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Main components and human health risks assessment of PM₁₀, PM_{2.5}, and PM₁ in two areas influenced by cement plants

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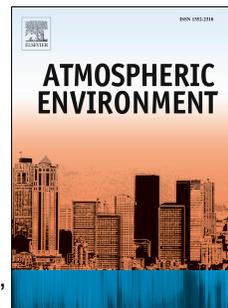
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1 Main components and human health risks assessment of
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3 plants

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Abstract

51

52 Particulate matter (PM) is widely recorded as a source of diseases, being more harmful
53 those particles with smaller size. PM is released to the environment as a consequence of
54 different activities, being one of them cement production. The objective of this pilot
55 study was to characterize PM of different sizes around cement facilities to have a
56 preliminary approach of their origin, and evaluate their potential health risks. For that
57 purpose, three fractions of PM (10, 2.5, and 1) were collected in the nearby area of two
58 cement plants with different backgrounds (urban and rural) in different seasons.
59 Subsequently, main components, outdoor and indoor concentrations, exposure, and
60 human health risks were assessed. Greatest levels of PM₁, organic matter, and metals
61 were found in urban location, especially in winter. Consequently, environmental
62 exposure and human health risks registered their highest values in the urban plant
63 during wintertime. Exposure was higher for indoor activities, expressing some metals
64 their peak values in the PM₁ fraction. Non-carcinogenic risks were below the safety
65 threshold (HQ<1). Carcinogenic risks for most of the metals were below the limit of 10⁻⁵,
66 except for Cr (VI), which exceeded it in both locations, but being in the range
67 considered as assumable (10⁻⁶-10⁻⁴).

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Key words

69

70
71 Cement

72 Particulate matter fractions

73 Indoor/outdoor exposure

74 Human risk assessment

75

Highlights

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- 77
- 78 ➤ Characterisation of PM₁₀, PM_{2.5}, and PM₁ was carried out around two cement
- 79 plants.
- 80 ➤ Outdoor and indoor exposure and human health risk to toxic elements were
- 81 assessed.
- 82 ➤ Higher concentrations and human health risks were observed in urban site in
- 83 winter.
- 84 ➤ Maximum human health risk levels were found due to PM₁ fraction exposure.

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1. Introduction

World Health Organization has recently estimated that ambient pollution is responsible for 3.7 million premature deaths yearly (WHO, 2014). Among the substances comprising air pollution, particulate matter (PM) is seen by some studies as the most harmful (Cohen et al., 2005; EEA, 2013). PM can cause a wide variety of health impacts, such as asthma, bronchitis, cardiovascular diseases, and lung cancer (Anderson et al., 2012)

Most influent parameters in PM hazardous potential are size and chemical composition (Harrison and Yin, 2000). PM size range spreads from micrometers to nanometres. PM with a diameter smaller than 10 μm (PM_{10}) are able to enter into the respiratory tract and reach the lungs (US EPA, 2013). The coarse fraction of these particles, those with a diameter between 10 and 2.5 μm ($\text{PM}_{10-2.5}$), remains in the upper part of the respiratory tract, while the fine particles, those PM smaller than 2.5 μm ($\text{PM}_{2.5}$), can undergo deeper in the lung system, being the smallest fraction capable of reaching the bloodstream (Anderson et al., 2012). The potential effects that can be developed after entering into the circulatory system could be more pernicious, concluding several publications (Cifuentes et al., 2000; Schwartz et al., 1996) that the smaller the PM, the more harmful it is. Regarding their chemical composition, the presence of toxic substances (e.g. acids, metals, and PAHs), plays an important role in health impacts (Casseo et al., 2013). PM size and chemical composition depend on several parameters, such as the weather, period of the year, and emission source (Casseo et al., 2013).

One of the industrial activities that releases PM into the environment is the cement production. In this activity, PM are generated as a consequence of subjecting lime to high temperatures (from 900 to 1,500°C) for yielding cement (EU Commission, 2013). Furthermore, raw materials processing and clinker milling and packaging could lead to PM fugitive emissions (Abdul-Wahab, 2006). Currently, there are few papers focusing on the study of health risks produced by PM around cement facilities (Abdul-Wahab, 2006; Mari et al., 2009; Rovira et al., 2014, 2011a). Although it is stated that almost 50% of the PM emitted from the cement industry is smaller than 2.5 μm (Gupta et al., 2012), no one of the previous cited articles is focused on the fine fraction of particles.

The aim of this study is to characterize PM around cement facilities to have a preliminary approach of their origin and assess their potential risk for human health. For that purpose, three PM fractions (10, 2.5, and 1) were collected in the surrounding of two cement factories. Concentrations of metals, ions, and carbon were measured in order to better know the main PM components. Human health risks were evaluated having into account the carcinogenic and non-carcinogenic risks derived from the particles metal content. To our knowledge, this is the first study focused in revealing potential health effects of PM fine fraction in the surrounding of cement facilities.

2. Materials and Methods

2.1. Site description and PM monitoring

A better description of the area and cement plant characteristics could be found in Supplementary Materials. Briefly, the first cement plant is placed in Barcelona (northeast Spain) metropolitan area, within an urban sector affected by several

150 industries, while the second is set 165 km south in the Mediterranean coastline,
151 integrated in a rural background. Both plants are similar in production volume and air
152 cleaning devices.

153

154 After performing previous studies (Rovira et al., 2011b, 2010), we selected one single
155 point in every location. These points were those in which PM concentrations were the
156 highest, besides being located into populated nuclei including especially sensitive
157 groups of population (children, seniors, etc.). Therefore a worst case scenario was
158 conducted in this study. In location A the sampling point was located 300 m away from
159 the cement plant, while in location B it was located 500 m away from the facility. To
160 evaluate differences among seasons with different meteorological conditions, samples in
161 location A were collected in three periods: autumn 2013 (AA), winter 2013/2014 (AW),
162 and summer 2014 (AS). Location B was used as control site. Samples in this location
163 were obtained during autumn 2014 (BA), since in this season emissions from traffic and
164 heating systems show medium values between summer and winter. For every period,
165 samples were collected during five consecutive days. Samples were collected
166 simultaneously with three high-volume active samplers, one for each analyzed fraction.
167 PM₁₀ and PM_{2.5} were sampled using two TE-6070-DV devices (Tisch Environmental),
168 while PM₁ samples were collected using CAV-A/mb sampler (MCV SA). Volume
169 sampled was around 1700 m³ for PM₁₀ and PM_{2.5} and around 600 m³ for PM₁. All the
170 three fractions were collected in quartz microfiber filters (QFF).

171

172 *2.2. Analytical methods*

173

174 A full description of the undergone procedures could be seen in Supplementary
175 Materials. Briefly, PM levels were calculated by gravimetric determination after
176 acclimatising (40% humidity and 20°C). Filters were then divided in three portions. The
177 first one was used for analysis of metals by means of ICP-OES. The second portion was
178 used for determining ionic content by ionic chromatography and specific electrode. Last
179 portion was used for knowing the carbon content by pyrolysis in presence of oxygen.

180

181 Some indirect calculations were performed in order to find out the contents of different
182 compounds. To establish the OC content we solved the equation $OC = 0.7 \times (OC + EC)$,
183 and organic matter (OM) was estimated by applying a factor of 1.6 to organic carbon
184 concentrations (Pérez et al., 2008). Carbonate and SiO₂ content were estimated from Ca
185 and Mg ($1.5 \times Ca + 2.5 \times Mg = CO_3^{2-}$), and Al₂O₃ concentrations ($2 \times Al_2O_3 = SiO_2$),
186 respectively. We assume that the totality of Al analysed was in oxide form (Al₂O₃)
187 (Querol et al., 2001).

188

189 *2.3. Main components determination*

190

191 PM were divided in six main components: mineral matter (Sum of CO₃²⁻, SiO₂, Al₂O₃,
192 Ti, P, Mn, Mg, K, Fe, and Ca), sea spray (sum of Na⁺ and Cl⁻), organic matter and
193 elemental carbon (OM+EC), secondary inorganic aerosols (sum of SO₄²⁻, NH₄⁺, and
194 NO₃⁻), trace elements (the sum of the rest of elements), and unaccounted (the difference
195 between the PM concentration and the sum of the rest of fractions).

196

197 *2.4. Exposure Model*

198

199 Concentrations of harmful metals (As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Se, V, and U) in
 200 the different PM fractions, seasons, and locations were used for assessing the human
 201 exposure. This metal selection was done according toxicological parameters availability
 202 in the risk assessment information system (RAIS, 2013). Exposure was estimated by
 203 considering only the inhalation route for an average adult individual (from 16 to 65
 204 years old) in a mean daily routine based on annual data (Generalitat de Catalunya,
 205 2012). Average exposure was calculated as divided in three different activities:
 206 sleeping, working/leisure, and outdoor time. Sleeping and working/leisure were
 207 considered as fully indoor activities. Numerical expression and parameters used to
 208 evaluate the exposure (Exp) for the different activities are shown in Equation 1:
 209

$$210 \quad Exp = \frac{C_{air} \times IR \times EF}{BW \times 365} \times \frac{AcT}{24} \quad (\text{Eq. 1})$$

211 Descriptions and values of the different parameters are presented in **Error! Reference**
 212 **source not found..** C_{air} used differed between indoor (sleeping and working/leisure) and
 213 outdoor activities. C_{air} for outdoor activities was the obtained from analytical
 214 determinations. C_{air} for indoor activities was calculated from outdoor C_{air} through the
 215 software IAQX v 1.1, developed by the United States Environmental Protection Agency
 216 (US EPA, 2000). We set an average room volume of 30 m³. Ventilation rates were
 217 taken according to the RD 1027/2007 specification for domestic and office buildings
 218 (IDA 2), published by the Spanish Ministry of Tourism, Energy, and Industry
 219 (MINETUR, 2013). Deposition and infiltration rates used in our simulations were
 220 obtained from previous studies (He et al., 2005; Hoek et al., 2008). Total exposure was
 221 calculated as the sum of every activity exposure (sleeping, work/leisure, and outdoor).
 222

223 2.5. Human Health risks assessment

224 Non-carcinogenic and carcinogenic risks calculations through inhalation were
 225 previously described (Rovira et al., 2010). Briefly, exposure concentrations (EC),
 226 Hazard Quotient (HQ) and cancer risk are described in equations 2, 3, and 4,
 227 respectively.
 228

$$230 \quad EC = \frac{C_{air} \times AcT \times EF \times ED}{AT \times 365 \times 24} \quad (\text{Eq. 2})$$

$$231 \quad HQ = \frac{EC \times 10^6}{RfC} \quad (\text{Eq. 3})$$

$$232 \quad \text{CancerRisk} = EC \times 10^6 \times IUR \quad (\text{Eq. 4})$$

233 All parameters used in these equations are depicted in Table 1.
 234

235 In order to know the carcinogenic potential of Cr, we assumed Cr (VI) concentration as
 236 1/6 of the total Cr concentration (Brown et al., 2014). It was also assumed that the
 237 totality of the As measured was inorganic (Huang et al., 2014).
 238

239 2.6. Statistical Treatment

240 We assumed a concentration equal to half the limit of detection for that species under
 241 the detection limit. Statistical processing was carried out by means of the statistical
 242 software package SPSS Statistics 20.0. For elucidating if the data present a parametric
 243

244 distribution a Levene test was performed. Subsequently, student T tests and ANOVA
245 (parametric data), and Kruskal Wallis (non parametric data) tests were undergone. We
246 considered difference as significant for those cases with a probability below 0.05
247 ($p < 0.05$).

248

249 3. Results and discussion

250

251 3.1. PM concentrations

252

253 Statistically significant differences ($p < 0.05$) were found between winter and the other
254 seasons in plant A (**Error! Reference source not found.**). The highest concentrations
255 for the three fractions were reported during winter, with average values of 51.2 ± 13.9 ,
256 31.9 ± 9.9 , and $31.3 \pm 7.1 \mu\text{g}/\text{m}^3$ for PM_{10} , $\text{PM}_{2.5}$, and PM_1 , respectively. Comparing the
257 samples collected in summer and autumn, significantly ($p < 0.05$) higher concentrations
258 of PM_{10} were recorded during autumn. No statistically significant differences were
259 found between PM_{10} and $\text{PM}_{2.5}$ concentrations obtained in plant B and those obtained in
260 plant A in samples collected during autumn. However, regarding PM_1 , statistically
261 significant ($p < 0.05$) smaller concentrations were found in plant B.

262

263 Mean values of the three particle fractions and the seasonal pattern obtained in plant A
264 are similar to those reported previously in the metropolitan area of Barcelona (Pérez et
265 al., 2008). In his turn, levels found in plant B are similar to those described in rural
266 areas previously (Pey et al., 2010c). In our research, yearly limits established by the EU
267 for $\text{PM}_{2.5}$ ($25 \mu\text{g}/\text{m}^3$), and yearly and daily values set for PM_{10} (40 and $50 \mu\text{g}/\text{m}^3$,
268 respectively) (EU Parliament, 2008) were surpass only in the plant A in winter.

269

270 3.2. Main components of PM

271

272 **Error! Reference source not found.** shows the main components of the collected
273 particles. Concentrations of all analysed elements and ions for the three fractions can be
274 seen in supplementary materials (Table S1).

275

276 3.2.1. Organic matter (OM) and elemental carbon (EC)

277

278 OM+EC is mainly attributable to combustion sources (Pérez et al., 2008). Our results
279 show that this component increases its contribution to the PM in the fine fraction of
280 particles. This trend was described in previous studies (Pérez et al., 2008; Reche et al.,
281 2012). Maximum levels of OM+EC were registered during winter, and reached their
282 minimum in summer for every fraction. An increase in the use of heating systems and
283 road traffic associated to low temperatures seems to be the cause for such result
284 (Galindo et al., 2010).

285

286 In our study, mean levels of OM+EC obtained during winter for PM_{10} and $\text{PM}_{2.5}$ (19.8
287 and $16.8 \mu\text{g}/\text{m}^3$, respectively) were higher than those recorded previously within the
288 Barcelona metropolitan area (around $11.9 \mu\text{g}/\text{m}^3$ for both fractions) (Viana et al., 2006).
289 These differences could have their origin in different meteorological conditions during
290 sampling collection, differences in heating systems between both places and/or
291 combustion from cement facility. Comparing both cement plants, B location presented
292 smaller values of OM+EC, explained by the lower traffic density.

293

3.2.2. Sea spray (SS)

Sea spray was mainly taking part into the PM₁₀ and PM_{2.5} fractions, experiencing a great decrease in PM₁. These results are in agreement with previous studies carried out by other authors (Kelly and Fussell, 2012; Mazzei et al., 2008). Higher contributions from this component are recorded in B location due to its proximity to the coastline.

3.2.3. Mineral matter (MM)

Maximum contributions of mineral matter are shown in PM₁₀ in winter. During this period, mineral matter contribution decreases notably when the particle size decreases to PM_{2.5}. In autumn, mineral matter shows similar contributions in every fraction. In summer, this component remains constant, between 8-13% for every fraction. Comparing both sites in autumn, cement plant B showed smaller contribution of this parameter in PM₁₀, but similar values to those experienced in plant for the rest of fractions.

3.2.4. Secondary Inorganic Aerosols (SIA)

Ammonium and sulphate have been recorded to be present mainly in the fine fraction, while nitrate is usually part of the coarser fraction. For every season and location, SIA contributions show a homogeneous distribution among the three fractions, with values ranging between 12-22%. Comparing plant A and B in the same season, higher ammonium contributions are shown in location B, suggesting a bigger influence from farming activities (Pey et al., 2010b).

3.2.5. Trace elements (TE)

Levels of toxic metals regulated under the European legislation were much lower in our study (**Error! Reference source not found.**) than the annual average limits set by the European Commission (6, 5, 20, and 500 ng/m³ for As, Cd, Ni, and Pb, respectively) (EU Parliament, 2008, 2005).

Higher statistically significant ($p < 0.05$) concentrations for almost every metal were observed during the winter within the three analyzed fractions. Especially high are the levels of V within the PM₁₀ fraction in winter. This could be a result of changes in the composition of fuel used in the cement facility (Reche et al., 2012). Levels of Cu and Sb in the coarser fraction (Pant and Harrison, 2013), which are used as traffic tracers, show similar values in winter and autumn, experiencing a great decrease in summer. Comparing both plants in the same season, statistically significant higher ($p < 0.05$) concentrations were recorded in A location for almost the totality of metals analyzed in every fraction. The only metals which registered higher significant levels in plant B were Sc, Mo, and V. These differences were especially clear in the PM_{2.5} and PM₁ fractions, and could be a consequence of the differences in fuel composition between the two plants (Arbuzov et al., 2014; Lane et al., 2013; Santacatalina et al., 2010). Levels of Cu and Sb were lower in the coarser fraction of B location, indicating a smaller contribution from traffic sources. Comparing our study with previous studies performed in the area (Pey et al., 2010c; Pérez et al., 2008; Minguillón et al., 2014), similar metal concentrations and seasonal patterns are observed. Plant A shows levels of

343 metals similar to an urban-industrial site, while B presents a slightly higher metal
344 concentrations than those reported for a rural background (Querol et al., 2007).

345

346 3.2.6. Unaccounted (U)

347

348 Unaccounted contributions range between 2-46% for $PM_{2.5}$ and PM_1 . This range
349 decreases in the PM_{10} fraction, having values between 2-35%. The origin of the
350 unaccounted component is diverse. Previous studies have related this component with
351 water bound to secondary inorganic aerosols, measurement errors or underestimations
352 in the content of OM+EC (Pey et al., 2010a; Santacatalina et al., 2010).

353

354 Except for the concentrations of OM+EC during winter, levels and seasonal patterns of
355 the components in location A for every fraction present in this study are similar to those
356 reported previously in the Barcelona metropolitan area (Pérez et al., 2008; Pey et al.,
357 2010b, 2010c). Location A seems to be more influenced by traffic emissions than
358 location B. Higher contributions in OM+EC could have their origin in traffic exhaust
359 emissions, and contributions to coarse TE could have their source in traffic non-exhaust
360 emissions.

361

362 3.3. Exposure Model

363

364 Indoor PM levels and exposure values are shown in **Error! Reference source not**
365 **found.** In order to better assess the exposure to different size of particles, we calculated
366 the health risks for three diameter ranges: $PM_{10-2.5}$ (result of subtracting $PM_{2.5}$ levels to
367 PM_{10} levels), $PM_{2.5-1}$ (result of subtracting PM_1 levels to $PM_{2.5}$ levels) and PM_1 .

368

369 Indoor concentrations represent around 65% of the outdoor concentrations for $PM_{2.5-1}$
370 and PM_1 , and around 45% of the outdoor PM_{10} concentrations. In location A, the
371 highest values of indoor concentrations are reached in the PM_1 fraction, while location
372 B reaches its greatest values of indoor concentration in the $PM_{10-2.5}$ fraction. This result
373 is a direct consequence of the higher proportion of PM_1 in PM_{10} found in location A,
374 and a bigger infiltration rate for fine PM. Regarding the activities, working and leisure
375 showed the highest exposures for every period and PM fraction. Consequently, indoor
376 exposure was the highest for every PM fraction due the most of time expended in indoor
377 environment.

378

379 The results of specific metal exposure are shown in **Error! Reference source not**
380 **found.** Maximum exposure was reached by V in winter, with a value of $5.2 \cdot 10^{-6}$
381 $mg/(kg \cdot day)$. More than half of this value (54%) was reached in the $PM_{10-2.5}$. Se and Hg
382 were not detected in any sampling period. Winter was the period that showed highest
383 metal exposure for most of the metals analyzed. During this period, Pb and V levels of
384 exposure were considerably higher (1.6 and 3.1 times respectively) than highest values
385 for the rest of periods. Comparing the two sites in the same season, smaller levels of
386 exposure were detected in location B. In this location, most of the exposure was
387 addressed in the fine fraction, while in location A it was located in the $PM_{10-2.5}$ fraction.
388 The higher metal content from traffic non-exhaust emissions in location A could explain
389 this result.

390

391 Regarding the distribution of different metals, Co, Cd, and Be showed their maximum
392 exposure values in the $PM_{10-2.5}$ fraction. Uranium showed its maximum exposures in

393 PM_{2.5-1}. Peak exposure values of As, Mn, and Pb were experienced in the PM₁ fraction.
394 Apart from traffic, cement facilities could be also a supplementary source of Cd, Co, Cr,
395 Mn, and Ni, and the main contributor for As, Pb, and V (Gupta et al., 2012;
396 Santacatalina et al., 2010). Levels of exposure in plant A were similar to those reported
397 before for the same area (Rovira et al., 2011b).

398

399 3.4. Human health risks assessment

400

401 Regarding non-carcinogenic risks, HQ for all the chemicals was below the safety
402 threshold, established in 1. Winter in plant A was the sampling period experiencing the
403 highest levels of non-carcinogenic risks. Within this period, the highest HQ value
404 corresponded to Mn allocated in PM₁, with a HQ value of 0.1. The rest of the HQ
405 values were below 10% of the safety limit.

406

407 Additional carcinogenic risks due to metal inhalation are depicted in **Error! Reference**
408 **source not found.** Hexavalent Cr was the only metal above the threshold for cancer
409 risk established as 10^{-5} in Spain (MAGRAMA, 2007). This threshold was surpassed in
410 every sampling period, except for plant A during summer. However, cancer values were
411 assumable (10^{-6} – 10^{-4}) depending on the variable characteristics of each individual (US
412 EPA, 1996). The sampling period performed in winter experienced the highest levels of
413 carcinogenic risk for most of metals. This period reached the highest overall value of
414 additional cancer risk, with a value of $2.9 \cdot 10^{-5}$ for Cr (VI). In winter, most of the
415 additional carcinogenic risks observed were part of the PM_{2.5-1} or PM₁ fractions. Unlike
416 winter, most of the additional carcinogenic risks observed in autumn and summer were
417 located in the PM_{10-2.5} fraction. As observed with OM+EC, a higher contribution from
418 combustion sources (such as heating systems) in winter could be the explanation to this
419 fact.

420

421 Carcinogenic risks were smaller in plant B if compared with plant A in the same season
422 of the year. In this location, most of additional carcinogenic risks were in the PM₁
423 fraction. The presence of toxic metals in the fine fraction in location B suggests a higher
424 contribution to metal content from combustion processes, such as the cement production
425 (Kelly and Fussell, 2012).

426

427 PM₁ registers the maximum carcinogenic risk in the case of As and Pb, and the highest
428 overall value for Cr (IV), evidencing thus the damage potential of PM₁. As said
429 previously, As and Pb are elements suitable for coming principally from the cement
430 plant. Although Cr (VI) is not an exclusive metal from cement production, it is feasible
431 a contribution to this metal levels from the cement facility, especially in plant B, where
432 traffic is less intense and no other industrial activities are developed. Levels of risks for
433 most of the metals here described are similar to those previously reported in the same
434 area (Rovira et al., 2011b).

435

436 4. Conclusions

437

438 Three fractions of PM (10, 2.5, and 1) were collected in the nearby area of two cement
439 plants in different seasons. Main components, exposure, and human health risks were
440 calculated to preliminary know the main contributors to the PM mass and evaluate the
441 potential health effects on the population. Our results show greatest levels of PM₁₀,
442 PM_{2.5}, and PM₁ during winter. During this season, the highest levels of OM+EC and

443 toxic metals were registered for every PM fraction. Consequently, exposure and human
444 health risks experienced their highest values. Summer and autumn show similar levels
445 of PM mass, but with a greater contribution from combustion sources in autumn.
446 Comparing both plants in the same season, statistically significant differences were
447 found in the levels of PM₁ and TE, presenting lower values plant B. Differences in the
448 concentrations of Sc, Mo, and V between the two locations suggest the influence of the
449 cement plant fuel used in the ambient particles composition, especially in the PM₁
450 fraction. Traffic had a major contribution to ambient PM in location A, while in location
451 B, less impacted by traffic, cement plant had more influence, especially in the fine
452 fraction.

453

454 Exposure values were higher for indoor activities (working/leisure and sleeping) due the
455 most of time expended in indoor environment. Non-carcinogenic risks were below the
456 safety threshold (HQ<1). Carcinogenic risks for most of the metals were below the limit
457 of 10⁻⁵, except for Cr (VI), which exceeded it in both locations, but being in the range
458 considered as assumable (10⁻⁶-10⁻⁴).

459

460 In this preliminary study, the importance of working on fine PM in areas influenced by
461 cement plants is revealed. Maximum values of carcinogenic and non-carcinogenic risks
462 were observed in the ambient PM₁. A possible contribution from cement plants to
463 OM+EC and elements (especially As and Pb) in the ambient PM₁ is observed in this
464 work. Further research, with greater number of samples and more detailed exposure
465 evaluation for different ages and activities of indoor concentrations, is needed in order
466 to elucidate the real contribution from different sources to human health damages.

467

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469

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475

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1 **Table 1: Parameters used for calculating human exposure and health risks**

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Parameter	Description	Value		Units	Reference
IR	Inhalation rate	Sleeping	7.58	m ³ /day	OEHHA 2012
		Work/Leisure	38.8		
		Outdoor	38.8		
EF	Exposure frequency	350		days/year	MAGRAMA, 2007
BW	Body weight	70		kg	US EPA, 1989
AcT	Activity Time	Sleeping	8.88	hours/day	Generalitat de Catalunya, 2012
		Work/Leisure	12.7		
		Outdoor	2.40		
ED	Exposure duration	30		years	MAGRAMA, 2007
AT	Averaging time	Carcinogenic: 70		years	MAGRAMA, 2007
		Non-carcinogenic: 30			
RfC	Reference inhalation concentration	As	1.50E+01	ng/m ³	RAIS, 2013
		Be	2.00E+01		
		Cd	2.00E+01		
		Co	6.00E+00		
		Cr	1.00E+02		
		Hg	3.00E+02		
		Mn	5.00E+01		
		Ni	9.00E+01		
		Se	2.00E+04		
		V	1.00E+02		
		U	4.00E+01		
IUR	Inhalation Unit Risk	As	4.3E-06	m ³ /ng	RAIS, 2013
		Be	2.4E-06		
		Cd	1.8E-06		
		Co	9.0E-06		
		Cr	8.4E-05		
		Ni	2.6E-07		
		Pb	1.2E-08		
	Conversion factor	365	days/year		
	Conversion factor	24	hour/day		
	Conversion factor	10 ⁶	ng/mg		
C _{air}	Concentration in air	Site Specific		mg/m ³	Present study

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28 **Table 2: Levels (mean \pm standard deviation) of toxic elements for both cement plants (A and B),**
 29 **and sampling periods: autumn (A), winter (W), and summer (S). Results are expressed in ng/m³**
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	AA			AW			AS			BA		
	PM ₁₀	PM _{2.5}	PM ₁	PM ₁₀	PM _{2.5}	PM ₁	PM ₁₀	PM _{2.5}	PM ₁	PM ₁₀	PM _{2.5}	PM ₁
As	0.63 \pm 0.09	0.38 \pm 0.07	0.36 \pm 0.11	0.62 \pm 0.13	0.59 \pm 0.06	0.39 \pm 0.21	0.19 \pm 0.07	ND	ND	0.36 \pm 0.16	0.30 \pm 0.02	0.15 \pm 0.10
Be	0.09 \pm 0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.68 \pm 0.35	0.31 \pm 0.13	0.26 \pm 0.05	0.47 \pm 0.01	0.20 \pm 0.01	0.20 \pm 0.01	ND	ND	ND	ND	ND	ND
Co	0.33 \pm 0.06	0.09 \pm 0.03	0.08 \pm 0.06	0.45 \pm 0.27	0.15 \pm 0.09	0.10 \pm 0.02	0.15 \pm 0.02	ND	ND	0.20 \pm 0.10	0.11 \pm 0.02	0.08 \pm 0.01
Cr	7.28 \pm 0.22	ND	ND	8.49 \pm 3.09	4.20 \pm 1.32	4.18 \pm 3.26	3.26 \pm 0.53	ND	ND	6.05 \pm 0.70	6.02 \pm 2.84	ND
Mn	6.98 \pm 3.94	4.38 \pm 1.02	3.32 \pm 3.67	8.13 \pm 2.82	7.48 \pm 1.38	5.29 \pm 2.47	7.85 \pm 2.30	1.91 \pm 0.91	1.89 \pm 0.46	5.10 \pm 3.32	2.83 \pm 1.23	1.33 \pm 0.70
Ni	4.07 \pm 0.91	1.74 \pm 0.14	1.6 \pm 0.18	6.96 \pm 2.42	5.94 \pm 4.33	1.69 \pm 0.94	7.0E \pm 2.42	ND	ND	3.47 \pm 0.47	3.24 \pm 0.66	2.88 \pm 0.69
Pb	11.9 \pm 3.19	4.96 \pm 1.76	4.07 \pm 2.64	16.8 \pm 3.03	13.2 \pm 4.89	13.1 \pm 3.88	3.16 \pm 1.62	1.70 \pm 2.21	1.29 \pm 0.86	3.57 \pm 2.57	2.88 \pm 1.93	1.61 \pm 0.96
U	0.11 \pm 0.01	0.10 \pm 0.01	0.10 \pm 0.06	0.15 \pm 0.04	0.15 \pm 0.03	0.15 \pm 0.07	0.02 \pm 0.02	ND	ND	0.08 \pm 0.06	0.08 \pm 0.06	ND
V	6.87 \pm 3.03	3.15 \pm 0.57	2.22 \pm 0.85	23.5 \pm 8.95	9.09 \pm 2.57	4.44 \pm 1.02	6.57 \pm 3.79	3.04 \pm 0.05	2.85 \pm 0.15	7.28 \pm 1.02	6.36 \pm 2.52	6.07 \pm 1.85

ND: Not detected.

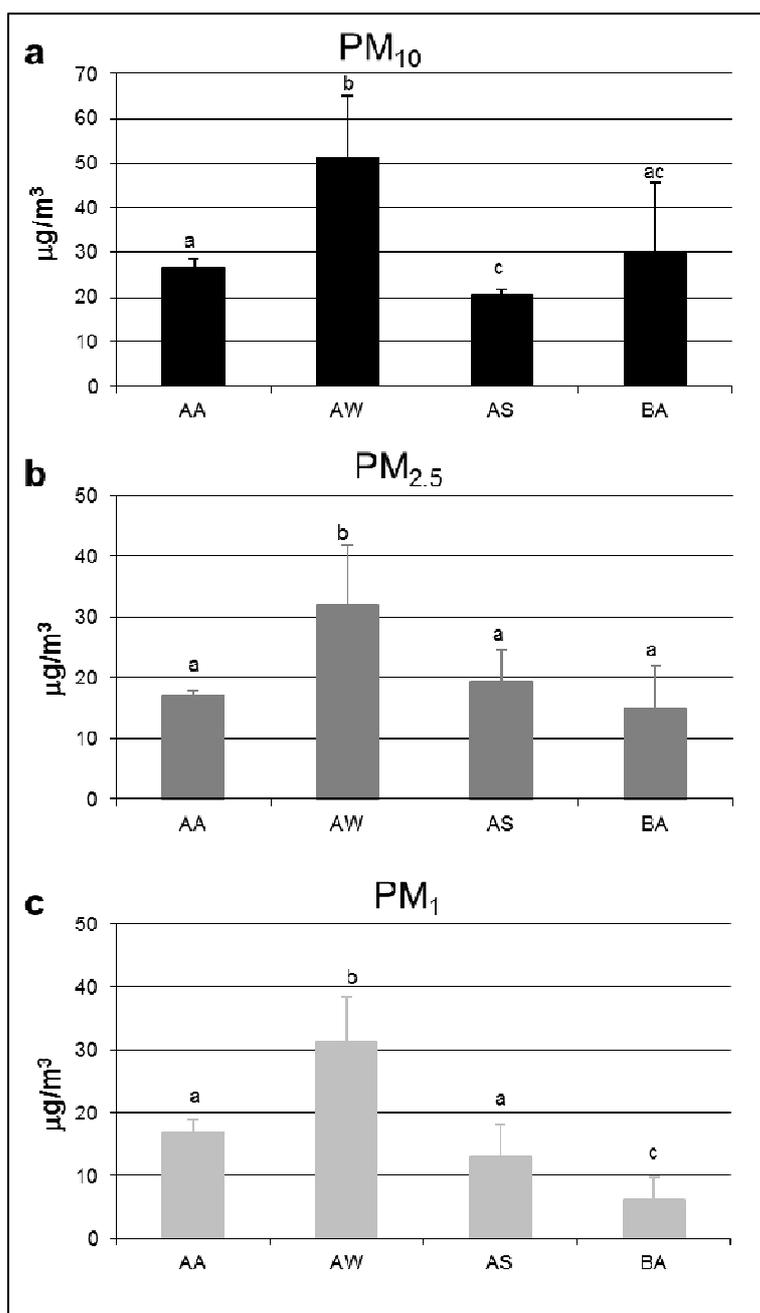
Table 3: Indoor and outdoor PM concentrations and exposure levels for both cement plants (A and B), and sampling periods: autumn (A), winter (W), and summer (S).

		PM concentration ($\mu\text{g}/\text{m}^3$)		Exposure ($\text{mg}/(\text{kg}\cdot\text{day})$)		
		Outdoor	Indoor	Sleeping	Working/Leisure	Outdoor
AA	PM _{10-2.5}	9.68	4.36	1.7E-04	1.2E-03	5.1E-04
	PM _{2.5-1}	0.16	0.10	4.0E-06	2.9E-05	8.5E-06
	PM ₁	16.8	10.9	4.2E-04	3.1E-03	9.0E-04
	Total	26.7	15.4	5.9E-04	4.3E-03	1.4E-03
AW	PM _{10-2.5}	19.3	8.68	3.3E-04	2.4E-03	1.0E-03
	PM _{2.5-1}	0.67	0.44	1.7E-05	1.2E-04	3.6E-05
	PM ₁	31.3	20.3	7.8E-04	5.7E-03	1.7E-03
	Total	51.2	29.4	1.1E-03	8.3E-03	2.7E-03
AS	PM _{10-2.5}	1.04	0.47	1.8E-05	1.3E-04	5.5E-05
	PM _{2.5-1}	6.51	4.23	1.6E-04	1.2E-03	3.5E-04
	PM ₁	13.0	8.42	3.2E-04	2.4E-03	6.9E-04
	Total	20.5	13.1	5.0E-04	3.7E-03	1.1E-03
BA	PM _{10-2.5}	15.0	6.76	2.6E-04	1.9E-03	8.0E-04
	PM _{2.5-1}	8.82	5.73	2.2E-04	1.6E-03	4.7E-04
	PM ₁	6.12	3.98	1.5E-04	1.1E-03	3.3E-04
	Total	30.0	16.5	6.3E-04	4.6E-03	1.6E-03

Table 4: Carcinogenic risk due to the exposure to metals associated to different PM fractions for both cement plants (A and B), and sampling periods: autumn (A), winter (W), and summer (S).

		As	Be	Cd	Co	Cr (VI)	Ni	Pb
AA	PM _{10-2.5}	2.2E-07	4.3E-08	1.4E-07	4.5E-07	2.1E-05	1.3E-07	1.7E-08
	PM _{2.5-1}	2.4E-08	NC	2.8E-08	3.4E-08	NC	1.0E-08	3.0E-09
	PM ₁	4.3E-07	NC	NC	1.3E-07	NC	1.2E-07	1.4E-08
	Total	6.8E-07	4.3E-08	1.7E-07	6.1E-07	2.1E-05	2.5E-07	3.4E-08
AW	PM _{10-2.5}	2.5E-08	NC	1.0E-07	5.6E-07	1.2E-05	5.5E-08	8.8E-09
	PM _{2.5-1}	2.4E-07	NC	1.4E-09	1.1E-07	6.5E-08	3.1E-07	4.7E-10
	PM ₁	4.7E-07	NC	1.0E-07	2.6E-07	1.6E-05	1.2E-07	4.4E-08
	Total	7.4E-07	NC	2.0E-07	9.4E-07	2.9E-05	4.9E-07	5.4E-08
AS	PM _{10-2.5}	1.7E-07	NC	NC	2.8E-07	9.5E-06	3.8E-07	3.6E-09
	PM _{2.5-1}	NC	NC	NC	NC	NC	NC	1.4E-09
	PM ₁	NC	NC	NC	NC	NC	NC	4.4E-09
	Total	1.7E-07	NC	NC	2.8E-07	9.5E-06	3.8E-07	9.4E-09
BA	PM _{10-2.5}	5.4E-08	NC	NC	1.6E-07	7.9E-08	1.2E-08	1.7E-09
	PM _{2.5-1}	1.8E-07	NC	NC	9.6E-08	2.0E-05	2.5E-08	4.3E-09
	PM ₁	1.8E-07	NC	NC	1.9E-07	NC	2.1E-07	5.4E-09
	Total	4.2E-07	NC	NC	4.5E-07	2.0E-05	2.5E-07	1.1E-08

NC: Not calculated. Values under the limit of detection



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2 Fig. 1: Daily mean PM₁₀ (a), PM_{2.5} (b), and PM₁ (c) levels for both cement plants (A and B), and
3 sampling periods: autumn (A), winter (W), and summer (S). Different superscripted letters denote
4 statistical significant differences ($p < 0.05$).
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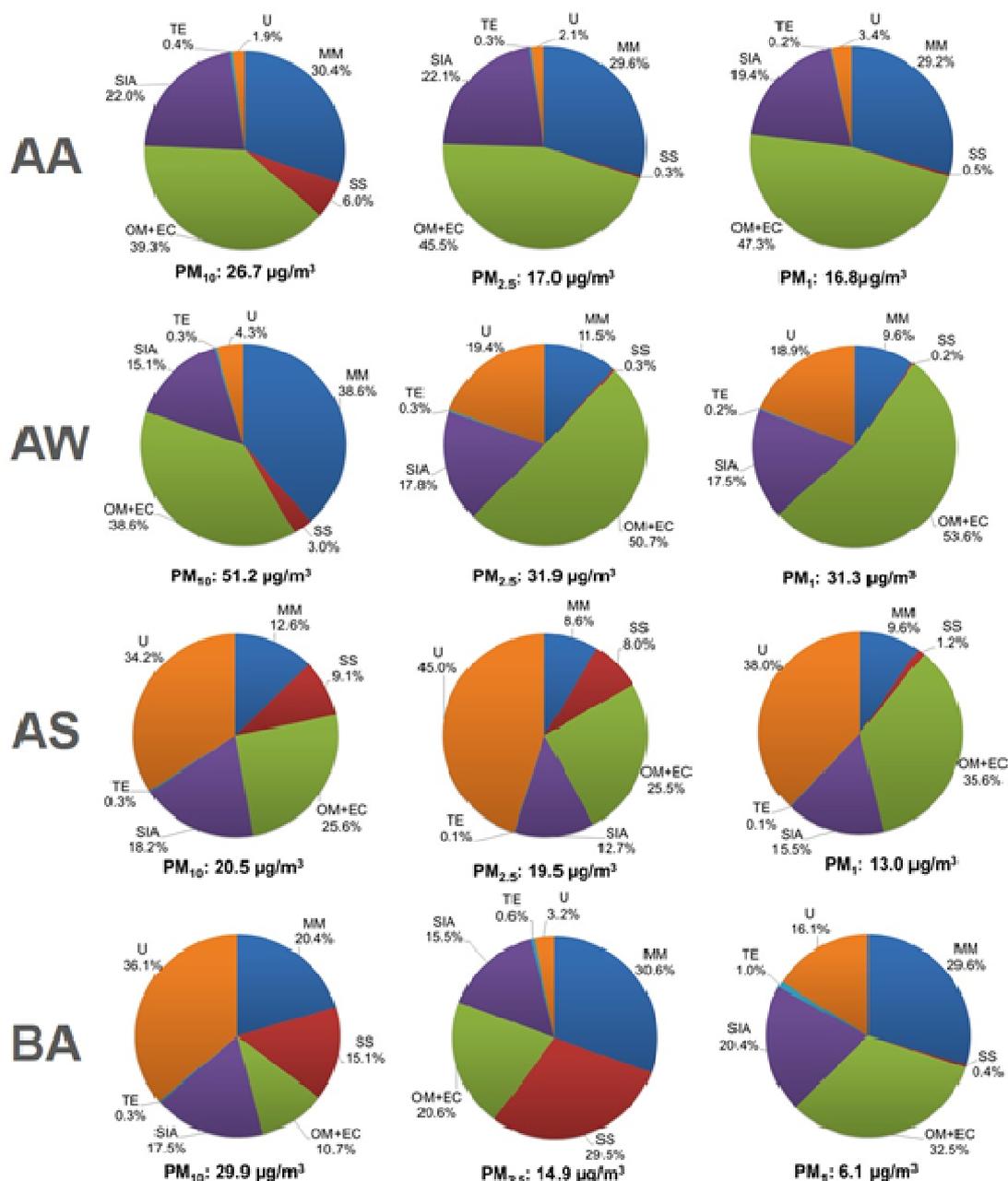


Fig. 2: Main components of collected PM for both cement plants (A and B), and sampling periods: autumn (A), winter (W), and summer (S). Results are expressed as percentage of the mass.

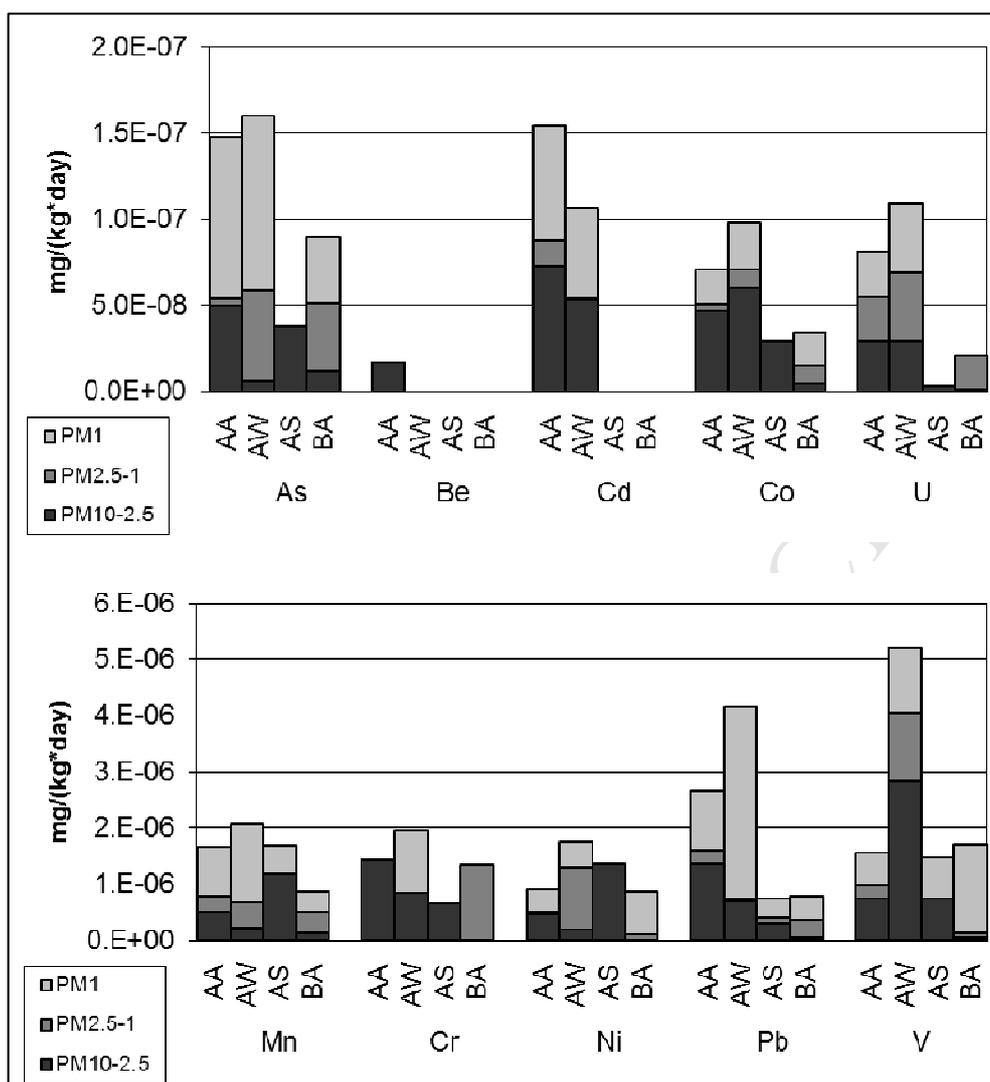
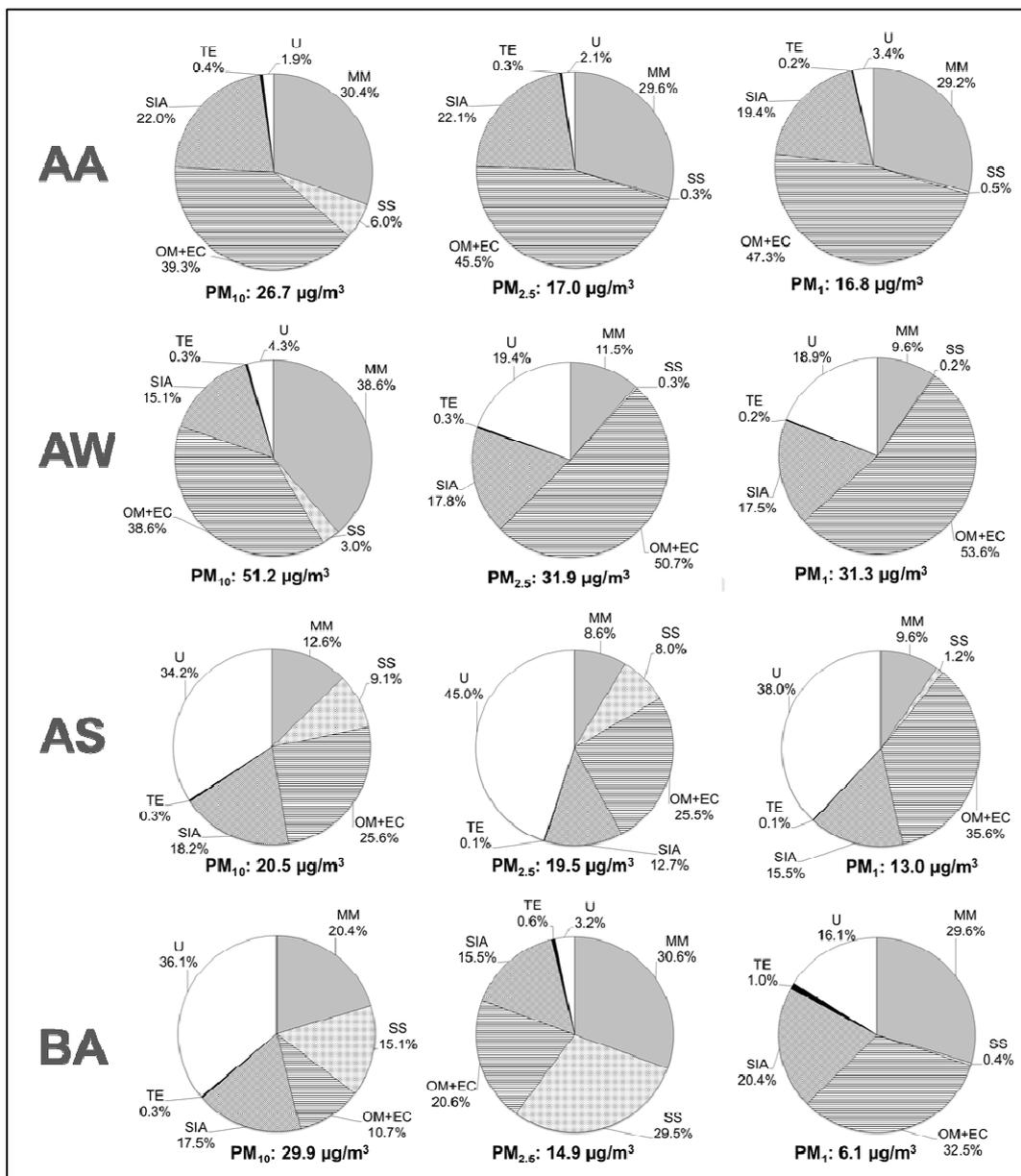


Fig. 3: Metal exposure levels for both cement plants (A and B), and sampling periods: autumn (A), winter (W), and summer (S).

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 33 printed version of the article.
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 36 **Fig. 4: Main components of collected PM for both cement plants (A and B), and sampling periods:**
 37 **autumn (A), winter (W), and summer (S). Results are expressed as percentage of the mass.**
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1 Supplementary materials for the paper entitled:

2 **Main components and human health risks assessment of**
3 **PM₁₀, PM_{2.5}, and PM₁ in two areas influenced by cement**
4 **plants**

5

6 Francisco Sánchez-Soberón, Joaquim Rovira, Montse Marí, Jordi Sierra, Martí Nadal,
7 José L. Domingo, Marta Schuhmacher*

8

9

Content

10

11

- Materials and methods

12

13

- Tables

14

15

16

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18

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20

21

22

23

24

25

26

27

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48 1. Materials and Methods

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50 1.1. Area of Study

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52 The two studied facilities are located in Catalonia (Northeast Spain). The first one (A) is
53 placed in Barcelona metropolitan area, within an urban sector profoundly affected by a
54 number of different industries. This settlement is crossed by two highways with an
55 average daily traffic of 49,199 and 160,558 vehicles per day, respectively (Ministerio de
56 Fomento, 2012). According to the company ruling the installation, the plant has an
57 annual production of 900,000 metric tons of cement annually. Non-conventional fuels
58 (sewage sludge, animal flours, refuse derived fuels, biomass) account 20% of the total
59 energy consumed. The second plant (B) is set in the coastline of southern Catalonia,
60 integrated in a rural background. Apart from the cement manufacture process, limestone
61 mining activities are performed in the nearby of the plant. Close to the cement plant
62 there is a road with an average daily traffic of 12,380 vehicles per day, being 34.4 % of
63 them considered as heavy vehicles (Ministerio de Fomento, 2012). In 2012 the plant
64 reached a production of about 867,000 metric tons of cement annually. During the same
65 year 31.9% of the total energy consumption came from alternative fuels, which means
66 more than 85.5 thousands metric tons yearly. Half of this number is composed by
67 biomass, while the other half is made from refuse derived fuels. Both plants are 165 km
68 away from each other, and both present same air cleaning devices i.e. electrostatic
69 precipitator for cleaning the exhaust gases from kiln and oil mill, and a baghouse for
70 gases coming from stone crusher, cement mill and coal mill.

71

72 1.2. Analytical methods

73

74 Before sampling, filters were heated at 200°C for 4 h. PM levels were calculated by
75 gravimetric determination. Filters were acclimated and weighted at constant humidity
76 (40%) and temperature (20°C) during consecutive days until constant weight before and
77 after sampling campaign. Subsequently, filters were divided into three portions to
78 perform different analytical determinations.

79

80 The first portion of filter was used for elemental analysis. It was treated with a mixture
81 of 2 mL of HNO₃ (65% Suprapur, E.Merck) and 3 mL of HF (37.5%, Panreac) in
82 hermetic Teflon bombs for 8 h at room temperature, and 8 additional hours at 80°C.
83 After cooling, extracts were filtered and made up to 25 mL with ultrapure water. They
84 were kept frozen at -20 °C until further analysis (Mari, Nadal, Schuhmacher, &
85 Domingo, 2009). Aluminium (Al), arsenic (As), beryllium (Be), bismuth (Bi), cadmium
86 (Cd), cerium (Ce), cobalt (Co), chromium (Cr), caesium (Cs), copper (Cu), dysprosium
87 (Dy), erbium (Er), europium (Eu), gadolinium (Gd), germanium (Ge), hafnium (Hf),
88 holmium (Ho), lanthanum (La), lithium (Li) mercury (Hg), manganese (Mn),
89 molybdenum (Mo), niobium (Nb), neodymium (Nd), nickel (Ni), lead (Pb),
90 praseodymium (Pr), rubidium (Rb), antimony (Sb), scandium (Sc), selenium (Se),
91 samarium (Sm), tin (Sn), strontium (Sr), Tantalum (Ta), terbium (Tb), thorium (Th),
92 titanium (Ti), thallium (Tl), uranium (U), vanadium (V), wolfram (W), yttrium (Y),
93 ytterbium (Yb), and zirconium (Zr) were determined by means of Inductively Coupled
94 Plasma Mass Spectrometry (ICP-MS, Perkin Elmer Elan 6000). Calcium (Ca), iron
95 (Fe), potassium (K), magnesium (Mg), sodium (Na) and phosphorus (P) concentrations
96 were determined by Inductively Coupled Plasma Optical Emission Spectrometry
97 techniques (ICP-OES, Perkin Elmer, Optima 3200RL). Detection limits, in ng/m³, were;

98 0.01 for Bi, Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Nb, Nd, Rb, Sm, Ta, Tb, Tl, U, Y, Yb, and
99 W; 0.02 for Rb; 0.03 for Cd and Pb; 0.06 for Co, Cu, Mn, Mo, Sn, Sr, Th, and Zr; 0.12
100 for As, Be, Hf, and Li; 0.13 for Hg; 0.31 for Cr and V; 0.59 for Ge; 0.63 for Se; 1.18 for
101 Sc and Ti; 3.13 for Fe; 5.88 for B; 6.25 for Mn and Zn; 15.7 for Ca; 29.4 for Mg; 31.3
102 for Al; 156 for K, P, and Na.

103

104 Another portion of filter was used for the determination of soluble inorganic ions (Cl⁻,
105 SO₄²⁻, NO₃⁻, and NH₄⁺). The piece of filter was cut in smaller portions and mixed with
106 15 mL of deionised water in a falcon tube. Then, it was shaken during 4 hours and
107 submerged in a sonication bath at 60°C during 1 hour. The extract was then filtered with
108 a 250 µm sieve, and the filtered liquid analyzed by means of Ionic Chromatography and
109 specific electrode (DX-300 Dionex) to elucidate the ionic content. For obtaining the
110 total carbon (TC) content, the last portion of filter was submitted to pyrolysis with
111 oxygen at 1,000 °C. Resulting gases (CO₂ and NO_x) were driven by a helium flow,
112 which was subsequently analyzed by means of gas chromatography (Thermo EA 1108
113 CHNS-O Carlo Erba Instruments) (Tiessen & Moir, 2000a, 2000b). To address the joint
114 content of organic carbon (OC) and elemental carbon (EC), sample was previously
115 exposed to a HCl enriched atmosphere in order to remove the carbon from carbonates.
116 After that it was analyzed following the same methodology described for TC.

117

118 Laboratory reagents blanks and duplicates were performed in order to control the
119 quality of the process. As external standard, Loamy clay soil (National Institute of
120 Standards and Technology) was used for metal and sulphanilamide for carbonic content.

121

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136

137

138

2. Tables

Table S1: Levels of elements, in ng/m³, for both cement plants (A and B), and sampling periods: autumn (A), winter (W), and summer (S).

	AA					
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
Al	624	114	83.5	42.2	45.7	23.6
As	0.63	0.09	0.38	0.07	0.36	0.01
Be	0.09	0.03	ND	-	ND	-
Bi	1.59	0.50	0.37	0.11	3.54	0.30
Ca	2142	1108	1586	844	1631	2239
Cd	0.68	0.35	0.31	0.13	0.26	0.05
Ce	1.30	0.48	0.69	0.36	1.11	1.01
Co	0.33	0.00	0.09	0.03	0.08	0.07
Cr	7.29	0.06	ND	-	ND	1.45
Cs	0.11	0.04	0.03	0.01	0.06	0.04
Cu	42.6	9.50	18.9	2.51	6.80	3.73
Dy	0.06	0.02	0.03	0.00	0.06	0.06
Er	0.05	0.02	0.02	0.00	0.05	0.06
Eu	0.11	0.05	ND	-	ND	-
Fe	407	103	131	42.0	106	72.5
Gd	0.21	0.07	0.04	0.00	0.12	0.14
Ge	ND	-	ND	-	ND	-
Hf	0.30	0.11	0.23	0.06	0.34	0.35
Hg	ND	-	ND	-	ND	-
Ho	0.01	0.01	ND	-	ND	-
K	1600	662	1304	60.9	1107	1843
La	0.48	0.17	0.20	0.02	0.34	0.46
Li	0.64	0.31	ND	-	1.45	1.77
Mg	64.3	52.9	45.0	18.6	103	96.7
Mn	6.98	3.94	4.38	1.02	3.32	3.67
Mo	1.06	0.22	ND	-	0.24	0.19
Na	904	473	45.2	29.8	39.4	17.7
Nb	0.25	0.04	ND	-	0.22	0.10
Nd	0.36	0.15	0.15	0.02	0.29	0.39
Ni	4.07	0.91	1.74	0.14	1.60	0.18
P	118	59.9	123	47.5	117	37.7
Pb	11.9	3.19	4.96	1.76	4.07	2.64
Pr	0.10	0.04	0.04	0.00	0.08	0.09
Rb	3.55	1.57	0.32	0.07	ND	3.73
Sb	3.88	0.90	1.29	0.17	1.47	0.32
Sc	2.90	2.41	2.33	2.80	1.57	0.32
Se	ND	-	ND	-	ND	-
Sm	0.08	0.03	0.04	0.01	ND	-
Sn	4.76	1.37	1.81	0.36	0.98	1.42
Sr	9.00	2.77	5.44	0.31	6.16	8.34
Ta	0.05	0.01	ND	-	ND	-
Tb	0.01	0.01	ND	-	ND	-
Th	0.14	0.04	0.09	0.01	0.16	0.13
Ti	46.8	14.4	7.69	2.97	ND	-
Tl	0.05	0.03	0.03	0.01	0.07	0.05
U	0.11	0.01	0.10	0.01	0.10	0.06
V	6.87	3.03	3.15	0.57	2.22	0.85

W	0.33	0.34	0.03	0.01	0.14	0.10
Y	0.24	0.10	0.05	0.01	ND	-
Yb	0.03	0.01	ND	-	ND	-
Zr	10.4	4.19	9.04	2.88	0.07	14.4
AW						
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
Al	2596	539	355	434	195	108
As	0.62	0.13	0.59	0.06	0.39	0.21
Be	ND	-	ND	-	ND	-
Bi	3.97	2.06	0.30	0.43	1.33	1.23
Ca	4743	1076	319	347	351	533
Cd	0.47	0.01	0.20	0.01	0.20	0.01
Ce	2.12	0.75	1.31	0.83	0.40	0.42
Co	0.45	0.27	0.15	0.09	0.10	0.02
Cr	8.50	3.09	4.20	1.32	4.18	3.26
Cs	0.12	0.04	ND	-	ND	-
Cu	41.4	18.2	28.6	9.84	12.38	4.85
Dy	0.15	0.03	ND	-	ND	-
Er	0.11	0.03	ND	-	ND	-
Eu	0.42	0.11	ND	-	ND	-
Fe	627	197	168	69.0	121	76.0
Gd	0.29	0.07	ND	-	ND	-
Ge	ND	-	ND	-	ND	-
Hf	0.71	0.10	ND	-	0.49	0.30
Hg	ND	-	ND	-	ND	-
Ho	0.03	0.01	ND	-	ND	-
K	3093	871	1892	236	1593	1272
La	1.04	0.22	0.07	0.05	0.16	0.20
Li	0.84	0.28	ND	-	ND	-
Mg	85.6	26.0	38.2	25.5	49.3	69.1
Mn	8.13	2.82	7.48	1.38	5.29	2.47
Mo	2.04	0.61	0.11	0.17	0.94	0.52
Na	1495	451	96.0	49.1	47.8	364
Nb	0.30	0.08	ND	-	0.13	0.07
Nd	0.89	0.19	ND	-	ND	-
Ni	6.96	2.42	5.94	4.33	1.69	0.94
P	ND	-	ND	-	ND	-
Pb	16.8	3.03	13.2	4.89	13.11	3.88
Pr	0.25	0.06	0.01	0.01	ND	0.04
Rb	4.90	1.23	ND	-	0.31	0.02
Sb	5.76	1.95	2.89	0.55	2.29	0.77
Sc	2.68	1.15	ND	-	ND	-
Se	ND	-	ND	-	ND	-
Sm	0.18	0.04	ND	-	0.04	0.03
Sn	8.05	2.39	3.56	1.38	1.75	0.84
Sr	21.2	3.67	7.84	1.97	5.00	9.45
Ta	0.25	0.35	ND	-	ND	-
Tb	0.03	0.01	ND	-	ND	-
Th	0.34	0.10	ND	-	0.10	0.04
Ti	71.0	20.3	26.4	11.9	10.5	13.6
Tl	0.07	0.01	0.11	0.05	0.06	0.02
U	0.15	0.04	0.15	0.03	0.15	0.07
V	23.5	8.95	9.09	8.95	4.44	1.02

W	0.62	0.39	ND	-	0.41	0.24
Y	0.60	0.17	ND	-	ND	-
Yb	0.08	0.02	ND	-	ND	-
Zr	21.3	3.75	7.06	2.84	7.32	8.81
AS						
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
Al	428	58.7	390	146	328	49.2
As	0.19	0.07	ND	-	ND	-
Be	ND	-	ND	-	ND	-
Bi	0.24	0.16	0.20	0.05	0.14	0.05
Ca	391	142	285	153	169	71.4
Cd	5.88	0.12	ND	-	ND	-
Ce	0.19	0.09	1.48	1.94	ND	-
Co	0.15	0.02	ND	-	ND	-
Cr	3.26	0.53	ND	-	ND	-
Cs	0.02	0.01	0.02	0.01	ND	-
Cu	9.62	14.8	10.2	3.55	ND	-
Dy	0.02	0.01	ND	-	ND	-
Er	0.01	0.00	ND	-	ND	-
Eu	0.01	0.00	ND	-	ND	-
Fe	314	84.2	53.2	27.1	28.4	10.7
Gd	0.02	0.01	0.01	0.01	ND	-
Ge	0.29	0.00	ND	-	ND	-
Hf	ND	-	ND	-	ND	-
Hg	ND	-	ND	-	ND	-
Ho	ND	-	ND	-	ND	-
K	309	202	ND	-	ND	-
La	0.15	0.04	0.11	0.03	0.09	0.02
Li	0.29	0.07	0.25	0.15	0.33	0.14
Mg	54.1	42.5	48.7	32.1	35.7	17.6
Mn	7.85	2.30	1.91	0.91	1.89	0.46
Mo	2.39	0.35	ND	-	3.91	1.41
Na	1539	285	1471	265	116	98.71
Nb	ND	-	ND	-	ND	-
Nd	0.11	0.03	0.04	0.05	0.10	0.04
Ni	7.00	0.00	ND	-	ND	-
P	ND	-	ND	-	ND	-
Pb	3.16	1.62	1.70	2.21	1.29	0.86
Pr	0.03	0.01	0.02	0.01	ND	-
Rb	0.51	0.13	0.19	0.12	0.30	0.07
Sb	1.62	0.59	1.15	1.25	ND	-
Sc	3.94	1.71	3.32	2.16	3.54	1.52
Se	0.59	0.00	ND	-	ND	-
Sm	0.02	0.01	0.01	0.01	ND	-
Sn	1.86	0.74	0.48	0.14	0.43	0.16
Sr	3.03	0.12	ND	-	ND	-
Ta	ND	-	ND	-	ND	-
Tb	ND	-	ND	-	ND	-
Th	ND	-	ND	-	ND	-
Ti	24.1	8.12	6.33	11.53	8.79	5.90
Tl	0.02	0.00	ND	-	ND	-
U	0.02	0.02	ND	-	ND	-
V	6.57	3.79	3.04	0.05	2.85	0.15

W	0.08	0.03	0.01	0.01	0.03	0.03
Y	0.10	0.03	ND	-	0.20	0.06
Yb	ND	-	ND	-	ND	-
Zr	2.60	1.35	2.42	1.76	4.88	2.92
BA						
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
Al	390	312	197	31.6	425	252
As	0.36	0.16	0.30	0.02	0.15	0.10
Be	ND	-	ND	-	ND	-
Bi	ND	-	ND	-	ND	-
Ca	1941	1279	1511	664	200	70.0
Cd	ND	-	ND	-	ND	-
Ce	1.40	1.56	0.28	0.07	0.19	0.14
Co	0.20	0.10	0.11	0.02	0.08	0.01
Cr	6.05	0.70	6.02	2.84	ND	-
Cs	0.09	0.12	0.08	0.09	0.04	0.02
Cu	32.0	31.6	27.2	24.4	11.8	7.26
Dy	0.05	0.00	0.05	0.02	ND	-
Er	0.02	0.01	0.02	0.02	0.01	0.00
Eu	ND	-	ND	-	ND	-
Fe	221	201	104	52.3	11.6	1.86
Gd	0.05	0.03	0.03	0.02	ND	-
Ge	ND	0.00	0.63	0.04	ND	-
Hf	ND	-	ND	0.14	ND	-
Hg	ND	-	ND	-	ND	-
Ho	ND	-	ND	-	ND	-
K	702	84.2	415	163	350	152
La	0.19	0.15	0.12	0.04	0.10	0.03
Li	0.39	0.23	0.32	0.13	0.43	0.11
Mg	154	15.5	264	70.9	ND	-
Mn	5.10	3.32	2.83	1.23	1.33	0.70
Mo	6.30	4.53	15.10	4.52	5.37	1.89
Na	3985	1043	4320	379	ND	-
Nb	0.06	0.05	ND	-	0.07	0.03
Nd	0.16	0.14	0.10	0.05	0.09	0.02
Ni	3.44	0.47	3.23	0.66	2.88	0.69
P	ND	-	ND	-	ND	-
Pb	3.57	2.57	2.88	1.93	1.61	0.96
Pr	0.06	0.03	0.02	0.01	0.02	0.01
Rb	0.71	0.69	0.46	0.45	0.42	0.22
Sb	0.88	0.36	2.08	0.65	1.52	0.31
Sc	11.2	8.85	8.97	7.54	20.2	12.7
Se	ND	-	ND	-	ND	-
Sm	0.16	0.15	0.02	0.01	ND	-
Sn	0.54	0.21	0.54	0.17	0.39	0.20
Sr	3.44	3.49	1.78	0.89	0.77	0.04
Ta	ND	-	ND	-	ND	0.02
Tb	ND	-	ND	-	ND	-
Th	ND	-	ND	-	ND	-
Ti	21.8	21.5	8.95	6.21	7.29	2.97
Tl	0.29	0.29	0.06	0.09	0.03	0.03
U	0.08	0.06	0.08	0.06	ND	-
V	7.28	1.02	6.36	2.52	6.07	1.85

W	0.03	0.00	0.02	0.01	0.04	0.02
Y	0.21	0.17	0.15	0.09	0.13	0.04
Yb	0.03	0.01	ND	-	ND	-
Zr	5.00	3.13	7.08	4.73	7.96	4.79

ND: not detected. Values Under the limit of detection

Table S2: Levels of PM, carbon and ions in location A during Autumn period (AA). Results are expressed in $\mu\text{g}/\text{m}^3$.

	AA					
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
PM	26.7	1.85	17.0	0.95	16.8	1.91
TC	8.01	1.09	5.51	0.87	5.69	0.96
OC+EC	7.38	1.33	5.45	0.70	5.59	0.88
Cl ⁻	0.69	0.35	0.01	0.00	0.04	0.02
SO ₄ ²⁻	2.48	0.74	2.55	0.63	2.06	0.76
NH ₄ ⁺	0.08	0.07	0.11	0.09	0.01	0.01
NO ₃ ⁻	3.31	0.97	1.10	0.14	1.19	0.17

TC: total carbon

OC + EC: organic carbon and elemental carbon

Table S3: Levels of PM, carbon and ions in location A during winter period (AW). Results are expressed in $\mu\text{g}/\text{m}^3$.

	AW					
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
PM	51.2	13.9	31.9	9.94	31.3	7.12
TC	17.5	5.61	14.9	3.98	15.3	3.72
OC+EC	13.9	5.48	11.4	2.43	11.8	3.52
Cl ⁻	0.05	0.03	0.01	0.01	0.02	0.03
SO ₄ ²⁻	2.47	0.42	2.85	0.39	1.90	0.24
NH ₄ ⁺	0.24	0.09	0.70	0.22	0.20	0.17
NO ₃ ⁻	5.02	1.29	2.11	0.43	3.38	2.51

TC: total carbon

OC + EC: organic carbon and elemental carbon

Table S4: Levels of PM, carbon and ions in location A during summer period (AS). Results are expressed in $\mu\text{g}/\text{m}^3$.

	AS					
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
PM	20.5	1.28	19.5	5.02	13.0	5.22
TC	3.04	0.47	1.36	0.58	1.32	1.19
OC+EC	3.69	0.43	3.51	0.57	3.26	1.14
Cl ⁻	0.34	0.50	0.09	0.04	0.04	0.00
SO ₄ ²⁻	2.46	0.44	1.88	0.26	1.80	0.27
NH ₄ ⁺	0.27	0.05	0.23	0.06	0.08	0.06
NO ₃ ⁻	1.00	0.26	0.37	0.03	0.14	0.01

TC: total carbon
 OC + EC: organic carbon and elemental carbon

Table S5: Levels of PM, carbon and ions in location B during autumn period (BA). Results are expressed in $\mu\text{g}/\text{m}^3$.

	BA					
	PM ₁₀		PM _{2.5}		PM ₁	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Stan. Dev.
PM	29.9	15.9	14.9	6.98	6.10	3.67
TC	2.18	1.30	2.20	0.85	1.46	0.06
OC+EC	2.26	1.17	2.16	0.83	1.40	0.06
Cl ⁻	0.52	0.54	0.07	0.05	0.03	0.00
SO ₄ ²⁻	2.53	1.06	1.74	0.78	1.06	0.65
NH ₄ ⁺	0.28	0.16	0.23	0.22	0.10	0.11
NO ₃ ⁻	2.42	1.99	0.34	0.19	0.09	0.02

TC: total carbon
 OC + EC: organic carbon and elemental carbon