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A two-year database of BC measurements at the biggest European crude oil pre-treatment plant: a comparison with organic gaseous compounds and PM_{10} loading

Mariarosaria Calvello [a,*], Francesco Esposito [b], Marina Lorusso [a], Giulia Pavese [a]

[a] IMAA, Istituto di Metodologie per l'Analisi Ambientale, CNR, C. da S. Loja, Z.I., 85050 Tito Scalo, PZ, Italy
[b] Scuola di Ingegneria, Università degli Studi della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

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ABSTRACT

A two-year data-set of black carbon (BC) measurements collected in a site in South Italy close to the biggest European pre-treatment plant (COVA) of crude oil has been studied. The area named Val d'Agri, in Basilicata Region, is also crossed by the main road SS598. Data have been collected by using a 7 wavelength aethalometer allowing the measurement of equivalent black carbon (EBC) content, the estimation of Ångström absorption exponent (AAE), and the detection of organic fraction presence through UVPM (UV-absorbing particulate matter) quantity. Data have been analyzed to distinguish seasonal behaviors and characteristics of carbonaceous aerosols. No evident seasonal patterns have been observed for EBC concentrations with a mean value of 643 ± 415 ng/m^3 and a large short-term variability, with frequent periods (few days or few weeks) of intense emissions associated to COVA activities. EBC averaged daily trends show two main peaks, one in the morning and one in the evening suggesting a contribution of traffic as a background source of BC on a long-term basis, due to the SS598 passing near the measurement site. On a four month period in 2013, a comparison with co-located PM_{10} concentrations data has been carried out showing a relevant contribution of EBC to the total particle loading at the site. Unlike EBC, AAE shows higher values (maximum value 1.3 ± 0.3) during cold periods and lower values (minimum value 0.9 ± 0.2) in the warmer seasons. Anti-correlation has been observed when comparing AAE with both solar radiation and temperature. In addition, enhanced values during night time for AAE average daily patterns have been observed despite the seasons, suggesting relevant additional sources of organic carbon other than traffic related to COVA emissions during the year. Moreover a good agreement, on a short-term basis, has been found among UVPM, benzene, toluene.

1. Introduction

BC is recognized to be a fundamental variable to estimate the Earth's radiation budget for its property of strongly absorbing solar radiation at all wavelengths. BC also has severe health impacts (Anenberg et al., 2011) and contributes to air quality worsening, so to raise the issue of BC as an additional indicator of the adverse health and pollution effects of airborne particles, compared to other indicators as PM_x (Janssen et al., 2011). At the same time, due to its shorter lifetime if compared to greenhouse gases, attempts of BC reduction could represent a more efficient way to mitigate such negative effects, as for example the Artic surface warming due to BC deposited on snow and ice (Bond et al., 2013; Sand et al., 2013). Recently the attention is growing on the necessity to enlarge the spatial and temporal coverages for BC experimental data, with a focus on its optical properties, in order to better assess its radiative forcing in models (Bond et al., 2013; Zhu et al., 2013). To this aim, studies on long-term databases of BC in different geographical areas and emission conditions play a fundamental role, and the scientific community has been carrying out an effort to extend the studied areas (Doumbia et al., 2012; Nair et al., 2012; Ni et al., 2014; Querol et al., 2013; Sandrini et al., 2014). Organic carbon (OC) and brown carbon (BrC) can be emitted together with BC during combustion processes when BC particles can act as carriers for toxic semi-volatile organic compounds, as for example polycyclic aromatic hydrocarbons (PAHs), due to the demonstrated strong affinity of these compounds with BC surfaces (Fernandez et al., 2002; Kim et al., 2009). The hypothesis of a modification of BC properties associated with the presence of particulate-phase organics, especially related to specific sources of emissions as oil production activities, is worth to be studied thoroughly.

The possibility to analyze a long-term dataset of BC measurements in the vicinity of the biggest European crude-oil pre-treatment plant (COVA) with continuous combustion processes, as such as in Agri Valley (South Italy), represents a useful field study as in an open air laboratory. The combustion processes occurring at the COVA plant are recognized to be one of the main sources of atmospheric pollution in the area due

* Corresponding author. Tel.: +39 0971 427205; fax: +39 0971 427271.
E-mail address: mariarosaria.calvello@imaa.cnr.it (M. Calvello).

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to both gaseous and particulate emissions, causing possible impacts on the air quality and health risks on the population (Calvello et al., 2014; Trippetta et al., 2014). Since 2006, the site has been subjected to special controls by the ARPA Basilicata (Basilicata Region Environmental Protection Agency) with a focus on gaseous emissions (volatile organic compounds—VOCs; benzene, toluene, etilbenzene, xilenes—BTEX; carbon monoxide—CO; sulfur oxides—SOx; nitrogen oxides—NOx). Recent results, obtained from the integration of data from the ARPA Basilicata network and independent experimental measurements of BC and PM_1, demonstrated the impact of COVA especially on the air quality of the area closest to it (Calvello et al., 2014). In literature, the production of carbonaceous aerosols by crude oil extraction and pre-treatment activities has been poorly studied, except from some works about extreme events (Mather et al., 2007; Perring et al., 2011). More works exist on oil extraction and treatment related gaseous emissions as VOCs (Grec and Maior, 2008; Lin et al., 2008), BTEX or PAHs (Lopes Oliveira et al., 2014; Sakari, 2012). A recent work by Pavese et al. (2012) described equivalent black carbon (EBC) measurements obtained near the Agri Valley oil pre-treatment plant by means of a multiwavelength aethalometer, and compared them with those obtained in a semi-rural site in South Italy close to a main road, highlighting the peculiarities of the former respect to the latter. Starting from those results, the present study aims to investigate the temporal variations of EBC concentrations in aerosol samples collected near the Agri Valley oil pre-treatment plant on a long-term basis, searching for possible seasonal trends, influence of the main meteorological parameters, and EBC contribution to PM_{10} loading at the site. Moreover the characteristics of carbonaceous aerosol at this peculiar site have been analyzed looking at AAE variations, and comparing temporal trends of UVPM with those of benzene, toluene and methane concentrations measured by ARPA Basilicata at the same measurement point.

2. Site and dataset description

2.1. Measurement site and instrumentation

The measurement site is in the Agri Valley (Basilicata Region, South Italy) that, with 25 oil wells, represents one of the biggest European onshore oil fields producing about 82,000 barrel of oil equivalent (BOE) per day (ENI, 2013). Oil wells are connected to the largest existing pre-treatment oil plant (170,000 m^2) in a populated area named "Centro Olio Val d'Agri" (COVA), where continuous combustion processes take place due to the presence of four control flames and three incinerators. The oilfield together with the COVA represents almost a unicum in such urbanized and agriculture-dedicated areas. Agri Valley is in fact a rural site with crops, woods and a large biodiversity, so that it is included in the protected area of the "Appennino Lucano Val d'Agri Lagonegrese" National Park. The valley is crossed by a rather busy main road named SS598 and surrounded by few villages, with a total of about 50,000 inhabitants, and a density of 34.5 inhabitants per square kilometer. The measurement site is "Viggiano Zona Industriale" (VZI) ARPA Basilicata monitoring station (40.18°N, 15.54°E, 565 m a.s.l), located at less than 1 km East from the COVA and North from SS598. A map with the COVA plant and the measurement site is reported in Fig. 1.

The instrument used in the present work is a Rack-Mount 7-wavelength Magee Scientific aethalometer AE31 (370, 470, 520, 590, 660, 880, 950 nm) measuring the attenuation of light transmitted from 7 lamps through a quartz fiber filter collecting absorbing carbonaceous aerosol. Absorption coefficients σ_{aer} at the 7 wavelengths were calculated from attenuation measurements and EBC concentrations were obtained from σ_{aer} assuming a mass absorption cross section (MAC) inversely proportional to the wavelength (Hansen, 2005). In the present work, a value of 16.6 $m^2\ g^{-1}$ was used for MAC at 880 nm. Measurements of σ_{aer} at UV wavelengths could lead to a qualitative detection of the organic fraction (OC) in carbonaceous aerosols, when present, due to the enhanced absorption of OC at the shorter wavelengths (Chen and Bond, 2010). The instrument was equipped with a cut size-selective cyclone for particles with aerodynamic diameters of less than 2.5 μm, and had been operating with a flow-rate of 4 L/min, a time-resolution of 5 min and a tape advancing time of 1 h. EBC concentrations were measured almost continuously from June 2011 to October 2013 at the VZI site.

Additional continuous measurements of methane concentrations by PID (photo-ionization detection), and of benzene and toluene concentrations by GC–PID (gas chromatography with photo-ionization detection), were provided by the ARPA Basilicata monitoring station for the period June 2011–October 2013. Moreover, for the period January–April 2013, gravimetric measurements of PM_{10} concentrations were available at the same monitoring station. More details on the ARPA Basilicata monitoring network can be found in Calvello et al. (2014).

Meteorological data (temperature, solar radiation, relative humidity, wind speed and direction) were obtained by the ARPA Basilicata monitoring station at the same site. In Table 1 the main seasonal meteorological parameters are presented indicating similar conditions for the three years and a clear separation between the warm season (spring and summer) and the cold one (fall and winter), typical of a continental

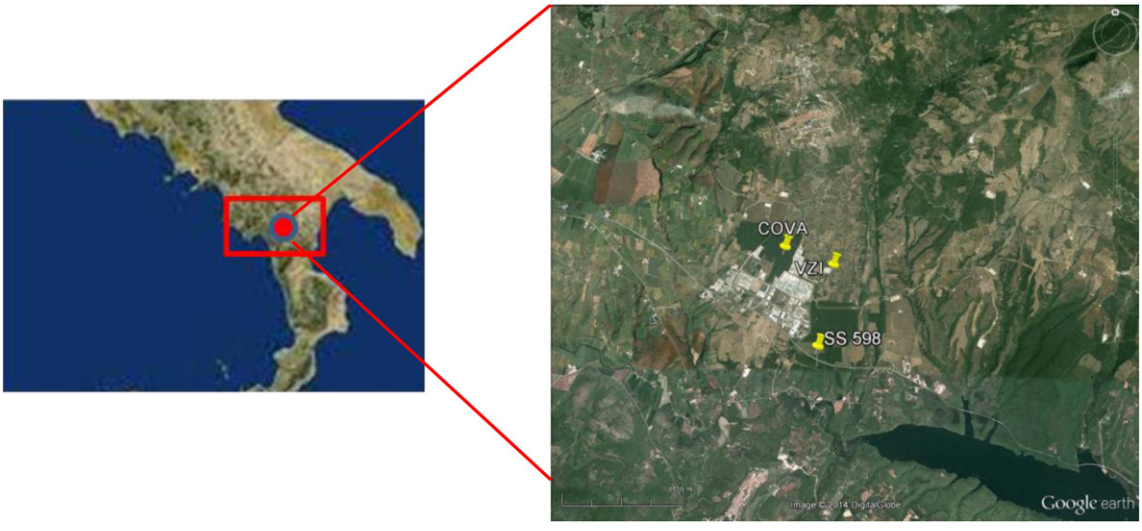

Fig. 1. Map of South Italy (left). Location of the COVA and of the measurement site VZI (right). Aerial photography courtesy of Google Earth (http://earth.google.com).