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MONOGRAPH

Identification of emission sources from data of $PM_{2.5}$ chemical speciation measured with automatic monitors: application in a coastal site of the Mediterranean basin

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ABSTRACT High-time resolution (1 hour) measurements of 11 species (organic carbon, elemental carbon, chloride, nitrite, nitrate, sulfate, sodium, ammonium, potassium, magnesium, calcium) within the $PM_{2.5}$ were conducted, from 3rd May to 30th June 2010, in a coastal site of Basilicata (Italy). Acquired data were analysed through Positive Matrix Factorization (PMF) method in order to individuate potential emission sources. This source apportionment evaluation revealed 5 factors separated as Vehicular traffic, Combustion of biomass, Secondary aerosol, Aged marine, Marine fresh and Dust. For each factor were defined profile, temporal trend, 24h-cycle and percentage contribution to measured $PM_{2.5}$, also emphasizing the relationship between factors and different wind conditions.

KEY WORDS Automatic monitors; High-time resolution $PM_{2.5}$ measures; Positive Matrix Factorization; Rural background site; Source apportionment.

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INTRODUCTION

The study presented here had as its overall objective the identification of emission sources (source apportionment) from $PM_{2.5}$ chemical speciation data collected by automatic monitors, and was conducted at a coastal site within the Mediterranean basin. In particular, attention was focused on the use of non-conventional measuring systems such as automatic monitor, in an intensive monitoring campaign with acquisition of high-time resolution data; it was verified the application of multivariate statistical methods to such resolution data typology (likely high variability), in order to detect and identify potential emission sources by a source apportionment receptor model approach for a rural background site where the sources are not particularly evident; finally, it was attempted to solve the emissive framework using a limited number of $PM_{2.5}$ chemical parameters, as described below.

MATERIAL AND METHODS

The study site, localised at the ENEA - Trisaia Research Centre (Rotondella, Matera), is a coastal area in Basilicata (Italy), 4 km away from the sea (Gulf of Taranto) and about 10 km distant from Appennino Calabro-Lucano (Fig. 1). In relation to the

potential emission sources it is considered as rural background (according to the criteria in Italian Decr. Leg. 13 agosto 2010, n. 155) where the main activities in the area are agriculture and handicraft, thus missing important punctual emission sources. The distance from the nearest town of great extent (Taranto) is 60 km, while the distances from the nearest towns of medium size are 4 km (Nova Siri Scalo) and 6 km (Policoro). The distance from the main roads is around 600–700 meters, with the presence of a four lane motorway (SS106-Jonica) and a two lane motorway (SS653-Sinnica).

The weather framework regarding the wind for the entire sample period shows a prevalent direction along the NW-SE axis, where to phenomena of local breeze were alternating continuative perturbation events from NW; in fact more in detail were differentiated three wind condition periods: in addition to the local breeze situation, emerged situations of continuous perturbation from NW, and situations of local breeze associated with sand transport.

Instrumental set-up was consisting in a transportable container-laboratory hosting inside an URG 9000D Ambient Ion Monitor associated with two ion chromatographs to analyse the major soluble inorganic ions (Cl^-, NO_2^-, NO_3^-, SO_4^{--}, Na^+, NH_4^+, K^+, Mg^{++}, Ca^{++}), an SUNSET semi-continuous EC/OC analyzer for organic carbon (OC) and elemental carbon (EC), a control unit for the acquisition of weather data.

Other than the facility to work standing-alone via remote control, additional important advantages of automated sampling and measurement systems are the reduction or absence of positive and negative artefacts in the sample (due to the non-manipulation of specimen, the presence of denuder that allows the separation of the gas phase and of the aerosol phase, and the minimum sampling interval) and a low limit of detection value, with possibility to reveal even very low mass concentrations. Finally these tools allow to perform measurement campaigns for limited periods with anyhow a consistent number of data available, sufficient for advanced statistical analysis such as multivariate techniques through which is possible the identification and quantification of the emission sources. On the other hand the high-time resolution of data from automated monitors permits to obtain further information on the emission sources' activity, for example any possible variation within the daily cycle.

The sampling periods accounted for 59 days, from 3rd May to 30th June 2010, with an 1 hour-time resolution of measures; 11 species (organic carbon, OC; elemental carbon, EC; chloride, Cl^-; nitrite, NO_2^-; nitrate, NO_3^-; sulfate, SO_4^{--}; sodium, Na+; ammonium, NH_4^+; potassium, K^+; magnesium, Mg^{++}; calcium, Ca^{++}) within the $PM_{2.5}$ (aero-suspended particles < 2.5μm of diameter) were measured.

Factorial analysis with PMF (Positive Matrix Factorization) was applied at the concentration data; PMF allows to obtain information on the contribution of emission sources in a specific receptor site without knowing the sources' emissivity reference profiles. The solution to the factorial model

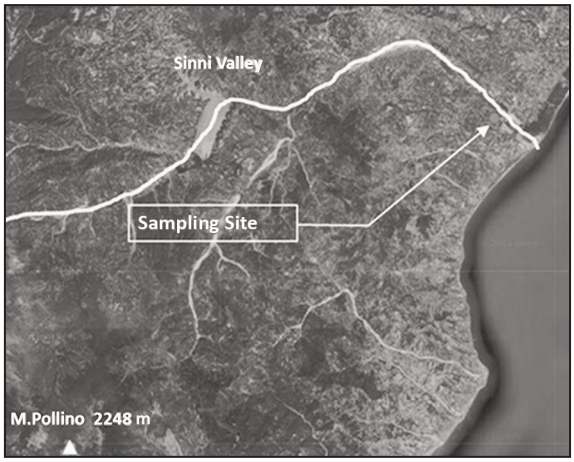

Figure 1. Localisation of the sampling site.

μg/ m³	average	std	min	max
OC	**1.66**	0.55	0.82	2.94
EC	**0.42**	0.23	0.12	1.04
Cl^-	**0.48**	0.33	0.03	1.66
NO_2^-	**0.16**	0.04	0.06	0.26
NO_3^-	**0.51**	0.24	0.20	1.17
SO_4^{2-}	**1.90**	0.81	0.54	3.78
Na^+	**0.764**	0.151	0.479	1.120
NH_4^+	**1.020**	0.505	0.148	2.279
K^+	**0.112**	0.049	0.015	0.212
Mg^{2+}	**0.023**	0.017	0.015	0.092
Ca^{2+}	**0.097**	0.108	0.015	0.481

Table 1. Average, standard deviation, minimum and maximum for each sampled component.

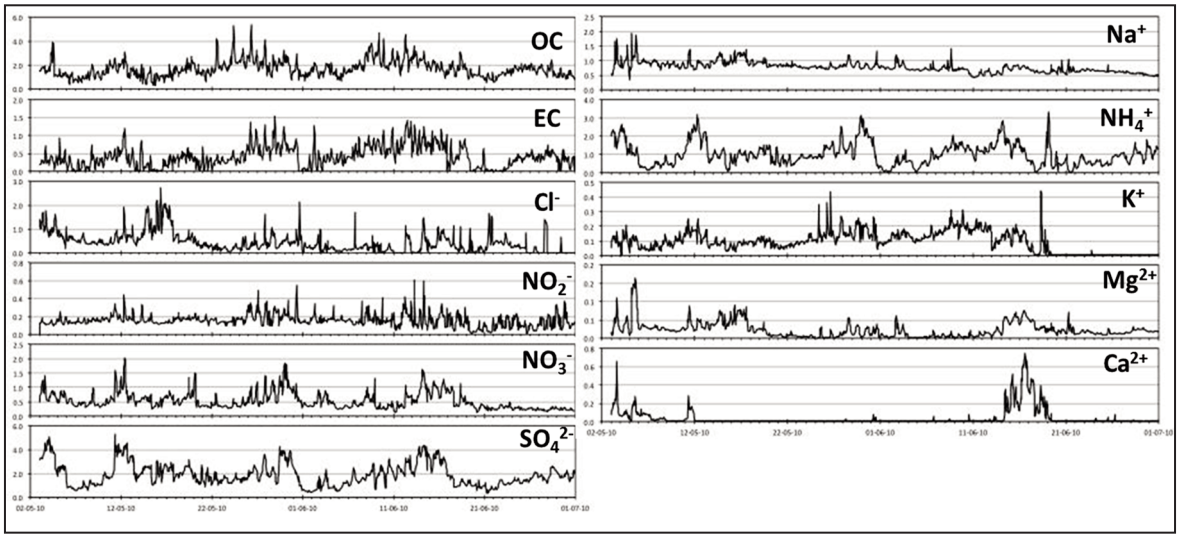

Figure 2. Species' time series.

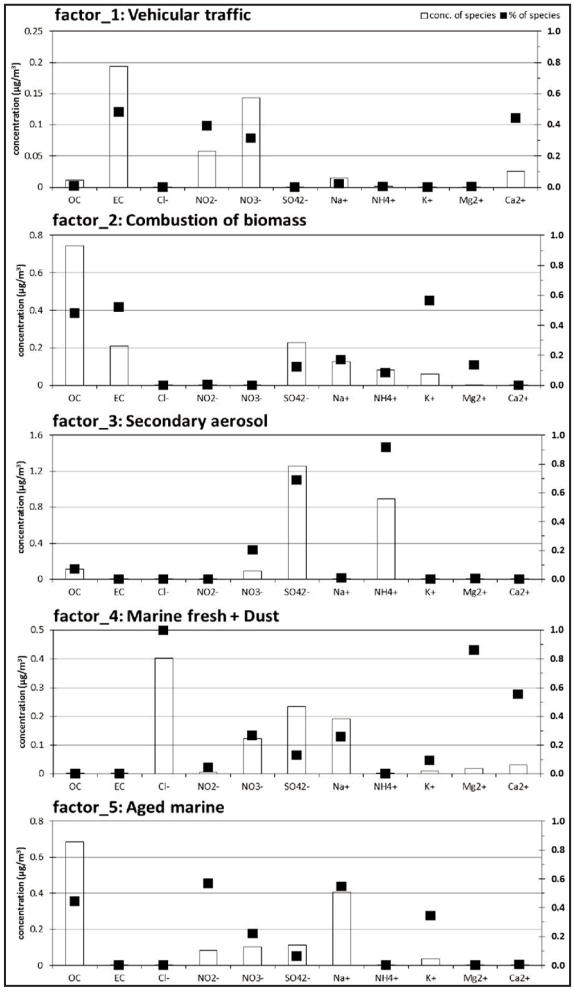

Figure 3. Individuated factors through PMF analysis.

with PMF explains the correlation between the variables observed through their linear combinations called "factors", associated to sources, which originate from common latent characteristics of the observed variables. The input model needs certain defined parameters such as the errors associated with the individual specimen and the number of factors in which clustering the experimental data, corresponding to the theoretically expected sources.

RESULTS AND DISCUSSION

The figure 2 shows sampled species' time series, where is noticeable the high variability of the values along the sampling period and the Table 1 shows a summary of mean, standard deviation, minimum and maximum for each sampled component, highlighting also how low are concentrations.

For the case studied, the PMF analysis permitted to individuate and recognise 5 factors (Fig. 3), as follows.

The first factor is Vehicular traffic with a high percentage of EC, NO_2^-, NO_3^-, linked to vehicular exhaust emissions, together with the presence of Ca^{++} related to road resuspension. Another recognized factor was the Combustion of biomass with high percentage of organic carbon, elemental carbon and potassium, all components derived from combustion processes. A third emission factor has been identified as Secondary aerosol with preval-

ence (high % contribution) of sulfate and ammonium as well, so a secondary aerosol present as ammonium sulfate. Another factor was composed of Marine fresh aerosol and Dust, with a very high value of chlorine (which characterize the fresh marine aerosol component) associated to a high value of sodium, and the presence of magnesium and calcium associated to both marine and sand transport. The fifth factor was the so-called Aged marine, defined as such because differently than the fresh marine presents no chlorine (which comes to be lost rapidly) but only the sodium. This factor is mixed with a component of anthropogenic nature, as evidenced by the organic carbon and nitrite (both of non-marine origin) probably carried by the wind at the time of the air masses displacement.

In the Figure 4 are presented for each factor the time series along the whole sampling period (left) and the trends within the 24h-cycle (right).

Vehicular traffic presents a bimodal trend almost coincident with the main hours of moving vehicles: around 6:00–7:00 a.m. and 8:00 p.m.,

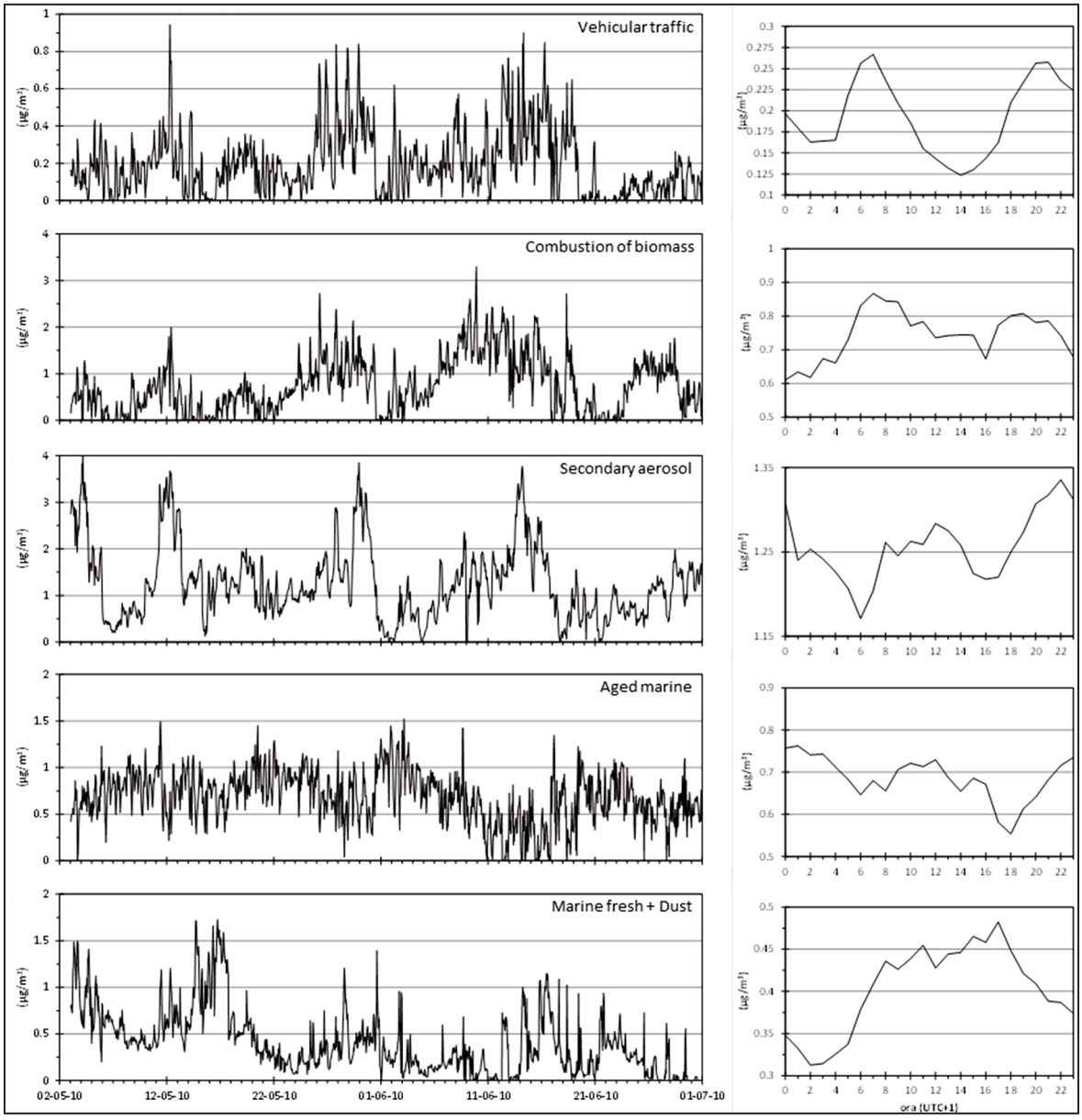

Figure 4. Time series and 24h-cycle of each factor.

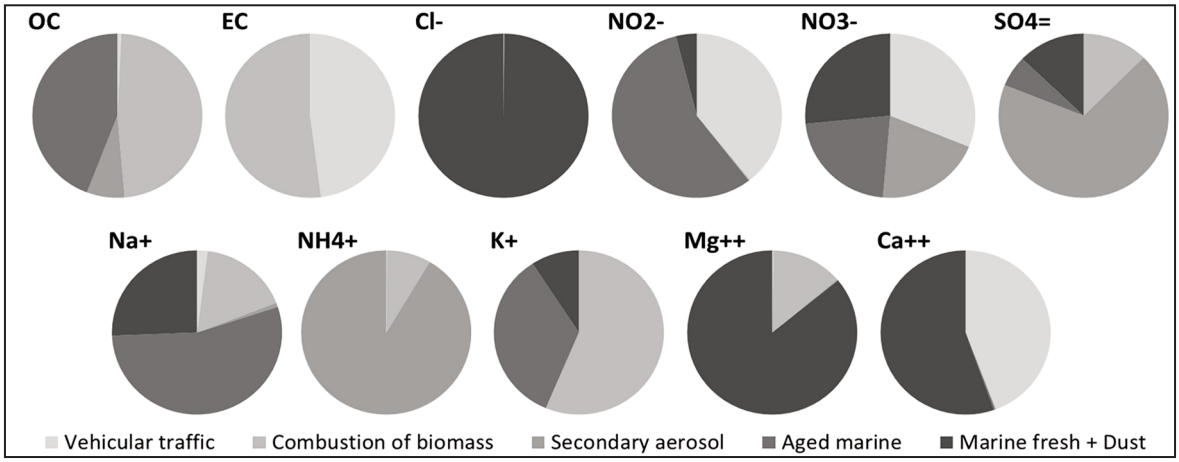

Figure 5. Contribution % of each species to the 5 factors.

when traffic flows are greater, the Vehicular traffic factor has the highest values. Combustion of biomass, probably connected to agricultural activities such as stubbles burning, has higher concentrations during the daytime. Secondary aerosol has daily changes that can be associated with both photochemical processes and movements of air masses involving the area. Marine fresh and Aged marine are obviously influenced by sea-land breezes, so when the breeze blew from the sea during the day the highest concentrations of Marine fresh were recorded; when the breeze blew from the land, Aged marine returns as the air masses are beckoned.

Also, as mentioned before, it was made a differentiation into three periods cumulating the days similar according three main anemological situations: 24 days combined with a NW perturbation; 16 days combined with situation of local breeze; 19 days combined with local breeze to which is associated a transport of sand. In the period when the perturbation comes from NW, so the Tyrrhenian, the wind is stronger, while in situations of local breeze and sand transport the wind maintains lower speeds.

What happens to individual sources during various anemological typologies. Vehicular traffic as expected shows bimodal daily trend similar in the all three periods although concentrations are different; this factor occurs with lowest values throughout NW perturbation maybe depending from dispersion and dilution concerns, in consideration that the height of the mixing layer is greater during the periods of perturbation. Combustion of biomass concentrations are lower as well during NW perturbations, again probably because of greater dilution; it shows within the 24h-cycle higher values more during daytime because of human activity. Even Secondary aerosol is lower during NW perturbation, with an almost constant trend over the 24 hours; therefore this secondary aerosols is likely associated with a regional background pollution. Aged marine increases during the NW perturbation because maybe linked to marine aerosol from the Tyrrhenian that depletes chlorine during the way; in this factor are also present components related to pollution from human activities (eg. OC, NO_2^-) because they are probably dragged by air masses passing through the mainland. Marine fresh aerosol shows higher values during the periods of local breeze and sand transport for accumulation-dilution question and with 24h-cycle increasing in daytime according to sea-land breeze phases.

Then, other data of most interest is the percentage contribution of each species to the 5 factors (Fig. 5) where it is seen that some components enter more in certain factors rather than in others like for example the SO_4^{--} which most enters into Secondary aerosol, or as the chlorine which enters completely into Marine fresh; instead other components such as NO_3^- are distributed in several factors more or less abundantly in one rather than in another.

Finally, regarding the contribution of the 5 factors on the total $PM_{2.5}$ detected, it is seen that the main factor in terms of mass is attributable to Secondary aerosol with 30%, then follows Combustion of biomass with 22%, then Aged marine with 21%, then

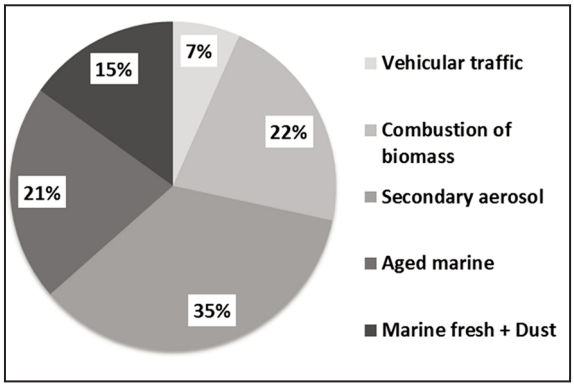

Figure 6. Contribution of the 5 factors on the total PM2.5 detected.

Marine fresh & Dust with 15%, and finally Vehicular traffic with 7% (Fig. 6).

CONCLUSIONS

In general the source apportionment techniques, through multivariate statistical analysis, allow to have information about air pollution factors that insist on a specific area, with the possibility of differentiating anthropogenic sources and natural sources, and discriminating primary and secondary sources. In particular for a rural background site, as this study case, PMF model leads to the predetermination of factors although the concentrations of species are highly variable and near to the detection limit. The use of PMF model is therefore to be considered a valid basis for the identification of the most probable emission profiles at a site where the sources are not particularly evident; hence it becomes essential to improve that receptor analysis with weather studies, in particular anemology and mixing layer height both locally and regionally. For certain investigations as our situation is eventually important rather temporal trends with cycles in the short and medium term as well as occasional events, and high-time resolution monitors can provide an important contribution to the identification of potential emission sources *a fortiori* in case of limited number of parameters and limited sampling period.

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