Atmospheric Pollution Research 7 (2016) 40–48

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Contents lists available at ScienceDirect

Atmospheric Pollution Research

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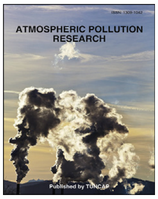

Original article

OC/EC from PM_{10} in the vicinity of Turów lignite open-pit mine (SW Poland): Carbon isotopic approach

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ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form
6 July 2015
Accepted 7 July 2015
Available online 21 October 2015

Keywords:
PM_{10}
$\delta^{13}C$
Organic/elemental carbon
Lignite open-pit mine

ABSTRACT

Concentrations of PM_{10} (particulate matter less than 10 μm in diameter) were measured at sampling points located in the vicinity of the Turów open-pit mine, southwest Poland, in April 2008. The samples were analysed by isotope ratio mass spectrometry (IR-MS) to determine the stable carbon isotope compositions of organic carbon ($\delta^{13}C_{OC}$) and elemental carbon ($\delta^{13}C_{EC}$). The daily PM_{10} concentrations ranged from 15 to 99 μg m^{-3} with an average value of 50 ± 24 μg m^{-3}. The analysed $\delta^{13}C_{OC}$ values ranged from −25.1 to −19.9‰ with an average value of −23.1 ± 1.9‰, and the values of $\delta^{13}C_{EC}$ ranged from −25.6 to −24.1‰ with an average value of −25.0 ± 0.5‰. Additionally, the average $\delta^{13}C_{TC}$ value of lignite from the open-pit mine reached −25.8‰, and calculated $\delta^{13}C_{OC}$ of lignite using an isotopic mass balance (IMB) value reaches −25.7 ± 0.1‰, whereas lignite $\delta^{13}C_{EC}$ value reaches −25.9 ± 0.2‰. The calculated major possible sources indicated that organic carbon (OC) in PM_{10} are represented probably by primary OC originated from the local lignite open-pit mine, whereas elemental carbon (EC) in PM_{10} are probably derived from local coal/lignite combustion products. If a data base of $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ values from other possible "pure" sources (coal/gasoline/diesel/biomass/etc) is created, it will be possible to calculate individual isotopic mass balances for OC and for EC, which would yield more information than was obtained for total carbon (TC). The method could be a new and very helpful tool for calculating the percentage input of possible sources of OC and EC in atmospheric particles, and it can be applied to data from locations throughout the whole world.

1. Introduction

Nowadays, unpolluted and contaminant-free air is of great importance to the people of the world. Good air quality has become one of the main aims of environmental management. International efforts are currently directed towards improving and controlling air quality to allow the population to live in a cleaner environment (Dockery et al., 1993; Dockery and Pope, 1994; Schwartz, 1994; Ackermann-Liebrich et al., 1997; Braun-Fährlander et al., 1997; Harrison and Yin, 2000; Pope et al., 2002; Hueglin et al., 2005). The most important and significant pollutant is atmospheric particulate matter, which is a mixture of fine and coarse particles containing elemental and organic carbon, nitrates, sulphates, mineral dust, trace elements, and water (Hueglin et al., 2005). A substantial fraction of total suspended particles (TSP) are particles with diameters of less than 10 μm (PM_{10}). Carbonaceous aerosols, one of the major components of PM_{10}, contributes 20 to 80% of PM_{10} by mass in urban and industrialized areas (Gray et al., 1986; Chow et al., 1993; Nunes and Pio, 1993; Rogge et al., 1993; Park et al., 2001; Harrison et al., 2003). Nevertheless, the contributions of different sources of carbonaceous aerosols along with their formation mechanism, atmospheric transitions, and modes of transport are still not well known (Anderson et al., 2003; Huang et al., 2006). Carbonaceous particles are generally divided into three fractions: (a) organic carbon (OC); (b) elemental carbon (EC), also called black carbon (BC) or soot (Liousse et al., 1993; Castro et al., 1999; Jacobson, 2001; Sanchez de la Campa et al., 2009); and (c) carbonate carbon (CC) (Johnson et al., 1981; Chow et al., 1993; Pio et al., 1994; Birch and Cary, 1996; Schauer et al., 2003). Piazzalunga et al. (2013) stated that at most European sites, CC accounts for a negligible part of total carbon (TC) in PM_{10}; CC is present in low concentrations, accounting for less than 5% of TC

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2015.07.003

(Appel et al., 1976; Ohta and Okita, 1984; Hamilton and Mansfield, 1991; Pio et al., 1994). In urban areas, CC usually represents only 1% of the fine fraction and between 2% and 3% of the coarse fraction (Clark and Karani, 1992). OC in atmospheric aerosols can originate directly from primary anthropogenic emission sources (Cachier et al., 1995; Duan et al., 2005) and natural biogenic sources (e.g., bacteria, viruses, many types of fungal spores, pollens and plants, and fragments of insects) (Hildemann et al., 1991, 1994; Schauer et al., 1996). OC can also be produced by atmospheric reactions (secondary OC) involving gaseous organic precursors (Pandis et al., 1992; Pankow, 1994; Jimenez et al., 2003; Schwarz et al., 2008; Górka et al., 2012). Elemental carbon is a primary pollutant emitted by the incomplete combustion of coal, oil, petrol and different kinds of biomass (Larson and Cass, 1989; Larson et al., 1989; Hildemann et al., 1991, 1994; Hitzenberger, 1993; Schauer et al., 1996; Schwarz et al., 2008). EC has a residence time of about six days and can be transported hundreds or thousands of kilometres from its source area (Husain et al., 2007). Sillanpää et al. (2005) reported that in urban European sites, the contribution of EC to PM varied from 5 to 9% by mass for $PM_{2.5}$ and from 1 to 6% by mass for $PM_{2.5-10}$ fractions.

Due to the nature of carbonaceous materials, the $^{13}C/^{12}C$ isotope ratios for individual coal fractions (OC and EC) in airborne particulate matter (PM_{10} and $PM_{2.5}$) are different. Significant seasonal variations in the $\delta^{13}C$ values of TC were observed in Mexico City (Lòpez-Veneroni, 2009), Wroclaw, Poland (Górka et al., 2012, 2014) and the East China Sea in Jeju (Kundu and Kawamura, 2014). As a result of the carbon isotopic compositions of organic and elemental carbon differ from each other, it is possible to distinguish the origins of carbonaceous materials. It is important that $\delta^{13}C_{EC}$ is unreactive; thus, it can be attributed to primary sources. In contrast, the main origin of $\delta^{13}C_{OC}$ is photochemical transformations; thus, $\delta^{13}C_{OC}$ can be transmuted into different types of $\delta^{13}C$ over time (Ho et al., 2006; Huang et al., 2006, 2009).

The major goal of this study is to determine whether carbon isotope ratios from OC and EC can be used to identify different sources of these carbon fractions within area dominated by one specific dust emission source (lignite open-pit mine) and to determine if other important PM sources are affecting the investigated area. Recently, using $\delta^{13}C_{TC}$ data concerning possible sources (Widory et al., 2004; Górka and Jędrysek, 2008; Kawashima and Haneishi, 2012) we can construct and use a very helpful tool which is premised on isotopic mass balance (IMB) (Górka et al., 2014) which yield quantity information about the input of coal/bio/diesel sources. If data base of $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ values from other possible "pure" sources (coal/gasoline/diesel/biomass/etc) is created, it will be able to calculate individual IMB for OC and for EC. It could be a new tool for calculating OC and EC input in TC and derives more information about relations between specific carbon form in atmospheric global budget of C in particulate matter.

2. Materials and methods

2.1. Study area

Measurements of 24-h PM_{10} concentrations were carried out in the vicinity of the Turów lignite mine from 9 to 26 April, 2008. The Turów lignite mine, which is a large open-pit mine located in south-western Poland, represents one of the largest lignite reserves in Poland. Ten sampling points located up to 1.5 km from the edge of the mine were selected (Fig. 1); these sites were potentially exposed to dust pollution coming (deflated) from the outcrop.

2.2. Sampling methodology

Atmospheric PM_{10} was collected on quartz fibre filters with diameters of 47 mm (QM-A Whatman). All filters were pre- and post-conditioned in a clean room with environmentally controlled temperature and humidity prior to weighing. Weighing was carried out with an electronic microbalance (Sartorius M5P 000 V001) with a sensitivity of ±1 μg and a capacity in the range of 500 mg. The PM_{10} measurements were conducted using an automatic outdoor station for continuous atmospheric PM_{10} monitoring with the sequential substitution system of 16 filtering membranes (Tecora Skypost PM HV certified by TUV in accordance with the EN 12341 Council Directive 1999/30/EC). The electronic flow rate controller allows continuous operation. The pumps were set at an airflow of 2.3 m^3 per hour according to EN 12341. Before the field campaign we tested the accuracy of an instrument by a reference calibrator (Flowcal Air, TECORA).

2.3. Organic carbon and elemental carbon isotope analysis

According to Connin et al. (1997), Collins et al. (1999) and Cao et al. (2011), samples containing both EC and OC were oxidized to CO_2 and burned at two temperatures for a specified period of time. The first dry combustion, in which the organic carbon fraction burns, was carried out in a muffle furnace at 375 °C for three hours. Subsequently, CO_2 was cryogenically purified, and the carbon remaining on the quartz fibre filter was burned in a quartz filter at 850 °C for five hours; the elemental carbon fraction burns during this process (Szidat et al., 2004; Ho et al., 2006). The obtained CO_2 was cryogenically purified on a vacuum line. The $\delta^{13}C$ values of OC and EC were determined using a Finnigan Delta E mass spectrometer. The isotopic abundances presented herein were calculated and compared with the international standard V-PDB (Vienna Pee Dee Belemnite) as follows:

$$\delta^{13}C = \left(\frac{^{13}C/^{12}C_{SAMPLE}}{^{13}C/^{12}C_{STANARD}} - 1\right)\cdot 1000[‰]$$

The error of the $\delta^{13}C$ determination was below 0.1‰.

2.4. Meteorological conditions

Meteorological conditions were compiled from on-site observations and the National Weather Service (International Centre for Mathematical and Computational Modelling, Warsaw University; Material produced using Met Office Software) and are summarized in Table 1. The sampling period (from 7 to 23 April) was dominated by low-pressure weather systems. The weather was variable with several fronts (on the 7th, 10th, 16th, 19th and 22nd) affecting the region. Periods of rain along with changes in temperature, humidity, cloudiness and wind direction were recorded. Light to moderate winds from the western directions prevailed during the study period. A high-pressure system formed over the Baltic Sea on 23 April, and warm, dry air remained over the region until 27 April.

3. Results and discussion

3.1. PM_{10} concentration

The concentration of PM_{10} during the analysed period ranged from 15 to 99 μg m^{-3} with an average 49 ± 23 μg m^{-3} (Table 1 and Fig. 2).

It must be emphasized that the reported PM_{10} concentrations refer to different time periods and different sites. The data in Table 1 show that the PM_{10} level varied significantly among different days