

## Long-term measurements of carbonaceous aerosols in the Eastern Mediterranean

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Even though, carbonaceous material (organic and elemental carbon) constitutes an important fraction of aerosol mass, its role in the Mediterranean atmosphere is yet to be unraveled. This study focuses on 12 years aerosol measurements (2001-2013) at Finokalia, a remote area representative of the E. Mediterranean. Filters were analyzed for Organic Carbon (OC), Elemental Carbon (EC), Water Soluble Organic Carbon (WSOC) and main ions.

Organic matter constitutes an important part of the total PM<sub>10</sub> mass (approximately 20%). The median OC to EC ratios exceeded 2, 6.58 in winter and 6.66 in summer, indicating that OC was mostly secondary. Calculated Secondary Organic Carbon (SOC) percentages were found to exceed 80% of the total carbon and showed no seasonal variability between summer and winter. The latter suggesting the presence of “aged” aerosols, all over the year, as confirmed by recent continuous measurements with aerosol mass spectrometer.

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## 1 Introduction

Atmospheric aerosol particles can be emitted either directly by anthropogenic and natural sources (dust, sea salt, soot, biological particles, etc.), or they are formed in the atmosphere by condensation of low volatility compounds (e.g. sulfuric acid or oxidized organic compounds) (Andreae and Rosenfeld 2008).

Carbonaceous aerosols are classified into two types, organic carbon (OC) and elemental carbon (EC). A significant and at times major (20-90%) mass fraction of the submicron aerosol is represented by organic species (Kanakidou et al. 2005). OC is emitted directly as primary particulate matter but is also secondary, formed by chemical reactions of volatile organic compounds in the atmosphere (Seinfeld and Pandis 1998). EC is emitted directly in the particulate phase and is a good tracer of combustion processes (fossil fuel and biomass burning).

To evaluate the contribution of carbonaceous material in the aerosol mass and identify their sources over the Mediterranean, PM<sub>10</sub> samples were collected over a 12-year period at Finokalia, a remote area representative of the E. Mediterranean. The aerosol samples were analyzed for organic, elemental carbon, dissolved organic carbon and main anions and cations.

## 2 Data and Methodology

PM<sub>10</sub> (bulk) samples were collected on Quartz filters (QMA, 47mm, Whatman and Flex Tissuquartz, 2500QAT-UP 47mm, Pall) at Finokalia monitoring station with an average sampling time of 1-3days per week during the period September 2001 to December 2013. OC and EC analyses were performed for a total of 1907 samples. For WSOC samples were analyzed from April 2009 to March 2010.

### 2.1 Data

Sampling was performed at approximately 3m above the ground. The sampling site of Finokalia is characterized as a natural background site, located at a central position in the Mediterranean Basin, relatively far from natural (Sahara) and anthropogenic sources. Consequently, the data from this site could be considered as representative of the open Eastern Mediterranean Sea.

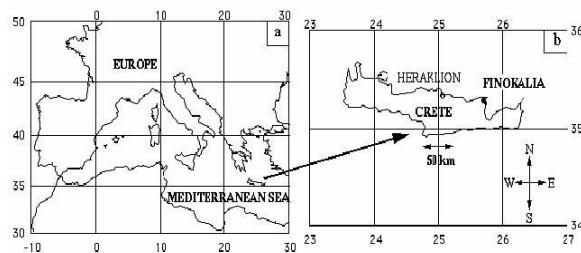


Fig. 1. The location of the sampling site at Finokalia (35°20'N, 25°40'E).

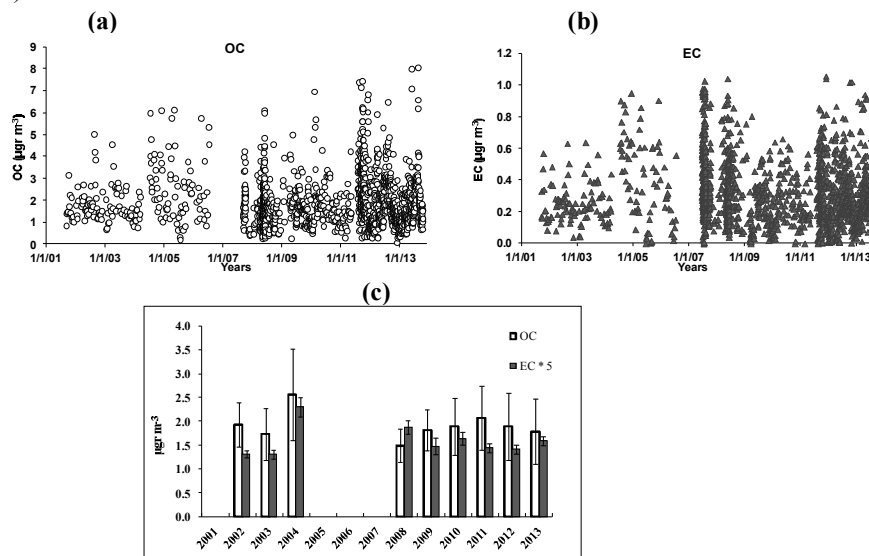
### 2.2 Methodology

A Sunset Laboratory OC/EC Analyzer (Birch and Cary 1996) was used to analyze all filters for OC and EC, while WSOC was determined using an OC analyzer (TOC-VCSH, Shimadzu) as described in details by Theodosi et al. (2010). The particulate organic matter (POM) was estimated by multiplying the measured OC by a conversion factor (CF) of 2.1, corresponding to the ratio of organic mass to organic carbon in the region.

### 3 Results

Daily and annual variations of OC and EC for the whole sampling period from 2001 to 2013 are presented in Figure 2. OC and EC concentrations correlate well throughout the year, showing similar trends for maximum and minimum values (slope=6.1,  $R^2=0.3$ ,  $n=1867$ ).

Fig. 2c shows the annual mean OC and EC concentrations ( $\mu\text{g m}^{-3}$ ). As observed for the whole sampling period OC and EC concentrations remain almost constant through the sampling period (only years with sampling coverage higher or equal to 60% were considered for this analysis).



**Fig. 2.** (a) Daily OC, (b) daily EC and (c) variation of the annual mean PM<sub>10</sub> levels collected at Finokalia Station (2001-2013).

For both OC and EC there is a net seasonal variability with higher values during the warm and lower during the cold season (Figure 2, 3). For OC the increase during the warm season can be explained by enhanced photochemistry, absence of precipitation and biomass burning events during summer (Sciare et al. 2008). The same behavior with spring/summer maxima and winter minima is also observed for EC. However, two maxima can be clearly seen: One in spring (April-May) and the second in August, in agreement with Sciare et al. (2008) observations. These authors explained the presence of these two maxima in EC concentrations by biomass burning activities in NE countries and especially Ukraine and countries of former Soviet Union and subsequent transport of pollution to our site by the northerlies.

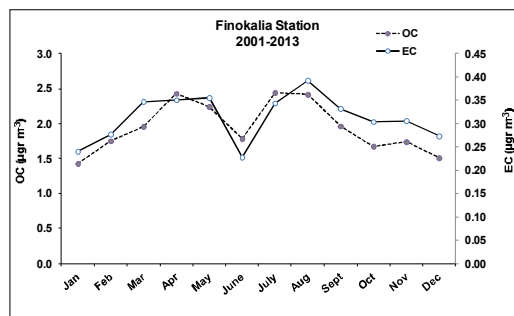


Fig. 3. Monthly average variations of OC and EC ( $\mu\text{g m}^{-3}$ ) in Finokalia for the studied period 2001-2013.

The substantial formation of secondary organic carbon is also indicated by the values of the OC/EC ratio which was higher than 2 (Favez et al. 2008). On an annual basis and for the entire sampling period 2001-2013, median OC/EC ratios both in winter (6.58) and summer (6.66) were significantly higher than 2 indicating considerable contribution of SOC at our site. It is noteworthy that OC/EC ratio remains constant all year-long (Fig. 4) without any clear seasonal pattern suggesting the absence of primary sources at our site and that aged and processed aerosol accounts for the majority of OC (see below). This result was also confirmed by recent continuous measurements with aerosol mass spectrometer.

Secondary Organic Carbon (SOC) was calculated by using the equation ( $\text{SOC} = \text{OC} - (\text{OC}/\text{EC})_{\text{primary}} * \text{EC}$ ) described by Turpin and Huntzicker (1995), where the  $\text{OC}/\text{EC}_{\text{primary}}$  ratio was set equal to 1. SOC percentages were equal to  $83.6 \pm 6.1\%$  without any significant seasonal variability (winter 84.3%, summer 85.7%), further supporting the processed nature of the aerosol all year round (Fig. 5a, b). The average concentration of WSOC was equal to  $0.86 \pm 0.62 \mu\text{g m}^{-3}$  with higher values during summer compared to winter, 1.00 and  $0.73 \mu\text{g m}^{-3}$  respectively. During summer the WSOC/OC ratio was equal to 0.53, indicating the existence of secondary OC with oxygen containing functional groups, which increase water solubility. This ratio decreased during winter (0.47), due to the weak photochemical oxidation. However WSOC levels were significantly smaller compared to SOC indicating that only a part of SOC (about 60%) is soluble.

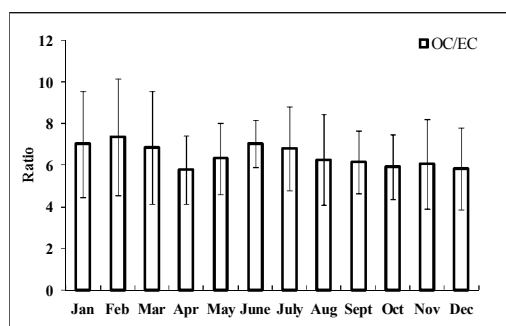


Fig. 4. The OC/EC ratio at Finokalia from 2001 to 2013.

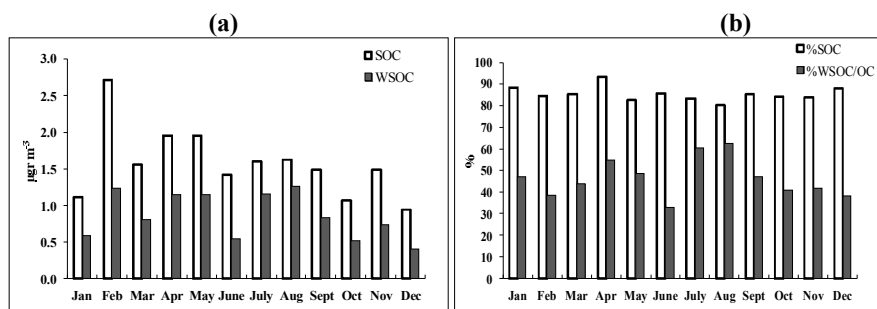


Fig. 5. (a) Monthly average concentrations of SOC and WSOC in  $\mu\text{g m}^{-3}$  and (b) percentages of SOC and WSOC/EC.

OC may be formed by gas-to-particle conversion processes in the atmosphere and, as EC, it can also originate from biomass burning and fossil fuel burning, whilst  $K^+$  comes only from biomass burning. Thus,  $K^+$  has been used as a biomass-burning tracer and the nss- $K^+$  to OC and EC ratios have been proposed as indicators of the relative contributions of biomass and fossil-fuel burning. The median nss- $K^+$ /OC ratio at Finokalia equals 0.06 (0.07±0.05). It is comparable to ratios reported for agricultural residue burning (0.04-0.13) and charcoal burning (0.08) and higher than those for biofuel burning (0.01; Andreae and Merlet, 2001). The nss- $K^+$ /EC ratio at Finokalia of 0.36 was in the range of ratios reported for agricultural residue burning (0.23-0.52) and higher than those reported for charcoal (0.27) and biofuel burning (0.06-0.18). Thus, in the region OC and EC are emitted from similar sources with significant contribution from biomass combustion.

Finally, organic matter as calculated for the period 04/2009-05/2011 accounts for a significant part of the total  $PM_{10}$  mass, ranging from 21.3±9.6% for Particulate Organic Matter and 1.44±0.88 % for EC.

## 4 Conclusions

This study reports on carbonaceous measurements of aerosols in the Eastern Mediterranean Sea on a 12-year basis (2001 – 2013). Carbonaceous matter constitutes a significant part of the total  $PM_{10}$  mass (21.3±9.6% POM and 1.44±0.88% EC).

OC, EC concentrations present similar seasonal trend with higher values during the warm season. High OC/EC ratios and increased SOC values throughout the year can be explained by the absence of primary local sources contribution and they reflect the presence of “aged” aerosols that have been subject to all possible chemical evolution before arriving to our site. The examination of the OC and EC ratios with nss- $K^+$  showed significant contribution from biomass burning.

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## **Relationship between atmospheric circulation types and storm surges over the Greek seas.**

**Tolika K., Anagnostopoulou C., Krestenitis Y.**

Using a flexible automatic circulation type classification scheme, an attempt is made to study and analyze the atmospheric circulation over Greece, during the days when storm surges were detected. This classification scheme provides daily circulation type calendars (with five anticyclonic and seven cyclonic types). The center of this classification was chosen to be at the center of the Aegean Sea. Sixteen cases of storm surges were observed over Greece from 2005 until 2012 in different parts of the domain of study. The first results showed, that in all cases, during the day of the storm surge, only cyclonic types are observed over Greece, with the cyclonic type C (centered over Greece) to prevail with a percentage of 38%, followed by the cyclonic type Cne (at the northeast of Greece) with a percentage of 25%. One day before the storm surge event, the percentages of the prevailing cyclonic type do not seem to change much (C (38%) and Cne (31%)). However, it is worth mentioning the two days before the event, the cyclonic circulation type Cne is the one presenting the highest percentage (44%).

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