Carbonaceous Aerosols Over the Mediterranean and Black Sea

C. Theodosi, D. Smouliotis, P. Zarmpas, M. Kocak, and N. Mihalopoulos

Abstract The role of carbonaceous material (organic and elemental carbon) in the Mediterranean and Black sea atmosphere is yet to be unraveled. To fill this gap the present work is focused on the study of carbonaceous aerosols over the Mediterranean and Black Sea. Thus, aerosol samples were simultaneously collected at a remote site in Greece (Finokalia, Crete), a highly populated urban (Istanbul), a remote (Imbros) and two rural sites in Turkey (Sinop, Erdemli). Approximately 1,200 aerosol samples were collected and analyzed for Organic and elemental carbon (OC and EC), as well as water-soluble organic carbon (WSOC). Their seasonal variation, the factors controlling their variation and their relative contribution to aerosol mass is presented and thoroughly discussed. More specifically, organic matter constitutes a significant part of the total PM_{10} mass (21–33% of Particulate Organic Matter and 2–11% EC). The percentage of WSOC ranges from 37% to 40% of the OC for the four remote and rural regions, while in Istanbul constitutes 27% of OC and 10% of the total PM_{10} mass. Correlations with potassium and sulfate showed that the sources of organic matter in Istanbul are mainly due to the anthropogenic activities, while in rural and suburban areas to long range transport and biomass burning.

1 Introduction

Aerosols in the atmosphere arise from natural sources, such as windborne dust, sea-spray, volcanoes, and from anthropogenic activities, such as combustion of fossil fuels (Seinfeld and Pandis 1998). They are introduced into the atmosphere

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either directly (primary aerosols) or as a product of gaseous reactions in the atmosphere (secondary aerosols) and they play a significant role in the climate forcing.

Carbonaceous aerosols constitute an important fraction of aerosol mass and are classified into two types, elemental carbon (EC) and organic carbon (OC). EC is produced during incomplete combustion and emitted directly in the particle phase, whereas OC is not only emitted directly in particulate matter (primary) but it also forms by chemical reaction of volatile organic compounds in the atmosphere (secondary; Seinfeld and Pandis 1998). In general, secondary organic aerosol (SOA) compounds are water-soluble because they have polar functional groups (e.g. hydroxyl, carbonyl and carboxyl) produced by the oxidation reaction (Saxena and Hildemann 1996). Secondary OC can therefore be considered to be water-soluble organic carbon (WSOC), which in atmospheric particles influences aerosol behavior inside respiratory tracts and wet-scavenging processes in the atmosphere (Saxena and Hildemann 1996).

To evaluate the significance of carbonaceous material in the chemical composition of aerosols and identify their sources over the Mediterranean and the Black Sea, PM_{10} samples have been collected at five different locations around the two basins, during one year period. The aerosol samples were analyzed for organic, elemental carbon and dissolved organic carbon and main anions and cations.

2 Data and Methodology

PM_{10} particles were collected on Quartz filters (Quartz filter, QMA, 47 mm, Whatman) at five different sampling sites (Finokalia, Imbros, Erdemli, Sinop and Istanbul) on the frame of CITYZEN project, using a constant flow (16 L/min) Genk type sampler.

Sampling was conducted within the period April 2009–February 2010, with a 24-h sampling frequency, covering approximately more than 95% of each month.

2.1 Data

A map indicating the location of the aforementioned regions across the Mediterranean and Black Sea are depicted in Fig. 1.

2.2 Methodology

All filters were analyzed for Organic and elemental carbon (OC and EC), with the Thermal-Optical Transmission (TOT) technique (Birch and Cary 1996), using

Fig. 1 Location of the sampling sites: Finokalia (35°20′N, 25°40′E), Istanbul (41.12°N, 29.00°E), Erdemli (36.56°N, 34.25°E), Imbros (40.23°N, 254.90°E), Sinop (42.04°N, 35.04°E)

a Sunset Laboratory OC/EC Analyzer, while water-soluble organic carbon (WSOC) using an organic carbon analyser (TOC-VCSH, Shimadzu) as described in details by Theodosi et al. 2010. Water insoluble organic carbon (WIOC) concentrations were also calculated by subtracting WSOC concentrations from OC concentrations (WIOC = OC–WSOC). Secondary Organic Carbon (SOC) was determined by subtracting the OC/EC primary ratio multiplied by the EC concentrations from OC concentrations ($SOC = OC-(OC/EC)_{primary}*EC$ by Turpin and Huntzicker (1995), where the $OC/EC_{primary}$ ratio defined as the OC/EC from combustion sources and equal to 1). The particulate organic matter (POM) was estimated by multiplying the measured OC by a conversion factor (CF), which corresponds to the ratio of organic mass to organic carbon and depending on the site varies between 1.4 and 1.8 (Sciare et al. 2005).

3 Results

The OC, EC temporal variation (n = 260), representatively for Erdemli, one out of the five sampling sites are presented in Fig. 2.

Both OC and EC in the region of Finokalia, Istanbul, Sinop and Erdemli depict a distinct seasonal variability characterized by summer minimum and winter maximum concentrations, while in the region of Imbros the opposite seasonal variability is observed (Fig. 3).

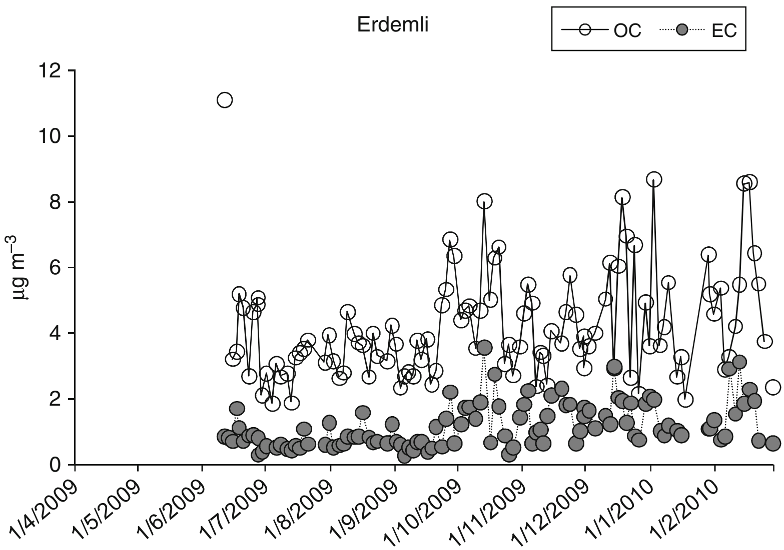

Fig. 2 Daily variation of OC and EC for PM_{10} levels collected at Erdemli

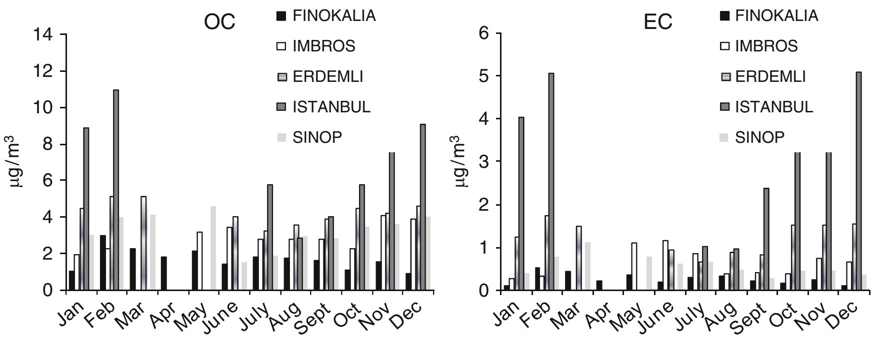

Fig. 3 Monthly average variations of OC and EC for all sampling sites in this study

The OC to EC carbon ratios, which are used to identify the presence of primary organic aerosols, indicate that in the case of Finokalia and Imbros (with OC/EC ratios exceeding 2; 3.2 and 2.3, respectively) OC is mostly secondary, whilst primary in Istanbul (OC/EC = 1.7).

The SOC percentages are higher for Finokalia, Sinop, Imbros and Erdemli (average 79%) than Istanbul's (average 53%) as presented in Fig. 4 (left). The low value of the Istanbul ratio underlines the major role of uncontrolled traffic-related or/and industrial originated emissions in Istanbul, as documented by Theodosi et al. (2010).

The determination of WSOC, WIOC and other elements can provide additional information regarding the carbon sources, such as the presence of secondary OC

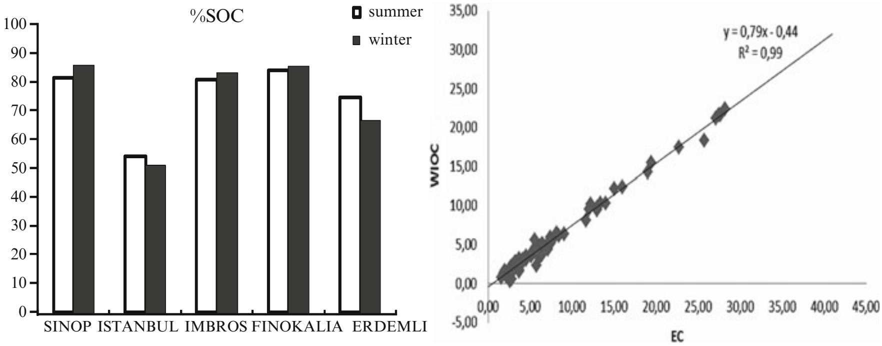

Fig. 4 The %SOC and WSIOC/EC ratio for Istanbul for summer and winter for all sampling sites, respectively

and primary emissions using WSOC and WIOC as indicators respectively (Theodosi et al. 2010).

A good correlation between WIOC and EC ($r^2 = 0.99$) was found in Istanbul indicating the influence of fossil fuel primary emissions (Fig. 4, right).

The WSOC to OC ratio in Istanbul during summer was found to be 0.36, slightly higher than the one observed in Cairo (0.33; Favez et al. 2008) indicating the existence of secondary (oxidised and more soluble) organic species, which increase water solubility. This ratio decreased during winter (0.25), due to the lack of photochemical oxidation, as well as to less wet depositional losses of WSOC relative to the insoluble carbon in winter (Kleefeld et al. 2002).

In addition the regression of OC and EC with no-sea-salt Potassium, showed that carbonaceous sources are mainly due to combustions of fossil-fuel especially those linked to traffic and vehicular exhausts. Moreover, during winter additional sources like household heating contribute to the total carbon loadings. In Sinop the main source of carbonaceous aerosol is biomass burning.

The total organic mass and the elemental carbon constitute a significant part in the PM_{10} mass of the measured samples (30% of POM and 11% EC in Istanbul, 33% of POM and 5% of EC in Imbros), while in Sinop and in Erdemli of relatively least (23% of POM and 2% of EC, 21% POM and 4% EC respectively).

4 Conclusions

This study reports on carbonaceous measurements of aerosols in the Mediterranean and Black Sea.

The average concentrations of OC and EC at Istanbul was much higher than the concentrations measured at the other sampling sites due to the abundance of anthropogenic sources at the greater Istanbul area.

OC and EC at Finokalia, Istanbul, Sinop and Erdemli demonstrate a clear seasonal variation with a minimum during summer and a maximum during winter.

In the case of Imbros the opposite tendency is observed. This can be explained by the fact that the aforementioned sampling site is located downwind of Istanbul, where the increased urbanization of megacities such as Istanbul can affect neighboring sites.

Regarding the carbonaceous composition, organic matter constitutes a significant part of the total mass of PM_{10} (21–33% POM and 2–11% EC). The percentage of WSOC ranges from 37% to 40% of the OC for the four remote regions, while in Istanbul constitutes 27% of OC and 10% of the total PM_{10} mass.

The correlation between OC and EC with no-sea-salt Potassium and with other ions (NO_3^-, Ox^-, SO_4^{2-}), showed that the sources of the OC and EC in Istanbul are due to combustions of fossil-fuels and vehicular exhausts, while in Sinop from biomass burning.

SOC values are higher in Finokalia, Sinop, Imbros and Erdemli than Istanbul's, reflecting the abundance of direct sources of pollution at the greater Istanbul area.

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