Atmospheric Environment 79 (2013) 681–688

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Relationship between methanesulfonate (MS^-) in atmospheric particulate and remotely sensed phytoplankton activity in oligo-mesotrophic central Mediterranean Sea

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HIGHLIGHTS

- Primary production is calculated for the sea around Lampedusa by bio-optical and WDRM models.
- Significant relationship between atmospheric MS^- and productivity index is found.
- Significant relationship between atmospheric MS^- and solar radiation dose is found.
- MS^- is related to the phytoplankton physiology, in turn related to variation of stress factors.
- High MS^- concentrations in spring 2005 could be related to NAO negative phase.

ARTICLE INFO

Article history:
Received 19 November 2012
Received in revised form
8 July 2013
Accepted 15 July 2013

Keywords:
Primary productivity
Methanesulfonate
MSA
Aerosol
Central Mediterranean Sea
North Atlantic Oscillation

ABSTRACT

The coupling between oceanic and atmospheric sulfur cycles is fundamental for the understanding of the role of sulfate particles as potential climate regulators. We discuss existing relationships among methanesulfonate (MS^- – one of the end products of oxidation of biogenic dimethylsulfide – DMS) in the atmospheric particulate, phytoplankton biomass, and remotely-sensed activity in the central Mediterranean. The MS^- concentration in the aerosol particles is based on PM_{10} sampling (from 2005 to 2008) of atmospheric aerosols at the island of Lampedusa (35.5°N, 12.6°E) in the central Mediterranean Sea.

The marine primary production in the sea sector surrounding the sampling site is obtained by using Ocean Color remote sensed data (SeaWiFS, MODIS-Aqua). In particular, primary production is calculated using a bio-optical model of sea reflectance and a Wavelength-Depth-Resolved Model (WDRM), fed by elaborated satellite data (chlorophyll concentration in the euphotic layer – Chl, sea surface temperature) and daily solar surface irradiance measurements.

The multi-year evolution of MS^- atmospheric concentration shows a well-defined seasonal cycle with a summer maximum, corresponding to the annual peak of solar radiation and a minimum of phytoplankton biomass (expressed as Chl).

Statistically significant linear relationships between monthly means of atmospheric MS^- and both the phytoplankton productivity index P^B ($r^2 = 0.84$, $p < 0.001$) and the solar radiation dose (SRD; $r^2 = 0.87$, $p < 0.001$) in the upper mixed layer of the sea around Lampedusa are found. These correlations are mainly driven by the common seasonal pattern and suggest that DMS production in the marine surface layer is mainly related to the phytoplankton physiology. High values of P^B are also the expression of stressed cells. The main stress factors in Mediterranean Sea during summer are high irradiance and shallow depth of the upper mixed layer, which lead to enhanced DMS emissions and higher MS^- amounts in the atmosphere.

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1352-2310/$ – see front matter
http://dx.doi.org/10.1016/j.atmosenv.2013.07.032

During spring 2005 high biomass and primary productivity values are observed in February and April, just one month before the peaks of atmospheric MS^- (March and May). The occurrence of anomalously high values at this time is hypothesized to be related to the negative phase of the North Atlantic Oscillation, and to related oceanic and atmospheric processes. The possible role of the taxonomic composition of phytoplankton assemblages is also discussed.

1. Introduction

The ocean atmospheric coupled sulfur cycle has received considerable attention in the last two decades due to its potential for climate regulation. However, due to the complexity of the cycle, some important features regarding its seasonal dynamics are still poorly understood. In addition, currently it is not possible to predict surface ocean concentrations of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) with any type of empirical correlations anywhere at any time of the year. Phytoplankton is the primary producer of DMSP, the biochemical precursor of DMS, a volatile compound that is ubiquitous in the global surface ocean which undergoes to atmospheric oxidation processes yielding methanesulfonate (MS^-) and sulfate. Emission of oceanic DMS to the atmosphere contributes to non-sea-salt sulfate ($nssSO_4^{2-}$) production (Bates et al., 1992; Kettle and Andreae, 2000) which affects the Earth's radiative budget by direct and indirect effects (e.g. Kaufman et al., 2002). In this regard, a negative feedback between oceanic DMS production and Earth albedo has been postulated (CLAW hypothesis, Charlson et al., 1987).

In polar regions, methanesulfonate peaks in summer, simultaneously to the chlorophyll maximum. For this reason several studies aim at reconstructing biogenic marine activity and other linked climatic parameters (i.e., sea ice extent) from the MS^- record from firn/ice core (e.g. Becagli et al., 2009). In particular in Antarctica, DMS oxidation is the dominant source of $nssSO_4^{2-}$, in addition to MS^-, and $nssSO_4^{2-}$ is used as marker of marine phytoplankton activity for the last 800 kyr (Wolff et al., 2006).

In the Mediterranean atmosphere, anthropic dominate over the biogenic sources of sulfate (Bardouki et al., 2003; Mihalopoulos et al., 2007), and the evaluation of the biogenic source contribution is a complex task. In temperate sea chlorophyll peaks in winter, while DMS in surface water peaks in late spring–summer. Hence, in spite of the importance of the correlation between oxidized sulfur compounds in the aerosol and biogenic activity, the processes determining the emission of DMS by phytoplankton are not well understood. Actually, the amount of DMSP released to the water depends on the different phytoplankton groups (prymnesiophytes, dinophytes but also chrysophytes, pelagophytes, prasinophytes and polar diatoms are stronger DMSP producers; Keller et al., 1989; Orellana et al., 2011) as well as on the physiological state of the cells within each group (Keller and Korjeff-Bellows, 1996; Sunda et al., 2002). In particular, healthy and exponentially growing cells release little amounts of DMSP, while high quantities of DMSP are released by stressed stationary or senescent cells (Laroche et al., 1999; Zhuang et al., 2011), by phytoplankton subjected to grazing (Wolfe and Steinke, 1996) or infected by viruses (Hill et al., 1998).

Recently, Vila-Costa et al. (2006) found that not only heterotrophic bacteria but also cyanobacteria (*Prochlorococcus* and *Synechococcus*) and picoeukaryotes (small diatoms) could contribute to DMSP uptake in surface waters. DMSP can be enzymatically lysed to DMS by phytoplankton, in particular by the prymnesiophytes *Emiliania huxleyi* and *Phaeocystis* sp. (Wolfe and Steinke, 1996; Orellana et al., 2011), and bacteria (Taylor and Visscher, 1996), though the bacterial contribution to DMS production is small (Kiene et al., 2000).

Sunda et al. (2002) assessed the antioxidant role for DMSP and DMS in microalgae, in fact, increases of DMSP and DMS concentrations are detected under conditions of oxidative stress in cultures, for instance high UV and photosynthetic active radiation (PAR) irradiance and Fe-limitation (Sunda et al., 2002; Zhuang et al., 2011).

Ocean primary production (PP) is a crucial component of the Earth's biogeochemical cycles of carbon, sulfur, and other chemical elements (Field et al., 1998). Net primary production (NPP, $g\ C\ m^{-2}\ d^{-1}$), i.e., total primary production minus the losses due to respiration of the phytoplankton, provides the upper bound for production at higher trophic levels (Behrenfeld et al., 2005). In situ measurements of PP or NPP are extremely time-consuming and do not represent a large area because of high spatial and temporal variability. Estimating PP at the regional and global scales or for long-term time periods is therefore difficult without the quasi-synoptic view provided by satellite data or numerical models (Kahru et al., 2009). Current satellite-based estimates of primary production have however achieved limited success (e.g., Friedrichs et al., 2008).

Another important parameter in defining phytoplankton status is the chlorophyll specific production index or assimilation number (P^B), i.e. the rate of photosynthetic carbon assimilation per weight of chlorophyll a (production/biomass, day^{-1}). P^B is related to both the phototrophic growth rate and the Carbon to Chlorophyll ratio (C:Chl $g\ g^{-1}$). C:Chl ratio is related to microalgae physiological adaptations and it has a well-established eco-physiological dependence on both the spatial and temporal variability of light, nutrients, and temperature (Behrenfeld and Boss, 2003; Behrenfeld et al., 2005) which are the main environmental factors limiting microalgae growth rate. The eco-physiological variability of these processes has been reconstructed through the C:Chl and growth rate fields, for large scale areas and long-term time series, as obtained from both satellite derived data of phytoplankton carbon biomass (Behrenfeld et al., 2005) and from in situ particulate organic carbon (POC) data and photosynthesis-irradiance (P–E) curves (Sathyendranath et al., 2009).

In this paper the monthly mean MS^- concentration in the aerosol at Lampedusa Island (Sicily Channel) in the period 2005–2008 is compared with monthly means phytoplankton biomass, activity and most probable taxonomic composition, aiming to improve the knowledge of biogenic and the environmental factors affecting DMS emission and MS^- concentration in the atmosphere. Special attention is given to the spring 2005 event, which shows exceptionally high MS^- values when comparing data sets between years. The possible reasons of this peculiarity are discussed.

2. Methods and data

2.1. Aerosol sampling and analysis

The aerosol sampling was carried out at the Station for Climate Observations, maintained by ENEA (the National Agency for New Technologies, Energy, and Sustainable Economic Development of Italy) at Lampedusa (35.5°N, 12.6°E). Lampedusa is a small island located south of the Sicily Channel and it is at least 100 km from the nearest coastline (Tunisia). The Station is located on a 50 m a.s.l. promontory on the North-Eastern coast of Lampedusa, in which continuous observations of greenhouse gases (Artuso et al., 2009), aerosol properties (di Sarra et al., 2011; Meloni et al., 2006), total ozone, ultraviolet irradiance (Meloni et al., 2005; Mateos et al., 2011), and other climatic parameters are carried out.

The aerosol sampling was started in June 2004 at daily resolution, alternating in sequence sampling of PM_{10}, $PM_{2.5}$, and $PM_{1.0}$ (particulate matter with aerodynamic diameter lower than 10, 2.5 and 1.0 μm respectively). Since 2007 only PM_{10} is sampled on a daily basis. During the sampling period some breaks in the sampling occurred due to technical problems. Here results on the PM_{10} sampling for the years 2005–2008 are reported.

Aerosol samples were collected on 47 mm Teflon filters (2 μm nominal porosity) using a Tecora Skypost automatic sampler operating at constant flow rate (2.3 m^3 h^{-1}). A quarter of each Teflon filter was extracted using MilliQ water (about 10 ml, accurately evaluated by weighing) in ultrasonic bath for 15 min, and the ionic content was determined by ion chromatography. Methanesulfonate was determined in every sample together with other organic anions (acetate, formate, glycolate, oxalate), inorganic anions (F^-, Cl^-, NO_3^-, SO_4^{2-}), and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Field blanks show MS^- values always below the detection limit. Detailed description of procedures for handling aerosol filters and analytical condition is reported elsewhere (Becagli et al., 2011).

2.2. Chl data

The Aqua MODIS remote sensing reflectance (at 443, 488, and 551 nm) Level-3 images were downloaded from the NASA browser at http://oceancolor.gsfc.nasa.gov/cgi/l3. The downloaded images with a 2 × 2 km^2 resolution are grouped on a monthly basis. The average chlorophyll concentration is derived in the geographic area between 35 and 36°N, and 12°–13°E, and covers 10,124 km^2 around the island of Lampedusa. Since the lifetime of DMS over the Mediterranean basin is from minute to 1–2 h (Kouvarakis and Mihalopoulos, 2002 and references therein), the selected geographical area can be considered the main DMS source affecting the aerosol MS^- concentration at the sampling site. Actually, MS^- is mainly distributed on the sub-micrometric fraction of aerosol, which can be transported over long distances. Thus, MS^- measured at Lampedusa cannot be directly linked to emissions from the local marine biota. However, the overall evolution and features of the four annual cycles, obtained from monthly averages, do not significantly change if we increase the considered area to 220 × 220 km^2, and to 330 × 330 km^2 around Lampedusa. Consequently, we assume that the patterns of the biological parameters evolution are representative for a large area around Lampedusa.

In the Mediterranean Sea, the standard NASA algorithms lead to a significant overestimation of the chlorophyll concentration compared to in situ data (Bricaud et al., 2002; D'Ortenzio et al., 2002; Volpe et al., 2007). This observed bias can have a strong impact on primary production models for the Mediterranean. To reduce the difference between the chlorophyll-a estimated by the remote sensed reflectance and the in situ measurements, its concentration (given as input to the PP model) was computed by using the MODIS MedOC3, an ocean color algorithm specifically designed for the Mediterranean Sea whose theoretical bases are fully described in Santoleri et al. (2008).

2.3. PAR data and SRD calculation

PAR (W m^{-2}) was derived from measurements of global downward irradiance. The downward shortwave flux was measured at Lampedusa with Eppley Precision Spectral Pyranometers (PSP); the radiometers were ventilated and regularly cleaned. Instrument calibration was updated to the World Meteorological Organization World Radiation Reference on a yearly base; corrections for instrumental thermal offset and cosine response were made as described by Di Biagio et al. (2010).

The calculation of the daily solar radiation dose (SRD) in the upper mixed layer, was performed as detailed in Vallina and Simo (2007) using the above mentioned daily irradiance measured at Lampedusa, the Mixed Layer Depth (MLD) climatology of the Naval Research Laboratory, and PAR attenuation coefficients from ocean color satellite-derived climatologies (SeaWiFS, http://disc.sci.gsfc.nasa.gov/giovanni/overview/index.html).

2.4. Daily PP estimate

To assess the pelagic primary production within the euphotic layer we used the semi analytical model of Morel (1991), a bio-optical and physiologically based model of the WRDM (Wavelength-Depth-Resolved-Model) type. Combining an atmospheric (Tanré et al., 1979) with a bio-optical model of the water column (Morel, 1988) it gives an estimate of photosynthetic irradiance at the sea surface and within the water column which, joined to a parameterization of the main physiological processes (Morel et al., 1987; Morel, 1991) allows the calculation of daily primary production, starting from the concentration of microalgae biomass. The main remote sensing inputs used by the model are the concentration of chlorophyll-a [CHL MedOC3], the sea surface temperature (SST) and the daily PAR. Starting from the surface concentration of chlorophyll-a the model calculates the chlorophyll profile in the euphotic layer (Morel and Berthon, 1989). After some assumptions and approximations (as discussed by Antoine and Morel, 1996) the computation of daily primary production (PP) has been obtained, through the basic photosynthesis-irradiance relationship (P–E curve) and the following equation:

$$\mathrm{PP} = 12\, a^*_{\max} \phi_{\mu\ \max} \times \int_0^L \int_0^D \int_{400\ \mathrm{nm}}^{700\ \mathrm{nm}} \mathrm{Chl}(z) \mathrm{PUR}(z,t,\lambda) f[x(z,t)] \mathrm{d}t\mathrm{d}z\mathrm{d}\lambda$$

where L indicates the length of day, D is the depth of euphotic layer, $a^*_{\max}$ is the maximum value of specific absorption in the chlorophyll spectrum (about at 435 nm), $\phi_{\mu\ \max}$ is the maximum quantum yield of phototrophic growth, PUR is the fraction of PAR potentially absorbed by all algal species (Morel et al., 1987), while $f(x)$ is a function reproducing the P–E curve, where x is the ratio between PUR and Ek (photo-adaptation irradiance). In the absence of local phytoplankton physiological parameters, these have assumed to be constant and equal to their average value (Antoine and Morel, 1996).

The sea surface temperature (SST) provided by MODIS Aqua is associated with a climatological temperature profile from MODB (Mediterranean Oceanic Data Base) to obtain the temperature vertical profiles (0–200 m). The surface PAR value is used by the model to reconstruct a depth profile of PAR through the average attenuation coefficient of the euphotic layer (Morel and Berthon, 1989). The process of calculating primary production over the entire study area is described by Lazzara et al. (2010). The pelagic primary production in the study area is calculated pixel by pixel starting from Chl, SST, and daily PAR data, and using the bathymetric data. The bathymetry is extracted from one of the same Chl images downloaded from the NASA ocean color website. These images are processed with SeaDAS 6.2, a suite of programs provided by NASA for Ocean Color studies. The bathymetric limit is used to improve the estimates of the primary production integrated in the water column, especially useful to avoid an overestimation in neritic and coastal waters.

The bio-optical model of PP chosen for this study (Morel, 1991; Antoine and Morel, 1996) has been widely validated and extensively used in the world ocean (Antoine et al., 1996) and more specifically in the Mediterranean Sea (Bricaud et al., 2002; Bosc et al., 2004). Besides, a validation of the integrated primary production estimates was performed in the Sicily Channel and Western Mediterranean waters from phytoplankton vertical profiles of variable fluorescence (pump & probe) measured during the spring season (Bohm et al., 1998; Nardello et al., 2004). The data show a good correlation between the daily and vertically integrated PP estimates from the variable fluorescence model and the bio-optical model applied to remotely sensed data.

The P^B index was calculated as the ratio of the integrated values of P (Carbon) and B (Chlorophyll) for the shallower depth between the entire water column and the euphotic layer, as bathymetry can be lower than euphotic layer.

3. Results and discussion

Four annual cycles (2005–2008) of monthly mean Chl, SRD, PP, P^B and MS^- in PM_{10} samples collected at Lampedusa are shown in Fig. 1.

Previous studies performed in the Eastern Mediterranean basin have shown that MS^- reproduces the general pattern of atmospheric DMS; however, in spite of the very low DMS lifetime in the Mediterranean, there is no point to point correlation between DMS and MS^- (Kouvarakis and Mihalopoulos, 2002). For this reason, monthly averages are used in this work. In order to give information on monthly variability the standard deviation calculated over the month is also reported in Fig. 1.

MS^- concentrations maxima are observed in late spring – early summer; whereas Chl concentration peaks in winter. Indeed, our

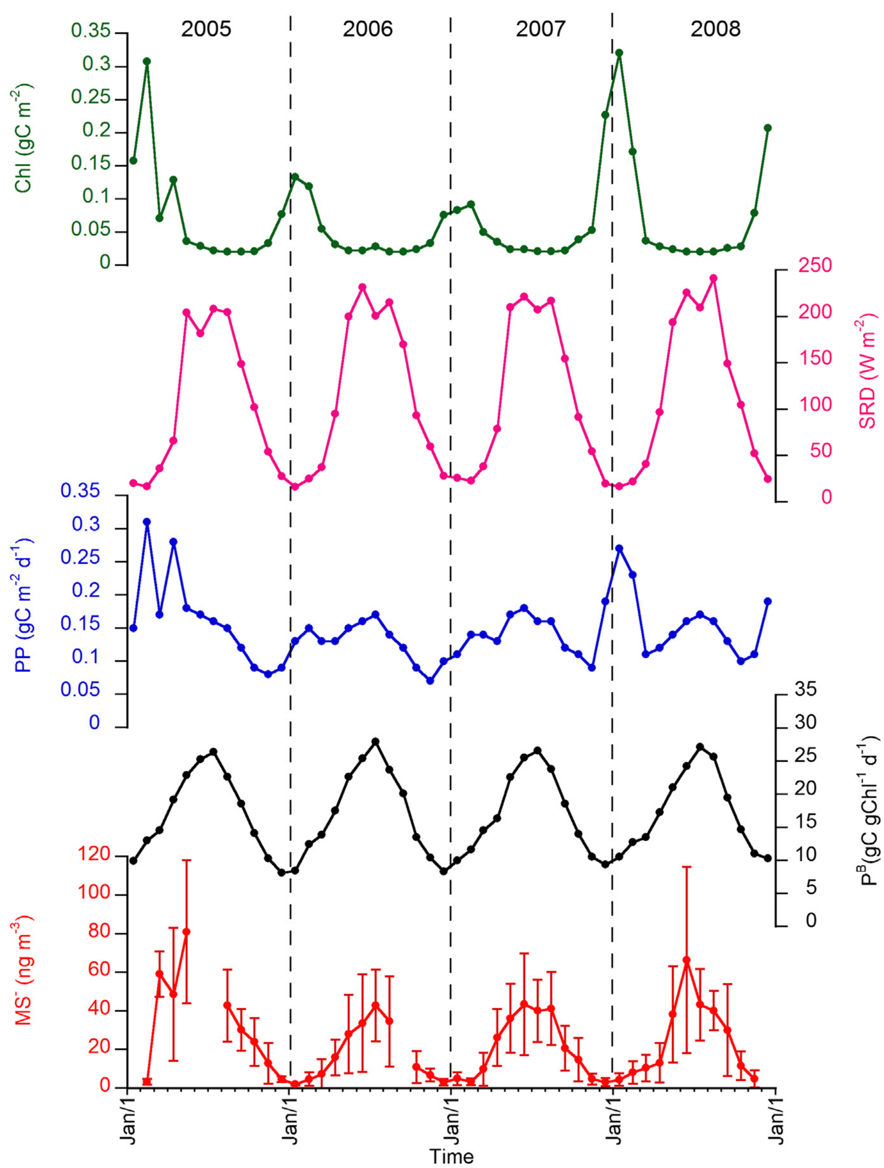

Fig. 1. Temporal evolution of monthly mean Chlorophyll a (green line), solar radiation dose (pink line) primary production (blue line), specific production index (P^B black line), and methanesulfonate in the aerosol (red line) during the years 2005–2008. Vertical lines in MS- profile represent the standard deviation calculated over the month. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

data show an inverse relationship between aerosol MS^- and Chl concentrations around Lampedusa throughout the four years 2005–2008 ($r^2 = 0.66$, not including spring 2005 data), corroborating those observed between DMS and Chl in the Sargasso Sea and in the north western coastal Mediterranean Sea (Toole and Siegel, 2004; Vallina and Simo, 2007).

The summer paradox could be explained by a different phytoplankton composition in summer and/or as a result of phytoplankton stress due to high UV irradiance and low nutrient availability, in turn due to shallow mixed layer depth during this season. Concerning the phytoplankton composition, few data exist for the Sicily Channel; in particular, there are no comprehensive data sets enabling an adequate assessment of the relative contribution of each phytoplankton size-fraction (micro-, nano- and picoplankton) to the assemblage (Siokou-Frangou et al., 2010 and references therein). Nevertheless, several authors reported the dominance of the smallest phytoplankton fractions throughout the year, and especially in summer, since their population growth is favored by the oligotrophic conditions which are typical of this area. During summer the phytoplanktonic assemblages resulted generally dominated by prokaryotes; in particular, *Synechococcus* spp. abundance was high in surface waters (Brunet et al., 2006), while *Prochlorococcus* spp. resulted the most abundant species at deep chlorophyll maximum (DCM) and upwelling (Bohm et al., 1998; Brunet et al., 2007). Among picoeukaryotes, pelagophytes and prymnesiophytes were the most abundant in surface waters (Brunet et al., 2006, 2007). Recently, the substantial contribution of picoeukaryotes to the DMSP production has been outlined by Archer et al. (2010). Thus, the MS^- maximum could be partially explained by the dominant contribution of DMSP producers to the phytoplanktonic assemblage during summer.

The summer increase in atmospheric MS^- concentration (Fig. 1) is also related to the higher solar radiation dose (SRD, in W m^{-2}) in the upper mixed layer (Fig. 2, $r^2 = 0.87$, $n = 40$, $p < 0.001$), as it has been shown for the atmospheric DMS in Vallina and Simo (2007). High levels of UV radiation are typical in summer at Lampedusa, when the daily erythemal dose may exceed 6.5 kJ m^{-2} (Meloni et al., 2005). The relationship between irradiance and DMS production is intricate; it is known that DMSP cleavage to DMS is promoted by high irradiance and UV (Vallina and Simo, 2007).

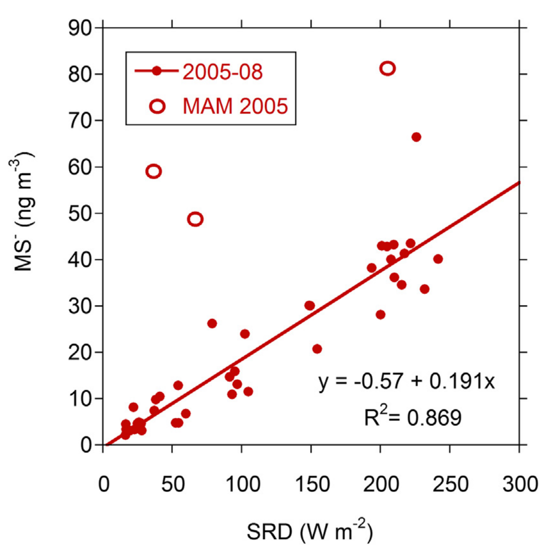

Fig. 2. Monthly average methanesulfonate concentration in aerosol versus solar radiation dose at Lampedusa in the years 2005–2008 (March, April and May 2005 are indicated with empty dots).

Sunda et al. (2002) assessed the antioxidant role of DMSP cleavage products under conditions of acute light stress and the DMS summer paradox has already been linked to high UV, long photoperiods and shallow mixed layer depth (Dacey et al., 1998).

Thus, the observed summer paradox could also be the direct result of a photo-protection mechanism through DMS release, hence stressing its defense role against excessive irradiance (Archer et al., 2010). However, the correlation between the two parameters does not imply a direct correlation. Indeed, several other atmospheric factors, such as DMS sea–atmosphere exchange, DMS oxidation pathways and reaction yield to MS^- in the atmosphere, control the aerosol MS^- concentration in addition to changes in DMS production. All these processes are characterized by a high temporal variability and depend in some way on solar irradiation.

The main factor affecting the DMS atmospheric flux is wind speed. Higher sea surface temperatures in summer than in winter reduce the solubility of the gaseous DMS in seawater, and could contribute to the high concentration of MS^- in summer. However, modeling studies have shown that on global scale DMS sea to air flux is closely related to the DMS sea surface distribution (Kloster et al., 2006 and references therein).

The MS^- formation in the aerosol from DMS in the Mediterranean occurs mainly (80%) by hydroxyl radical (OH) in heterogeneous phase (Mihalopoulos et al., 2007). Due to high solar UV irradiation (e.g., Casasanta et al., 2011), the OH radical shows a very high concentration over the Mediterranean basin in summer, mostly under cloudless condition, favoring photochemical oxidative processes from DMS to MS^-. All these processes have seasonal pattern with summer maxima and contribute to the good correlation between SRD (which is derived from the total irradiance) and MS^-.

Primary production (Fig. 1) shows a more complex seasonal pattern with high values in correspondence of both high phytoplankton biomass and solar radiation. Furthermore PP has no evident and direct relationship with atmospheric MS^-. Conversely, phytoplankton productivity (P^B) shows a seasonal pattern similar to MS^- (Fig. 1) with generally high values in summer correlated with the solar radiation dose peaks.

High primary production values appear related to an unusually high winter-spring bloom (spring 2005 special event). In fact, anomalous high values were observed in spring 2005 for all the considered parameters (Chl, PP, P^B and MS^-). Such an anomaly will be further discussed in Section 3.1.

Excluding the 2005 event, a linear relationship between atmospheric MS^- and the chlorophyll specific production index (P^B) is found (Fig. 3, $r^2 = 0.84$, $n = 40$, $p < 0.001$). Such correlation suggests that DMS production (and the related aerosol MS^-) is not simply related to phytoplankton biomass but to the phytoplankton acclimation processes (numerically expressed by P^B) which in turn, are induced by the variation of stress factors that, in Mediterranean Sea during summer, are mainly light excess and the low thickness of the marine upper mixed layer. The low thickness of the marine upper mixed layer acts in two ways: (i) it prevents the nutrient supply by upwelling waters, and (ii) it is responsible for exposition of phytoplankton cells living in this layer to a higher solar radiation dose.

The correlation between MS^- and P^B is a very important result, suggesting the possibility to experimentally derive P^B by atmospheric parameters and thus allowing the validation of biogeochemical models which could be able to predict phytoplankton growth rates under light and nutrient limitation.

The overall similar evolution of these two quantities is the result of the influence of different complex mechanisms, and not necessarily a mutual dependence, as discussed above. Data which fall outside of the main relationship between MS^- and P^B, such as those

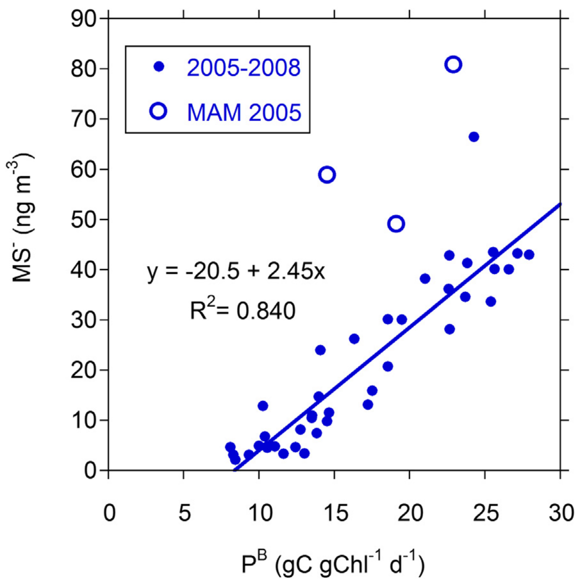

Fig. 3. Monthly average of methanesulfonate concentration in aerosol versus phytoplankton productivity P^B (gC $gChl^{-1}$ d^{-1}) in the seawater around Lampedusa, in the years 2005–2008 (March, April and May 2005 are indicated with empty dots).

discussed in the next section, suggest cases in which specific processes, other than those identified above, play a relevant role. Thus, the found relationship may also be used to identify cases in which other factors are dominant.

3.1. The spring 2005 special event

The correlation between P^B, MS^- and SRD is mainly driven by factors having common seasonal patterns. A relevant exception occurs during spring 2005, when high biomass and PP values are observed in February and April, while MS^- peaks in March and May. In general, during springtime the composition of phytoplankton assemblages is expected to be different with respect to summer, with the largest phytoplanktonic organisms (diatoms, coccolithophores, and dinoflagellates) being dominant in the late winter-spring blooms in the Mediterranean Sea (Siokou-Frangou et al., 2010). However, a relevant contribution by large-size cells to the phytoplankton assemblage was reported by Bohm et al. (1998) in the Sicily Channel during spring 1996 and 1998, when microplanktonic diatoms were the largest fraction in the coastal upwelling. Prymnesiophytes resulted generally widespread and abundant as well, and in particular *E. huxleyi* was the most abundant species offshore (Bohm et al., 1998). Observations made in spring 2007 south of Lampedusa, in the Gulf of Gabes, showed that nanoeukaryotes (chlorophytes, pelagophytes, prymnesiophytes and cryptophytes) accounted for more than 77% of total chlorophyll-a in few offshore stations which were sampled by Bel Hassen et al. (2009). Thus, the available data for this area indicate high spring abundances of the major DMSP producers, i.e. prymnesiophytes (*E. huxleyi*) and small nano-eukaryotic flagellates.

Satellite determinations of particulate inorganic and organic carbon (PIC and POC), obtained through the NASA ocean color data base suggest that a somewhat special spring bloom occurred in 2005 in the Sicily Channel. Observing the SeaWiFS time series data for this area, PIC and POC values are more than twice higher in the first 4 months of 2005 than in the corresponding periods of 2006 and 2007, and nearly twice than in the whole period from 1998 to 2010. It is well known, since the earliest satellite observations, that high PIC values such as those measured in spring 2005 can reveal the presence of a coccolithophorides bloom (Balch et al., 1991; Tyrrell and Merico, 2004) and, as previously stated, coccolithophorides (prymnesiophytes) are known to be efficient DMSP producers.

An exceptionally high spring 2005 maximum in pelagic primary production due to an exceptional phytoplankton bloom was observed also by Olita et al. (2011) in the Algero-Provencal Basin (from the Gulf of Lion to the east coasts of Corse and Sardinia), by means of a satellite-based model. In addition to the anomalies in Chl and PP evolution in winter-spring 2005, also the spring 2005 MS^- displays anomalously high values with respect to the same period of the following years. No information can be derived for summer 2005 for MS^- due to missing data.

SRD and P^B do not show any anomalous features in this spring, and the correlation between these parameters and MS^- is lost for these points (Figs. 2 and 3).

Fig. 4 shows that spring 2005 is characterized by a strong negative North Atlantic Oscillation (NAO) phase. March, April, and May 2005 appear to correspond with an exceptionally hot spring season, due to a prominent extension of the subtropical high over the western Mediterranean basin. The high pressure condition is evidenced by a positive anomaly, recorded over the whole atmospheric column, which presumably leads to strong subsidence cloud free conditions, and weak winds. Fromentin and Planque (1996) suggested that coccolithophorides blooms may be favored by NAO negative index conditions. They suggest that the weak winds associated with a negative NAO index promote the stability of the water column, preventing a deep mixing of surface water, reducing the marine mixing layer depth and by this way producing effects similar to those induced by an increase of SRD.

These steady conditions could have allowed an earlier initiation of the spring bloom, which could have favored the growth of small flagellates and prymnesiophytes instead of diatoms, as found by Irigoien et al. (2000) in the English Channel. This hypothesis could be also supported by findings of high *E. huxleyi* abundances in the Sicily Channel in spring 1996 (Bohm et al., 1998), when the other negative NAO index had been registered (Fig. 4).

As mentioned before, the occurrence of MS^- in the aerosol particles is also related to various atmospheric processes. The meteorological analysis for the 20 days showing the highest MS^- show stagnant atmospheric conditions characterized by a consistent core of positive geopotential height (GPH) and temperature anomalies positioned over the Lampedusa region at all atmospheric levels, and dry air at shallow tropospheric layers (Fig. S1). The MS^- residence time in the atmosphere is expected to increase due to this stagnant condition, leading to an enhanced loading in the marine boundary layer. This mechanism may have produced in spring 2005

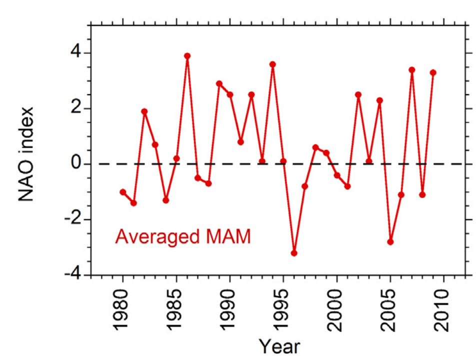

Fig. 4. Time series of March, April, May mean North Atlantic Oscillation index (NAO). NAO Index Data are provided by the Climate Analysis Section, NCAR, Boulder, USA, Hurrell (1995). Updated regularly. Accessed 01 January 2012.

higher MS^- concentrations than usually measured in summer, even if the irradiance promoting the DMS oxidation in the atmosphere is not as high as in summer.

4. Conclusions

Measurements of MS^- in PM_{10} and solar irradiance at Lampedusa, satellite determinations of Chl and SST, and NCEP/NCAR meteorological data were used to derive estimates of PP, and P^B and to assess the influence of biogenic emissions on measured MS^- in the central Mediterranean. Measurements made in the period 2005–2008 were considered.

The MS^- showed in the different years a distinct annual cycle for this area with higher concentration in summer. The summer maximum occurred in correspondence with the maximum of solar radiation. Conversely, Chl and pelagic primary production appeared negatively correlated with MS^- (summer paradox). The summer paradox for the studied area was explained as the combination of seasonal changes in the phytoplankton composition, and phytoplankton stress due to high irradiance (UV–visible) and low nutrient availability associated with a shallow mixed layer depth during summer.

A statistically significant linear relationship between atmospheric MS^- and both the phytoplankton productivity index P^B ($r^2 = 0.84$, $p < 0.001$), and the solar radiation dose ($r^2 = 0.87$, $p < 0.001$) in the upper mixed layer of the sea around Lampedusa was found. These correlations suggest that the MS^- seasonal behavior was mainly related to the phytoplankton physiology (growth rate, photo adaptation), which in turn depends on stress factors (i.e., excess radiation and water column stratification during summer in the Mediterranean).

The occurrence of a linear correlation between MS^- and P^B is a very important result and, although it needs confirmation over an enlarged data set covering a larger marine sector, it suggests the possibility to experimentally derive P^B from atmospheric parameters, thus allowing the validation of biogeochemical model results, and the improvement in their ability to predict phytoplankton growth rates under light and nutrient limitation. Such ability is fundamental for a correct modeling of the ocean carbon cycle at the global scale.

High biomass and PP values were observed in February and April 2005, just one month before unusually high values of atmospheric MS^- (March and May). The high values in this season could be related to the negative phase of North Atlantic Oscillation by two mechanisms driven by stable atmospheric condition: (i) the weak winds over the Mediterranean Sea prevent a strong vertical mixing of the water column, thus reducing the upper mixed layer depth and producing effects similar to an increase of SRD and (2) the stable atmospheric condition determine the accumulation of the newly formed MS^- in the marine boundary layer.

The link between anomalously high MS^- atmospheric concentrations and NAO requires further investigations on an extensive data set. If confirmed, it would imply important consequences on climatic feedbacks which involve sulfur species in the atmospheric aerosol.

Acknowledgments

The study has been partially supported by the Italian Ministry for University and Research through Projects SUMMAMS and RITMARE.

Contributions by Claudia Di Biagio and Francesco Monteleone are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.07.032.

References

Antoine, D., Morel, A., 1996. Oceanic primary production. 1. Adaptation of a spectral light photosynthesis model in view of application to satellite chlorophyll observations. Glob. Biogeochem. Cycles 10, 43–55.
Antoine, D., André, J.M., Morel, A., 1996. Oceanic primary production. 2. Estimation at global scale from satellite (coastal zone color scanner) chlorophyll. Glob. Biogeochem. Cycles 10, 57–69.
Archer, S.D., Ragni, M., Webster, R., Airs, R.L., Geider, R.J., 2010. Dimethyl sulfoniopropionate and dimethyl sulfide production in response to photoinhibition in *Emiliania huxleyi*. Limnol. Oceanogr. 55 (4), 1579–1589.
Artuso, F., Chamard, P., Piacentino, S., Sferlazzo, D.M., De Silvestri, L., di Sarra, A., Meloni, D., Monteleone, F., 2009. Influence of transport and trends in atmospheric CO_2 at Lampedusa. Atmos. Environ. 43, 3044–3051.
Balch, W.M., Holligan, P.M., Ackleson, S.G., Voss, K.J., 1991. Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine. Limnol. Oceanogr. 36 (4), 629–643.
Bardouki, H., Liakakou, H., Economou, C., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Mihalopoulos, N., 2003. Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter. Atmos. Environ. 37, 195–208.
Bates, T.S., Calhoun, J.A., Quinn, P.K., 1992. Variations in the methanesulphonate to sulfate molar ratio in submicrometer marine aerosol particles over the south Pacific Ocean. J. Geophys. Res. 97 (D9), 9859–9865.
Becagli, S., Castellano, E., Cerri, O., Curran, M., Frezzotti, M., Marino, F., Morganti, A., Proposito, M., Severi, M., Traversi, R., Udisti, R., 2009. Methanesulphonic acid (MSA) stratigraphy from a Talos Dome ice core as a tool in depicting sea ice changes and southern atmospheric circulation over the previous 140 years. Atmos. Environ. 43, 1051–1058.
Becagli, S., Ghedini, C., Peeters, S., Rottiers, A., Traversi, R., Udisti, R., Chiari, M., Jalba, A., Despiau, S., Dayan, U., Temara, A., 2011. MBAS (Methylene Blue Active Substances) and LAS (Linear Alkylbenzene Sulphonates) in Mediterranean coastal aerosols: sources and transport processes. Atmos. Environ. 45, 6788–6801.
Behrenfeld, M.J., Boss, E., 2003. The beam attenuation to chlorophyll ratio: an optical index of phytoplankton physiology in the surface ocean? Deep-Sea Res. P I 50, 1537–1549.
Behrenfeld, M.J., Boss, E., Siegel, D.A., Shea, D.M., 2005. Carbon-based ocean productivity and phytoplankton physiology from space. Glob. Biogeochem. Cycles 19 (1), GB1006. http://dx.doi.org/10.1029/2004GB002299.
Bel Hassen, M., Drira, Z., Hamza, A., Ayadi, H., Akrout, F., Messaoudi, S., Issaoui, H., Aleya, L., Bouaïn, A., 2009. Phytoplankton dynamics related to water mass properties in the Gulf of Gabes: ecological implications. J. Mar. Sys. 75, 216–226.
Bosc, E., Bricaud, A., Antoine, D., 2004. Seasonal and interannual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of SeaWiFS observations. Glob. Biogeochem. Cycles 18, GB1005. http://dx.doi.org/10.1029/2003GB002034.
Bohm, E., Buongiorno Nardelli, B., Brunet, C., Casotti, R., Conversano, F., Corato, F., D'Acunzo, E., D'Ortenzio, F., Iudicone, D., Lazzara, L., Mangoni, O., Marcelli, M., Marullo, S., Massi, L., Mori, G., Nardello, I., Nuccio, C., Ribera d'Alcala, M., Saggiomo, V., Santoleri, R., Scardi, M., Sparnocchia, S., Tozzi, S., Zoffoli, S., 1998. SYMPLEX experiment: first results on oceanic mesoscale dynamics and related primary production from AVHRR and SeaWiFS satellite data and field experiments. In: EOS 5th Eur Symp Aeropsace Remote Sensing, 21–24 September, Barcelona. SPIE, 3496, pp. 137–149.
Bricaud, A., Bosc, E., Antoine, D., 2002. Algal biomass and sea surface temperature in the Mediterranean Basin. Intercomparison of data from various satellite sensors, and implications for primary production estimates. Remote Sens. Environ. 81, 163–178.
Brunet, C., Casotti, R., Vantrepotte, V., Conversano, F., 2007. Vertical variability and diel dynamics of picophytoplankton in the Strait of Sicily, Mediterranean Sea, in summer. Mar. Ecol. Prog. Ser. 346, 15–26.
Brunet, C., Casotti, R., Vantrepotte, V., Corato, F., Conversano, F., 2006. Picophytoplankton diversity and photoacclimation in the Strait of Sicily (Mediterranean Sea) in summer. I. Mesoscale variations. Aquat. Microb. Ecol. 44, 127–141.
Casasanta, G., di Sarra, A., Meloni, D., Monteleone, F., Pace, G., Piacentino, S., Sferlazzo, D., 2011. Large aerosol effects on ozone photolysis in the Mediterranean. Atmos. Environ. 45, 3937–3943.
Charlson, R., Lovelock, J.E., Andreae, M.O., Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326 (6114), 655–661.
Di Biagio, C., di Sarra, A., Meloni, D., 2010. Large atmospheric shortwave radiative forcing by Mediterranean aerosol derived from simultaneous ground-based and spaceborne observations, and dependence on the aerosol type and single scattering albedo. J. Geophys. Res. 115, D10209. http://dx.doi.org/10.1029/2009JD012697.
Dacey, J.W.H., Howse, F.A., Michaels, A.F., Wakeham, S.G., 1998. Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea. Deep Sea Res. I 45 (12), 2085–2104.

di Sarra, A., Di Biagio, C., Meloni, D., Monteleone, F., Pace, G., Pugnaghi, S., Sferlazzo, D., 2011. Shortwave and longwave radiative effects of the intense Saharan dust event of 25–26 March, 2010, at Lampedusa (Mediterranean sea). J. Geophys. Res. 116, D23209. http://dx.doi.org/10.1029/2011JD016238, 2011.

D'Ortenzio, F., Marullo, S., Ragni, M., d'Alcala, M.R., Santoleri, R., 2002. Validation of empirical SeaWiFS algorithms for chlorophyll-alpha retrieval in the Mediterranean Sea – a case study for oligotrophic seas. Remote Sens. Environ. 82 (1), 79–85.

Field, C.B., Beherenfeld, M.J., Randerson, J.T., Falkowski, P., 1998. Primary production of the Biosphere: integrating terrestrial and oceanic components. Science 281 (5374), 237–240. http://dx.doi.org/10.1126/science.281.5374.237.

Friedrichs, M.A.M., et al., 2008. Assessing the uncertainties of model estimates of primary productivity in the tropical Pacific Ocean. J. Mar. Syst.. http://dx.doi.org/10.1016/j.marsys.2008.05.010.

Fromentin, J.M., Planque, B., 1996. Calanus and environment in the eastern North Atlantic. II. Influence of the North Atlantic Oscillation on *C. finmarchicus* and *C. helgolandicus*. Mar. Ecol. Prog. Ser. 134, 111–118.

Hill, R., White, B., Cottrell, M., Dacey, J.H., 1998. Virus-mediated total release of dimethylsulfoniopropionate from marine phytoplankton: a potential climate process. Aquat. Microb. Ecol. 14 (1), 1–6.

Hurrell, J.W., 1995. Decadal trends in the North Atlantic Oscillation: regional temperatures and precipitation. Science 269, 676–679.

Irigoien, X., Harris, R.P., Head, R.N., Harbour, D., 2000. North Atlantic Oscillation and spring bloom phytoplankton composition in the English Channel. J. Plankton Res. 22 (12), 2367–2371.

Kahru, M., Kudela, R., Manzano-Sarabia, M., Mitchell, B.G., 2009. Trends in primary production in the California Current detected with satellite data. J. Geophys. Res. 114, C02004. http://dx.doi.org/10.1029/2008JC004979.

Kaufman, Y.J., Tanre, D., Boucher, O., 2002. A satellite view of aerosols in the climate system. Nature 419 (6903), 215–223.

Keller, M.D., Korjeff-Bellows, W., 1996. Physiological aspects of the production of dimethylsulfoniopropionate (DMSP) by marine phytoplankton. In: Kiene, R.P., Visscher, P.T., Keller, M.D., Kirst, G.O. (Eds.), Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds. Plenum Press, New York, pp. 131–142.

Keller, M.D., Bellows, W.K., Guillard, R.R.L., 1989. Dimethylsulfide production in marine phytoplankton. In: Saltzman, E.S., Cooper, W.J. (Eds.), Biogenic Sulphur in the Environment, Am. Chem. Soc. Symp. Ser., vol. 393, pp. 167–182,. Washington, D.C.

Kettle, A.J., Andreae, M.O., 2000. Flux of dimethylsulfide from the oceans: a comparison of updated data sets and flux models. J. Geophys. Res. 105 (D22), 26,793–26,808.

Kiene, R.P., Linn, L.J., Bruton, J.A., 2000. New and important roles for DMSP in marine microbial communities. J. Sea Res. 43, 209–224.

Kloster, S., Feichter, J., Maier-Reimer, E., Six, K.D., Stier, P., Wetzel, P., 2006. DMS cycle in the marine ocean-atmosphere system – a global model study. Biogeosciences 3, 29–51. SRef-ID: 1726-4189/bg/2006-3-29.

Kouvarakis, G., Mihalopoulos, N., 2002. Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulphate in the aerosol phase in the Eastern Mediterranean atmosphere. Atmos. Environ. 36, 929–938.

Laroche, D., Vezina, A.F., Levasseur, M., Gosselin, M., Stefels, J., Keller, M.D., Matrai, P.A., Kwint, R.L.J., 1999. DMSP synthesis and exudation in phytoplankton: a modeling approach. Mar. Ecol. Prog. Ser. 180, 37–49.

Lazzara, L., Marchese, C., Massi, L., Nuccio, C., Maselli, F., Santini, C., Pieri, M., Sorani, V., 2010. Sub-regional patterns of primary production annual cycle in the Ligurian and North Tyrrhenian seas, from satellite data. Ital. J. Remote Sens. 42 (2), 87–102.

Mateos, D., di Sarra, A., Meloni, D., Di Biagio, C., Sferlazzo, D.M., 2011. Experimental determination of cloud influence on the spectral UV radiation and implications for biological effects. J. Atmos. Solar Terr. Phys. 73, 1739–1746.

Meloni, D., di Sarra, A., Herman, J.R., Monteleone, F., Piacentino, S., 2005. Comparison of ground-based and Total Ozone Mapping Spectrometer erythemal UV doses at the island of Lampedusa in the period 1998–2003: role of tropospheric aerosols. J. Geophys. Res. 110, D01202. http://dx.doi.org/10.1029/2004JD005283.

Meloni, D., di Sarra, A., Pace, G., Monteleone, F., 2006. Optical properties of aerosol over the central Mediterranean. 2. Determination of single scattering albedo at two wavelengths for different aerosol types. Atmos. Chem. Phys. 6, 715–727.

Mihalopoulos, N., Kerminen, V.M., Kanakidou, M., Berresheim, H., Sciare, J., 2007. Formation of particulate sulphur species (sulphate and methanesulphonate) during summer over the Eastern Mediterranean: a modeling approach. Atmos. Environ. 41, 6860–6871.

Morel, A., 1988. Optical modelling of the upper ocean in relation to its biogenous matter content (case I waters). J. Geophys. Res. 93 (C9), 10,749–10,768.

Morel, A., 1991. Light and marine photosynthesis: a spectral model with geochemical and climatological implications. Prog. Oceanogr. 26, 263–306.

Morel, A., Lazzara, L., Gostan, J., 1987. Growth rate and quantum yield time response for a diatom to changing irradiances (energy and color). Limnol. Oceanogr. 32 (5), 1066–1084.

Morel, A., Berthon, J.F., 1989. Surface pigments, algal biomass profiles, and potential production of the euphotic layer: relationships reinvestigated in view of remote-sensing applications. Limnol. Oceanogr. 34, 1545–1562.

Nardello, I., Marcelli, M., e Lazzara, L., 2004. Stime di biomassa e produzione primaria nel Canale di Sicilia, attraverso misure di fluorescenza in vivo della clorofilla a. In: Casagrandi, R., Melià, P. (Eds.), Ecologia. Atti XIII Congresso Nazionale della Società Italiana di Ecologia, p. S11.8. Aracne, Roma, S.It.E. Atti XXVII.

Olita, A., Sorgente, R., Ribotti, A., Fazioli, L., Perilli, A., 2011. Pelagic primary production in the Algero-Provençal Basin by means of multisensor satellite data: focus on interannual variability and its drivers. Ocean Dyn. 61, 1005–1016.

Orellana, M.V., Matrai, P.A., Janer, M., Rauschenberg, C.D., 2011. Dimethylsulfoniopropionate storage in Phaeocystis (Prymnesiophyceae) secretory vesicles. J. Phycol. 47, 112–117.

Santoleri, R., Volpe, G., Marullo, S., Buongiorno Nardelli, B., 2008. Open waters optical remote sensing of the Mediterranean Sea. In: Barale, V., Gade, M. (Eds.), Remote Sensing of the European Seas. Springer, Netherlands, pp. 103–116. http://dx.doi.org/10.1007/978-1-4020-6772-3. Part 2.

Sathyendranath, S., Stuart, V., Nair, A., Oka, K., Nakane, T., Bouman, H., Forget, M.H., Maas, H., Platt, T., 2009. Carbon-to-chlorophyll ratio and growth rate of phytoplankton in the sea. Mar. Ecol. Prog. Ser. 383, 73–84.

Siokou-Frangou, I., Christaki, U., Mazzocchi, M.G., Montresor, M., Ribera d'Alcalà, M., Vaqué, D., Zingone, A., 2010. Plankton in the open Mediterranean Sea: a review. Biogeosciences 7, 1543–1586.

Sunda, W., Kleber, D.J., Kiene, R.P., Huntsman, S., 2002. An antioxidant function for DMSP and DMS in marine algae. Nature 418, 317–320.

Tanré, D., Herman, M., Deschaps, P.Y., De Leffe, A., 1979. Atmospheric modelling for space measurements of ground reflectances, including bidirectional properties. Appl. Opt. 18, 3587–3594.

Taylor, B.F., Visscher, P.T., 1996. Metabolic pathways involved in DMSP degradation. In: Kiene, R.P., Visscher, P.T., Keller, M.D., Kirst, G.O. (Eds.), Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds. Plenum, New York, pp. 265–276.

Toole, D.A., Siegel, D.A., 2004. Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: closing the loop. Geophys. Res. Lett. 31, L09308. http://dx.doi.org/10.1029/2004GL019581.

Tyrrell, T., Merico, A., 2004. *Emiliania huxleyi*: bloom observations and the conditions that induce them. In: Thierstein, H.R., Young, J. (Eds.), Coccolithophores: from Molecular Processes to Global Impact. Springer, Berlin, pp. 75–97.

Vallina, S.M., Simo, R., 2007. Strong relationship between DMS and the Solar Radiation Dose over the global Surface Ocean. Science 315, 506–508.

Vila-Costa, M., Simo, R., Harada, H., Gasol, J.M., Slezak, D., Kiene, R.P., 2006. Dimethylsulfoniopropionate uptake by marine phytoplankton. Science 314, 652–654.

Volpe, G., Santoleri, R., Vellucci, V., Ribera d'Alcalà, M., Marullo, S., D'Ortenzio, F., 2007. The colour of the Mediterranean Sea: global versus regional bio-optical algorithms evaluation and implication for satellite chlorophyll estimates. Remote Sens. Environ. 107 (4), 625–638.

Wolfe, G.V., Steinke, M., 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. Limnol. Oceanogr. 41, 1151–1160.

Wolff, E.W., et al., 2006. Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles. Nature 440, 491–496. http://dx.doi.org/10.1038/nature04614.

Zhuang, G., Yang, G., Yu, J., Gao, Y., 2011. Production of DMS and DMSP in different physiological stages and salinity conditions in two marine algae. Chin. J. Oceanogr. Limnol. 29 (2), 369–377.