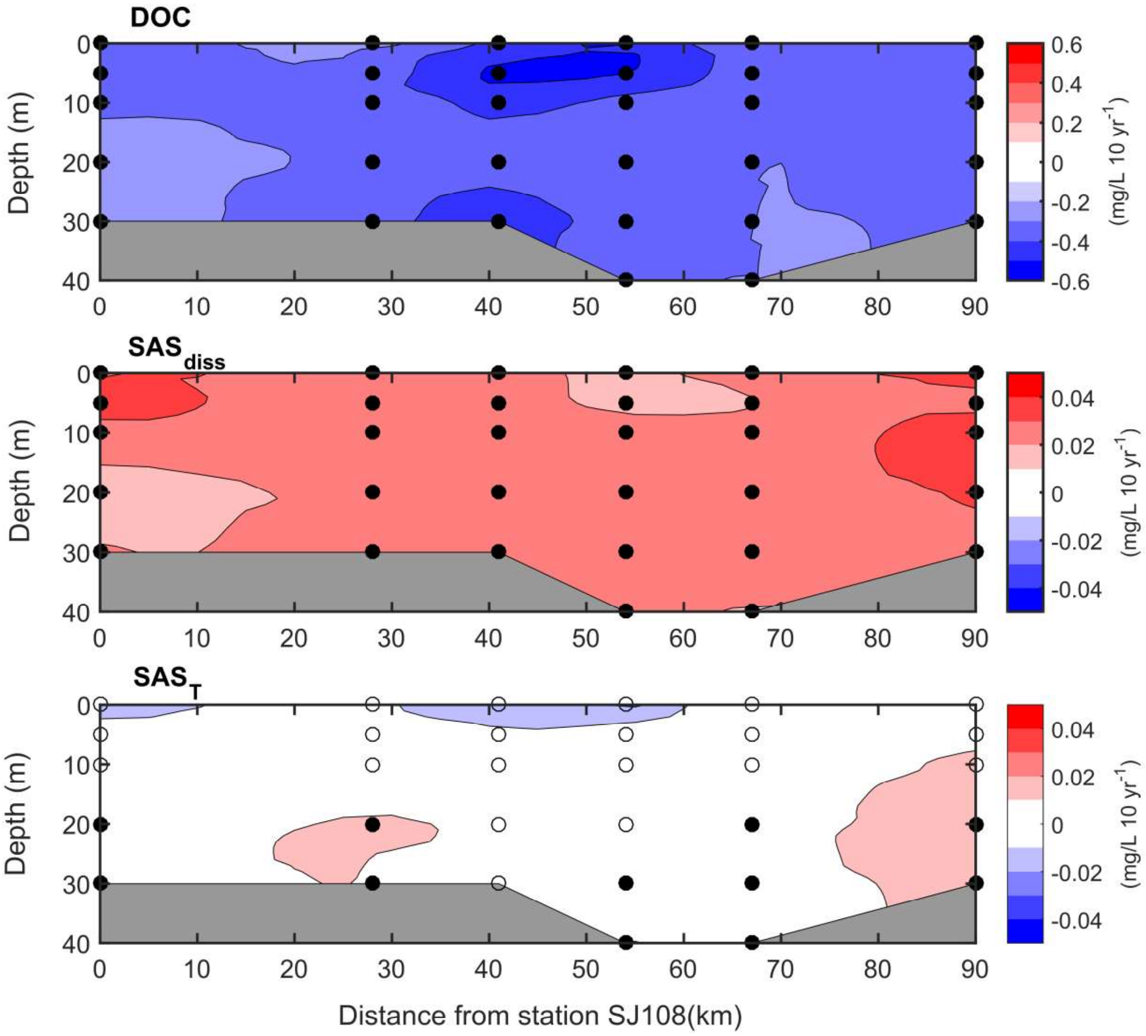

DOC
Depth (m)
(mg/L 10 yr^{-1})
SAS$_{diss}$
Depth (m)
(mg/L 10 yr^{-1})
SAS$_{T}$
Depth (m)
(mg/L 10 yr^{-1})
Distance from station SJ108(km)

Figure 5

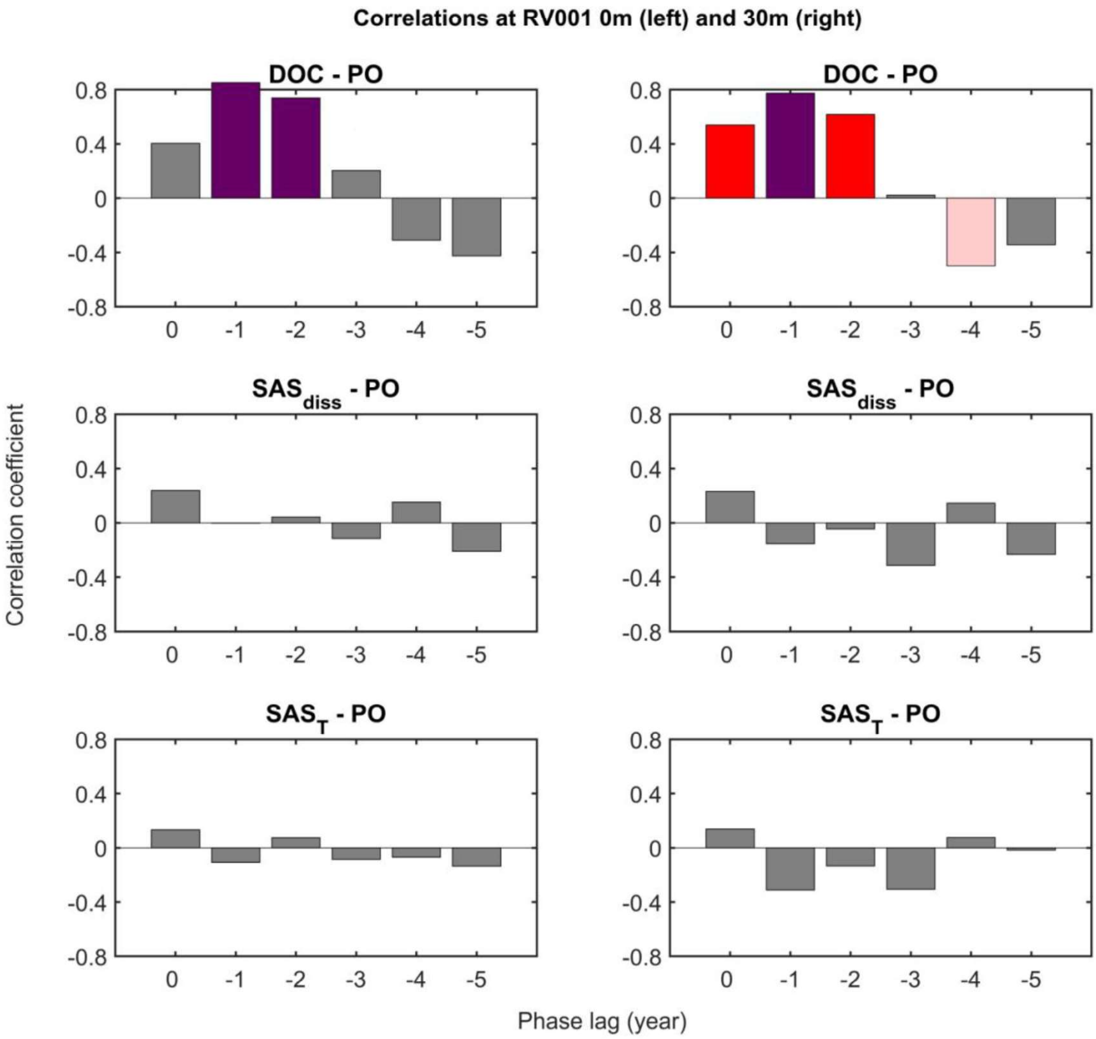

Correlations at RV001 0m (left) and 30m (right)
DOC - PO
DOC - PO
SAS$_{diss}$ - PO
SAS$_{diss}$ - PO
SAS$_T$ - PO
SAS$_T$ - PO
Correlation coefficient
Phase lag (year)
0.8
0.4
0
-0.4
-0.8
0
-1
-2
-3
-4
-5

Figure 6

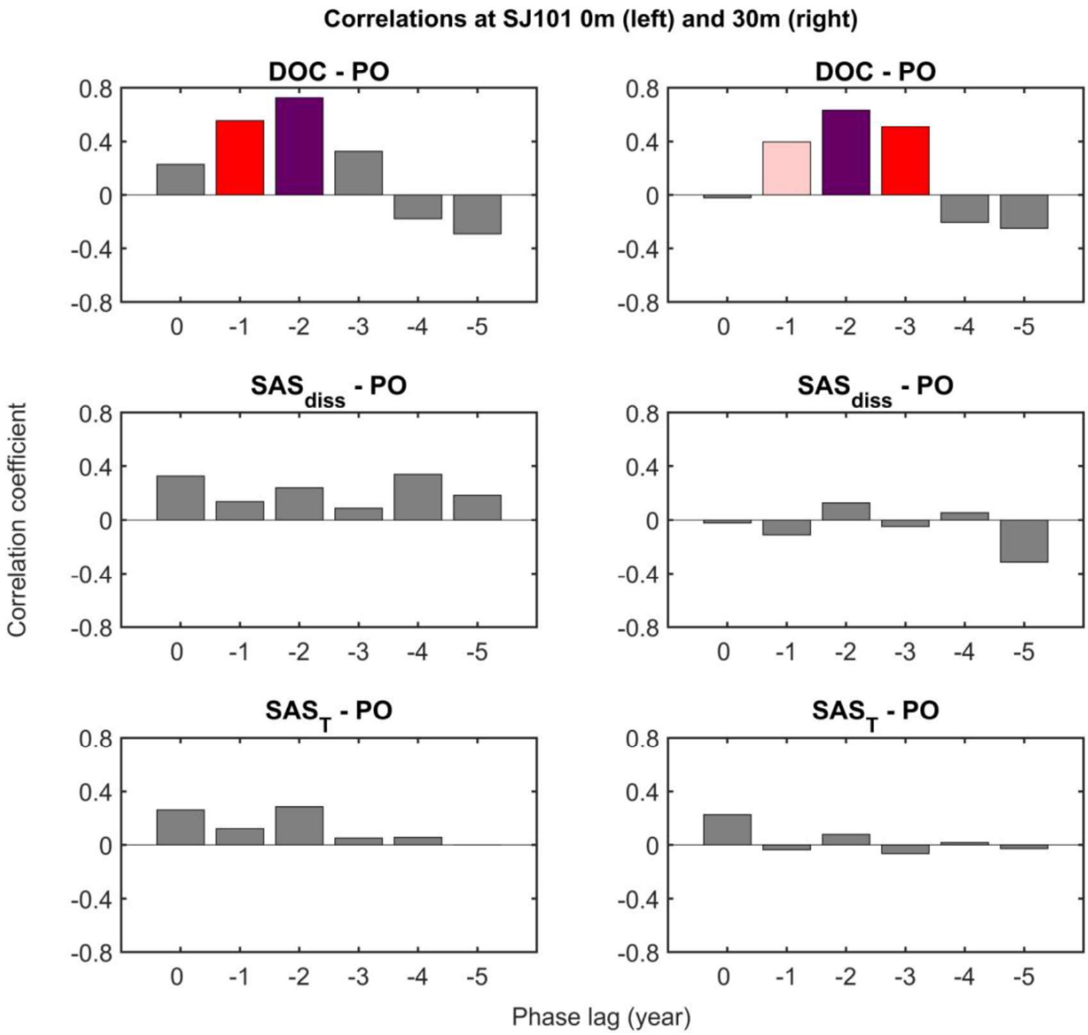

Correlations at SJ101 0m (left) and 30m (right)
DOC - PO
DOC - PO
SAS_{diss} - PO
SAS_{diss} - PO
SAS_T - PO
SAS_T - PO
Correlation coefficient
0.8
0.4
0
-0.4
-0.8
0
-1
-2
-3
-4
-5
Phase lag (year)

Figure 7

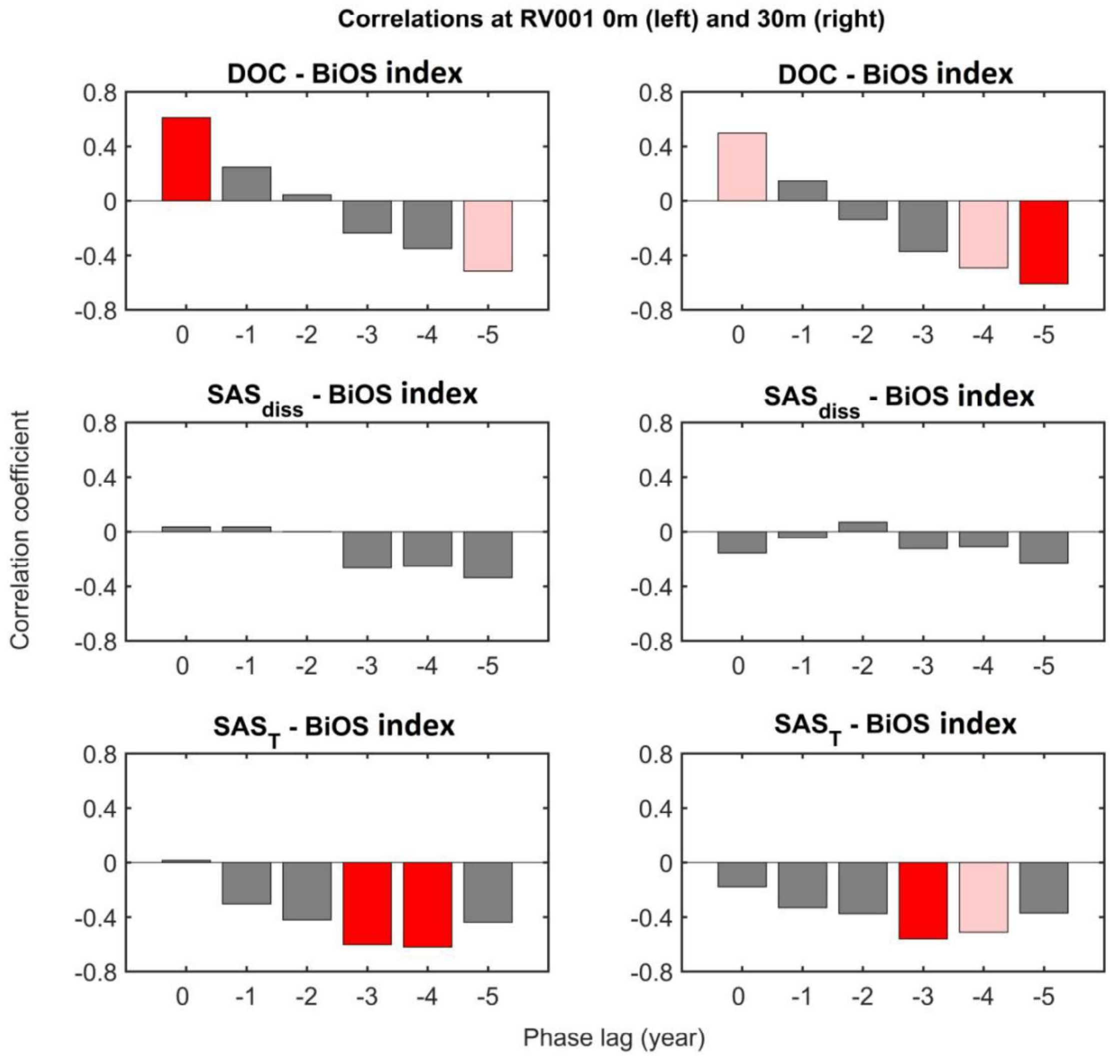

Correlations at RV001 0m (left) and 30m (right)
DOC - BiOS index
DOC - BiOS index
SAS$_{diss}$ - BiOS index
SAS$_{diss}$ - BiOS index
SAS$_{T}$ - BiOS index
SAS$_{T}$ - BiOS index
Correlation coefficient
0.8
0.4
0
-0.4
-0.8
0
-1
-2
-3
-4
-5
Phase lag (year)

Figure 8

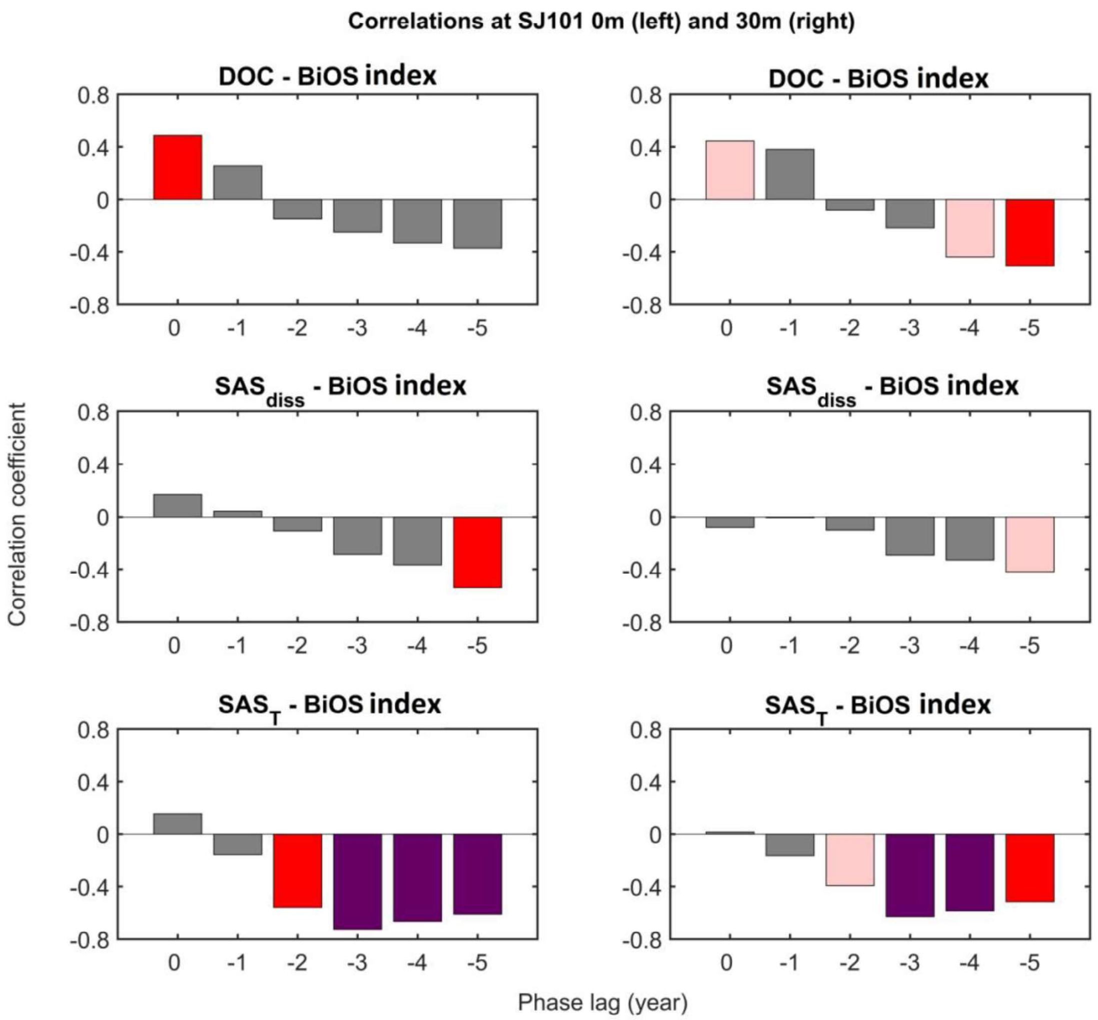

Correlations at SJ101 0m (left) and 30m (right)
DOC - BiOS index
DOC - BiOS index
SAS$_{diss}$ - BiOS index
SAS$_{diss}$ - BiOS index
SAS$_T$ - BiOS index
SAS$_T$ - BiOS index
Correlation coefficient
Phase lag (year)
0.8
0.4
0
-0.4
-0.8
0
-1
-2
-3
-4
-5

Figure 9