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Main components of PM_{10} in an area influenced by a cement plant in Catalonia, Spain: Seasonal and daily variations

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ABSTRACT

Particulate matter (PM) composition has a key role in a wide range of health outcomes, such as asthma, chronic obstructive pulmonary disease, lung cancer, cardiovascular disease, and death, among others. Montcada i Reixac, a municipality located in the Barcelona metropolitan area (Catalonia, Spain), for its location and orography, is an interesting case- study to investigate air pollution. The area is also characterized by the presence of different industrial emission sources, including a cement factory and a large waste management plant, as well as an intense traffic. In this study, PM_{10} levels, trace elements, ions, and carbonaceous particles were determined for a long time period (2013–2016) in this highly polluted area. PM_{10} samples were collected during six consecutive days in two campaigns (cold and warm) per year. A number of elements (As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, K, La, Li, Hg, Mg, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Tb, Th, Ti, Tl, U, V, W, Y, Yb, and Zr), ions (Cl^-, SO_4^{2-}, NO_3^-, and NH_4^+), and carbonaceous content (total carbon, organic plus elemental carbon, and CO_3^{2-}), were analysed. These data were used to identify the PM_{10} main components: mineral matter, sea spray, secondary inorganic aerosols, organic matter plus elemental carbon, trace elements or indeterminate fraction. Although a clear seasonality (cold vs. warm periods) was found, there were no differences between working days and weekends. Obviously, the cement plant influences the surrounding environment. However, no differences in trace elements related with the cement plant activity (Al, Ca, Ni and V) between weekdays and weekends were noted. However, some traffic-related elements (i.e., Co, Cr, Mn, and Sb) showed significantly higher concentrations in weekdays.

1. Introduction

Nowadays, air pollution, especially in cities and metropolitan areas, is one of the most challenging problems that governments and local authorities must face. Road traffic, industrial activities (e.g., power plants, cement factories, waste incineration facilities, etc.) or the presence of harbours and airports, are pointed out as potentially important sources of air pollution in urban areas (Amato et al., 2016; Grigoratos and Martini, 2015; Sánchez-Soberón et al., 2015; Squizzato et al., 2017; Tolis et al., 2015; Wang et al., 2017). Among others, particulate matter less 10 µm of aerodynamic diameter (PM_{10}) is one of the pollutants that receive most of the attention. Particulate matter (PM) presents a wide variety of constituents, such as metals and trace elements, organic compounds, and acids (Cassee et al., 2013; Sánchez-Soberón et al., 2015, 2016). Not only PM composition, but also its size, depend on different parameters, such as meteorological conditions, season of the year, and emission sources (Cassee et al., 2013). PM composition has a key role in a wide range of health effects, which include –but are not limited to– asthma, chronic obstructive pulmonary disease, lung cancer, cardiovascular disease, premature birth, low birth weight, and even death (Deepak and Devi, 2016; Ebisu et al., 2016; Falcon-Rodriguez et al., 2016; Franchini et al., 2016; Morakinyo et al., 2016; Morales-Suárez-Varela et al., 2017; Wang et al., 2016).

Montcada i Reixac is a municipality (34,802 inhabitants in 2016) located in Catalonia (NE Spain). Since it is located in the metropolitan area of Barcelona (4,793,592 inhabitants in 2016), it means an interesting case study to investigate air pollution. The area is also characterized by a particular orography, being located in a river basin flanked by hills. There is also a wide variety of industrial emissions sources, two dense highways (daily crossed by around 50,000 and 160,000 vehicles), a waste treatment facility which manages approximately 240,000 t of organic waste/year (Vilavert et al., 2014), and a cement plant with an annual capacity of 900,000 t of clinker (Rovira et al., 2016, 2011; Sánchez-Soberón et al., 2015). In addition, a

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municipal waste incinerator was operating in the zone until 2004, when it ceased to operate (Schuhmacher and Domingo, 2006). Altogether, it makes this zone an area of a special environmental interest, and consequently, various studies and environmental surveys have been conducted in recent years (Abad et al., 2003; Domingo et al., 1999a, 1999b, 2000; Gallego et al., 2016; Meneses et al., 1999; Nadal et al., 2002, 2009; Rovira et al., 2016; Schuhmacher et al., 1997, 1998a, 1998b, 2006; Schuhmacher and Domingo, 2006; Vilavert et al., 2012, 2014). Despite these investigations, the inhabitants of Montcada i Reixac are still concerned regarding air quality and possible health outcomes.

In this study, PM_{10} levels, constituents (trace elements, ions, and carbon) and main components were studied for a long time in an area influenced by a cement plant in Montcada i Reixac. Seasonal and daily variations were also studied in detail. To the best of our knowledge, this is the first study facing in deep, and for a long period of time, the PM_{10} characterization in this complex area.

2. Materials and methods

2.1. Study area and sampling

Sampling points (41°28'11"N; 2°11'04"E) were located in "Can Sant Joan", a neighbourhood of Montcada i Reixac. The studied area is located in the Besòs river basin, with a cement plant situated at approximately 600 m from the sampling point and two highways nearby. Additional details on the area of study are available elsewhere (Rovira et al., 2011, 2016). A daily (between 0:00 am to 11:59 pm) PM_{10} sample was collected for 6 consecutive days, in two periods per year, between 2013 and 2016. Sampling campaigns were carried out in October and December of 2013, July and November of 2014, October and December of 2015, and July and December of 2016. Meteorological data during the sampling campaigns are summarized in Table 1. A high volume sampler MicroPNS HVS16PM10 (MCZ, Bad Nauheim, Germany), which allows the sampling of daily PM_{10} levels with the reference method UNE EN 12341, was used. A volume around 1630 m^3 was collected for each sample in quartz microfiber filters (QFFs) of 150 mm of diameter, being previously heated at 200 °C for 4 h to remove any volatile organic compound. Before and after sampling, QFFs were acclimated at 25 °C and 40% relative humidity. Then, at the same conditions, they were weighed until the weight of each filter was stabilized.

2.2. Trace elements determination

A ¼ fraction of each QFF was digested with 2 mL of 65% nitric acid (Suprapur, E. Merck, Darmstadt, Germany) and 3 mL of hydrofluoric acid (37.5% Panreac, Barcelona, Spain) in a Teflon vessel for 8 h at room temperature and 8 h at 80 °C. The digested solution was evaporated until dryness on a sand bath at 250 °C. The residue was dissolved in 2.5 mL of nitric acid and then diluted to a final volume of 25 mL with ultrapure water. They were kept at −20 °C until analysis (Mari et al., 2009).

The concentrations of aluminium (Al), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), cerium (Ce), cobalt (Co), chromium (Cr), caesium (Cs), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gallium (Ga), gadolinium (Gd), germanium (Ge), hafnium (Hf), holmium (Ho), lanthanum (La), lithium (Li) mercury (Hg), manganese (Mn), molybdenum (Mo), niobium (Nb), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), rubidium (Rb), antimony (Sb), scandium (Sc), selenium (Se), samarium (Sm), tin (Sn), strontium (Sr), terbium (Tb), thorium (Th), titanium (Ti), thallium (Tl), uranium (U), vanadium (V), tungsten (W), yttrium (Y), ytterbium (Yb) and zirconium (Zr), were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000). Rhodium was used as internal standard. In turn, the levels of barium (Ba), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg) and sodium (Na) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 3200RL).

Detection limits were 0.01 ng/m^3 for Bi, Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Nb, Nd, Pr, Sm, Ta, Tb, U, W, Y and Yb; 0.03 ng/m^3 for Cd, Pb, Tl, and Rb; 0.06 ng/m^3 for Co, Cu, Hf, Mn, Mo, Sn, Sr, Th and Zr; 0.13 ng/m^3 for As, Be, Hg, Li, Ni and Sb; 0.25 ng/m^3 for Ga; 0.31 ng/m^3 for Cr, Ge and V; 0.63 ng/m^3 for Se; 1.25 ng/m^3 for Sc; 3.13 ng/m^3 for Ba and Fe; 6.25 ng/m^3 for Ti and Zn; 15.6 ng/m^3 for Ca; 31.3 ng/m^3 for Al and Mg; 123 ng/m^3 for Na; and 156 ng/m^3 for K.

Quality control/quality assurance of the analytical process was carried out through the analysis of duplicate samples, blanks, and standards (Loamy clay, National Institute of Standards and Technology, LCS-4).

2.3. Ions determination

A portion of another QFF piece was extracted with 15 mL of ultrapure water for 12 h of axial agitation, and 3 rounds of ultrasound at 60 °C for 10 min. The resulting extract was filtered with a 0.47 µm membrane filter. For the analysis of Cl^-, SO_4^{2-} and NO_3^-, an ion chromatograph (Dionex D-300) was used, while the determination of ammonium (NH_4^+) was made by the reaction of Berthelot, whereby indofenol is formed and subsequently determined by spectrophotometry at a wavelength of 640 nm (Patton and Crouch, 1977). Detection limits were 0.002 µg/m^3 for Cl^-; 0.02 µg/m^3 for NO_3^-; 0.10 µg/m^3 for SO_4^{2-} and 0.008 µg/m^3 for NH_4^+.

2.4. Total (TC), organic (OC) and elemental (EC) carbon determination

For the analysis of total carbon (TC), a piece of filter (2.8 cm^2) was burnt through combustion with an oxygen atmosphere at a temperature of 1000 °C. The resulting gases (CO_2, SO_2 and NO_X), dragged by a stream of helium, were analysed by gas chromatography (Thermo EA 1108 CHNS-O Carlo Erba Instruments) (Tiessen and Moir, 2000). For the analysis of organic carbon (OC) plus elemental carbon (EC), a sample was previously digested in a HCl atmosphere to remove the carbon from carbonates (CC), being subsequently analysed with the same methodology used to determine TC. The detection limit was 0.01 µg/m^3. The OC was calculated from the ratio reported by Pérez

Table 1
Meteorological conditions in each sampling campaign.

Period	Mean temperature (°C)	Minimum temperature (°C)	Maximum temperature (°C)	Rainfall during sampling (mm)	Rainfall the week before sampling (mm)	Relative humidity (%)
October 2013	21.0	17.6	25.2	0.0	3.0	76
December 2013	9.7	3.7	15.5	0.0	0.0	70
July 2014	22.8	15.8	31.4	0.0	0.8	65
December 2014	6.7	0.5	15.1	0.3	34.3	65
October 2015	18.1	9.5	27.8	7.9	46.8	67
December 2015	10.5	3.4	16.4	0.3	0.0	79
July 2016	24.2	17.6	30.7	0.0	1.4	56
December 2016	8.0	−0.3	17.0	0.0	2.1	75