



The preliminary study of the PM₁ main components and of their seasonal variation using a linear parametric model

A. Speranza^{1*}, G. Jona Lasinio² and R. Caggiano¹

¹IMAA, Istituto di Metodologie per l'Analisi Ambientale, CNR, 85050 Tito Scalo, PZ, Italy; rosa.caggiano@imaa.cnr.it; antonio.speranza@imaa.cnr.it

²Department of Statistical, Sciences, University of Rome "la Sapienza" - P.le Aldo Moro 5, 00185 Rome, Italy; giovanna.jonalasinio@uniroma1.it

*Corresponding author

Abstract. This study presents the mass concentration PM₁ (aerosol particles with an aerodynamic diameter below 1 μm) together with sixteen related trace elements (i.e. Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti, Zn) measured during Summer and Winter periods in a characteristic anthropized area. Soil, Sulfate, total-metal-oxide (TMO) and the carbonaceous material (CM) masses were evaluated and considered as the main components of PM₁. All variables were log transformed to smooth extreme recording influence. A linear parametric model was estimated to assess components influence on the log PM₁ and to evaluate the possible differential effect of observation periods on the components contribution. Results showed that CM, Sulfate, Soil and TMO explained about 44.32%, 33.56%, 11.4% and 0.2% of the total variance of PM₁, respectively. The contributions of CM, Sulfate and Soil to PM₁ were significant with an error of 5%. The contribution of TMO to PM₁ was significant with an error of 10%. CM, Soil and TMO contributed to PM₁ with a significant difference between Summer and Winter, whereas Sulfate contributed to PM₁ with non significant difference between Summer and Winter. Therefore, the CM, Sulfate and TMO components which were mainly related to anthropogenic origin explained about 78% of the PM₁ total variance, whereas the Soil component which was mainly related to natural origin explained about 11.4% of the PM₁ total variance. CM, Soil and TMO components contributed differently to PM₁ in Summer and Winter. This result suggested possible seasonal sources activities for these components.

Keywords. PM₁; Linear parametric model; Seasonal sources.

1 Introduction

Human activities and natural processes contribute to the formation and emission in the air of aerosol particles, which are also known as particulate matter (PM). These particles have different sizes, shapes and masses and they are made of many chemical compounds some of which potentially harmful. The size of particle is an important physical parameter because it provides relevant information on particles origin, their formation process and harmful effects. Particles with an aerodynamic diameter smaller than 10 μm (thoracic particles) are of special interest because they can penetrate and be deposited in specific thoracic regions of the lung. It has been reported that PM toxicity increases with the aerodynamic diameter decrease, as particles with smaller aerodynamic diameter can easily reach deep regions of the lung and can vehicle potentially toxic substances. Indeed, physiological and

toxicological considerations have suggested that fine particles (i.e. aerosol particles with an aerodynamic diameter smaller than 2.5 μm) can play the largest role in affecting human health [1]. Fine particles have mainly an anthropogenic origin and they are mostly formed through the processes of combustion and relating condensation/reaction and gas-to-particle conversion of materials containing potentially toxic elements. PM₁ (i.e. aerosol particles with an aerodynamic diameter smaller than 1 μm) is a PM fraction that better represents the contribution of PM anthropogenic sources. The identification of the possible emission sources of PM₁ is a starting point to evaluate and plan actions aimed at mitigating the levels of PM to protect the public health and the environment. This preliminary study aims to evaluate the main components of PM₁ relating to natural and anthropogenic emission sources and to evaluate their seasonal variations using a linear parametric model.

2 Methods

The mass concentration of PM₁ measured during Summer and Winter periods in a characteristic anthropized area was determined and sixteen related trace elements (i.e. Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti, Zn) were analyzed. The area was characterized from natural emission sources and from diverse anthropogenic emission sources relating to several activities (i.e. industrial, agricultural, domestic heating and traffic).

2.1 PM₁ main components

The main components of PM₁ such as Soil mass, Sulfate mass and total metal oxide (TMO) mass were evaluated as follows:

$$[Soil] = 2.14[Si] + 1.89[Al] + 2.42[Fe] + 1.95[Ca] + 1.67[Ti] + 1.29[Mn] + 1.35[Na] + 1.67[Mg] \quad (1)$$

$$[Sulfate] = 3.063[S] \quad (2)$$

$$[TMO] = 2.15[Li] + 1.14[Cd] + 1.27[Ni] + 1.31[Cr] + 1.25[Cu] + 1.24[Zn] + 1.08[Pb] + 1.21[K] \quad (3)$$

with $[Al]1.89 = Al_2O_3$ and $3Al_2O_3 = SiO_2$ [2-3]. An estimate of the carbonaceous material mass was determined evaluating the PM₁ missing mass (MM) using the reconstructed mass approach as:

$$PM_1 = [Soil] + [Sulfate] + [TMO] + [MM] \quad (4)$$

Thus, it is expected that the missing mass was largely made of carbonaceous material (CM) [4].

2.2 Linear parametric model

It was originally demonstrated that air pollutants follow a lognormal distribution starting from the “law of proportionate effect” [5]. Davies [6] reported that aerosol atmospheric particles have a distribution that can be represented by lognormal distribution. Thus all considered variables were log transformed to smooth extreme recording influence. The following linear parametric model was estimated:

$$Y_i = \beta_{0s} + \sum_k \beta_{ks} X_{ki} \quad (5)$$

Where Y_i is the i^{th} observation of log-transformed PM₁, β_{ks} ($k=0,1,2,4$, $s=1,2$) are standard regression coefficients changing with the season s and X_{ki} denotes the log-transformed i^{th} value of Soil, TMO, MM and Sulfate. Model's components were evaluated with the usual ANOVA table and the percentage of total variation for each component computed.

This model was used to estimate and assess the role of PM₁ main components and to evaluate the possible differential effect of observation periods on the components contribution [7].

3 Results

Figure 1 shows the measured PM₁ mass fraction versus the fitted PM₁ mass fraction using the parametric linear model (see Equation 5). In this model CM, Sulfate, Soil and TMO explained about 44.32%, 33.56%, 11.4% and 0.2% of the total variance of PM₁, respectively (see Table 1). The contributions of CM, Sulfate and Soil to PM₁ were significant with an error of 5%.

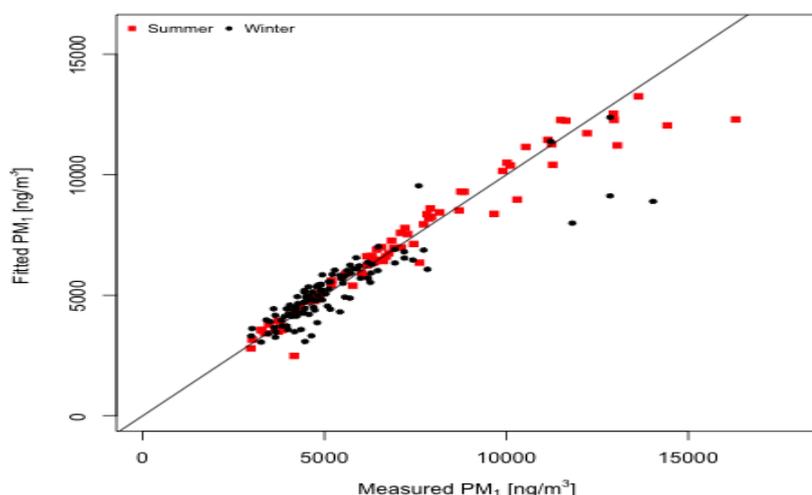


Figure 1: Observed PM₁ vs. fitted PM₁ according to model (5). The correlation between fitted and observed is $r=0.95$, the line is bisector ($y=x$)

The contribution of TMO to PM₁ was significant with an error of 10%. Carbonaceous material, Soil and TMO contributed to PM₁ with a significant difference between the two considered seasons. Sulfate contributed to PM₁ with non significant difference between Summer and Winter.

	Df	Sum Sq	Mean Sq	F value	Pr(>F)	% variance
MM	1	10.2835	10.283	738.228	0.000	40.320
Season	1	0.6292	0.629	45.167	0.000	2.470
Sulfate	1	8.5578	8.558	614.341	0.000	33.560
TMO	1	0.0490	0.049	3.519	0.062	0.200
Soil	1	2.9083	2.908	208.782	0.000	11.400
MM:Season	1	0.4127	0.413	29.623	0.000	1.620
Sulfate:Season	1	0.0003	0.0003	0.019	0.889	0.001
TMO:Season	1	0.1372	0.137	9.847	0.002	0.540
Soil:Season	1	0.1014	0.101	7.279	0.007	0.400
Residuals	174	2.4238	0.0140			
		25.5032				

Table1: ANOVA table from model (5).

The Carbonaceous material component and the Sulfate component which were mainly related to combustion of fossil fuels, industrial activities and inorganic aerosol formation (anthropogenic emission sources) explained about 78% of the PM₁ total variance. The Soil component which was mainly related to possible African dust and to the re-suspension from fields or bare lands of crustal material (natural emission sources) explained about 11.4% of the PM₁ total variance. The TMO which was also related to possible fuels-oils combustion and to traffic related activities explained about 0.2% of the PM₁ total variance. The carbonaceous material component, Soil component and TMO component contributed differently to PM₁ in Summer and Winter (see Table1). In Summer period the processes of resuspension of Soil can be facilitated from dry weather conditions which can involve significant variations of the emissions of crustal material in to the air. Whereas, during Winter the combustion of fossil fuels and firewood due to domestic heating come in to play determining a significant variations of the emissions of carbonaceous material and chemical elements in to the air. As such the observed seasonality for Soil, TMO and CM components. The Sulfate component contributed to PM₁ with non significant difference in the two seasons. This result indicates that the emission sources of Sulfate and the relating anthropogenic activities remain unchanged in the two considered seasons.

Eventually residuals analysis was elaborated showing a heavy tail for larger observations, homoscedastic behavior and negligible autocorrelation

4 Conclusions

The parametric linear model allows for the assessment of the main components of PM₁ and the evaluation of their seasonal variations. In the studied area the anthropogenic emission sources were responsible for about 78% of the PM₁ total variance, while natural emission sources explained about 11.4% of the PM₁ total variance. Significant differential effect of the observation periods on the CM, Soil and TMO components were observed. This suggests that the studied area is characterized from possible anthropogenic as well as natural emission sources with seasonal characteristics.

References

- [1] Pope III, C. A., and Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of the air & waste management association*, 56(6), 709-742.
- [2] Trippetta, S., Sabia, S., Caggiano, R. (2016). Fine aerosol particles (PM 1): natural and anthropogenic contributions and health risk assessment. *Air Quality, Atmosphere & Health*, 9(6), 621-629.
- [3] Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., & Cahill, T. A. (1994). Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research: Atmospheres*, 99(D1), 1347-1370.
- [4] Prakash, J., Lohia, T., Mandariya, A. K., Habib, G., Gupta, T., Gupta, S. K. (2018). Chemical characterization and quantitative assessment of source-specific health risk of trace metals in PM 1.0 at a road site of Delhi, India. *Environmental Science and Pollution Research*, 25(9), 8747-8764.
- [5] Aitchison, J., and Brown, J. (1957). *The lognormal distribution with special reference to its uses in economics*. New York, NY: Cambridge University Press.
- [6] Davies, C. N. (1974). Size distribution of atmospheric particles. *Journal of Aerosol Science*, 5(3), 293-300.
- [7] R Development Core Team (2008). *R: A language and environment for statistical computing*. R Foundation

