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.

Keywords

PM_{10}, characterization, trace elements, ions, carbon, cement plant

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 tons of organic waste/year (Vilavert et al., 2014), and a cement plant with an annual capacity of 900,000 tons of clinker (Rovira et al., 2016, 2011; Sánchez-Soberón et al., 2015). In addition, a 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 HVS16 PM10 (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 hours to remove any volatile organic compound. Before and after sampling, QFFs were acclimated at 25ºC 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 hours at room temperature and 8 hours at 80°C. The digested solution was evaporated until dryness on a sand bath at 250ºC. 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 $\mu g/m^3$ for Cl^-; 0.02 $\mu g/m^3$ for NO_3^-; 0.10 $\mu g/m^3$ for SO_4^{2-} and 0.008 $\mu g/m^3$ 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 1,000°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, 2000a, 2000b). 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 $\mu g/m^3$. The OC was calculated from the ratio reported by Pérez et al. (2008), according to which, OC = 0.7 (OC + EC). For particle organic matter (OM) calculation, the level of OC was multiplied by a factor of 1.6 (Malm et al., 1994; Russell, 2003; Turpin and Lim, 2001).

2.5 Indirect determinations

The concentrations of carbonates (CO_3^{2-}) were determined indirectly from the stoichiometric ratio: $CO_3^{2-} = 1.5Ca + 2.5Mg$ (Querol et al., 2001). Similarly, silicon oxide (SiO_2) was calculated from the following stoichiometry: $2Al_2O_3 = SiO_2$ (Querol et al.,

2001). Levels of aluminium oxide (Al_2O_3) were calculated assuming that all the aluminium was present in oxide form (Querol et al., 2001).

PM was classified into 6 main components: 1) mineral matter (sum of CO_3^{2-}, SiO_2, Al_2O_3, Ti, P, Mn, Mg, K, Fe, and Ca), 2) sea spray (sum of Na and Cl^-), 3) organic matter and elemental carbon (OM+EC), 4) secondary inorganic aerosols (sum of SO_4^{2-}, NH_4^+, and NO_3^-), 5) trace elements (the sum of the remaining elements), and 6) indeterminate (the difference between PM concentrations and the sum of the other main components) (Sánchez-Soberón et al., 2015).

2.7. Statistics

For the statistical analysis, values below the detection limit (LD) were assumed to be equal to one-half of that limit (ND = ½ LD). Statistical significance was established using firstly the Levene test to establish whether data showed a parametric distribution. Subsequently, the ANOVA or Kruskal-Wallis tests were applied. A difference was considered as statistically significant when the probability was lower than 0.05 ($p<0.05$).

3. Results and discussion

3.1. Elements, carbon, ions and indirect determinations

PM_{10} levels in each sampling campaign are depicted in Fig. 1. PM_{10} concentration showed a mean value of 30 μg/m^3, ranging from 14 to 65 μg/m^3. The 5th, 25th, 75th and 95th percentiles were 17, 20, 36, and 63 μg/m^3, respectively. Significantly higher levels were found in December 2013, December 2015 and December 2016 than those noted in July 2014, December 2014 and October 2015. Elevated PM_{10} concentrations were observed during anticyclone episodes, typical of winter in Mediterranean areas. In general terms, statistically similar (p=0.810) PM_{10} mean levels were found between July (23 μg/m^3) and October campaigns (23 μg/m^3), both presenting concentrations significantly lower (p<0.001) than those in December (38 μg/m^3). According to the week period, PM_{10} levels were similar (p=0.450), being mean levels 31 and 29 μg/m^3, in working days and

weekends, respectively. The daily (24 h) PM_{10} limit, which can be only exceeded 35 times a year and set at 50 $\mu g/m^3$ (European Union Parlament and Council, 2008), was overpassed in 2 of the 6 samples analysed in December 2013, and 1 of 6, in December 2015. According to the Catalan air quality network (Generalitat de Catalunya, 2017), PM_{10} mean annual levels in this same location were: 25 $\mu g/m^3$ in 2013 and 2016, and 28 $\mu g/m^3$ in 2014 and 2015, overpassing 6, 11, 8 and 4 times the daily threshold limit (50 $\mu g/m^3$) during 2013, 2014, 2015 and 2016, respectively.

The concentrations of trace elements in PM_{10} samples collected from 2013 to 2016 are shown in Table 2. Sodium (2,684 ng/m^3), Ca (1,495 ng/m^3), K (783 ng/m^3), Fe (641 ng/m^3) and Al (537 ng/m^3) were the elements with the greatest mean concentrations. Contrastingly, Be, Ge, Hg, Ho, Se and Tb were below their respective detection limits in most of the samples. In general terms, higher levels were found in the surveys of December and October than in July, with a few exceptions (i.e., Cd, Li, Sc and Se). Clear seasonal trends were observed for Cu, Pb, Sb and Sn, all of them presenting statistically significant differences among campaigns (July < October < December). Twenty elements (Al, As, Bi, Ca, Cr, Cu, Er, Hf, La, Nb, Pb, Sb, Sm, Sn, Th, U, W, Y, Yb and Zr) showed significantly different concentrations of PM_{10} between July and October campaigns ($p<0.05$). Moreover, significant differences between July and December were observed for As, Bi, Ca, Ce, Cr, Cs, Cu, Fe, K, Mo, Nb, Ni, Pb, Rb, Sb, Sn, Tl, U and W ($p<0.05$). Finally, only for a few elements (namely, Cu, Fe, Pb, Sb, and Sn) the difference in PM_{10} levels between October and December campaigns reached a level of statistical significance ($p<0.05$).

A specific analysis of daily trends in PM_{10} levels was conducted, with only a few elements presenting significantly different concentrations when comparing working days and weekends: Co (0.35 vs. 0.20 ng/m^3), Cr (6.16 vs. 3.61 ng/m^3), Mn (12.8 vs. 7.89 ng/m^3), and Sb (3.94 vs. 2.64 ng/m^3). Since the activity of the cement plant is continuous throughout the week, the main difference between weekdays and weekends is the reduction of road traffic in the highways crossing the area. No differences between weekdays and weekends in the levels of the elements related with the cement plant activity (Al, Ca, Ni and V) were noted (Mari et al., 2016). In addition, all these elements (Co, Cr, Mn, and Sb) have been related to traffic emissions such as wear brakes, brake linings, tyres, fossil fuels and lubricants combustion, and/or engine abrasion (Bosco et al., 2005; Ogunbileje et al.,

2013; Saradhi et al., 2014; Schauer et al., 2006; Taiwo et al., 2014; Golokhvast et al., 2015; Valotto et al., 2015; Wawer et al., 2015; Yu et al., 2014). Therefore, the PM content of Co, Cr, Mn and Sb might be a good surrogate to study the contribution of traffic in polluted areas with similar characteristics to our case study. Furthermore, the potential contribution of other emission sources cannot be disregarded, as some of these elements (Co, Cr, and Mn) may be also related to mineral fraction or cement dust (Gupta et al., 2012; Saradhi et al., 2014; Valotto et al., 2015).

The levels of total carbon (TC), organic plus elemental carbon (OC+EC), carbonates (CO_3^{2-}) and ions (Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-), as well as indirect determinations (OM, SiO_2, and Al_2O_3) calculated in the eight sampling campaigns between 2013 and 2016, are summarized in Table 3. The carbonaceous content (TC, OC+EC and OM) of PM_{10} samples showed a strong seasonal pattern (December>October>July), with significant differences among sampling campaigns. In contrast, no significant differences in carbonaceous content (TC, OC+EC and OM) were noted between working days and weekends. Regarding carbonates (CO_3^{2-}), levels in July were significantly lower ($p<0.05$) than in December and October. By contrast, ions (Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-) did not show notable differences among campaigns, with the only exception of NH_4^+, whose values were significantly higher in December ($p<0.05$). Like PM_{10} concentrations, the levels of ions (Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-) were not significantly different when comparing weekdays and weekends.

Pearson's correlations were calculated for all trace elements, ions, total carbon and PM_{10} total concentrations (Supplementary Information, Fig. S1). PM_{10} showed high Pearson's coefficients with TC (0.925; R^2=0.855), Sn (0.844; R^2=0.713) and Sb (0.793; R^2=0.628), all of them at $p<0.001$. In addition, TC was highly and positively correlated ($p<0.001$) with OC+EC (0.986; R^2=0.972), as well as with a number of elements: Sn (0.855; R^2=.783), Sb (0.843; R^2=0.711), Pb (0.780; R^2=0.609), Cu (0.764; R^2=0.583), Cr (0.709; R^2=0.503), and Fe (0.687; R^2=0.472). As above commented, all these elements are related to road traffic emissions (e.g., brake wear, fuel combustion, tyre), a fact that points out traffic as one of the main contributors to Total Carbon (TC) content in PM.

3.2. PM_{10} main components

PM_{10} main components in air samples collected around the cement plant, according to the sampling period and season, are depicted in Fig. 2 and 3, as well as in Supplementary Information (Fig. S2). The percentage of mineral matter decreased from 28-39% in 2013 to 8-16% during the period 2014-2016. In July, the levels of mineral matter (2.31 $\mu g/m^3$) were significantly lower than those registered in October (5.41 $\mu g/m^3$) and December (7.89 $\mu g/m^3$) campaigns. Sea spray, with a mean overall contribution of 5% (range: 1-10%) did not show significant differences in concentrations between sampling periods (1.46, 1.74, and 1.32 $\mu g/m^3$ in July, October and December, respectively). The relative contribution of sea spray was lower in the December (3%) campaigns than in October (8%) and July (6%) campaigns. Regarding the OM+EC fraction, significant differences were observed among sampling months, with a profile inversely proportional to ambient temperature (17.5, 8.61 and 4.34 $\mu g/m^3$ in December, October and July, respectively). The relative contribution of OM+EC fraction showed the same trends, with significant differences according to the season (46% in December, 37% in October, and 19% in July). These results are in agreement with the presence of more combustion processes and less dispersion of pollutants during cold seasons. Similarly, the concentrations of secondary inorganic aerosols (4.35, 4.07, and 4.99 $\mu g/m^3$ in July, October and December) were not significantly different among campaigns. However, significantly higher relative contribution was noted in July (19%) than in December (15%). For the trace elements fraction, a significant increase of levels was noted in parallel with decrease of the ambient temperature (0.05, 0.09, 0.13 $\mu g/m^3$, in July, October and December, respectively). Trace elements owned a relative contribution of 0.2% in July campaigns, and 0.4% in October and December surveys. When comparing weekdays and weekends, no significant differences were noted in the levels of main PM components, with the only exception of secondary inorganic aerosols, whose relative contribution was 14% and 16% in weekdays and weekends, respectively. However, despite the relative contribution was different, total levels of secondary inorganic aerosols did not show significant differences between working days (4.46 $\mu g/m^3$) and weekends (4.85 $\mu g/m^3$). Finally, for indeterminate fractions the relative contributions were: 46% (10.8 $\mu g/m^3$), 15% (3.43 $\mu g/m^3$) and 17% (6.64 $\mu g/m^3$) in the July, October and December campaigns, respectively. However, no significant differences were

noted between working days (24%; 7.49 μg/m^3) and weekends (20%; 5.74 μg/m^3). Indeterminate fraction varies across the campaigns, from 5% and 3% in October and December 2013, to 49% in ther July 2014 campaign. Indeterminate fraction has different origins such as measurement errors, underestimations in OM+EC fraction, or water bound to secondary inorganic aerosols (Sánchez-Soberón et al., 2015)

The dendrogram (Supplementary Information Fig. S3) with all the data set showed two main groups. The first one was mainly formed by samples obtained in anticyclone periods (December 2013, 2015 and 2016), while the other included the rest of sampling periods. In turn, the anticyclone group was divided in two sub-groups: 1) December 2013, and 2) December 2015 and December 2016. Similarly, the second main group was also divided in two subgroups: 1) warm season campaigns (July 2014 and 2016), and 2) colder surveys (October 2013 and 2015, and December 2014). The same classification was obtained after applying a principal component analysis (PCA), whose plots explained 81.1% of the data variance in a 3-D model (Fig. 4). Cold period cluster (December campaigns) was characterized by high scores of OM+EC and trace elements due to combustion process, while July campaigns cluster (especially in 2014) showed a great score of sea spray and indeterminate component. An explanation could be the difference in wind regimes according to the season, as winds blowing from the sea are increased in summer in this Mediterranean area. In addition, both 2013 campaigns had high scores of mineral matter.

Emissions of a cement facility could be classified mainly in three groups. The first group corresponds to those emissions produced in handle, crushing and milling of raw materials; the second group is that coming from milling, storage and packaging of clinker and cement; and finally, the third group corresponds to the stack emissions produced in kiln combustion of fuel (traditional or alternative), and also raw materials not retained in air cleaning devices. The first two groups could be classified as diffuse emission sources, not focused on any point source, but in large area across the facility. The last group, kiln emissions, are released from the stack of the plant. Fugitive emissions related with raw materials, mainly, but not exclusively limestone and quartz, and clinker or cement, could be detected mainly with Ca levels (Jorquera et al. 2013, Yubero et al. 2011), but also Si, Fe or Al. In the current study, raw material fugitive emissions are classified as mineral materials and cannot

be distinguished from soil resuspension. In a similar way, in this survey cement or clinker fugitive emissions are indistinguishable from mineral mater resuspension using elemental analysis. However, it is possible to identify alite and belite, calcium silicates present in cement, using X-ray diffraction. In fact, in the present study, Ca and Al, highly positively correlated, were found to be associated with mineral industries (Mari et al. 2016). Cement stack or kiln emissions are even hard to distinguish from other combustion sources, especially in the complex background of Montcada i Reixac municipality. In order to assess the influence of the cement plant a different sampling approach should be considered. Two options could be considered: i) to program sampling campaigns in different cement plant operational status, or ii) to include an additional sampling point with the same background and without cement plant influence.

4. Conclusions

In the current study, the main PM_{10} components of samples collected near a cement plant were investigated. The concentrations of a number of trace elements, ions, and carbonaceous fraction content were analysed. Some parameters, including PM_{10} levels and main components, showed significant differences among sampling campaigns. Most of them were related to seasonal patterns (cold vs. warm periods), likely due to differences in emission sources and meteorological conditions. Higher levels of PM_{10} and its components were detected in the samplings conducted in December, when the area is affected by anticyclone episode conditions. Contrastingly, PM_{10} levels and most of its components were lower during summer (July campaigns) or in rainy periods (December of 2014 and October of 2016). Despite the area is subjected to an important industrial activity including the cement plant, traffic might have a significant contribution on the surrounding environment given the strong correlation among PM_{10} levels, TC and several traffic-related trace elements (e.g., Sn, Sb, Cu, Cr, and Fe). Although no significant differences in PM_{10} main components were noted between weekdays and weekends, the levels of some traffic-related elements (e.g., Co, Cr, Mn, and Sb) were decreased in the weekend. However, no differences in the trace elements related with the cement plant activity (Al, Ca, Ni and V)

were noted between weekdays and weekends. In order to exhaustively establish the cement influence in PM_{10} levels and constituents in this extremely complex background, we suggest two different approaches: i) sampling at the same location when the cement plant is not working and comparing within the same period and meteorological conditions when the facility is working, and ii) to collect samples in other location with a similar background, but without any influence of cement plants. To the best of our knowledge, this is the longest PM_{10} characterization survey in an area concurrently influenced by a cement plant and traffic.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version.

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Table 1

Meteorological conditions in each sampling campaign.

Period	Mean Temperature (ºC)	Minimum Temperature (ºC)	Maximum Temperature (ºC)	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

Table 2

Levels of trace elements (ng/m^3) in PM_{10} samples collected near a cement plant in 8 campaigns performed between 2013 and 2016.

	Oct 2013 *n=6*	Dec 2013 *n=6*	Jul 2014 *n=6*	Dec 2014 *n=6*	Oct 2015 *n=6*	Dec 2015 *n=6*	Jul 2016 *n=6*	Dec 2016 *n=5*
Al	624 ± 114	2596 ± 539	91.0 ± 48.1	134 ± 98.0	186 ± 82.3	201 ± 71.5	261 ± 135	140 ± 113
As	0.63 ± 0.09	0.52 ± 0.15	0.19 ± 0.07	0.40 ± 0.15	0.33 ± 0.12	0.69 ± 0.16	0.19 ± 0.08	0.33 ± 0.10
Ba	ND	ND	8.39 ± 4.39	15.4 ± 10.7	19.3 ± 1.46	35.2 ± 9.82	17.9 ± 12.0	26.0 ± 7.81
Be	0.08 ± 0.03	ND	ND	ND	ND	ND	ND	ND
Bi	1.59 ± 0.50	3.97 ± 2.06	0.24 ± 0.16	0.36 ± 0.34	0.47 ± 0.22	0.72 ± 0.46	0.62 ± 0.54	1.64 ± 1.01
Ca	2686 ± 825	4744±1076	391 ± 142	867 ± 608	767 ± 81.3	1150 ± 373	612 ± 234	596 ± 199
Ce	1.29 ± 0.48	0.68 ± 0.24	ND	0.21 ± 0.13	0.49 ± 0.93	1.76 ± 2.18	0.05 ± 0.03	0.39 ± 0.07
Cd	0.68 ± 0.35	2.12 ± 0.76	0.19 ± 0.09	0.33 ± 0.08	0.27 ± 0.06	0.44 ± 0.12	0.54 ± 0.22	0.44 ± 0.12
Co	0.27 ± 0.09	0.45 ± 0.27	0.15 ± 0.02	0.12 ± 0.07	0.18 ± 0.05	0.54 ± 0.35	0.33 ± 0.09	0.37 ± 0.22
Cr	6.26 ± 1.23	8.48 ± 3.07	3.26 ± 0.53	3.35 ± 2.79	3.82 ± 2.14	8.06 ± 3.62	3.73 ± 1.34	7.31 ± 4.46
Cs	0.09 ± 0.06	0.12 ± 0.04	0.02 ± 0.01	0.04 ± 0.03	0.03 ± 0.01	0.05 ± 0.01	0.04 ± 0.02	0.03 ± 0.01
Cu	42.6 ± 9.50	41.4 ± 18.2	9.62 ± 14.8	22.2 ± 16.3	18.9 ± 3.76	38.8 ± 8.6	16.7 ± 6.06	58.7 ± 20.6
Dy	0.06 ± 0.02	0.15 ± 0.04	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Er	0.05 ± 0.02	0.11 ± 0.03	0.01 ± 0.01	ND	0.01 ± 0.01	0.01 ± 0	0.01 ± 0.00	0.01 ± 0.00
Eu	0.10 ± 0.05	0.42 ± 0.11	ND	ND	ND	0.01 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
Fe	407 ± 103	627 ± 197	313 ± 84.2	516 ± 285	518 ± 84.3	1250 ± 266	628 ± 209	912 ± 367
Ga	ND	ND	0.89 ± 0.21	0.35 ± 0.28	0.58 ± 0.05	1.28 ± 0.31	0.26 ± 0.20	0.47 ± 0.16
Gd	0.21 ± 0.07	0.29 ± 0.07	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Ge	ND	ND	ND	ND	ND	0.19 ± 0.08	ND	ND
Hf	0.30 ± 0.11	0.71 ± 0.10	ND	0.08 ± 0.05	0.05 ± 0.03	0.10 ± 0.04	0.08 ± 0.13	0.04 ± 0.02
Hg	ND	ND	ND	ND	ND	0.08 ± 0.03	ND	ND
Ho	0.01 ± 0.01	0.03 ± 0.01	ND	ND	ND	ND	ND	ND
K	1600 ± 662	3093 ± 871	309 ± 202	ND	186 ± 80.2	478 ± 63.1	188 ± 85.0	216 ± 139
La	0.47 ± 0.17	1.04 ± 0.22	0.15 ± 0.04	0.10 ± 0.03	0.18 ± 0.07	0.24 ± 0.04	0.16 ± 0.09	0.11 ± 0.02
Li	0.64 ± 0.31	0.84 ± 0.28	0.29 ± 0.07	0.21 ± 0.09	0.29 ± 0.19	ND	0.68 ± 0.36	0.3 ± 0.09
Mg	56.2 ± 51.3	85.6 ± 26.0	32.1 ± 42.5	ND	ND	ND	48.8 ± 30.8	105 ± 25.1
Mn	6.98 ± 3.95	6.87 ± 3.33	7.85 ± 2.30	9.83 ± 5.34	9.47 ± 2.22	22.8 ± 6.84	10.7 ± 3.31	15.1 ± 7.00
Mo	1.06 ± 0.23	2.04 ± 0.61	2.39 ± 0.35	0.92 ± 0.48	1.92 ± 0.26	2.88 ± 0.99	0.10 ± 0.16	0.96 ± 0.65
Na	904 ± 473	1494 ± 450	ND	62.2 ± 14.5	1371 ± 388	905 ± 196	779 ± 514	700 ± 535
Nb	0.25 ± 0.04	0.89 ± 0.19	ND	0.09 ± 0.05	0.06 ± 0.04	0.07 ± 0.04	0.04 ± 0.02	ND
Nd	0.36 ± 0.15	14.95 ± 4.51	0.11 ± 0.03	0.04 ± 0.02	0.10 ± 0.04	0.13 ± 0.04	0.12 ± 0.07	0.05 ± 0.02
Ni	4.07 ± 0.91	6.96 ± 2.42	ND	2.14 ± 1.16	4.01 ± 0.88	7.31 ± 2.04	4.89 ± 1.00	5.57 ± 4.02
Pb	11.9 ± 3.20	16.8 ± 3.04	3.16 ± 1.62	10.8 ± 5.66	8.36 ± 4.14	17.6 ± 3.49	4.60 ± 1.52	17.8 ± 6.56
Pr	0.10 ± 0.04	0.24 ± 0.06	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.02	0.01 ± 0.01
Rb	3.55 ± 1.57	4.90 ± 1.23	0.51 ± 0.13	0.65 ± 0.20	0.46 ± 0.13	0.79 ± 0.08	0.86 ± 0.34	0.70 ± 0.17
Sb	3.88 ± 0.90	5.76 ± 1.94	1.62 ± 0.59	2.63 ± 2.13	2.44 ± 0.67	5.83 ± 1.92	1.60 ± 0.89	4.38 ± 1.92
Sc	2.03 ± 2.30	2.69 ± 1.15	2.56 ± 1.71	1.90 ± 1.04	1.03 ± 1.02	ND	0.93 ± 2.27	0.06 ± 0.13
Se	ND	ND	ND	ND	ND	ND	ND	ND
Sm	0.08 ± 0.03	0.18 ± 0.04	0.02 ± 0.01	ND	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
Sn	4.32 ± 1.42	8.05 ± 2.38	1.86 ± 0.74	4.09 ± 2.82	4.36 ± 0.88	7.81 ± 1.84	3.57 ± 1.63	6.97 ± 2.28
Sr	7.52 ± 4.37	21.2 ± 3.67	3.03 ± 0.12	2.57 ± 1.14	2.61 ± 0.50	2.70 ± 0.48	4.77 ± 1.63	2.59 ± 0.51
Ta	0.05 ± 0.01	0.25 ± 0.35	ND	ND	0.07 ± 0.15	0.01 ± 0.02	ND	ND
Tb	0.01 ± 0.01	0.03 ± 0.01	ND	ND	ND	ND	ND	ND
Th	0.15 ± 0.04	0.33 ± 0.10	ND	ND	0.04 ± 0.03	0.03 ± 0.02	ND	ND
Ti	46.8 ± 14.4	70.9 ± 20.3	24.1 ± 8.12	21.5 ± 14.9	22.0 ± 5.93	32.6 ± 4.30	42.1 ± 16.3	29.7 ± 9.61
Tl	0.04 ± 0.04	0.07 ± 0.03	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.02	0.06 ± 0.01	0.01 ± 0.01	0.04 ± 0.05
U	0.09 ± 0.02	0.15 ± 0.04	0.02 ± 0.00	0.05 ± 0.02	0.05 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
V	6.86 ± 3.02	23.5 ± 8.95	6.57 ± 3.79	6.09 ± 2.04	8.41 ± 3.47	16.4 ± 3.14	9.42 ± 1.35	5.40 ± 5.03
W	0.33 ± 0.34	0.61 ± 0.39	0.08 ± 0.03	0.10 ± 0.11	0.12 ± 0.07	3.36 ± 3.12	ND	0.55 ± 0.73
Y	0.24 ± 0.10	0.60 ± 0.17	0.10 ± 0.03	0.05 ± 0.03	0.06 ± 0.05	0.08 ± 0.02	0.02 ± 0.01	0.05 ± 0.08
Yb	0.03 ± 0.01	0.08 ± 0.02	ND	ND	ND	0.01 ± 0.00	ND	ND
Zr	10.4 ± 4.20	21.3 ± 3.72	2.60 ± 1.35	2.49 ± 1.56	3.87 ± 0.74	3.39 ± 1.17	0.72 ± 0.50	0.90 ± 1.41

Levels in ng/m^3. Oct: October; Dec: December; Jul: July. ND: Not detected.

Table 3

Levels of Total Carbon (TC), organic plus elemental carbon (OC+EC), ions (Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-) and indirect determinations (OM, CO_3^{2-}, SiO_2, and Al_2O_3) in PM_{10} collected in 8 sampling campaigns from 2013 to 2016.

	Oct 2013 n=6	**Dec 2013** n=6	**Jul 2014** n=6	**Dec 2014** n=6	**Oct 2015** n=6	**Dec 2015** n=6	**Jul 2016** n=6	**Dec 2016** n=5
TC	8.01 ± 1.10	17.5 ± 5.61	3.04 ± 0.47	8.00 ± 2.79	5.51 ± 0.90	17.4 ± 3.86	3.77 ± 0.80	13.9 ± 3.95
OC+EC	7.38 ± 1.34	13.9 ± 5.48	2.77 ± 0.43	6.24 ± 2.17	4.74 ± 0.85	16.2 ± 3.90	3.11 ± 0.60	13.2 ± 3.81
OM	8.27 ± 1.49	15.6 ± 6.14	3.10 ± 0.48	6.99 ± 2.44	5.40 ± 4.70	18.6 ± 4.38	3.74 ± 0.97	14.8 ± 4.26
CO_3^{2-}	2.19 ± 1.12	4.83 ± 1.06	0.42 ± 0.10	0.90 ± 0.60	0.77 ± 0.08	1.15 ± 0.37	0.66 ± 0.23	0.70 ± 0.22
SiO_2	0.34 ± 0.06	1.43 ± 0.30	0.07 ± 0.03	0.08 ± 0.05	0.11 ± 0.05	0.11 ± 0.04	0.13 ± 0.07	0.08 ± 0.06
Al_2O_3	1.18 ± 0.22	4.91 ± 1.02	0.23 ± 0.12	0.27 ± 0.16	0.37 ± 0.16	0.38 ± 0.14	0.46 ± 0.25	0.26 ± 0.21
Cl^-	0.69 ± 0.35	0.05 ± 0.03	0.34 ± 0.50	0.13 ± 0.03	0.51 ± 0.73	0.47 ± 0.14	0.33 ± 0.54	1.65 ± 0.71
SO_4^{2-}	2.48 ± 0.74	2.47 ± 0.42	2.16 ± 0.44	1.05 ± 0.09	0.95 ± 0.70	1.85 ± 0.84	1.63 ± 0.76	3.13 ± 0.98
NH_4^+	0.08 ± 0.07	0.24 ± 0.09	0.08 ± 0.08	0.09 ± 0.05	0.22 ± 0.26	0.62 ± 0.06	0.08 ± 0.04	0.15 ± 0.07
NO_3^-	3.31 ± 0.97	5.02 ± 1.29	0.85 ± 0.26	1.13 ± 0.43	1.09 ± 0.50	2.38 ± 0.62	3.92 ± 0.46	1.88 ± 0.24

Levels in µg/m^3. TC: Total carbon; OC+EC: organic carbon plus elemental carbon; OM: organic matter.
Oct: October; Dec: December: Jul :July

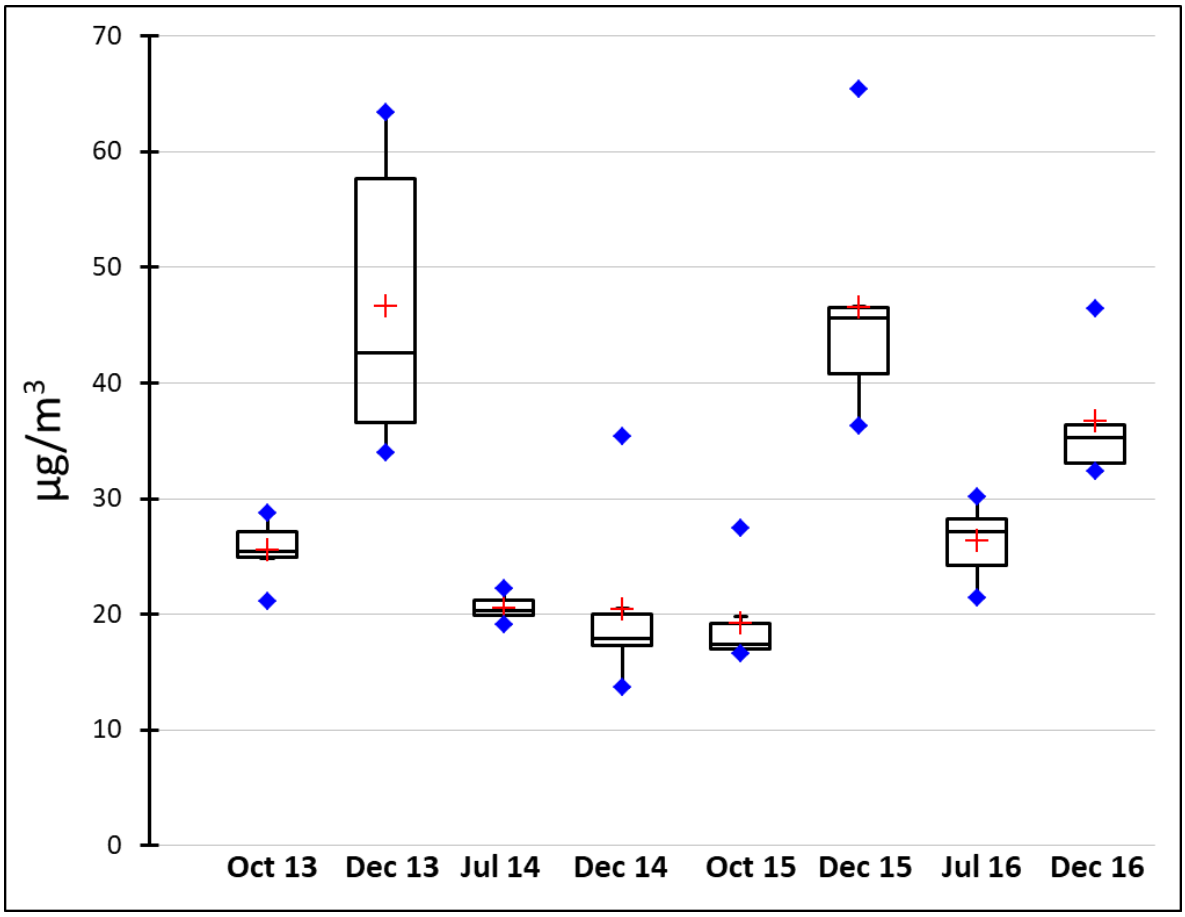

Fig. 1. Box-plot of PM_{10} levels ($\mu g/m^3$) in the eight campaigns performed from 2013 to 2016. Mean levels are marked with a red cross. Maximum and minimum values are marked with blue diamonds.

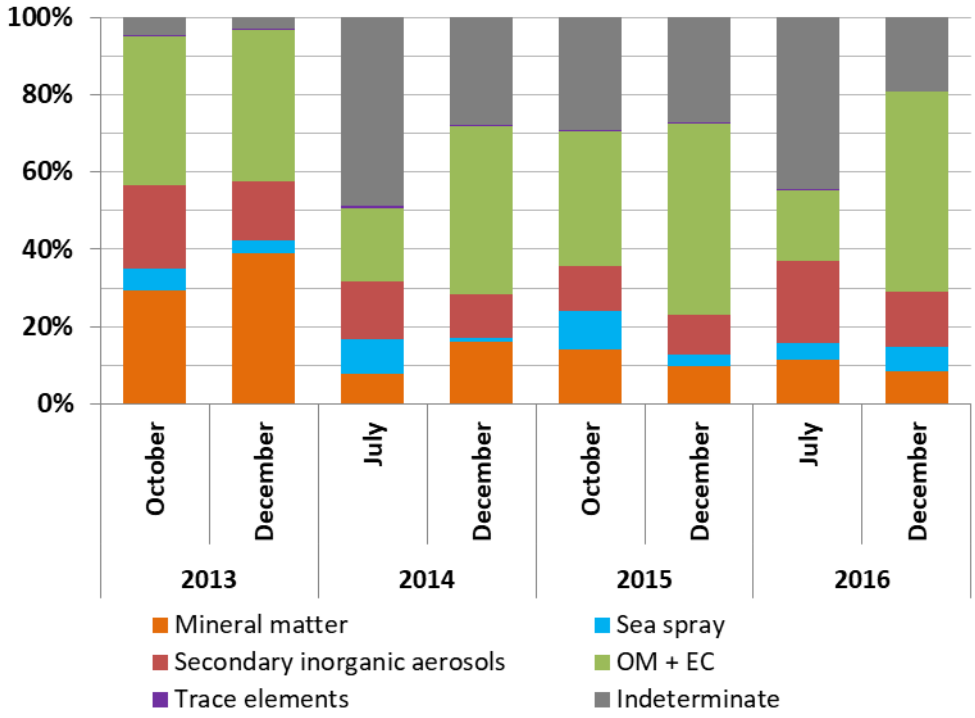

Fig. 2. PM_{10} principal components sampled during 2013 to 2016 near a cement plant.

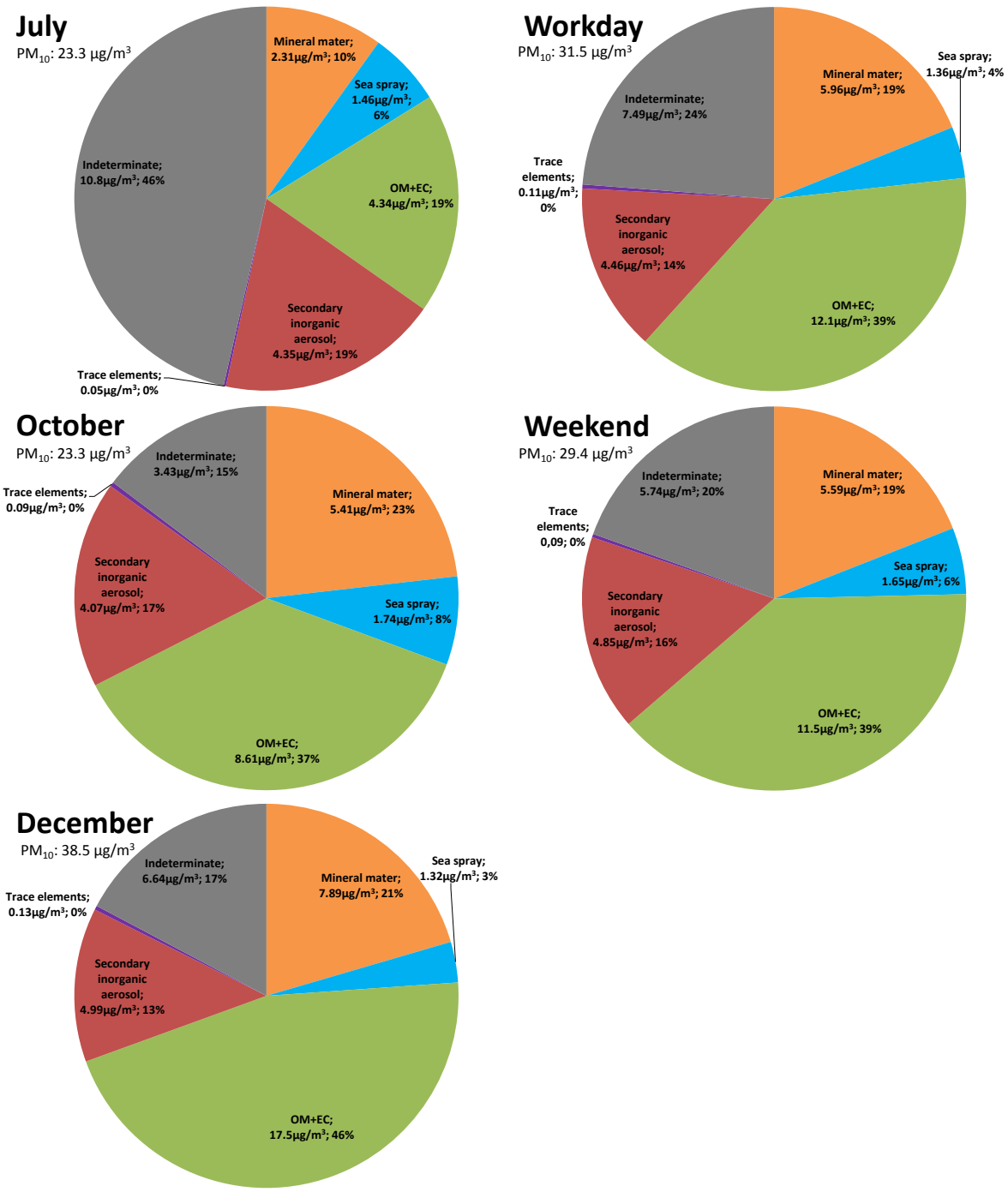

Fig. 3. PM_{10} main components in June, October, and December, and during working days and weekends.

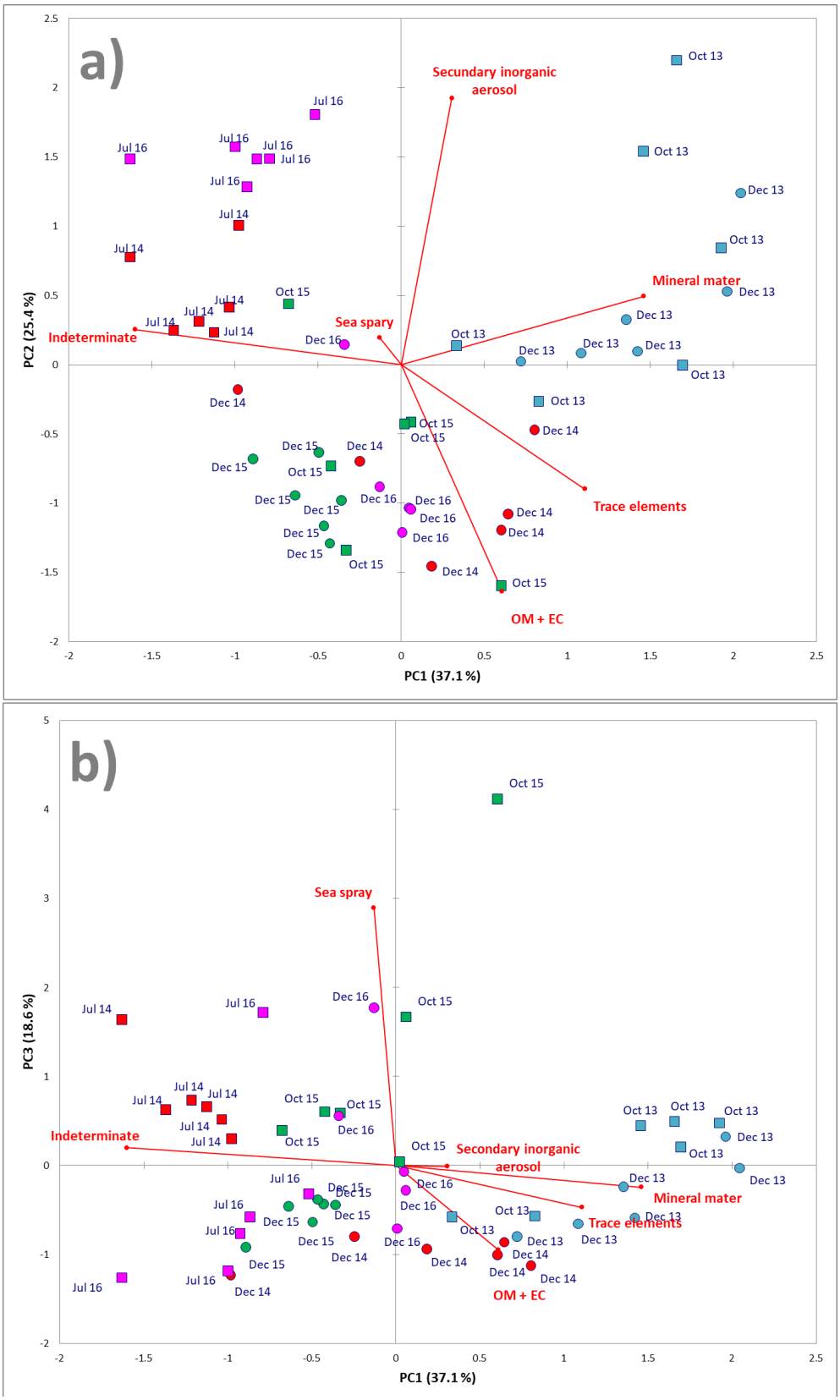

Fig. 4. Principal components analysis with main components of PM_{10} collected around a cement plant between 2013 and 2016.

Supplementary Material

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