FINAL REPORT

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Review on contribution of emission sources

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AIRUSE

Testing and development of air quality mitigation measures in Southern Europe

Contents

1. SUMMARY

Source apportionment of ambient PM has been carried out at many urban areas (Portugal, Spain, Italy and Greece). Different receptor modelling approaches were employed for this purpose, based on the ambient concentration levels of particles and their chemical speciation. The different sources identified and their relative contributions (%) are reported in this review, along with the source apportionment models used and the size fraction studied. The main sources identified include road/soil dust, traffic, fuel oil, biomass burning, marine aerosol, secondary sulphate and industry. In the studies where PMF and ME-2 was employed the generated factors provided information on chemical source profiles and source contribution. For the CMB modelling the chemical source profiles from the receptors were successfully reconstructed by local source profiles. In the cases were simple statistical procedures were used (PCA and MLR), unidentified sources were resolved. The main conclusion of this literature search is that sophisticated factor analysis methods like PMF and hybrid models like ME-2 can provide useful information on the source mass contribution in cases where the local emission profiles are not known.

2. INTRODUCTION

In the field of atmospheric sciences, source apportionment (SA) models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants, e.g., particulate matter (PM), based on ambient data registered at monitoring sites. There are three main groups of SA techniques:

(a) Methods based on the evaluation of monitoring data. Basic numerical data treatment is used to identify sources.

(b) Methods based on emission inventories and/or dispersion models to simulate aerosol emission, formation, transport and deposition. These models require detailed emission inventories that are not always available, and they are limited by the accuracy of emission inventories, especially when natural emissions are important.Asignificant advantage of thesemethods is that they may be used in scenario studies to evaluate the impact of emission abatement strategies on the anthropogenic contribution to ambient PM concentrations.

(c) Methods based on the statistical evaluation of PM chemical data acquired at receptor sites (**receptor models**). The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass.

The two main extremes of receptor models are chemical mass balance (CMB) and multivariate models. The CMB model assumes knowledge of the composition of the emissions for all relevant sources. If changes of the source profiles between the emitter and the receptor may be considered minimal, CMB can be regarded as the ideal receptor model. However, these requirements are almost never completely fulfilled, and thus, pure CMB approaches are often problematic. One important characteristic of CMB is that secondary aerosols must be included not as components of emission source profiles but as specific, single chemical compounds. This absence of mixture with other tracer elements is often regarded as a limitation, and may lead to misinterpretation of results. Principal

component/factor analysis (e.g., principal component analysis or PCA, positive matrix factorisation or PMF, UNMIX) attempts to apportion the sources on the basis of observations (internal correlations) at the receptor site alone. These are commonly used tools, because software to perform this type of analysis is widely available and detailed prior knowledge of the sources and source profiles is not required. The choice of the model dimension and the search for non-negative solutions by axis rotations can be based entirely on mathematical criteria. Nevertheless, it has been suggested that factor analysis attempts to get more information out of atmospheric data than is really there (Henry, 1987). Furthermore, it is a common problem that the resulting components or factors may represent mixtures of emission sources, as opposed to clearly independent source profiles. Source signatures that change with time are a limitation for this and other types of receptor models. To combine the advantages and reduce the disadvantages of CMB and factor analysis hybrid models have been developed. Examples are confirmatory or target transformation factor analysis,which offer some control of the solutions by “fixing” or “freeing” specific parameters, set according to the theoretical expectation of the researcher (Hopke, 1988). The multilinear engine is a hybrid receptor model (ME, Paatero, 1999) that can solve multilinear problems with the possibility of implementing many kinds of constraints using a script language. The program allows choosing hybrid versions in the full range between PMF and CMB type models, with the difference that individual data points can be properly weighed (not possible in any eigenvector analysis).

The main objective of receptor models is, therefore, to identify the possible sources of PM (if not assumed already from the source profiles) and to obtain data on their contributions to the bulk PM mass. Furthermore, policy-makers require sound scientific knowledge of the PMsources and their contributions to atmospheric PM levels and associated health risks for the development and implementation of policies to protect human health and the environment. Thus the information provided by receptor models is key to the design of effective mitigation strategies on the local- and meso-scale.

3. METHODOLOGY

The compilation of meta-data on SA publications was carried out by means of a literature search among existing publications in international scientific journals or public reports concerning urban areas in Southern Europe. Only studies that used receptor models are reported here as in the framework of the AIRUSE project the source apportionment analysis will be conducted my means of receptor models. Tables 1-4 provides the source apportionment studies conducted in South Europe using receptor models.

4. RESULTS

4.1. Size fraction and analytical methodologies

Until 2005, PM10 was on average the preferred target metric followed by PM2.5. After 2007 the new studies found in the literature targeted mostly on PM2.5, thus confirming a change in focus in SA studies in Southern Europe. This focus on the sources of fine aerosols ismost probably related to stronger recent evidence on the adverse effects of fine particulates on health (Pope and Dockery, 2006).

A large variety of sampling methodologies was employed throughout Europe. The choice of method influences the PM and chemical data due to artefacts. High-volume samplers (typical flow >30m^3/h) were used in the majority of the SA studies reported with 24h as the standard sampling period . This duration was the most commonly used as it allows for the comparison with the daily limit value for PM concentrations. The second widespread method of sampling was for 24h with a low-volume sampler (typically 1m3/h) both in terms of number of studies and of groups applying this methodology. The use of new sampling and monitoring methodologies (e.g., streaker sampler) were reported for newer studies.

A broad spectrum of techniques was described. Ion chromatography (IC) was most commonly used for the determination of ionic species, while major and trace elements were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry), ICP-MS

(inductively coupled plasma mass spectrometry), PIXE (Particle induced X-ray emission spectrometry) and XRF (X-ray fluorescence).

Discrimination between organic (OC) and elemental (EC) carbon was carried out in a limited number of the studies. The low percentage of OC/EC analyses, as well as the almost complete absence of data on speciation of organic aerosols (OA) in these studies, implies an evident difficulty to detect and interpret sources of organic PM, such as different vehicular sources (e.g., diesel vs. gasoline vehicles).

4.2. Emission sources and mass contributions

The studies considered in the present review have been carried out with varying objectives and the SAs have been obtained with a range of different techniques, which do not necessarily produce directly comparable results. Often contributions have been estimated from mixed sources (e.g. by composite profiles in CMB and by mixed factors in PMF). In order to be able to compare all the SA results and to attain useful conclusions, sources have been pooled into seven major categories covering those most frequently observed in the individual studies: Road/Soil dust, Traffic, Fuel oil, Biomass Burning, Marine aerosol, Secondary Aerosol, and Industry. Tables 1-4 provide the mass contributions (%) to the ambient PM mass in urban ares in Italy, Greece, Portugal and Spain.

Road and Soil dust is characterized by elements abundant in the earth's crust and soils like: Al, Si, Ca and Fe. This component of the PM is associated with the re-suspension of dust by local winds. Also long-range transport during Saharan dust events is frequently reported in Mediterranean countries. The mean contribution of Road/Soil dust to PM varies from 5 to 54% with the lowest valus reported for the very small size fraction (e.g: PM1, Vecchi et al., 2006) and the highest ones for the coarser fractions (e.g: PM10-2, Karanasiou et al., 2009). It shoulbe be also mentioned that this source revealed high contributions in areas that are frequently affected by Saharan dust intrusions, like Athens and Barcelona.

Traffic is a source category that encompasses different kinds of emission deriving from many different vehicle types and associated processes. In addition to the primary PM emissions from exhaust and the emissions of organic and inorganic gaseous PM precursors from the

combustion of fuel and lubricant, vehicles emit significant amounts of particles through the wear of brake linings, clutch, and tyres. These are deposited onto the road and subsequently resuspended by vehicle traffic together with mineral dust particles and road wear material. Traffic source profiles usually contain elemental carbon, EC, Fe, Ba, Zn, Cu and aswell as organic compounds like hopanes and steranes that can be used to distinguish exhaust emissions from gasoline and diesel powered engines. Cu, Zn, Mn, Sb, Sn, Mo, Ba, and Fe are markers of brake wear and can serve as indicators of traffic re-suspension (Amato et al., 2009). In this review with the term traffic we mainly refer to exhaust emissions as in most studies the Road dust source was seperated by the exhaust emissions. The mean relative contribution from traffic to PM is 7-57%. Traffic along with secondary aerosol is the most important source in Southern Europe. Unsurprisingly, there is no clear geographical pattern in the traffic contributions to PM among southern European countries. In urban sites where the porportion of diesel vehicles is high e.g: like Florence and Barcelona traffic contribution is elevated.

The **Fuel oil** combustion is characterised by the high contribution of V and Ni trace elements. This source might also include emissions from shipping. This source was resolved in Barcelona, Thessaloniki, Florence and Athens, in sites affected by power plants and port emissions.

Biomass burning has recently started to cause concern due to the impact that domestic wood burning and open fires may have on atmospheric PM levels. Potassium, K is the most common species used to trace biomass burning along with organic tracers like levoglucosan. The mean relative contribution of biomass burning to PM is 1-49%. As expected, the relative contribution of biomass burning to PM2.5 or PM1 is higher than to PM10. Considering that biomass burning in urban areas is associated wit domestic heating, the contributions during the cold season are higher than those in the warmer part of the year.

Marine aerosol includes profiles characterized by Na, Cl and Mg. As it was expected this source had higher contribution in coarse fraction and in areas close to the coast.

Secondary aerosol is mainly composed of ammonium- sulphate and nitrate deriving primarily from the gaseous precursors ammonia (NH3), sulphur dioxide (SO2), and nitrogen

oxides (NOx). In factor analysis, the source including these inorganic species and also OC is often referred to as sulphate or secondary aerosol. The mean contribution of this source is relatively high as it contains components that are formed from a big variety of sources like traffic emissions, biomass burning, industrial and port emissions etc. In most studies this sources contributed up to 50% to PM mass concentrations.

Industry is a rather heterogeneous category including mainly emissions from power plants together with emissions from different types of industry emissions (petrochemical, metallurgic, ceramic, pharmaceutical, etc. The sources are sometimes mixed with unidentified combustion sources or traffic. For this reason the mean contribution of this source revealed high variability between the studied areas, from 1-66%.

5. CONCLUSIONS

Source apportionment of PM and has been conducted over the past two decades with a variety of receptor models shifting from principal component analysis techniques, enrichment factors and classical factor analysis towards more sophisticated models able to handle uncertainties on the input and output such as e.g. Positive Matrix Factorization. A wider use of advanced factor analysis techniques able to deal with heterogeneous and complex data and to provide improved uncertainty estimations should be promoted. On the other hand, PCA technique should be preferably used for qualitative or preliminary estimations. The Chemical Mass Balance requires the detailed informatin on the local chemical emission profiles. Nevertheless, the scarcity of measured source profiles for south European countries and the lack of long term, speciated PM series, especially in urban areas, make its use less practical. The definition and documentation of the source categories in South Europe has improved swiftly but there is still a need of harmonization of the different SA approaches in order to facilitate the interpretation and comparability of the results and their application in the design of abatement measures.

Table 1. Mean source contributions (%) to the ambient PM mass in Italy

Site/PM fraction, study	Model	Road/Soil dust	Traffic	Fuel oil	Biomass burning	Marine aerosol	Secondary aerosol	Industry
Florence, Genoa, Milan/PM1, Vecchi et al., 2006	PMF	5-7	7-16	9	12-49 (combustion)		8–48 (sulphate)	16-50 (mixed anthropogenic)
Florence/PM10, Lucarelli et al., 2004	APCA	20-32	26-50				20-37 (sulphate)	
Florence, Tuscany/PM10, Patos 2006	PMF	18	23		24	6	30	
Milan/PM10,Bernardoni et al.,2011	PMF	4-28 (construction)	14-16		14		7-30 (nitrate)	8-11
Milan/PM10, PM2.5, Marcazzan et al. 2003	APCA	14	27				47-54 (sulphate)	8-47 (mixed anthropogenic)
Genoa/PM10, PM2.5, PM1, Mazzei et al.,2008	PMF	17-33	9-34	12-35		0.6-1	11-36	
Milan/PM10, PM2.5, Perrone et al., 2012	CMB	10	23		1		15 (sulphate)	
Venice/ PM10, Masiol et al. 2012	PMF	19	7		10 (combustion)	8-25	10-17 (nitrate)	
Bari-Taranto/ PM2.5, Amodio et al, 2010	APCA	7			15 (combustion)		78	
Montelupo, Florence/PM10, Chiari et al. 2005	APCA	21				2	11	16-41
Cimone/PM10, Marenco et al. 2006	APCA	27				1	60	

Table 2. Mean source contributions (%) to the ambient PM mass in Greece

Site/PM fraction, study	Model	Road/Soil dust	Traffic	Fuel oil	Biomass burning	Marine aerosol	Secondary aerosol/Unidentified
Thessaloniki/ TSP, Samara et al., 1994	PCA	7-11	4-5	25-33			54-66
Thessaloniki /fine, Manoli et al., 2002	PCA	28	38	14			20
Thessaloniki/ coarse, Manoli et al., 2002	PCA	57	9	26			8
Thessaloniki/ PM_{10}, Samara et al., 2003	PCA	18-22	45-65	10-35			
Athens/ fine, Karanasiou et al., 2009	PMF	20	27	12	15	19	7
Athens/ coarse, Karanasiou et al., 2009	PMF	54	8			16	22
Rhodes Island/ PM_{10} Argyropoulos et al., 2012		10-22	32-41		9-12	3-10	17-20

Table 3. Mean source contributions (%) to the ambient PM mass in Spain

Site/PM fraction, study	Model	Road /Soil dust	Traffic	Fuel oil	Biomass burning	Marine aerosol	Secondary aerosol	Industry
Barcelona/PM10, Querol et al., 2001	PCA	26	54 (secondary included)			4		
Barcelona/PM2.5, Querol et al., 2001	PCA	8	73 (secondary included)					
Barcelona/PM10, Querol et al., 2004	PCA, MLRA	31	32			5		30 (secondary included)
Barcelona/PM10, Rodriguez et al., 2004	PCA	25	33			4		10 (secondary included)
Barcelona/PM2.5, Rodriguez et al., 2004	PCA	10	43			1		28 (secondary included)
Barcelona/PM10, Viana et al., 2007	PCA, MLRA	26	19			9	23	8
Barcelona/PM2.5, Viana et al., 2007	PCA, MLRA	15	19			5	36	9
Barcelona/PM10, Amato et al., 2009	ME-2, PMF2	41-42	18-21	5-6		10-11	24	1-2
Barcelona/PM2.5, Amato et al., 2009	ME-2, PMF2	18-21	25-32			3	36-45	2-3
Barcelona/PM10, Reche et al., 2012a,b	ME-2	29-48	14-23		3	6-10	16-24	1-6
Barcelona/PM2.5, Reche et al., 2012a,b	ME-2	11-34	22-33		3	2-3	25-33	1-9
Madrid/PM10,	PMF	19-29	31				21	

Karanasiou et al., 2011								
Madrid/PM10, Rodriguez et al. 2007	PMF	17-31	18			6	19	
Madrid/PM2.5, Rodriguez et al., 2007	PMF	13-26	29				18	

Table 4. Mean source contributions (%) to the ambient PM mass in Portugal

Site/PM fraction, study	Model	Road /Soil dust	Traffic	Fuel oil	Biomass burning	Marine aerosol	Secondary aerosol	Industry
Lisbon/PM10, Almeida et al., 2006	PCA, MLRA	19-20		0.04-5		19-47	10-15	13-16
Lisbon/PM2.5, Almeida et al., 2006	PCA, MLRA	9-16	22-45	0.1-8		6-8	23-25	0.1-14
Areao/PM0.95, Pio et al., 1996	PCA, MLRA		25			14	31	
Areao/PM0.95-10, Pio et al., 1996	PCA, MLRA					88	3	

APCA: Absolute Principal Component Analysis, PCA: Principal Component Analysis, PMF: positive Matrix Factorization, CMB: Chemical Mass Balance, ME-2: Multilinear Engine 2, MRL: Multilinear Regression

6. REFERENCES

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., Hopke, P.K. Quantifying road dust resuspension in urban environment by Multilinear Engine: A comparison with PMF2 (2009) Atmospheric Environment, 43 (17), pp. 2770-2780.

Amodio M., Andriani E., I. Cafagna, et al., A statistical investigation about sources of PM in South Italy, Atmospheric Research 98 (2010) 207–218

Argyropoulos G., Manoli E., Kouras A., Samara C., 2012. Concentrations and source apportionment of PM_{10} and associated major and trace elements in the Rhodes Island, Greece. Science of the Total Environment 432, 12-22.

Bernardoni V., Vecchi R., Valli G., Piazzalunga A., Fermo P., PM10 source apportionment in Milan (Italy) using time-resolved data. The Science of the Total Environment, 409, (2011) 4788-4795

Chiari M., Lucarelli F., Mazzei F., Nava S., Paperetti L.. Prati P., Valli G., Vecchi, R. Characterization of airborne particulate matter in an industrial district near Florence by PIXE and PESA' X-Ray Spectrometry 34, 4 (2005), 323-329.

Karanasiou A., Siskos P.A., Eleftheriadis K., 2009. Assessment of source apportionment by Positive Matrix Factorization analysis on fine and coarse urban aerosol size fractions, Atmospheric Environment, 43, 3385 – 3395.

Lucarelli F., Mandò P.A., Nava S., Prati P., Zucchiatti A., 'One-year Study of the Elemental Composition and Source Apportionment of PM10 Aerosols in Florence, Italy' Journal of the Air & Waste Management Association, 54 (2004) 1372-1382.

Manoli E., Voutsa D. Samara C., 2002. Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece, Atmospheric Environment 36, 949-961.

Marcazzan G.M., Ceriani M., Valli G., Vecchi R., Source apportionment of PM10 and PM2.5 in Milan (Italy) using receptor modelling, Science of The Total Environment, Volume 317, (2003), 137-147

Marenco F., P. Bonasoni, F. Calzolari, M. Ceriani, M. Chiari, P. Cristofanelli, A. D'Alessandro, P. Fermo, F. Lucarelli, F. Mazzei, S. Nava, A. Piazzalunga, P. Prati, G. Valli and R. Vecchi, 'Characterization of atmospheric aerosols at Monte Cimone, Italy, during summer 2004: Source apportionment and transport mechanisms', Journal of Geophysical Research 111 (2006) D24202.

Masiol M., Squizzato S., Ceccato D., Rampazzo G., Pavoni B., Determining the influence of different atmospheric circulation patterns on PM_{10} chemical composition in a source apportionment study, Atmospheric Environment 63 (2012) 117-124

Mazzei F., D'Alessandro A., Lucarelli F., Nava S., Prati P., Valli G., Vecchi R. Characterization of particulate matter sources in an urban environment, Science of the Total Environment 401 (2008) 81-89

Perrone M.G., Larsen B.R., Ferrero L., Sangiorgi G., De Gennaro G., Udisti R., Zangrando R., A. Gambaro, E. Bolzacchini Sources of high PM2.5 concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling, Science of the Total Environment 414 (2012) 343–355

Pio CA, Castro LM, Cerqueira MA, Santos IM, Belchior F, Salgueiro ML (1996). Source assessment of particulate air pollutants measured at the southwest European coast. Atmos Environ, 30(19), 3309 –20.

Progetto regionale PATOS:
http://servizi.regione.toscana.it/aria/img/getfile_img1.php?id=21169 Cuccia E., Piazzalunga A., Bernardoni V., Brambilla L., Fermo P., Massabò D., Molteni U., Prati P., Valli G., Vecchi R. (2011). Carbonate measurements in PM10 near the marble quarries of Carrara (Italy) by infrared spectroscopy (FT-IR) and source apportionment by Positive Matrix Factorization (PMF). Atmospheric Environment, 45, 6481-6487

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O. PM10 and PM2.5 source apportionment in the Barcelona Metropolitan area, Catalonia, Spain (2001) Atmospheric Environment, 35 (36), pp. 6407-6419.

Querol, X., Alastuey, A., Ruiz, C.R., Artiñano, B., Hansson, H.C., Harrison, R.M., Buringh, E., Ten Brink, H.M., Lutz, M., Bruckmann, P., Straehl, P., Schneider, J. Speciation and origin of PM10 and PM2.5 in selected European cities (2004) Atmospheric Environment, 38 (38), pp. 6547-6555

Reche, C., Viana, M., Amato, F., Alastuey, A., Moreno, T., Hillamo, R., Teinilä, K., Saarnio, K., Seco, R., Peñuelas, J., Mohr, C., Prévôt, A.S.H., Querol, X. Biomass burning contributions to urban aerosols in a coastal Mediterranean City (2012a) Science of the Total Environment, 427-428, pp. 175-190.

Reche, C., Moreno, T., Amato, F., Viana, M., van Drooge, B.L., Chuang, H.-C., Bérubé, K., Jones, T., Alastuey, A., Querol, X. A multidisciplinary approach to characterise exposure risk and toxicological effects of PM 10 and PM 2.5 samples in urban environments (2012b) Ecotoxicology and Environmental Safety, 78, pp. 327-335.

Rodríguez, S., Querol, X., Alastuey, A., Viana, M.-M., Alarcón, M., Mantilla, E., Ruiz, C.R. Comparative PM10-PM2.5 source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain (2004) Science of the Total Environment, 328 (1-3), pp. 95-113.

Samara C. et al., (1990), Characterization of airborne particulate matter in Thessaloniki, Greece. 1. Source related heavy-metal concentrations within TSP, Toxicological and Environmental Chemistry, 29, 107-119.

Samara C. et al., (2003), Chemical mass balance source apportionment of PM10 in an industrialized urban area of Northern Greece, Atmospheric Environment, **37**, 41–54.

Samara C., Voutsa D., 2005. Size distribution of airborne particulate matter and associated heavy metals in the roadside environment. Chemosphere 59, 1197-1206.

Samara, C., Kouimtzis, T.H., Katsoulos, G.A., 1994. Characterisation of airborne particulate matter in Thessaloniki, Greece Ð Part III: comparison of two multivariate modelling approaches for the sources of apportionment of heavy metal concentrations within total suspended particles. Toxicology and Environmental Chemistry 44, 147-160.

Vecchi R., Chiari M., D'Alessandro A., Fermo P., Lucarelli F., Mazzei F., Nava S., Piazzalunga A., Prati P., Silvani F., Valli G. (2008) A mass closure and PMF source apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy. Atmospheric Environment, 42, 2240-2253

Viana, M., Maenhaut, W., Chi, X., Querol, X., Alastuey, A. Comparative chemical mass closure of fine and coarse aerosols at two sites in south and west Europe: Implications for EU air pollution policies (2007) Atmospheric Environment, 41 (2), pp. 315-326

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