

PARTICULATE MATTER SOURCE APPORTIONMENT IN COMPLEX URBAN AND INDUSTRIAL CITIES: THE CASE OF TARRAGONA, SPAIN

EDSON PLASENCIA SÁNCHEZ¹, MANEL SÁNCHEZ-GUIJARRO¹,
FRANCISCO SÁNCHEZ-SOBERÓN², JOAQUIM ROVIRA², JORDI SIERRA²,
MARTA SCHUHMACHER², MÓNICA ROSELL¹ & ALBERT SOLER¹

¹Grup MAiMA, Mineralogia Aplicada, Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Spain

²Universitat Rovira i Virgili (URV), Environmental Analysis and Management Group, Departament d'Enginyeria Química, Spain

ABSTRACT

In the framework of UltraPAR project (Assessing the Exposure and the Health Effects of Ambient Fine and Ultrafine Particles in areas of intensive industrial activity) the outdoor air quality of 12 schools in Tarragona (Catalonia, Spain) was monitored in winter 2016–2017. High volume air samplers equipped with quartz filters were used for sampling airborne particulate matter equal or smaller than 10, 2.5, and 1 μm (known as PM_{10} , $\text{PM}_{2.5}$, and PM_1 respectively). These ambient samples together with some sources samples (harbour, industrial complexes, incinerator and road traffic) were chemically, mineralogically, and isotopically characterized and it is expected to help assessing the contribution of different emission sources. Preliminary results show that the maximum PM concentrations reached 37 $\mu\text{g}/\text{m}^3$ for PM_1 , 30 $\mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$ and 54 $\mu\text{g}/\text{m}^3$ for PM_{10} while the lead content varies in the range of 10 to 13 ng/m^3 . Through XRD and SEM the marine aerosol influence is confirmed in this coastal city. The carbon isotopic signatures of the different PM sizes could be a potential tracer of its origin (mineral vs combustion sources). These findings were also compared with recent and older environmental data from other studies in similar cities or specifically in this zone to explore its consistency and possible temporal variations.

Keywords: PM_{10} , $\text{PM}_{2.5}$, Carbon Isotopes, Tarragona.

1 INTRODUCTION

The metal profile and the isotopic composition of particulate matter (PM) have been used for identifying their emission sources, i.e. industrial or exhaust emissions, road dust, cement, biomass burning and others [1]–[3].

Several authors pointed out that industrial and coastal cities are principally affected by the industrial emission, marine aerosol, crustal and the traffic [4]–[7].

In Tarragona some studies have been performed in order to characterize the air quality and the potential health risk for exposed population, in most of them the principal component analysis (PCA) applied to a dataset of element abundance was the method used to estimate the source apportionment of pollutants [8]–[10].

2 METHODOLOGY

2.1 Site description and sampling campaign

Tarragona is located in northeast Spain on the shore of Mediterranean Sea at 90km southwest of Barcelona. Since 1960s it has experienced an extensive development in the chemical and petrochemical industries along with port activities and urban growing.



2.3 Data analysis

The total major element content in PM (Major-PM) was calculated as the sum of Al, Ca, Fe, K, Mg and Na content. The total trace element content in PM (Trace-PM) result of subtracting Major-PM from the sum of the 52 elements analysed (Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr) in each filter.

The total nitrogen content in PM (N) was calculated as the sum of the nitrogen content in NO_2^- , NO_3^- and NH_4^+ ions. The total major non-metal element content in PM (MajorNonM-PM) was calculated as the sum of N, C, S, Cl, P and Se.

When the value of an element was lower of its limit of quantification (LOQ) a half of the LOQ was assigned to perform numerical operations over the whole data.

Maps were generated in ArcGIS 10.2 and statistical analysis was performed in Statgraphics XVII.

3 RESULTS AND DISCUSSION

3.1 PM pollution levels

In general, the concentrations of PM were moderate and near to the European air quality standard (EU Directive 2008/50/EC; $50 \mu\text{g}/\text{m}^3$ for PM_{10} and $25 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$) in the outdoor air of the 12 sampled schools in Tarragona. However, samples from Vilallonga not only were exceeding these AQS for PM_{10} and $\text{PM}_{2.5}$, but also were above the percentile 95th of the whole dataset (Fig. 2).

Perafort have a PM profile lower than Cambrils which is considered as an urban background area, probably, because is located inland and Cambrils is near to the coast.

Similar to at Els Angels, La Pobla and Vilallonga the PM_1 fraction must be representing most of the $\text{PM}_{2.5}$ content due to their close values.

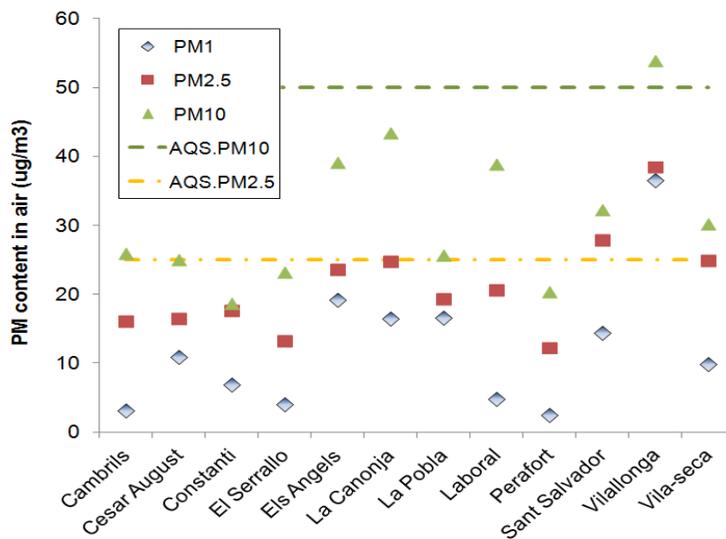


Figure 2: PM concentrations in the outdoor air of 12 schools in Tarragona respect air quality standards (AQS).

The metal content (Major-PM + Trace-PM) was quite similar for PM₁₀ and PM_{2.5} samples around 30% while for PM₁ is around 10%. There is not a clear relationship between the levels of metal content and PM, but, in general, as long as PM concentration increases the metal content decreases down to 20% in both PM₁₀ and PM_{2.5} particles and down to less than 1% in PM₁. In other words, the source of non-metal content for PM is larger than the source of metal content (i.e. sea aerosol or organic emissions vs particulate emission from engine wear) in such a way that metal content reach a maximum before than the non-metal content in PM.

The metal content suggests 3 areas of influence: near industrial source or roads (higher PM₁ content), urban or surrounding industrial complexes (similar PM₁₀ and PM_{2.5} content) and influenced by marine, dust or a secondary emission source (increasing the amount of PM but not the metal content).

Attending to its extreme low metal content, the road traffic apportionment at Cambrils, El Serrallo, Laboral and Perafort (all they near to the coast) can be considered negligible beside to other pollution sources, at least in a preliminary sense.

It has to be taken into consideration that a high variability of PM levels at Tarragona has been reported previously and it was explained by the influence of external air masses from Sahara, Barcelona and inner Europe [11], [12].

3.2 Elemental composition

The most abundant element (as weight percent) in PM₁₀ and PM_{2.5} samples was Na, indeed, Na, Al, Ca represent around 80% of the total metal content in all these samples. All samples had similar composition both in Major-PM and Trace-PM, except Cambrils where Na represent more than 60% in PM_{2.5} and Ca represent more than 80% in PM₁.

In Fig. 3 is shown the metal composition of PM₁ samples after Na, Al, Ca and K were removed. The contents of Mg, Cu, Fe, Sc, Sn and Zn were significant although different between samples. Vilaseca, Vilallonga and Sant Salvador got the most similar element composition (as weight percent), while Cesar August had the highest content of Fe, El Serrallo of Cu, Perafort of Mg and La Pobra of Sb and Sn.

From the major nonmetal elements, carbon was the most prevalent in all samples, except for Cambrils (PM₁₀, PM_{2.5} and PM₁), Laboral (PM₁₀), Sant Salvador (PM_{2.5}) and El Serrallo

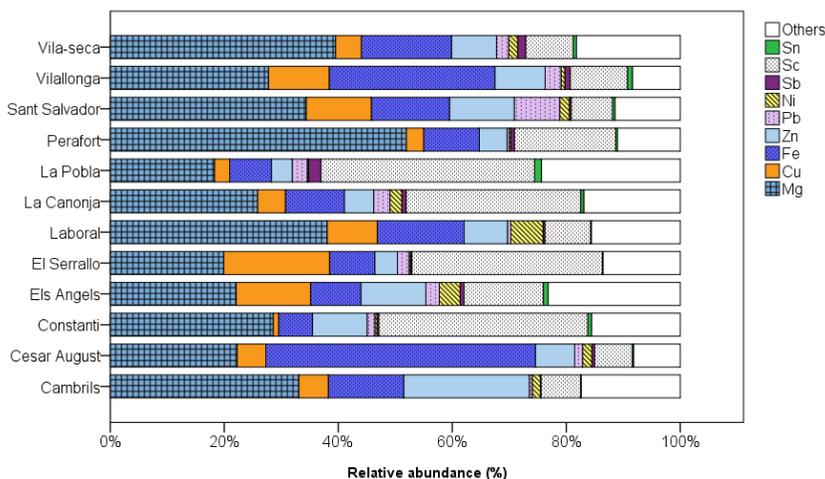


Figure 3: Trace metal element content in PM₁ outdoor air of 12 schools in Tarragona.

(PM_{2.5}), in which the most abundant elements were P and Cl for PM₁₀ and PM_{2.5}, and S for tPM₁.

3.3 XRD and SEM findings

A circular piece of each quartz filter was analyzed by XRD along with samples from sources. Due to the amorphous matrix of fibbers from which the filters are made, a typically diffractogram contains a high background level which has to be removed to find and identify the peaks compared with a mineral database (JCDPS) that represent the crystalline phases present in the samples. The most important phases identified were halite, feldspars, anhydrite and calcite.

Another piece of each sample was observed by SEM-EDS. These results confirmed the presence of halite, among other mineral phases as calcite, anhydrite, silvite, etc. Also, a significative amount of amorphous carbon was observed in most of the samples. These findings are in accordance to previous studies performed in Tarragona [15].

3.4 Spatial analysis of samples

From a comparative analysis of the elements and ratios used as traces for identifying the pollution sources in coastal and industrial areas [4], [5], [13], [16], [17], some of them were selected to examine our data, for example, the influence of the predominant wind (NW) thought the transport of the heaviest particles was reflected in the spatial distribution of both the PM content and in the ratios PM_{2.5}/PM₁₀ and PM₁/PM_{2.5} in Tarragona.

The Mn content profile (PM₁₀, PM_{2.5} and PM₁) was quite similar at La Canoja, Els Angels and Cesar August, while was the highest at Vilallonga, which confirms the industrial influence in these schools.

The Ni content, especially in PM₁, corresponded to refining and fuel-oil combustion places at Laboral, La Canoja, Els Angel, Cesar August, Sant Salvador and Vilallonga. The highest content was found at Cesar August.

Using Se content as tracer for coal combustion, Vilaseca, Laboral, La Canoja, Els Angel, Cesar August, could be grouped by its content in PM_{2.5}. Perafort had a similar content, but, appears as a northern isolated point.

Laboral, El Serrallo and Sant Salvador had the highest Cu/Sb ratios in PM₁ which could indicate that they are mostly influenced by road traffic, while El Serrallo and La Pobla had the highest Al/Ca ratio in PM₁₀, indicating the places where the resuspended effect is more relevant either by traffic or by construction works.

As previously mentioned, Na content profile (PM₁₀, PM_{2.5} and PM₁) was almost the same in every place representing the sea sprays and aged sea salts apportionment.

Another important tracer was the C/N ratio (see Fig. 4), which is used to evaluate the origin of the organic matter; the obtained ratios were between 0.4 (Cambrils, PM_{2.5}) and 53 (La Pobla, PM₁₀) with an average value of 13 for PM₁, 15 for PM_{2.5} and 13 for PM₁₀. While Cambrils, El Serrallo and VilaSeca had a profile ratio with values lower than 10 (planktonic source); Sant Salvador, Els Angels and Cesar August lower than 15 (terrestrial vascular plants); La Pobla and Vilallonga ratios were greater to 30: out of the literature reference.

3.5 Isotope analysis and source identification

The isotope composition of the whole carbon content in each filter ($\delta^{13}\text{C}$) was analyzed by taking a sample of 1x1 cm. The results are expressed in ‰ respect to the isotope composition



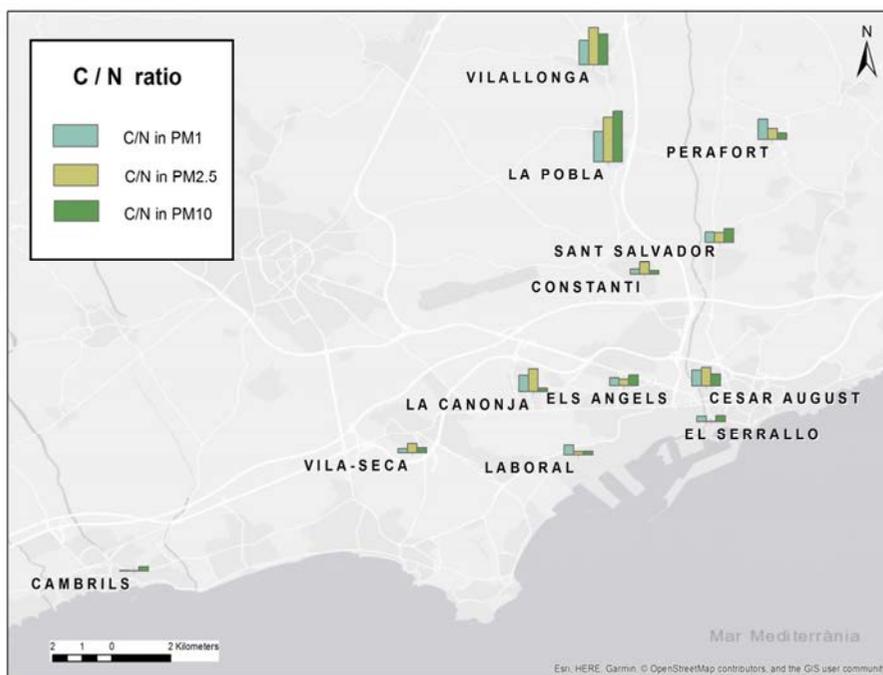


Figure 4: Spatial distribution of C/N ratio in PM outdoor air of 12 schools in Tarragona.

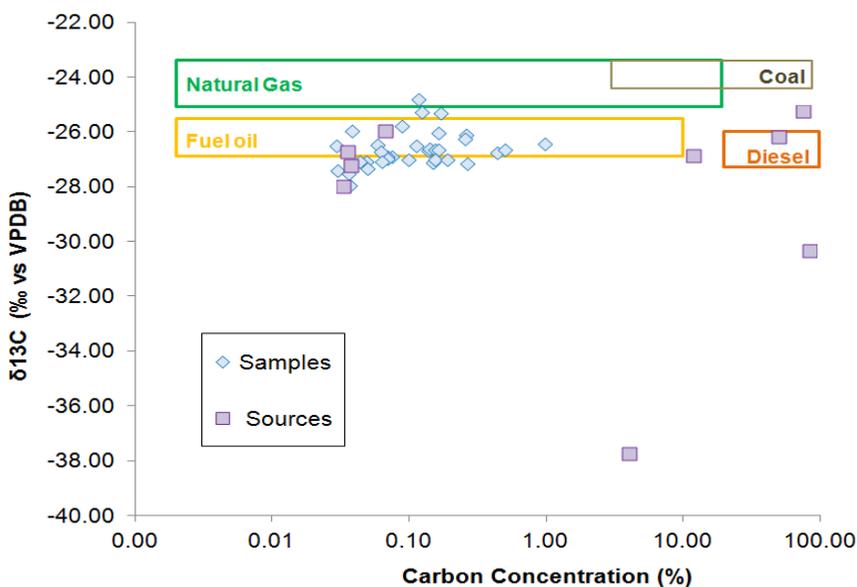


Figure 5: Carbon isotope characterization of PM samples and sources from Tarragona in comparison to reference boxes of different combustion emissions [1].

of the international standard for carbon, Vienna Pee Dee Belemnite (VPDB), and are presented in Fig. 5 along with some reference boxes which represent the isotope signature of the combustion products by fuels according to the study of Widory et al., 2004 [1].

All school samples had a $\delta^{13}\text{C}$ significantly different from those associated to mineral fraction ($>-17\text{‰}$) [13], instead, most of them had a $\delta^{13}\text{C}$ around -26.6‰ which can be associated to fuel oil combustion, in a wide range of carbon content between 0.05 to 1%. Most of the analyzed sources also showed a similar $\delta^{13}\text{C}$, but, its carbon concentration permitted identifying a different combustion fuel.

The overall carbon isotope signature for PM at Tarragona ($-26.1 \pm 0.8\text{‰}$ for PM_{10} , $-26.8 \pm 0.5\text{‰}$ for $\text{PM}_{2.5}$ and $-26.9 \pm 0.4\text{‰}$ for PM_1); was quite different of those which are reported for other cities, i.e. Beijing $-23.5 \pm 0.9\text{‰}$ for PM_1 or Delhi $-25.5 \pm 0.5\text{‰}$ for PM_{10} , but closer to Kolkata (Calcuta) $-26.0 \pm 0.4\text{‰}$ for PM_{10} [2,18].

The maximum $\delta^{13}\text{C}$ value for PM_{10} was -24.8‰ (El Serrallo), -25.7‰ (Cesar August) for $\text{PM}_{2.5}$ and -26.43‰ (Constanti) for PM_1 ; they are all aligned with the predominant wind direction from coast to inland. Whereas the minimum $\delta^{13}\text{C}$ values (-27.9‰ of Cambrils for PM_1 , -27.4‰ of Laboral for $\text{PM}_{2.5}$ and -26.7‰ of La Pobla for PM_{10}) were mainly upwind (near of the coast).

The farthest locations from the coast (Vilallonga, La Pobla and Perafort) shared a similar profile around -26.7‰ : $\delta^{13}\text{C}(\text{PM}_{10}) < \delta^{13}\text{C}(\text{PM}_{2.5}) < \delta^{13}\text{C}(\text{PM}_1)$.

In general, a spatial overview of the $\delta^{13}\text{C}$ signature revealed a profile that matches very well with the expected influence areas by the macro sources: petrochemical, industrial complex and harbour, although the range of the $\delta^{13}\text{C}$ signature is not large enough to identify the proportion of the different sources with a high level of certainly.

4 CONCLUSIONS

Selected elements and ratios seem to be appropriated for PM sources apportionment in Tarragona, while complementary isotopic characterization of PM could help to confirm these results. Moreover, isotopes have more accuracy and demand fewer resources both for pre and post sample analysis.

ACKNOWLEDGEMENTS

The present research work has been funded by UltraPAR (CTM2015-65303-P), REMEDIATION (CGL2014-57215-C4-1-R) and PACE (CGL2017-87216-C4-1-R) projects from Spanish Ministry of Economy and Competitiveness (MINECO) and co-financed by the European Union through the European Regional Development Fund (AEI/FEDER, UE). This work was also partly supported by the *Generalitat de Catalunya* through the consolidate research group (2017-SGR-1733). E. Plasencia Sánchez was supported by the Peruvian Government credit-fellowship “Reto Excelencia” and M. Rosell by “Ramón y Cajal” contract RYC-2012-11920. We thank the technical support from CCiT-UB.

REFERENCES

- [1] Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A. & Guerrot, C., The origin of atmospheric particles in Paris: a view through carbon and lead isotopes. *Atmospheric Environment*, **38**, pp. 953–961, 2004.
- [2] Sharma, S.K. et al., Variation of stable carbon and nitrogen isotopic composition of PM_{10} at urban sites of Indo Gangetic Plain (IGP) of India. *Bull Environ Contam Toxicol.*, **95**, pp. 661–669, 2015.



- [3] Widory, D., Nitrogen isotopes: Tracers of origin and processes affecting PM₁₀ in the atmosphere of Paris. *Atmospheric Environment*, **41**, pp. 2382–2390, 2007.
- [4] Mbengue, S., Alleman, L.Y. & Flament, P., Metal-bearing fine particle sources in a coastal industrialized environment. *Atmospheric Research*, **183**, pp. 202–211, 2017.
- [5] Di Palma, A. et al., Geochemistry and carbon isotopic ratio for assessment of PM₁₀ composition, source and seasonal trends in urban environment. *Environmental Pollution*, **239**, pp. 590–598, 2018.
- [6] Kunwar, B., Kawamura, K. & Zhu, Ch., Stable carbon and nitrogen isotopic compositions of ambient aerosols collected from Okinawa Island in the western North Pacific Rim, an outflow region of Asian dusts and pollutants. *Atmospheric Environment*, **131**, pp. 243–253, 2016.
- [7] Querol, X. et al., Speciation and origin of PM₁₀ and PM_{2.5} in selected European cities. *Atmospheric Environment*, **38**, pp. 6547–6555, 2004.
- [8] Aragón Guiol, M., Caracterització de l'atmosfera del port de Tarragona. PhD thesis, Tarragona, 2013 (in Catalan).
- [9] Alastuey, A. et al., Contribution of harbour activities to levels of particulate matter in a harbour area: Hada Project-Tarragona Spain. *Atmospheric Environment*, **41**, pp. 6366–6378, 2007.
- [10] Querol, X. et al., Levels of particulate matter in rural, urban and industrial sites in Spain. *Science of the Total Environment*, **334–335**, pp. 359–376, 2004.
- [11] Querol, X. et al., Speciation and origin of PM₁₀ and PM_{2.5} in Spain. *Aerosol Science*, **35**, pp. 1151–1172, 2004.
- [12] Rodriguez, S. et al., Comparative PM₁₀–PM_{2.5} source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. *Science of the Total Environment*, **328**, pp. 95–113, 2004.
- [13] Mari, M. et al., Source apportionment of inorganic and organic PM in the ambient air around a cement plant: Assessment of complementary tools. *Aerosol and Air Quality Research*, **16**, pp. 3230–3242, 2016.
- [14] Moreno, T. et al., Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail. *Atmospheric Environment*, **40**, pp. 6791–6803, 2006.
- [15] Alastuey, A. et al., Contribution of harbour activities to levels of particulate matter in a harbour area: Hada Project-Tarragona Spain. *Atmospheric Environment*, **41**, pp. 6366–6378, 2007.
- [16] Moreno, T. et al., Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail. *Atmospheric Environment*, **40**, pp. 6791–6803, 2006.
- [17] Sánchez de la Campa, A. et al., High concentrations of heavy metals in PM from ceramic factories of Southern Spain. *Atmospheric Research*, **96**(2010), pp. 633–644, 2010.
- [18] He, N., Kawamura, K., Kanaya, Y. & Wang, Z., Diurnal variations of carbonaceous components, major ions, and stable carbon and nitrogen isotope ratios in suburban aerosols from northern vicinity of Beijing. *Atmospheric Environment*, **123**, pp. 18–24, 2015.

