Impact of Traffic Flows and Meteorological Events on the Hourly Elemental Composition of Fine and Coarse Particles at an Urban Site

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Abstract

Hourly $PM_{2.5}$ and $PM_{2.5-10}$ samples were collected during a week at an urban site located on the Spanish Mediterranean coast by a Streaker sampler. Samples were subsequently analyzed to determine the elemental composition by the PIXE technique. Although elemental concentrations at the sampling site were influenced by traffic flows, atmospheric levels of traffic-related components lay in the lower range of the values reported for other urban stations of similar characteristics. Concentrations of elements used as tracers of non-exhaust emissions (Cu, Zn, Mn, Al, Ca and Fe) in $PM_{2.5-10}$ showed the best correlations with traffic densities ($R^2 > 0.5$). The correlation coefficients calculated for the fine fraction were lower. A short Saharan dust event identified during the study period increased the concentrations of crustal elements (Al, Ca, K, Ti, Sr and Fe) mainly in the coarse fraction. Nevertheless, the relative increase in the concentrations of sea-spray elements was higher, indicating that the Saharan dust plume reached the sampling site along a marine-path. Thanks to the high temporal resolution of PM sampling, the effect of a brief but intense precipitation event could be stablished. During this episode, peaking at a value of 17 l m^{-2} in one hour, a higher atmospheric removal efficiency was observed for coarse particles than for fine particles. The concentrations of most of the elements analysed in $PM_{2.5-10}$ were reduced to values below detection limits.

Keywords: Streaker; PIXE; Traffic; Saharan dust; Precipitation.

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INTRODUCTION

In urban environments with no industrial activity, road traffic is the main emission source of atmospheric particulate matter (PM). Vehicle emissions can be divided into exhaust and non-exhaust emissions. Direct (abrasion) and indirect (resuspension) emissions are included in the non-exhaust component (Pant and Harrison, 2013). Several previous studies (Thorpe and Harrison, 2008; Pant and Harrison, 2013; Lawrence *et al*., 2013; Alves *et al*., 2018) have identified and compiled the main elements associated with both processes. Specific elements are frequently associated with non-exhaust traffic-induced emissions. Cu, Fe, Zn, Mn, Sb, Ba and Sn are present in brake dust, Zn is considered as the key tracer of tyre wear, and crustal elements such as Al, Ca, Fe or Si are closely related to vehicle-induced resuspension. With regard to exhaust emissions, elemental markers such as Cu, Mn, Fe, Zn, Ba, Sn, Mo and Sb have been identified in previous studies. These elements can be emitted from different processes including fuel and lubricant combustion, catalytic converters, particulate filters and engine corrosion (Pant and Harrison, 2013).

Depending on the emitting process, these elements can be found either in the fine or the coarse mode. PM components emitted from combustion processes are mainly found in the fine fraction ($PM_{2.5}$), while elements derived from non-exhaust emissions are primarily associated with the coarse fraction ($PM_{2.5-10}$) (Handler *et al*., 2008; Pant and Harrison, 2013). In spite of this, the relationship of these elements with PM sources and particle size is not necessarily unequivocal, as shown in several studies (Moreno *et al*., 2013; Crilley *et al*., 2016). These works established the chemical profile of the main PM sources in urban environments using hourly data, which implies a substantial improvement in the identification of atmospheric aerosol sources (Crilley *et al*., 2016).

High-time resolution measurements can provide a more comprehensive view of the influence of specific atmospheric processes on the variability of PM components. Meteorological events such as rainfall, transport of mineral dust from arid areas or substantial variations in the mixing layer height can affect the size and composition of atmospheric particles. The influence of these events and the contribution of PM emissions from different sources, especially traffic-related sources, determine the temporal variability of PM concentrations in urban environments.

Rainfall and the transport of mineral dust from arid areas are two of the most important meteorological events, each having an opposite effect on PM concentrations. Precipitation scavenging is the most important sink of aerosols in the troposphere (Loosmore and Cederwall, 2004). Although the duration and intensity of precipitation events are key factors in the removal efficiency of atmospheric aerosols, different studies pointed out that coarse particles are removed more efficiently than fine particles (Andronache, 2003; Nicolás *et al*., 2009; Feng and Wang, 2012; Amato *et al*., 2012). Rainfall episodes also reduce road dust resuspension. Nevertheless, it is difficult to establish a correlation between the duration of the precipitation event and the time needed to reach PM concentrations previous to the episode. In general, road dust emissions recover faster after daytime precipitation because primary (traffic) emissions are still occurring and solar radiation accelerates the mobilization of particles by water evaporation (Amato *et al*., 2012).

In the western Mediterranean basin, Saharan dust events (SDE) can significantly contribute to PM concentrations in urban environments. Although increases in PM concentrations have been recorded for all particle sizes, the coarse fraction is more affected by these events than the fine fraction (Nicolás *et al*., 2014; Contini *et al*., 2014). Thus, SDE are the main cause of the exceedances of the PM_{10} daily limit value established by the European legislation (Escudero *et al*., 2007; Nava *et al*., 2012; Cuspilici *et al*., 2017). During SDE the concentrations of crustal

components such as Ti and Fe show significant increments; however, increases in the levels of non-crustal elements like Ni or V, mainly related to combustion processes, have also been observed. This is probably due to the transport of anthropogenic pollutants by Saharan dust plumes (Nicolás *et al*., 2011; Malaguti *et al*., 2015; Galindo *et al*., 2018). Likewise, SDE may produce an increase in the concentrations of marine elements (Na, Cl and Mg) as a result of the uptake of these species during the transport of Saharan air masses over the Mediterranean sea.

The purpose of this study is to determine the influence of traffic flows and some meteorological events (SDE and a short but intense rain period) on the elemental composition of $PM_{2.5}$ and $PM_{2.5-10}$ samples collected with a high time resolution (1 hour). The high temporal resolution of measurements will provide insights into the sensitivity of the analysed components to daily traffic cycles and different meteorological episodes. The results of this study can provide a scientific basis for improving urban air quality.

EXPERIMENTAL

Sampling Site

The sampling site was placed in the urban centre of Elche (38° 16′; 0° 41′; 86 m a.s.l). The city is located in the southeast of Spain, only 12 km from the Mediterranean coast. Elche is the third biggest city in the Valencian Community, with a population of about 192,000 inhabitants (data from 2016). The urban area is located on a plain and crossed by the Vinalopó River. Elche is also known by its high density of palm tree gardens and for being one of the largest shoe manufacturing centres in Europe. However, it should be noted that no large industries are present in the city, so the main PM source in the urban area is road traffic (Yubero *et al*., 2015).

The climate in Elche is considered as arid Mediterranean. In fact, rainfall is quite scarce, with annual values not exceeding 300 l m^{-2}. Precipitation episodes usually concentrate during the fall and spring months. Breeze regimes (E-SE) are very frequent during the summer months, while

during winter the wind usually blows from the northwest. The average temperature in the city ranges from about 27 °C (August) to 12 °C (January). During November, when this study was carried out, the average temperature is usually around 16 °C.

The measurement site was situated ~3-4 m above ground level, on a narrow street of about 7 m width. The street has two traffic lanes and is surrounded by buildings of approximately 25 m height. The average density of vehicles on working days varies between 8000 and 9000 vehicles day^{-1} (Data from the Elche traffic office). The sampling point can be considered as representative of an urban environment heavily influenced by traffic. In Galindo *et al*. (2018), graphic documentation related to the location of the sampling site can be found. Previous studies on the temporal variability of PM_{10} and PM_1 concentration and composition in this area can be found in Yubero *et al*. (2015), Galindo and Yubero (2017) and Galindo *et al*. (2018).

Instrumentation and data analysis

Fine and coarse particle elemental composition: Streaker and PIXE

The aerosol was collected during 1 week, from 15th to 21st November 2011, by a "Streaker" sampler (P.I.X.E. International Corporation-http://pixeintl.com/Streaker.asp). This device is designed to separate the fine (<2.5 μm aerodynamic diameter) and the coarse (2.5-10 μm) modes of the aerosol. A paraffin-coated Kapton foil is used as an impaction surface for coarse particles and a Nuclepore membrane as a fine particle collector. The two collecting plates are paired on a cartridge that rotates at a constant speed for a week, this produces a circular continuous deposition of particulate matter at both stages. The rotation speed during sampling (1.2 mm h^{-1}), the pumping orifice width (1.2 mm) and the beam size normally used for the subsequent PIXE (Particle-Induced X-ray Emission) analysis are such that an overall resolution of about one hour is obtained on the elemental composition of air particulate matter (Calzolai *et al.*, 2015; Chiari *et al*., 2006). PIXE analyses were performed with 3 MeV protons from the 3 MV Tandetron

accelerator of the LABEC laboratory of INFN in Florence, with the external beam set-up extensively described elsewhere (Calzolai *et al*., 2010; Lucarelli *et al*., 2014, Lucarelli *et al*., 2018). The beam scanned the streak in steps corresponding to one hour of aerosol sampling. Each spot was irradiated for about 60 s with a beam intensity ranging from 20 nA to 300 nA. PIXE spectra were fitted using the GUPIX software package (Campbell *et al*., 2010) and elemental concentrations (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Pb) were obtained via a calibration curve from a set of thin standards of known surface density. Concentration uncertainties were determined by a sum of independent uncertainties on standard thicknesses (5%), X-ray counting statistics (from 2 to 20% or higher when concentrations approach MDLs) and sampling parameters (10%). Field blank correction was applied to all the data sets. Accuracy of analysis was checked against certified reference materials (NIST standard SRM2783). The total number of hourly samples collected during the sampling period was 156.

Detection limits were about 10-20 ng m^{-3} for elements from Na to Ca, and 5 ng m^{-3} (or below) for elements from Ti to Pb. The percentage of valid samples in both fractions was higher than 70% for most of the elements (Na, Mg, Al, S, Cl, K, Ca, Cr, Fe, Ni, Cu and Zn). Br and Si in the fine fraction could not be quantified in this study due to the high background levels in the substrate.

Meteorology and traffic density

It should be indicated that all hours in this study are in local time (UTC+1), unless otherwise stated. Hourly values of the main meteorological variables were obtained from a station of the Environmental Monitoring Network of the Valencian Community located on the outskirts of the city. The Global Data Assimilation System (GDAS1) model from the NOAA Air Resources Laboratory (http://www.ready.noaa.gov/READYamet.php) was used for the determination of the planetary boundary layer (PBL) height. Saharan dust events were identified using back-trajectory

analysis supported by the outcomes of the BSC/DREAM model. During the study period, a low intensity SDE was detected between Sunday 20th at 07:00 h and Monday 21st at 11:00 h. The event finished due to a precipitation episode, occurring on Monday 21st between 05:00 h and 13:00 h. The accumulated precipitation during the event was 28 l m^{-2}, peaking at 17 l m^{-2} between 07:00 h-08:00 h (Fig. 1a). Throughout this time period, rainfall was heavy. Figs. 1(b) and 1(c) show the hourly evolution of wind speed and direction, PBL height and relative humidity. The impact of the PBL height on PM concentrations was established from particle number concentration (N) measurements obtained with a Grimm 365 optical spectrometer located on the roof of a university building. The instrument is able to determine particle number concentrations in 31 particle size channels from 0.25 to 32 μm. Fine particles concentrations has been obtained as a result of the N addition from 0.25 μm to 1 μm. Likewise, coarse particles concentrations is the result of the N addition from 1 μm to 32 μm. The site was 15 m above the ground and approximately 1.5 km northeast of the measurement site.

Figure 1

Fig. 1d shows the temporal evolution of fine and coarse number concentrations. As can be seen, the SDE had a greater impact on coarse particles, with a peak value of ~0.5 cm^{-3} at the end of the event. The Saharan outbreak was followed by a precipitation event which caused wet scavenging of atmospheric particles. The figure also shows an increase in particle number concentration during the breeze period and a rise in the concentration of submicrometric particles (the increase for particles larger than 1 μm was lower) when the PBL height was lowest. Fig. S1 included in the supplemental material shows the impact of the SDE on the study area at 12 UTC on November 20th along with the precipitation episode that occurred the following day.

Traffic density (TD) at the sampling point was obtained from the Elche traffic office. The hourly evolution of the number of vehicles during the sampling period is shown in Fig. 2.

Conclusions that can be drawn from the information presented in this figure are: a) the average number of vehicles during working days (8917) was clearly higher than that registered on Saturday (7636) and Sunday (6057); b) traffic densities on Saturday and Sunday significantly decreased between 14:00 h and 16:00 h, while on working days they remained high; c) during both working days and weekends two maxima were observed (around 13:00 h and 20:00 h); however, on week days the curve showed a third peak at the start of the working day (around 08:00 h-09:00 h). In addition, TD registered between 00:00 h and 06:00 h during the weekend was higher than that on working days. This can be seen in Fig. 2, where the percentage differences between TD on working days (WD) and Saturday (ST) are presented. The same pattern is generally observed throughout the year in the study area.

Figure 2

From now on only Saturday 19th will be considered as weekend day in the analysis of the influence of traffic flows on PM composition. Sunday 20th and Monday 21st will not be considered in this analysis because they were affected by a SDE and a precipitation episode that occurred afterwards.

RESULTS

Average elemental concentrations

Average elemental concentrations and standard deviations (SD) for the coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) fractions during the study period are shown in Table 1. Maximum and minimum hourly values are also presented. Concentrations of elements with percentages of valid samples below 20% are not included in this table.

Table 1

Typical marine elements like Na and Cl showed high concentrations in the coarse fraction (C) due to the close proximity of the sampling site to the Mediterranean coast. Levels of crustal

elements such as Si, Ca and Fe in the coarse size range were also significant. The mean Mg/Na ratio obtained for the whole study period (0.12) is typical of bulk sea-water (Bardouki *et al*., 2003). However, the Cl/Na ratio (~ 1.13) indicates a deficit of Cl due to the reaction of NaCl with sulfuric and nitric acids. In the fine fraction (F), S was found to be the most abundant element, followed by Na and Ca. There was no correlation between Na and Cl in this fraction because most of the Cl is missing due to the aforementioned reaction of NaCl with sulfuric and nitric acids which is more effective in the fine fraction due to the more favourable surface to volume ratio (Yao *et al*., 2003).

Regarding mass size distributions, marine and crustal elements such as Na, Mg, Cl, Al, Ca and Fe were found mainly in the coarse fraction. Ni, and especially S, were distributed primarily in the fine fraction, while elements like K, Ti, Cr, Mn, Cu and Zn were almost evenly distributed between the two fractions.

It is difficult to compare elemental concentrations obtained in Elche with those measured at other urban locations due to multiple factors: different measurement period, soil composition, distance to the sea and vehicle density. Even so, with the exception of marine elements (Na, Mg and Cl), concentrations obtained in this study were in the lower range of the values reported for other urban stations located in the western Mediterranean like Barcelona (Dall´Osto *et al*., 2013; Minguillon *et al*., 2014), Florence (Lucarelli *et al*., 2000) or Palma de Mallorca (insular suburban site) (Pey *et al*., 2009). It is noteworthy that Zn concentrations in both fractions were significantly lower than those previously measured at other Mediterranean urban areas.

As can be observed in Table 1, maximum hourly concentrations for some elements like Na, Cl or Fe, were considerably higher than the average values, particularly in the coarse fraction. This indicates that these elements are very sensitive to short-term episodes.

The influence of traffic on daily patterns of elemental concentrations

The relationship between daily patterns of TD on WD and ST (see Fig. 2) and daily patterns of elemental concentrations in both mass fractions is discussed in this section. The hourly evolution of elemental concentrations on WD and ST is presented in Fig. S2, included in the supplementary material. From the daily cycles shown in this figure, it can be inferred which elements are related to traffic emissions and which elements have a more regional origin.

Fig. 3a shows the determination coefficients (R^2) obtained by correlating elemental hourly concentrations (in the coarse fraction) with TD both on WD and ST. For many elements, the coefficients calculated for WD were higher than those obtained on ST. Some elements typically related to traffic, such as Cu, Fe and Mn, showed the highest coefficients (> 0.8 on WD). Other elements associated with vehicle emissions (Cr, Zn) or traffic resuspension (Ti, Ca, Al, Si) showed moderately high determination coefficients. Although S had a moderate correlation with TD, it is well-known that traffic is not a major source of sulfur-containing compounds. The hourly evolution of S concentrations in the coarse fraction on WD (Fig. S2) showed a broad peak during the hours of higher solar radiation. A similar pattern was observed for Na and Mg and, to a lesser extent, Ca. This points to the presence of secondary Na_2SO_4 and/or $CaSO_4$ in the coarse fraction. The increase in S concentrations at midday was lower in $PM_{2.5}$ than in the coarse fraction and is most likely associated with the photochemical formation of sulfate. The low correlations shown in Fig. 3a for Na and Cl (R^2<0.3) can be explained considering that traffic is not the main source of coarse Na and Cl at our sampling site. Elements such as Ni and P did not show a correlation with traffic flows. For the remaining elements, correlations on WD were statistically significant (p-value <0.05). Correlations calculated on ST were also statistically significant for most of the analysed elements.

The determination coefficients calculated for the fine fraction (not shown) were significantly lower. Significant correlations (> 0.5) on WD were only obtained for S, Ca, Fe and Zn. This

points to a greater impact of vehicle emissions on the detected elemental concentrations on the coarse fraction than on the fine fraction in the study area (Galindo *et al*., 2018).

Figure 3

The percentage differences between elemental concentrations on WD and ST for both mass fractions are presented in Figs. 3(b) and 3(c). Since the percentage differences between the number of vehicles on WD and ST were highest at around 03:00 h (- 83%), 08:00 h (+ 200%) and 15:00 h (+ 103%) (see Fig. 2), Figs. 3(b) and 3(c) only show the differences at these hours and for the whole period. Most of the elements in the coarse fraction (Fig. 3b) showed positive percentages for the whole period, meaning that concentrations during WD were higher than those registered on ST. The same was observed at 08:00 h and 15:00 h. Nevertheless, elements typically associated with vehicle emissions (Cu and Zn) or traffic-induced resuspension (Fe, Ca, Ti and Al) showed negative percentage differences at 03:00 h due to a reduction in the number of vehicles on weekdays relative to Saturday (see Fig. 2). In the fine fraction (Fig. 3c), traffic-related elements (Zn, Fe, Cr and Cu), as well as Cl and Ca, also showed negative percentage differences at 03:00 h.

Meteorological factors affecting the daily evolution of elements

The temporal evolution of elemental concentrations throughout the study period is plotted in Fig. 4. As can be observed, some elements did not show a well-defined daily pattern. Different factors may affect the daily profiles of the analysed elements. The influence of traffic, one of the main factors affecting PM levels and composition in urban environments, has been discussed in the previous section. Different meteorological scenarios that can also have a significant influence on the observed variability will be examined in the next sections.

Figure 4

Breezze

It is worth noting the significant increase in the concentrations of Na(C), Na(F), Cl(C), Mg(C), K(C), K(F), S(C) and S(F) on Thursday 17th during the central hours of the day. This was due to the intense sea breeze circulation (see Fig. 1). The concentrations of these elements in the coarse fraction were increased by a factor from 5 to 12, suggesting a strong impact of the sea breeze on the temporal evolution of these components. Conversely, the increase in the levels of Cl(F) was quite lower, possibly because Cl is mainly distributed in the coarse fraction and chloride depletion increases with the decrease in particle size (Yao *et al*., 2003).

SDE and wet scavenging

As already mentioned a SDE occurred between 20th and 21st of November, followed by a precipitation episode resulting in scavenging of particles by wet deposition. As shown in Fig. 1, this event had a stronger effect on larger particles. Throughout the event two well-defined concentration peaks were registered, one at the beginning (~14:00 h on 20th) and the other at the end (~07:00 h on 21st). The maximum impact of rainfall was around 08:00 h on 21st.

Significant increases in the concentrations of many elements were observed during the SDE (Fig. 4). For instance, the increase in the Fe(C) concentration at around 07:00 h coincided with the peak in the number concentration of coarse particles (see Fig. 1). To quantify the impact of SDE on elemental concentrations, mean levels were calculated for event and non-event periods (Table 2). These values were obtained from daily averages. For this reason, the time interval between 07:00 h on 19th and 07:00 h on the 20th was considered as a non-event day, while the period from 07:00 h on the 20th to 07:00 h on the 21st as an event day. Table 2 also presents increase factors for each element.

Table 2

As may be expected, the highest increase factors were obtained for coarse particles, confirming the greater impact of SDE on this fraction in the study area. Crustal elements showed significant

315 increases in the coarse fraction. In contrast, only Al showed a substantial increment in the fine
316 fraction, probably because other crustal elements have also a significant contribution from other
317 sources. Increases in the levels of marine elements (Na, Mg, Br and Cl) in the coarse fraction
318 were higher than for the other elements. This is probably the result of the uptake of these species
319 during the transport of Saharan air masses over the Mediterranean sea. Anthropogenic elements
320 (like V and Ni) emitted in the Mediterranean basin and north Africa (mainly from fuel oil
321 combustion in industries and ships) could also be transported to the sampling site by Saharan dust
322 plumes (Galindo *et al*., 2017b and 2018). Notable increases for Na and Mg were also observed in
323 the fine fraction.

324 The concentration of S in the coarse fraction significantly increased during the event most
325 likely due to the formation of coarse $CaSO_4$. In some previous studies performed in the study area
326 (Nicolás et al., 2009; Galindo et al., 2020), we have reported increases in the concentrations of
327 fine sulfate and ammonium during Saharan events, pointing to the formation of fine $(NH_4)_2SO_4$
328 during these episodes. However, for the studied event, an increase in sulfur concentrations in the
329 fine fraction was not observed. Therefore, the formation of fine calcium sulfate, as suggested by
330 Cesari et al. (2016), did not occur (notice that fine calcium concentrations also did not increase
331 during this particular event, Table 2). A plausible explanation is that there was not enough
332 ammonia present to neutralize the extra amount of sulfuric acid generated during the event.
333 Consequently, sulfuric acid was mostly neutralized by coarse $CaCO_3$.

334

335 As can be seen in Fig. 4, during this event, maximum hourly concentrations of some elements
336 can be twice (Na, S, Al, Ca or Ti) or even three times higher (Fe and Cl) than the average daily
337 values shown in Table 2

Rainfall affected most of the elements in both the fine and coarse fractions, as can be seen in Fig. 4. In some cases, concentrations decreased so much that even fell below detection limits (for example, Ti(C), Ti(F), Mg(C), Mg(F), K(C), K(F), etc.). On the other hand, the reduction in mass concentrations caused by precipitation was not uniform for both size fractions. In fact, elements in the coarse fraction were more affected by wet scavenging. Fig. 5 shows the decrease in elemental concentrations for Na, Ca, Fe and S during the precipitation event.

Figure 5

As can be seen in Figs. 5(a) and 5(d), during the episode, concentrations of Na(F), Na(C) and S(C) fell below detection limits. Regarding Ca (Fig. 5b), concentrations significantly decreased in both fractions; however, the decay factor (i.e., the ratio of calcium concentrations before and just after the precipitation event) was higher for the coarse fraction than for the fine fraction. A similar behaviour was observed for Fe (Fig. 5c). Table 3 shows decay factors for all the analysed elements in both fractions. These factors have been calculated using elemental hourly concentrations measured before (03:00-04:00 h) and after the precipitation event (11:00-12:00 h). <MDL indicates that concentrations during the episode fell below detection limits.

Table 3

All the elements in the coarse fraction (with the exception of Ni and Cr) were practically removed (concentrations <MDL) from the atmosphere during the event. The impact of rainfall on the fine fraction was significantly lower. In fact, elements like Cu and Cl did not show any decrease during the episode. This outcome highlights a greater removal efficiency by wet scavenging for coarse particles than for fine particles. Comparable results were found in Milan (Vecchi *et al*., 2009), where in a rainy episode similar to the one studied here (rainfall of 25 l m^{-2} in one hour), decreases of 90% in the coarse fraction and only 25% in the range 0.5-2.5 μm were

registered. In the same way, wet scavenging of coarse particles stopped abruptly an extreme Saharan outbreak observed in Lecce (SE Italy) (Conte et al., 2020).

From the plots in Fig. 5 the time needed to reach pre-event concentrations can be estimated. Around 18:00 h-19:00 h, concentration values previous to the event were re-established or, at least, they were above the MDL for most of the analysed elements. Therefore, a recovery period of approximately 10-12 hours can be established.

CONCLUSIONS

This study investigates the sensitivity of PM elemental composition to daily cycles of traffic flow as well as to some short-term meteorological events. The high temporal resolution of the dataset enabled the identification of elements typical of non-exhaust vehicle emissions (Cu, Zn, Mn, Al, Ca, Ti and Fe in the coarse fraction) as the best tracers of the variability of road traffic. Determination coefficients between concentrations of these elements and traffic volumes were higher than 0.5 on working days.

Likewise, elements in the coarse fraction were found to be good indicators of certain non-anthropic events. The concentrations of marine elements (Na, Mg, and Cl) not only increased under sea breeze conditions, but also under Saharan dust episodes. In fact, it is noteworthy that increase factors for crustal elements (for instance Ti, Fe, Si, Al or Sr in the coarse fraction) during these events were lower than those obtained for marine elements.

Coarse particles were more efficiently removed from the atmosphere by wet deposition than fine particles. The concentrations of most of the elements in the coarse fraction were reduced below detection limits during the precipitation event. For this type of short and intense rainfall event, the time needed to reach pre-event concentrations was about 10-12 hours.

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522

523 **FIGURE CAPTIONS**

524

525 Fig. 1: Hourly time series of: a) temperature and precipitation; b) wind direction and velocity; c)
526 PBL height and relative humidity and d) coarse and fine particle concentration. The Saharan dust
527 event occurred at the end of the sampling is also showed.

528 Fig. 2: Daily evolution of the number of vehicles at the sampling site on Saturday 20th, Sunday
529 21st and on working days (from Tuesday 15th to Friday 18th). The percentage difference
530 between the number of vehicles on Saturday and on working days is also presented.

531 Fig. 3: a) Values of the coefficient of determination (R^2) obtained in the regression analysis
532 between the daily evolution of elements in coarse fraction and the number of vehicles during the
533 weekday and Saturday; b) Percentage difference in concentration between weekdays and

Saturday obtained for each element in the coarse fraction; c) Percentage difference in concentration between weekdays and Saturday obtained for each element in the fine fraction.

Fig. 4: Time series of analysed elements in fine (F) and coarse (C) fractions. Red lines represent elements in coarse fraction (right Y axis) and grey lines in fine fraction (left Y axis). Concentrations are in ng m^{-3}.

Fig. 5: Impact of the precipitation episode on the concentrations of: a) Na, b) Fe; c) Ca; d) S.

FIGURES (Supplementary material)

Fig. S1: Maps from BSC-DREAM model of dust load for 20th November at 12:00 UTC and of precipitation for 21st November at 06:00 UTC.

Fig. S2: Elemental hourly evolution for: fine fraction (dotted grey line (Saturday) and continuous grey line (Working day average)) and coarse fraction (dotted red line (Saturday) and continuous red line (Working day average)). Concentrations are in ng m^{-3}.

TABLE CAPTIONS

Table 1: Average elemental concentrations in ng m^{-3} for the coarse and fine fractions. Maximum and minimum hourly levels are also shown.

Table 2: Elemental concentrations (ng m^{-3}) calculated for SDE and non-event periods. Increase factors are also shown.

Table 3: Decay factors for the analysed elements due to the precipitation event.