



## Source apportionment to PM<sub>10</sub> and PM<sub>2.5</sub> at multiple sites in the Bay of Gibraltar (S Spain) by PMF: estimate of shipping emission

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The recognized adverse health effect of the PM<sub>10</sub> and PM<sub>2.5</sub> particles leads to an increasing demand of a more efficient control of pollutant emissions especially in industrial and/or urban sites. The degree with which the control of the emissions can be accomplished depends on the identification of the pollutant sources and the estimation of their contribution. The chemical speciation of ambient PM coupled with receptor modelling can be considered as a powerful tool to estimate origin of the sources and their contribution to the PM<sub>10</sub> and PM<sub>2.5</sub> fractions. This work aims to evaluate the effect on air quality of the anthropogenic activities performed in one of the most important industrial estates of Southern Spain located in the Bay of Gibraltar. The area under study is characterized by the presence of metallurgy industries and oil refineries around which four urban agglomerates are located, namely: Los Barrios (36°11'7.39"N, 5°29'33.89"O), La Linea (36°9'40.24"N, 5°20'53.72"O), Algeciras (36°7'47.21"N, 5°26'51.71"O) y Puente Mayorga (36°10'54.60"N, 5°23'8.32"O). Traffic is consequently another important source of pollutants in the considered area together with an intense shipping activity. The estimation of the pollutant sources and their contribution was obtained by applying the Positive Matrix Factorization (PMF) model to the PM<sub>10</sub> and PM<sub>2.5</sub> levels and chemical speciation data simultaneously obtained in the four urban agglomerates during a period of 4 years (March 2003 – December 2007). Given the small size of the area under study, the PM data collected in all the four stations was simultaneously introduced within the PMF model. This procedure allowed the PMF to use a higher number of data rather than using the 4 database separately, thus improving the performances of the model. Following this procedure a total of 567 and 341 samples for the PM<sub>10</sub> and PM<sub>2.5</sub> fractions respectively were introduced within the PMF. Moreover, before running the model, a detailed inspection of the database was performed in order to look for the possible presence of weaker data such as contaminated data, below detection limit data, missing data etc. This procedure is important in order to improve the performances of the model, reducing the error associated with the calculated sources contributions. In the present work seven sources were obtained in both PM<sub>10</sub> and PM<sub>2.5</sub> fractions, namely: crustal (traced by Al, Ca, K, Ti, Fe, Rb, Sr), marine (traced by Na, Cl, Mg), industrial (Cr, Mn, P, Zn, Fe, As, Ni, Pb), oil combustion (traced by V, Ni y La from both oil refinery and shipping emissions), traffic (OC+EC, Cu, Sn, Sb), secondary sulphate (SO<sub>4</sub><sup>=</sup> and NH<sub>4</sub><sup>+</sup>), ammonium nitrate in PM<sub>2.5</sub> (traced by NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and sodium nitrate in PM<sub>10</sub> (Na and NO<sub>3</sub><sup>-</sup>). In PM<sub>10</sub> fraction the main contributing sources in all stations were secondary sulphate (19-22% of PM<sub>10</sub> mass), sodium nitrate (15-21%) and crustal (14-23%) followed by traffic (10-21%), marine (10-17%), oil combustion (6-9%) and industrial (1-5%). The main contributing sources in PM<sub>2.5</sub> were regional sulphate (28-34%), ammonium nitrate and traffic (10-15%), crustal (8-18%), oil combustion and marine (8-10%), and industrial (2-7%).

Further information on source contributions and locations were obtained by coupling PMF with wind direction data which show two privileged mean wind directions in the considered area: SSE-ESE (75% of occurrence) and W-NW (80% of occurrence). In this work wind data was used to separately evaluate the contributions from shipping and oil refinery which were not separated by the PMF model mainly as a consequence of the similarity in the fingerprints of these two sources.

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