RELAZIONE FINALE PROGRAMMA DI RICERCA
SHORT TERM MOBILITY (STM) 2014

INTERCOMPARISON OF RECEPTOR MODELS APPLIED TO THE CHARACTERISATION OF AEROSOL SOURCES IN HARBOUR-INDUSTRIAL AREAS OF THE ADRIATIC SEA AND OF THE AEGEAN SEA

Il Fruitore: Daniela Cesari

Istituto di afferenza: Istituto di Scienze dell'Atmosfera e del Clima – CNR UOS di Lecce

con qualifica: ricercatore T.D. **livello:** III

Istituzione ospitante: Aristotle University of Thessaloniki (Department of Chemistry 54124, Thessaloniki)
Supervisore: Prof. C. Samara

Periodo: 30 Aprile 2014 – 20 Maggio 2014

Introduction

Ship emissions of atmospheric pollutants are continuously growing due to the increase of global trade. Harbours are important for economic and social development of coastal areas but they are also an environmental burden often located near urban and industrial areas. In-port ship emissions are nowadays a concern for impact on air quality and climate in several European countries. Receptor models could represent useful tools to quantitatively characterise the main sources that affect air quality of harbour-industrial areas. However, the presence of multiple anthropogenic sources that could be characterised by chemical fingerprints (Kim & Hopke, Atmospheric Environment 42, 6047–6056, 2008) could make difficult to distinguish the contribution of specific sources. This could happen specifically with harbour emissions that have similarities with industrial and diesel emissions. This project is focalised on the source apportionment analysis of two dataset of concentration and chemical composition of $PM_{2.5}$ collected during the CESAPO project in Italy and during the ACEPT-AIR LIFE project in Greece. The Italian dataset was collected in the Brindisi harbour-industrial area while Greek dataset was collected in Thessaloniki harbour and SA will be performed using two different receptor models: the Positive Matrix Factorization (EPA PMF3.0 version) and the Chemical Mass Balance (CMB) approach. The application of CMB is often laborious and time consuming, for this reason it will be applied the Robotic Chemical Mass Balance, developed at the host institution (Argyropoulos & Samara, Environmental Modelling & Software 26, 469-481, 2011) that simplifies the procedure and minimises the personal judgment that could compromise the SA results. This will be applied with both literature source profiles and using the same profiles obtained with PMF for sensitivity tests. The intercomparison of the results of the two models will allow a statistically robust SA of the area and also to investigate the potentiality of the two SA approaches in characterising the contribution of harbour emissions to primary and secondary $PM_{2.5}$.

Description of the studied area

1. First studied area

The province of **Brindisi** is located in the Salentum peninsula (SE of Italy) in the Apulia region. The specific area of Brindisi investigated in this report is included in the list of SIN (National Sites of Interest) for relevant and potentially dangerous pollution, according to Italian Legislation (D.M. 471/99). The urban area of Brindisi is located near an international airport (at 3 km NNE of the urban area) having a typical yearly traffic of more than two millions passengers and about 75 tonns of cargo (ISPRA 2009). In the area of Brindisi there are three thermo-electric power plants. The largest is the coal power plant "Federico II" located at about 10 km SE of the urban area of Brindisi in Cerano (total capacity 2640 MW). The second one is the coal power plant Edipower (1280 MW) located at about 3 km ENE of the urban area of Brindisi (that could also work using oil) and the third one is the gas power plant of Enipower (1170 MW) located inside the industrial area. The aerosol emissions associated to coal power plants are expected to be characterised by sulphate and organic carbon (Kang et al., 2010) and trace metals like Al, Mn, V, Cr, As (Zhang et al., 2005). The aerosol emissions associated to gas combustion typically contain trace metals like Zn, V, Ni, Cr, Cd, Pb and Hg (Amaroli and PO, 2003). Near Brindisi it is located a large industrial area characterised by the presence of an important petrochemical plant (production of polyethylene, PVC and other polymers), a pharmaceutical industry, an industrial waste incinerator, an industry for construction of airplanes components and several artisan activities. The aerosol emissions of these mentioned sources are likely to have significant content of organic components (organic carbon in general and PAH) as well as trace metals. Brindisi includes a harbour area, characterised by both commercial and tourist ship traffic. Particularly, the internal harbour area is mainly dedicated to tourist activities and it includes the passenger terminal; while the intermediate part of the harbour is dedicated to commercial ships.

The dataset collected in the Brindisi harbour is composed of 100 daily samples of $PM_{2.5}$. Each sample has been analysed for 22 major and trace elements and ions (Al, Si, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, Sr, Pb, OC, EC, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}).

2. Second studied area

Thessaloniki (40° 62' E, 22° 95' N) is the second largest city in Greece hosting more than a million inhabitants in an area of about 200 km^2. The city is located at the mouth of the Thermaikos Gulf and is surrounded by low hills to the north and the mountain of Hortiatis (1,200 m) to the east. In the west, the area is flat, allowing connection of the city with the rest of the Macedonian mainland. Several industrial islands are located to the north (cement and lime production and marble quarry facilities), northwest (oil refining, polypropylene production, metal scrap incineration, non-ferrous metal smelting, iron and steel manufacturing, and electrolytic MnO_2 production), and west (oil hydro skimming, truck and auto painting, metal recovery facilities, and lubricating oil recovery facilities). Thessaloniki experiences a rather Mediterranean climate with mean temperatures during winter and summer at 7 °C and 25.3 °C, respectively, and mean annual rainfall at 445 mm.

The main air pollution sources are vehicular traffic (more than 500,000 automobiles are registered in the greater Thessaloniki area) and industrial activities (Kassomenos et al. 2011). The vehicle fleet profile during the study included around 90% gasoline-fueled private cars, 7 % diesel-powered vehicles (private cars, buses, trucks, and taxies), and 1 % two stroke engines. Diesel private cars were banned until November 2011. Residential heating also plays a significant role during the cold period of the year (October–April). Diesel oil and natural gas have been regularly used as fuel for residential heating in most of the city, while wood burning is also used as a supplementary heating source, mainly in the suburbs of

the city. After 2010, a great move of households towards wood and pellet burning was evidenced all over the city and the surrounding residential communities as a result of the economic crisis.
PM_{10} and $PM_{2.5}$ particle fractions were concurrently collected at two urban sites that, despite the short distance between them (around 2.5 km), usually exhibit the maximum and minimum levels of primary air pollution measured in Thessaloniki (Petrakakis et al. 2011). The urban-traffic site (UT) was located in the commercial center (22° 56′ 30″/40°38′ 15″, 11.6 m asl), next to a 6-lane asphalted busy road (about 58,000 vehicles/day) and to a metro station construction site. The urban-background site (UB) was located in a residential area in the upper part of the city (22° 57′ 38″/40° 38′34″, 174.0 m asl), next to a less busy road (<4,000 vehicles/day) covered with granite setts and approximately 800 m from the ring road that runs around the city carrying transit traffic. At both sites, the sampling devices were positioned on the roof of the air quality monitoring stations of the Municipality of Thessaloniki (about 3.0 m above ground level) in a short distance from the kerbside (about 2.5 m). Meteorological data (air temperature, relative humidity, wind speed, and wind direction) were also measured in situ.
The dataset collected in Thessaloniki is composed of PM_{10} and $PM_{2.5}$ samples, in total 219 samples, and each one was analyzed for 29 major and trace elements and ions (Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Pb, OC, EC, Cl^-, NO_3^-, SO_4^{2-} , Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}).

Receptor models used

1. The Robotic Chemical Mass Balance (RCMB)

Receptor modelling is founded upon the hypothesis of mass and chemical species conservation, assumed for the airborne PM collected at the receptor site, which allows for a mass balance analysis to be used, in order to identify and apportion sources of PM in the atmosphere. There is a wide range of receptor models whose main difference is the degree of knowledge required about the pollution sources prior to their application. The two main extremes of receptor modelling are multivariate models, which require little knowledge about pollution sources, and chemical mass balance (CMB) models, which require an almost complete knowledge, respectively.
The main assumptions on which CMB models rely are:

a. all the sources, contributing significantly to a receptor site, have been identified and have had their emissions chemically characterized
b. chemical species do not react with each other
c. compositions of source emissions are constant over the period of ambient and source sampling (d) the number of sources is less than the number of chemical species
d. the source compositions are linearly independent of each other
e. measurement uncertainties are random, uncorrelated and normally distributed (Henry et al., 1984; Thurston and Lioy, 1987).

If all the contributing sources are known, their chemical compositions remain constant during the sampling, and there is no interaction between their chemical species that would cause mass removal or formation, then the total airborne particulate mass concentration C_{mass} measured at the receptor site will be a linear sum of the contributions of the individual sources S_j (Henry et al., 1984):

$$(1) \quad C_{mass} = \sum_{j=1}^{n} S_j$$

Similarly, the mass concentration of an aerosol property i, C_i, will be (Henry et al., 1984):

$$(2)\quad C_i = \sum_{j=1}^{n} a_{ij} S_j$$

where a_{ij} is the mass fraction of source contribution j possessing property i.
Writing equation (2) for every measured chemical species defines the CMB problem, provided that the source contributions S_j will be considered as the dependent variables. The application of CMB is often laborious and time consuming, for this reason, in this case study, it will be applied the Robotic Chemical Mass Balance, developed at the host institution (Argyropoulos & Samara, Environmental Modelling & Software 26, 469-481, 2011) that simplifies the procedure and minimises the personal judgment that could compromise the SA results.

2. The Positive Matrix Factorization (PMF)

The receptor model PMF assumes that concentrations at receptor sites are impacted by linear combinations of source emissions, which are derived as factors in the model. In this cases study, PMF was applied to PM mass concentration that were collected at sampling sites to identify emission sources and quantify the contributions of these sources. We used the EPA PMF 3.0 version for the analysis, as shown in Eq. (3):

$$(3)\quad X_{ij} = \sum_{k=1}^{p} g_{ik} * f_{kj} + e_{ij}$$

The data set can be expressed as a matrix X of i by j dimensions, where i is the number of samples and j is the species measured. Additionally, g_{ik} is the concentration of chemical species, f_{kj} is the mass fraction, e_{ij} is the residual of the j_{th} species concentration measured in the i_{th} sample, and p is the total number of the independent factors. The objective of a PMF analysis is to determine the number of factors p, the chemical composition profile f_k, the factor contributions g_k, and residuals e. The PMF 3.0 determines signal-to-noise ratio (S/N) statistics for each input species and allows the user to downgrade the importance or remove species with small S/N values (Liu et al., 2014). Then, according with the S/N it is possible to categorize each variable in Strong (variables are treated by the model as they are), Weak (variables' uncertainties are tripled by the model) and Bad (variables are excluded by the model during the run).

1. First case study: the Brindisi dataset

To characterise the potential sources of $PM_{2.5}$, the Positive Matrix Factorization (PMF) method was applied using the EPA PMF3.0 software. Particularly, the elements Zn, Ti, Cl^-, Cr and Cd were considered ''weak'', meaning that PMF triple their uncertainties.
The best solution was obtained with eight factors. The average absolute and relative contributions of these factors to the $PM_{2.5}$ concentrations are reported in Table 1. The first factor, characterised by V, Ni and $C_2O_4^{2-}$, is commonly associated to oil combustions or its refining (Rodriguez et al., 2004; Querol et al., 2007). In the site analysed in this work, it likely represents a mixed industrial-oil combustion source, given the presence of petrochemical industry, including also ship emissions that are typical sources of V and Ni (Pandolfi et al., 2011). The second factor, characterised by Al, Fe, and Mn, represents a crustal contribution. The third factor, characterised by K^+ indicates a possible contribution from biomass

combustions or fires (not domestic heating given the high temperature in the measurement period) to $PM_{2.5}$ concentration. This factor is in agreement whit other source apportionment works which report K^+ as tracer of biomass burning (Belis et al., 2011; Samara, 2005). The PMF model reconstructs an important contribution for this factor especially in the first three weeks of July 2012. The average contribution during this period is 25.7% ± 1.5%, significantly larger than the average contribution of 7.9% ± 0.5% associated to the other measurement days. During the first three weeks of July 2012 several cases of fires, some of them likely associated to agricultural practice, have been recorded, active in the area studied, that explain the increase of this contribution in that period. The fourth factor, characterised by Cu, Pb and WSOC, represents the contribution of vehicular traffic emissions. The fifth factor, characterised by Sb and Cr, indicates an industrial contribution to $PM_{2.5}$. The average contribution of this factor is relatively low (0.4%± 0.3%), however, there are two events in which this contribution is relevant: the former is during the days 7-8/06/2013 in which a contribution of 6% is observed and the latter is during 03/08/2013 in which a contribution of 3% is observed. In both cases the prevalent wind directions were associated to the industrial area (ENE-SSE).

The sixth factor is characterized by Cl^-, NO_3^-, Na^+ and Mg^{2+}. This factor represents the sea spray and the presence of NO_3^- in the profile confirms that the sea spray was subjected to chlorine depletion with formation of sodium nitrate. The contribution of sea-spray to $PM_{2.5}$ concentration obtained by the PMF (2.6% ± 0.5%) is in very good agreement with the contribution (2.7% ± 0.3%) estimated from Cl^- and Na^+ concentrations.

The seventh factor, characterised by SO_4^{2-} and NH_4^+, is associated to ammonium sulphate of secondary origin. The ratio SO_4^{2-}/NH_4^+ in the profile of this factor is 2.7 in good agreement with the theoretical ratio of 2.66 expected in $(NH_4)_2SO_4$. The average relative contribution to $PM_{2.5}$ of this factor is 27.3% ± 0.8%. This is comparable, within the uncertainty, with the direct calculation of the average abundance of ammonium sulphate in $PM_{2.5}$ of 29% ± 0.9% (interval on daily samples between 7% and 52%).

The eighth factor is characterised by the species WSIC and Ca^{2+} and, to a lower extent, by Mg^{2+}. It could indicate a possible contribution of calcium and magnesium carbonates from upper crust or from resuspended dust and construction work, Ca being an element present in asphalt with elevated concentrations in dust from urban and paved roads (Chow et al., 2004). Magnesium is an element abundant in cement and also abundant in asphalt (Galindo et al., 2011). A contribution of carbonates to atmospheric particles in the Salentum peninsula was already observed in sites located at 35 km SSE of the measurement site (Perrone et al., 2011; Contini et al., 2014) and it is compatible with the limestone geological system of the Salentum peninsula (Cesari et al., 2012, 2014).

	Source contribution ($\mu g/m^3$)	**Source contribution (%)**
Industrial - oil combustion	2.30 (± 0.19)	15.3 (± 1.3)
Crustal	2.48 (± 0.13)	16.4 (± 0.9)
Biomass combustion - fires	1.77 (± 0.10)	11.7 (± 0.7)
Traffic	2.47 (± 0.26)	16.4 (± 1.7)
Industrial 2	0.06 (± 0.05)	0.4 (± 0.3)
Sea spray	0.39 (± 0.08)	2.6 (± 0.5)
Secondary Ammonium Sulphate	4.12 (± 0.12)	27.3 (± 0.8)
Crustal carbonates	1.17 (± 0.04)	7.7 (± 0.3)

Table 1) Absolute and relative contributions to $PM_{2.5}$ of the different sources obtained with PMF.

The comparison between daily $PM_{2.5}$ measured concentrations and those reconstructed by PMF indicates that PMF was able to give a good reconstruction having a determination coefficient R^2= 0.87. It is worth to mention that both the marine contribution and the ammonium sulphate contribution obtained by the PMF are in good agreement with the direct calculations (respectively 2.7% and 29% of $PM_{2.5}$).

The Brindisi dataset has been analysed also using the RCMB model. Particularly, it will be reported a preliminary analysis for 46 days. As input, the model needs the $PM_{2.5}$ composition dataset (the same used for PMF) and also the chemical source profiles relevant for the area studied. The profiles included are:

- Catalyst Equipped Passenger Cars;
- Non-catalytic Passenger Cars;
- EURO1 Compliant Diesel Vehicles;
- EURO3 Compliant Diesel Vehicles;
- EURO4 Compliant Diesel Vehicles;
- Taxi;
- 2-stroke Engine Motorcycles;
- Oil Combustion;
- Municipal waste Burns;
- Tire Burns;
- Agricultural Burns;
- Olive Wood Burning;
- Road Dust-Urban Background;
- Road Dust-Urban & Industrial Background;
- Zinc electroplating Industry;
- Steel Industry;
- Cement Industry;
- Sea Spray;
- Ammonium Sulphate;
- Ammonium Nitrate;
- Calcium Nitrate;
- Calcium Sulphate;
- Sodium Nitrate;
- Ammonium Chloride;
- Potassium Sulphate.

In table 2 a preliminary comparison between RCMB factor contributions and those determined with EPA PMF 3.0 is reported.

	PMF Source contribution (%)	R-CMB Source contribution (%)
Industrial + oil combustion	15.3 (± 1.3)	10.9 (± 2.6)
Crustal + Crustal Carbonates	**24.1 (± 0.9)**	**23.1 (± 2.4)**
Biomass combustion - fires	11.7 (± 0.7)	5.1 (± 0.2)
Traffic	16.4 (± 1.7)	25.1 (± 0.3)
Sea spray	**2.6 (± 0.5)**	**1.8 (± 0.3)**
Secondary Ammonium Sulphate	**27.3 (± 0.8)**	**29.3 (± 0.3)**

Table 2) Comparison between relative contributions to $PM_{2.5}$ of the different sources obtained with PMF and RCMB receptor models.

The comparison between daily $PM_{2.5}$ measured concentrations and those reconstructed by RCMB indicates that the model was able to give a good reconstruction having a determination coefficient R^2= 0.87 (similarly to PMF's result). Also the RCMB gave an ammonium sulphate contribution in good agreement with the direct calculation. However, this result is quite preliminary because related to only 46 days.

In this case study, it is possible to observe that both models gave similar contributions for the following sources: marine aerosol/sea spray, secondary sulphates and crustal matter. The differences related to the other factor contributions coming from PMF and RCMB could be related to the different source chemical profiles used in the CMB model. However, as already mentioned, this kind of intercomparison is only qualitative, because RCMB has been done for half of the dataset and further analysis are needed in order to definitively compare PMF and RCMB results. Further analysis will be done in order to improve this intercomparison study: particularly, an improvement of the solution could be to use different kind of chemical source profiles, more adequate to Brindisi sampling site: in this way, the RCMB could give factor contributions more similar to PMF's those.

2. Second case study: the Thessaloniki dataset

To characterise the potential sources of $PM_{2.5}$ and PM_{10} fractions collected in Thessaloniki, in both UT and UB sites, RCMB has been used with the follow chemical source profiles:

- CAT. CARS: Gasoline fuelled, catalyst equipped vehicles
- NON CAT.CARS: Gasoline fuelled, non-catalyst equipped vehicles
- DIESEL VEHICLES: Diesel fuelled vehicles
- 2 STROKE ENG.: 2 stroke engine motorcycles
- OIL COMB.: Oil combustion
- WASTE BURNS: Uncontrolled open burns of municipal solid waste
- TIRE BURNS: Uncontrolled open burns of used vehicle tires
- BIOMASS BURNS: Uncontrolled open burns of biomass
- ROAD DUST: Paved road dust
- MAVISO: Zinc electroplating industry
- SIDENOR: Steel Industry
- TITAN: Cement Industry
- SEA SPRAY: Marine aerosol
- SULFATES: Secondary Ammonium Sulphate
- NH_4NO_3: Secondary Ammonium Nitrate
- $Ca(NO_3)_2$: Secondary Calcium Nitrate
- $CaSO_4$: Secondary Calcium Sulphate
- $NaNO_3$: Secondary Sodium Nitrate
- NH_4Cl: Secondary Ammonium Chloride
- K_2SO_4: Secondary Potassium Sulphate

The Thessaloniki dataset was also analysed via PMF (EPA PMF 3.0). Different solutions were explored, considering different datasets separated for PM fractions and for sampling sites. At the end it was decides to work with the whole dataset (the two PM fractions together with the two sites) in order to obtain a more stable and strong solution. Different runs have been performed between 5 and 10 factors. In Table 3 e 4 results coming from RCMB are reported; while in Figure 1 the best solution for PMF has been reported for 7 factors: Secondary Nitrate, Marine Contribution, Road Dust, Biomass Burning - Combustions, Crustal Matter, Traffic Contribution, Ammonium Sulphate.

	ID $PM_{2.5}$		ID PM_{10}	
	$\mu g/m^3$	%	$\mu g/m^3$	%
NISSAN1	0.42 ± 0.02	1.29 ± .06	0.96 ± 0.06	1.77 ± 0.11
NONCAT	0.025 ± 0.003	0.08 ± .01	0.12 ± 0.01	0.21 ± 0.03
OASTH1	0.26 ± 0.05	0.81 ± 0.14	-	-
OASTH3	1.02 ± 0.05	3.14 ± 0.17	0.17 ± 0.06	0.32 ± 0.10
OASTH4	0.62 ± 0.03	1.90 ± 0.09	0.32 ± 0.06	0.59 ± 0.11
TAXI	1.65 ± 0.06	5.05 ± 0.18	1.36 ± 0.08	2.50 ± 0.14
2STROKE	0.34 ± 0.05	1.05 ± 0.15	0.88 ± 0.09	1.62 ± 0.17
KAYSTHRAS	0.08 ± 0.03	0.24 ± 0.08	0.31 ± 0.06	0.57 ± 0.10
WASTEBURN	0.68 ± 0.06	2.09 ± 0.2	1.42 ± 0.10	2.61 ± 0.18
TIREBURN	-	-	-	-
BIOMASS	4.44 ± 0.20	13.67 ± 0.5	1.95 ± 0.21	3.60 ± 0.39
OLIVE	2.11 ± 0.09	6.48 ± 0.3	0.38 ± 0.06	0.71 ± 0.11
XYLOSOMPA	3.56 ± 0.20	10.93 ± 0.5	3.66 ± 0.35	6.74 ± 0.64
CORWOOD	0.26 ± 0.03	0.79 ± 0.09	0.98 ± 0.08	1.81 ± 0.15
ASSKON	7.02 ± 0.20	21.56 ± 0.6	35.89 ± 0.64	66.10 ± 1.17
KORSKON	3.89 ± 0.20	11.94 ± 0.5	2.83 ± 0.17	5.22 ± 0.31
MAVISO	0.012 ± 0.001	0.04 ± 0.003	0.030 ± 0.003	0.050 ± 0.005
SIDENOR	0.067 ± 0.003	0.21 ± 0.01	0.08 ± 0.01	0.15 ± 0.01
TITAN	-	-	-	-
MARINE2	0.012 ± 0.001	0.04 ± 0.004	0.050 ± 0.004	0.09 ± 0.01
SULFATES	4.94 ± 0.06	15.17 ± 0.2	2.74 ± 0.06	5.05 ± 0.10
NH_4NO_3	2.69 ± 0.06	8.26 ± 0.2	2.78 ± 0.08	5.11 ± 0.15
$Ca(NO_3)_2$	0.084 ± 0.009	0.26 ± 0.03	1.30 ± 0.06	2.39 ± 0.12
$CaSO_4$	0.066 ± 0.009	0.20 ± 0.03	2.23 ± 0.06	4.11 ± 0.11
$NaNO_3$	0.089 ± 0.005	0.27 ± 0.01	0.19 ± 0.01	0.35 ± 0.03
NH_4Cl	0.008 ± 0.001	0.03 ± 0.003	0.060 ± 0.004	0.12 ± 0.01
K_2SO_4	0.017 + 0.002	0.05 ± 0.01	0.020 ± 0.003	0.05 ± 0.01

Table 3. RCMB results for $PM_{2.5}$ and PM_{10} aerosol fractions collected in ID site.

The comparison between daily $PM_{2.5}$ measured concentrations for the ID site and those reconstructed by RCMB indicates that the model was able to give a good reconstruction having a determination coefficient R^2= 0.96. However, by comparison between marine and secondary sulphates contributions obtained by direct calculations (respectively 1.5% and 13% of $PM_{2.5}$) with those estimated by the model, it is possible to note that the RCMB is not able to give a good reconstruction. Further elaborations, in this sense, are needed in order to improve the solution.

The same trend is observed for PM_{10} fraction results: despite the good reconstruction, having an R^2=0.92, the model is not able to reconstruct correctly the marine and the sulphate contributions (respectively 1.2% and 8.4% of PM10). Also in this case further elaborations are needed in order to improve the solution.

	EP $PM_{2.5}$		EP PM_{10}	
	$\mu g/m^3$	%	$\mu g/m^3$	%
NISSAN1	0.72 ± 0.03	2.55 ± 0.09	1.71 ± 0.05	4.58 ± 0.14
NONCAT	0.06 ± 0.01	0.20 ± 0.02	0.11 ± 0.01	0.30 ± 0.03
OASTH1	0.23 ± 0.04	0.81 ± 0.14	0.67 ± 0.09	1.80 ± 0.23
OASTH3	-	-	-	-
OASTH4	0.08 ± 0.01	0.27 ± 0.03	-	-
TAXI	-	-	0.02 ± 0.01	0.05 ± 0.02
2STROKE	0.25 ± 0.02	0.89 ± 0.08	0.08 ± 0.02	0.20 ± 0.06
KAYSTHRAS	0.06 ± 0.02	0.21 ± 0.07	0.99 ± 0.07	2.64 ± 0.19
WASTEBURN	0.27 ± 0.03	0.96 ± 0.10	-	-
TIREBURN	-	-	-	-
BIOMASS	9.82 ± 0.26	34.82 ± 0.93	-	-
OLIVE	1.58 ± 0.11	5.60 ± 0.38	2.04 ± 0.10	5.45 ± 0.26
XYLOSOMPA	1.77 ± 0.12	6.26 ± 0.43	9.02 ± 0.40	24.09 ± 1.06
CORWOOD	0.27 ± 0.04	0.97 ± 0.14	0.36 ± 0.04	0.95 ± 0.10
ASSKON	2.43 ± 0.09	8.60 ± 0.33	11.67 ± 0.26	31.20 ± 0.69
KORSKON	3.46 ± 0.10	12.27 ± 0.37	4.97 ± 0.15	13.27 ± 0.41
MAVISO	0.024 ± 0.001	0.084 ± 0.004	0.013 ± 0.001	0.036 ± 0.003
SIDENOR	0.025 ± 0.002	0.09 ± 0.01	0.079 ± 0.004	0.21 ± 0.01
TITAN	0.0005 ± 0.0003	0.002 ± 0.001	-	-
MARINE2	-	-	0.070 ± 0.004	0.19 ± 0.01
SULFATES	5.53 ± 0.08	19.60 ± 0.30	3.49 ± 0.07	9.33 ± 0.18
NH_4NO_3	3.17 ± 0.09	11.25 ± 0.31	3.01 ± 0.10	8.05 ± 0.28
$Ca(NO_3)_2$	0.07 ± 0.01	0.25 ± 0.02	1.05 ± 0.05	2.82 ± 0.13
$CaSO_4$	-	-	0.84 ± 0.03	2.25 ± 0.09
$NaNO_3$	0.067 ± 0.004	0.24 ± 0.01	0.50 ± 0.02	1.34 ± 0.06
NH_4Cl	0.005 ± 0.001	0.018 ± 0.004	0.046 ± 0.003	0.12 ± 0.01
K_2SO_4	0.22 ± 0.01	0.77 ± 0.04	0.009 ± 0.002	0.024 ± 0.005

Table 4. RCMB results for $PM_{2.5}$ and PM_{10} aerosol fractions collected in EP site.

The comparison between daily $PM_{2.5}$ measured concentrations for the EP site and those reconstructed by RCMB indicates that the model was able to give a good reconstruction having a determination coefficient R^2= 0.96. However, by comparison between marine and secondary sulphates contributions obtained by direct calculations (respectively 1% and 18% of $PM_{2.5}$) with those estimated by the model, it is possible to note that the RCMB is not able to give a good reconstruction. Probably, further elaborations are needed in order to improve the solution.

The same trend is observed for PM_{10} fraction results: despite the good reconstruction, having an R^2=0.93, the model is not able to reconstruct correctly the marine and the sulphate contributions (respectively 2% and 12% of PM10). Also in this case further elaborations are needed in order to improve the solution.

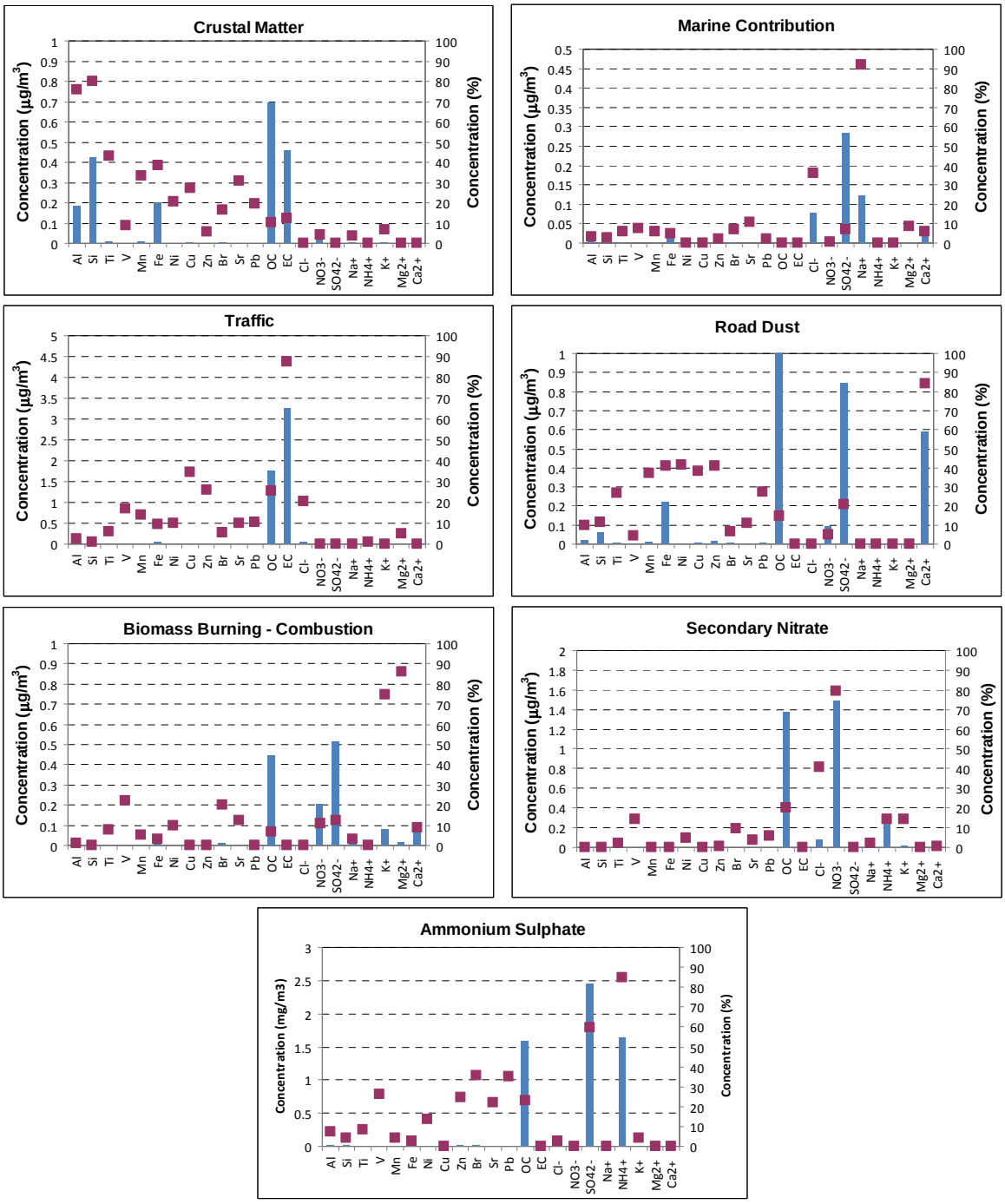

Figure 1. Source profiles obtained with the PMF for the whole Thessaloniki dataset.

Conclusions

The aim of this work was to perform a Source Apportionment study based on two complementary receptor models: the Positive Matrix Factorization (EPA 3.0 version) and the Robotic Chemical Mass Balance. The study has been done on two PM dataset collected in two harbour cities: Brindisi and Thessaloniki. Then, an intercomparison study on receptor models' results has been performed.
The $PM_{2.5}$ Brindisi dataset has been analyzed firstly via PMF. The model gave an 8-factor solution: crustal (16.4% ± 0.9% of $PM_{2.5}$); marine (2.6% ± 0.5%); carbonates (7.7% ± 0.3%); ammonium sulphate (27.3% ± 0.8%); biomass burning/fires (11.7% ± 0.7%); traffic (16.4% ± 1.7%); industrial (0.4% ± 0.3%) and, finally, a mixed source industrial/oil combustion (15.3% ± 1.3%). The comparison between daily $PM_{2.5}$ measured concentrations and those reconstructed by PMF indicates that PMF was able to give a good reconstruction having a determination coefficient R^2= 0.87. Moreover, the marine contribution and the ammonium sulphate contribution obtained by the PMF are in good agreement with the direct calculations (respectively 2.7% and 29% of $PM_{2.5}$). Also the preliminary analysis, performed with the RCMB on 46 daily samples of the Brindisi dataset, shown that the model was able to give a good reconstruction, similarly to PMF's result, giving a good reconstruction of the sulphates contribution in good agreement with the direct calculations.
By the comparison between PMF and RCMB results, it is possible note that both the models gave similar contributions for the sources: marine aerosol/sea spray, secondary sulphates and crustal matter. Instead, some differences related to the other factor contributions (Industrial – oil combustion, Biomass Burning – fires and Traffic) are observed. These differences could be related to the different source chemical profiles used in the RCMB: a chemical profile not adequate to the sampling site analysed could pull the RCMB model giving a different solution, if compared with another model that works in a different way (such as PMF). However, this kind of intercomparison is only qualitative, because RCMB has been done (up to now) for half of the dataset and further analysis are needed in order to definitively compare PMF and RCMB results.

The $PM_{2.5}$ and PM_{10} dataset of Thessaloniki has been analysed via PMF and RCMB. In this case study, even if both models seem to be able to give a good reconstruction of the aerosol mass concentration, they are not able to give a good reconstruction of the marine and of the secondary sulphate, as it appears by comparing the relative factor contributions with the direct calculations. However, by comparing the PMFs' and the RCMBs' solution, it is possible to note that both models found a similar solution in terms of sources affecting the sampling sites: a crustal contribution, a marine contribution, a road dust contribution, a biomass burning contribution and finally, the presence of secondary aerosol in terms of secondary nitrate and ammonium sulphate.

This work will be continued optimizing the intercomparison in collaboration with the Aristotle University of Thessaloniki (Department of Chemistry) with the aim to produce a paper for a scientific International journal, with the citation of the STM 2014 CNR Program.

Acknowledgments

This work was done under the program of Short Term Mobility 2014. I wish to thank the CESAPO project (Interreg Greece-Italy, www.cesapo.upatras.gr) and the ACEPT-AIR LIFE project (www.aceptair.prd.uth.gr) for providing data for Brindisi and Thessaloniki. Finally I wish to thank Prof. Costantini Samara, George Argyropoulos and Aristotle University of Thessaloniki for the hospitality, for running the RCMB and for helping me in the data elaboration.

Bibliography

Armaroli N., Po C., 2003. Emissioni da centrali termoelettriche a gas naturale. La letteratura corrente e l'esperienza statunitense. La Chimica e l'Industria, RICHMAC Magazine - Maggio 2003.

Argyropoulos, G., Samara, C. 2011. Development and application of a robotic chemical mass balance model for source apportionment of atmospheric particulate matter. Environmental Modelling & Software 26, 469-481.

Belis C.A., Cancelinha J., Duane M., Forcina V., Pedroni V., Passarella R., Tanet G., Douglas K., Piazzalunga A., Bolzacchini E., Sangiorgi G., Perrone M.G., Ferrero L., Fermo P., Larsen B.R., 2011. Sources for PM air pollution in the Po Plain, Italy: I. Critical comparison of methods for estimating biomass burning contributions to benzo(a)pyrene. Atmospheric Environment 45, 7266-7275

Cesari, D., Contini, D., Genga, A., Siciliano, M., Elefante, C., Baglivi, F., Laura, D., 2012. Analysis of raw soils and their re-suspended PM10 fractions: Characterisation of source profiles and enrichment factors. Applied Geochemistry 27, 1238-1246.

Cesari, D., Genga, A., Ielpo, P., Siciliano, M., Mascolo, G., Grasso, F.M., Contini, D. 2014, Source apportionment of PM2.5 in the harbour-industrial area of Brindisi (Italy): identification and estimation of the contribution of in-port ship emissions. Under review in Science of the Total Environment.

Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.G., Crow, D., Kohl, S.D., Engelbrecht, J.P., Green, M.C., 2004. Source profiles for industrial, mobile, and area sources in the big bend regional aerosol visibility and observational study. Chemosphere 54, 185–208.

Contini, D., Cesari, D., Genga, A., Siciliano, M., Ielpo, P., Guascito, M.R., Conte, M., 2014. Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy). Science of the Total Environment 472, 248–261

Galindo, N., Yubero, E., Nicolas, J.F., Crespo, J., Pastor, C., Carratala, A., Santacatalina, M., 2011. Water-soluble ions measured in fine particulate matter next to cement works. Atmospheric Environment 45, 2043–2049.

Henry, R.C., Lewis, C.W., Hopke, P.K., Williamson, H.J., 1984. Review of receptor model fundamentals. Atmospheric Environment 18 (8), 1507e1515.

ISPRA 2009 (in Italian) – Rapporto 95/2009. Traffico marittimo e gestione ambientale nelle principali aree portuali nazionali. 2009. ISBN: 978-88-448-0396-4.

Kang, C.M., Koutrakis, P., Suh, H.H., 2010. Hourly Measurements of Fine Particulate Sulfate and Carbon Aerosols at the Harvard–U.S. Environmental Protection Agency Supersite in Boston. Journal of the Air & Waste Management Association 60, 1327-1334.

Kassomenos, P.A., Kelessis, A., Paschalidou, A.K., Petrakakis, M. 2011. Identification of sources and processes affecting particulate pollution in Thessaloniki, Greece. Atmospheric Environment 45, 7293–7300.

Kim, E., Hopke, P.K., 2008. Source characterization of ambient fine particles at multiple sites in the Seattle area. Atmospheric Environment 42, 6047–6056.

Liu, Q.Y., Liu, Y.J., Zhang, M.G., 2014. Source apportionment of personal exposure to carbonyl compounds and BTEX at homes in Beijing, China. Aerosol and Air Quality Research 14, 330-337.

Pandolfi, M., Gonzalez-Castanedo, Y., Alastuey, A., de la Rosa, J., Mantilla, E., Sanchez de la Campa, A., Querol, X., Pey, J., Amato, F., Moreno, T., 2011. Source apportionment of PM10 and PM2.5 at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions. Environmental Science and Pollution Research 28, 260-269.

Perrone, M.R., Piazzalunga, A., Prato, M., Carofalo, I., 2011. Composition of fine and coarse particles in a costal site of the central Mediterranean: carbonaceous species contributions. Atmospheric Environment 45, 7470-7477.

Petrakakis, M.I., Kelessis, A.G., Tzoumaka, P.N., Zoumakis, N., Kassomenos, P., Kenellopoulou, Z., Tsaknia, A., Koutsari, E. 2011. Benzene and PM2.5 in the urban area of Thessaloniki. 4th Environmental Conference of Macedonia, Greece, Thessaloniki 18–20 March 2011 (in Greek)

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E.; Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmospheric Environment 41, 7219-7231.

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

Samara,C.,2005. Chemical mass balance source apportionment of TSP in a lignite burning area Of Western Macedonia, Greece. Atmospheric Environment 39, 6430-6443.

Thurston and Lioy, 1987 Thurston,G.D., Lioy , P.J., 1987. Receptor modelling and aerosol transport. Atmospheric Environment 21(3),687-698.

Zhang, C. F., Qiang Y., and Sun, J. M.: Characteristics of particulate matter from emissions of four typical coal-fired power plants in China. Fuel Processing Technol., 86(7), 757– 768, 2005.