JRC

EUROPEAN COMMISSION

9th intermediate technical / scientific report
Collaborative Research Project for Air Pollution Reduction in Lombardy Region
(2006- 2010)

Edited by
Alois Krasenbrink

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RegioneLombardia

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Collaborative Research Project for Air Pollution Reduction in Lombardy Region
(2006- 2010)

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(WP1 Leader: Bo Larsen)

WP1

Identification of air pollution origin
Source apportionment
Report IX: Final Report

Completion of deliverable VII.1.1. 2nd report on source apportionment based on the collected source profiles and the regional, long-term ambient air $PM_{2.5}$ / PM_{10} sampling campaign of winter (2008-2009).

General conclusions on WP1 activities under the “Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)”.

A devoted effort from the JRC source apportionment team during all phases of the five years project is the main reason for the success of WP1.

Preface

In order to provide relevant inputs to the Lombardy Region for the design of abatement strategies in the region with an adequate spatial coverage of the most representative areas of the region, a number of activities have been planned for this work package to be carried out in the period of 2006-2010. These activities have been divided into three categories: *(i) Receptor characterization:* Sampling and analysis of ambient particulate matter (PM) during smog episodes (focus on winter, comparison with summer/autumn) and of ozone precursor volatile organic compounds (VOC) in ambient air during smog episode (focus on summer, comparison with winter), *(ii) Source characterization:* Sampling and analysis of PM and VOC emitted from significant sources in the Lombardy Region (chemical source fingerprints), and *(iii) Receptor modelling*: Multivariate statistical analysis using receptor modelling to estimate the contribution of significant sources to the PM and ozone pollution of the ambient air. As a spin-off from the data acquired for source apportionment, useful information has been obtained on chemical substances associated with PM_{10}, for which the European Commission has established target limit values for annual mean concentration (benzo[a]pyrene, Pb, Cd and As).

The results of the activities carried out under WP1 for PM_{10} have been reported in Progress Reports I-VII. The present Report IX completes the work carried out under WP1 for the 2nd source apportionment exercise based on all the collected source profiles and the regional, long-term ambient air $PM_{2.5}$ / PM_{10} sampling campaign of winter 2008-2009, which has been focused on the completion of the chemical analysis of elementary carbon (EC), organic carbon (OC), PAH and levoglucosan and receptor modeling computations with 24 hours time resolution, using CMB and PMF.

The present report also summarizes and draws up conclusions on all WP1 activities carried out under the “Contract for the Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)”. The material presented in the present final report together with the material presented in the previous Progress Reports (I-VIII) completes the deliverables under WP1 as specified in above mentioned contract.

The JRC contributors to the present report are: *B. R. Larsen* – Receptor modelling and reporting, *M. Duane* – Analysis of levoglucosan and PAH.

The JRC contributors to WP1 activities (2006-2010) are: *B. R. Larsen* – overall responsibility, *V. Forcina* - Responsible for PM sample equipment, *J. Cancelinha* - Responsible for PM gravimetry, *M. Duane* – GC-MS and HPLC-MS, *K. Douglas* – OC/EC measurements *V. Pedroni* - ICP-MS, *R. Passarella* - Sample preparation, *G. Tanet* - Method development and inter-comparison. *J. Mønster* – PM sampling. . *L. Montero and T. Adam* – VOC characterization.

External contributions are thankfully acknowledged from C. Colombi, V. Gianelle and C. Belis in estimation of biomass burning’s contribution to PM; from A. Giudici, G. Lanzani + Local ARPA’s for campaign logistics; from A. Latella for VOC source apportionment activities; from G. Sangiorgi, A. Piazzalunga, M.-G. Perrone, E. Bolzacchini and P. Fermo for chemical analysis activities.

1. Source apportionment of PM with 24-hour temporal resolution

(Fulfilment of delayed aspects of deliverable VII.1)

The final deliverable to complete under WP1 of the "Collaborative Research Project for Air Pollution Reduction in Lombardia (2006- 2010)" is the source apportionment of particulate matter with a 24-hour temporal resolution. For that purpose positive matrix factorization (PMF) analysis was performed using chemical concentration data on PM_{10} and $PM_{2.5}$ from all samples collected analysed during 2007-2009, which amount to 32376 data points! Details on the sample collection and analysis are described elsewhere (Progress Reports III, IV, V, VII, VIII).

1.1. PMF and CMB modelling approach

PMF analysis was performed for many different combinations of input species to identify species critical for PMF factor differentiation. The PMF model runs evaluated different combinations of the 54 molecular markers listed in Table 1:

Table 1 input data.

Species	Category	S/N	Min	25th	Median	75th	Max
PM	Weak	9.81225	8.81130	46.25236	68.77806	96.60936	186.85137
NO3	Strong	5.82474	0.24750	7.05890	13.18791	21.93577	68.08680
NH4	Strong	5.50309	0.06427	2.41112	5.02492	8.10916	24.87221
SO4	Strong	6.78207	0.29914	1.76698	3.06914	4.78842	13.50662
CL	Bad	4.27063	0.00250	0.26692	0.56299	0.91244	2.30498
PO4	Bad	4.73103	0.00238	0.03936	0.06372	0.10318	0.51330
F	Weak	4.60895	0.00171	0.01118	0.01799	0.02897	0.13957
OC	Bad	2.78280	1.40094	8.04807	11.88913	16.44813	32.39650
Pk1C	Strong	2.63414	0.48047	1.82772	2.64809	3.69581	7.48621
Pk2C	Strong	2.47761	0.37530	1.35761	1.88087	2.49482	5.56060
Pk3C	Strong	2.60096	0.14304	0.56947	0.84532	1.20686	2.74173
Pk4C	Strong	2.42640	0.36781	1.16102	1.63917	2.10834	4.50718
PyrC	Strong	3.02290	0.25279	2.94142	4.68844	6.98487	14.67302
AS	Weak	3.08315	0.00001	0.00078	0.00126	0.00178	0.00722
V	Strong	4.94154	0.00027	0.00240	0.00337	0.00460	0.01027
CD	Strong	5.15251	0.00001	0.00039	0.00073	0.00113	0.00495
SOOT	Strong	0.98694	0.29300	1.61747	2.46535	3.62164	10.79256
ZN	Weak	2.81025	0.01325	0.22205	0.30942	0.42024	1.08756
MN	Strong	5.59001	0.00104	0.01358	0.02275	0.03843	0.14050
PB	Strong	4.54140	0.00224	0.01460	0.02688	0.04441	0.24761
CU	Strong	5.10690	0.00104	0.01781	0.03248	0.06834	0.21887
SB	Strong	2.52187	0.00029	0.00328	0.00539	0.01056	0.04135
SN	Strong	4.44039	0.00058	0.00444	0.00780	0.01474	0.05508
MO	Strong	4.58214	0.00036	0.00267	0.00471	0.00813	0.03124
BA	Strong	4.29130	0.00098	0.00916	0.01559	0.02764	0.07909
CO	Strong	3.62745	0.00004	0.00030	0.00045	0.00065	0.00166
CE	Strong	5.01870	0.00004	0.00030	0.00059	0.00093	0.00266
CR	Strong	4.69779	0.00099	0.00682	0.01036	0.01541	0.05841
NI	Bad	4.51329	0.00072	0.00591	0.00862	0.01263	0.04460
SR	Strong	4.59156	0.00013	0.00197	0.00334	0.00522	0.01420
FE	Strong	3.47012	0.05181	0.49255	0.90880	1.56761	5.98284
TCA	Strong	6.19731	0.01280	0.32783	0.57897	0.92617	3.45605
CA	Bad	6.12693	0.00152	0.37122	0.68450	1.13229	3.45605
TMG	Strong	6.00997	0.00500	0.10525	0.18119	0.32457	1.00171
MG	Bad	5.51544	0.00152	0.06237	0.11478	0.19998	1.00171
SI	Strong	2.60094	0.05069	0.54467	1.11520	1.76179	4.86648
AL	Strong	5.30604	0.02402	0.21174	0.42285	0.69904	2.15046

Table 1 (continued) input data.

TI	Strong	4.00267	0.00203	0.01265	0.02312	0.04043	0.16739
RB	Strong	4.82035	0.00018	0.00101	0.00153	0.00214	0.00688
K	Weak	5.53359	0.04627	0.26099	0.38740	0.54370	1.21242
LEV	Strong	3.27480	0.00362	0.27557	0.50746	0.89359	3.33249
BAA	Weak	0.84444	0.00002	0.00043	0.00083	0.00156	0.00966
CHRYS	Bad	0.91537	0.00013	0.00120	0.00216	0.00348	0.01245
BBFLU	Bad	4.12615	0.00007	0.00080	0.00135	0.00207	0.00737
BKFLU	Bad	3.91175	0.00006	0.00044	0.00083	0.00138	0.00710
BJFLU	Bad	3.81278	0.00008	0.00055	0.00092	0.00143	0.00495
BEPYR	Bad	5.64909	0.00005	0.00056	0.00098	0.00153	0.00574
BAPYR	Strong	5.78743	0.00005	0.00054	0.00102	0.00192	0.00974
IN123	Strong	5.55338	0.00006	0.00068	0.00123	0.00204	0.00769
DBAHA	Bad	6.14398	0.00002	0.00013	0.00024	0.00051	0.00604
BGPER	Strong	5.03566	0.00008	0.00074	0.00130	0.00212	0.00725
COR	Bad	3.60563	0.00002	0.00028	0.00086	0.00162	0.00557
PAH	Bad	3.38186	0.00073	0.00781	0.01310	0.02052	0.06646
PT	Bad	5.97994	0.00000	0.00002	0.00003	0.00007	0.00339
RH	Bad	4.66332	0.00000	0.00001	0.00002	0.00004	0.00021
PD	Bad	4.95325	0.00000	0.00002	0.00004	0.00007	0.00063
NA	Bad	5.73644	0.00152	0.15337	0.25800	0.38322	1.47906

The units for all data are µg/m3.

Each dataset was analyzed using the EPA positive matrix factorization model (v3.0.2.2), which uses a weighted least-squares fitting approach to find factor contributions and factor profiles from concentration data (http://www.epa.gov/heasd/products/pmf/pmf.html). Although many studies refer to the factors derived by PMF as sources, PMF only reveals which species temporally co-vary and since the temporal variability of pollutant concentrations is not solely determined by changes in emissions, one must be careful when linking factors to source classes. Given this ambiguity, we use the words ''*factor*'' and ''*factor profile*'' to refer to PMF results; ''*source profile*'' is used exclusively to refer to actual profiles measured by source tests.

The positive matrix factorization model used uncertainties on each individual input data for weighing in the iterative procedure of finding solutions to the mass balance; it uses realistic error estimates to weigh data values and imposes non-negativity constraints in the factor computational process. We took advantage of PMF's option of decreasing the weight for individual data points in the iterative solution of the mass balance to minimise the influence of partial fulfilment of the intrinsic assumption of mass conservation for semi-volatile receptor species (OC, NH_4NO_3, NH_4Cl, PAH) from source to receptor. A special emphasis was put on attributing uncertainties, which took into consideration the fact that measurement data increase as the ambient concentrations approaches the detection limits. A relative uncertainty of 1000% was assigned to the measurements made at the detection limit deriving from the simple fact that the detection limit was determined at a signal to noise ratio of 1/10. Detection limits for each species were determined from the analysis of handling and field blanks. All of the molecular marker data were above the detection limits. Missing data were approximated by linear interpolation from of the neighbour data assuming that the chemical composition of the PM remained unchanged. Additional uncertainty was attributed to reconstituted data proportional to the relative difference in the PM mass concentration.

Semi-volatile compounds - may be affected by temperature dependant partitioning from source to receptor, which infringe the assumption of mass conservation. It is unknown how much this will affect PMF solutions. However, we aimed at compensating for this with a novel approach in the setting of the input uncertainty, thereby assigning less weight in the PMF solution for the more volatile receptor compounds (H. Junninen et al., 2009. Environ. Sci. Techn. 43, 7964-7970). While a 10% additional uncertainty was attributed to OC, NH_4NO_3, and NH_4Cl a more advanced approach was taken for PAH. First of all only four-ring to six-ring PAH were used, and their input uncertainty, S_{ij}, was estimated by Equation 1-4.

$$S_{ij} = \frac{\Lambda_j + 0.2C_{ij}}{\Phi_{ij}} \qquad \text{Eq. 1}$$

$$\Phi = \frac{KpC_{PM}}{(1+KpC_{PM})} \qquad \text{Eq. 2}$$

$$\log Kp = m \log p_{Ls}^{o} + b \qquad \text{Eq. 3}$$

$$\log p_{Ls}^{o} = \log p_{L}^{o} + \tfrac{\Delta H}{R}\left(T^{-1} - T_s^{-1}\right) \qquad \text{Eq. 4}$$

in which, Λ_j nominates the detection limit of compound j, C_{ij} the concentration of compound j in sample i, Φ_{ij} the partition of compound j in particulate phase in sampling temperature of sample i, Kp the temperature corrected partitioning coefficient, C_{PM} the concentration of PM, $P_{Ls}{}^{O}$ the temperature corrected subcooled liquid vapour pressure, m and b are, constants, and T the sampling temperature. We have successfully used a similar approach for reactivity compensation in receptor modelling of volatile organic compounds (Latella et al., Journal of Chromatography A (2005) 1071, 29–39). For the non-volatile receptor compounds the optimized use of uncertainties in the dataset and intrinsic assumptions followed the standard approach recommended by the EPA.

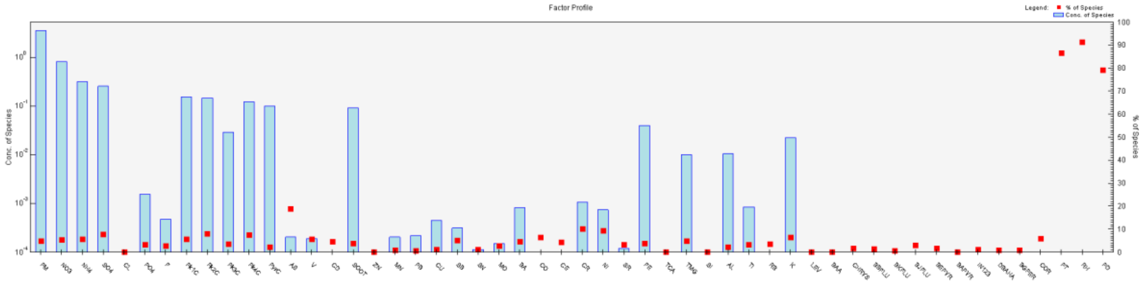
There is some evidence for atmospheric decay of PAHs, which may breach the assumption of mass conservation in areas, where prevalent sources for PAH impact through long-range transport - especially during summertime. The present study wascarried out during wintertime with low photochemical activity (average ozone concentrations < 10 ppbV). Thus, in comparison with all other sources of uncertainty for this study it is safe to assume that atmospheric decay of PAH did only play a minor role. Little is known about the atmospheric stability of levoglucosan, thus an additional uncertainty of 10% was added to this compound. Finally the propagated uncertainty was calculated from all individual uncertainties and used as the required input data to the PMF model.

PMF results depend on the number of factors included in the model and the amount of rotation imposed on the solution. Interpretability was the key basis for judging the optimum values for these parameters. Since we are interested in the sources of PM, interpretability was defined by how well PMF apportioned source-class-specific groups of molecular markers. Interpretable solutions were those that grouped source-class-specific sets of markers into distinct factors, with factor-profiles similar to measured source profiles (see Progress Reports III, IV, V, and VII). Models that grouped markers for multiple source classes into the same factor, distributed markers for one source class across multiple factors, or contained factors with no distinctive groupings of compounds were judged less interpretable and rejected. While no molecular marker pattern can be unambiguously associated with a specific source class, this approach provides a systematic basis for sorting through the possible PMF models.

For each combination of input species, we systematically varied the number of factors and found that the optimum number depends on the specific combination of input species. For a given dataset, PMF models with an insufficient number of factors clearly mixed markers from different source classes into the same factor. PMF models with too many factors contained factors that did not have distinct groupings of compounds. The best, most interpretable solution was defined as the solution with the maximum number of factors that had distinctive groupings of compounds and explained at least 90% of the PM. One optimum solution was identified for each combination of input species.

As a starting point, all compounds were included and set to STRONG in the model. Four to seven factors were tested, all of which gave R^2 values for the prediction of PM around 0.9 without giving always interpretable solutions. When Na was included the solutions contained factors that did not have distinct groupings of compounds. This may be explained by trace contamination of the samples during the handling of the filters and filter holders, thus it was decided to omit Na and Cl.

The first model runs demonstrated that when the platinum group elements (PGE) were included they came out in one factor (PGE factor) that had a very low SCE for PM. The factor was almost void of any other compounds as seen below.



The scrutinizing of the factor loading plots revealed that the PGEs occurred in a limited number of samples (rare events mostly occurring at the traffic site Milano VM) at concentration levels 10-20 times higher than in all other samples. A possible explanation for this is that PGEs are emitted from a low number of gasoline vehicles by mechanical degradation of the exhaust catalyst. No further information was obtained from PGEs and they were omitted from the dataset.

When all individual PAH were included they split into two factors i.e. one for 2007 (with levoglucosan) and one for 2009 (no levoglucosan). This is explained by the fact that individual PAH congeners are highly inter-correlated and it was decided to use a low number of individual PAHs, namely the most orthogonal congeners BAA, BaP, In123, and BGPer. Since a six-factor solutions contained factors that did not have distinct groupings of Levoglucosan and sulfate, a five-factor solution was identified as optimal. In order to test for robustness 20 model runs were completed with five factors and random seeding (Output: QA1 base and QA1 diag). No significant difference between individual runs was revealed (Q-robust = 39152, Q-true 41782). Bootraps (100) minimum R2 = 0.6, Block size 20). The effect of rotation on the PMF results was demonstrated to be insignificant by varying the FPEAK values between -0.8 and +0.8. Nickel and phosphate were modelled with R^2 below 0.3 and were omitted for the final run. As, K, Zn, and F produced predictions with R^2 around 0.4. Thus they were set to WEAK in the model. Two samples were excluded as evident outliers (Milano VM and Abiate Cerreto (PV) 24/02/2007)

1.1.1. Chemical mass balance (CMB) modelling

Source apportionment by CMB was carried out for $PM_{2.5}$ and PM_{10} as described in detail elsewhere (Progress Reports III, IV, V, and VII). The same approach for uncertainty estimation as for PMF was applied. However, CMB was performed on the average concentration data for each station and measurement campaign with the uncertainty on the pooled data calculated by propagating the uncertainties for each individual sample and dividing by √N. The data output from the CMB runs is shown in detail in Appendix 2.

Very good fitting statistics were obtained with R^2 in the range of 0.9-0.98. The mass balance for the source apportionments was good. Only 18.1 % of the observed mass could not be accounted for by the five to eight source profile included in the CMB. This tended to be better for $PM_{2.5}$ than for PM_{10}.

1.1.2. PMF modelling of polyaromatic compounds

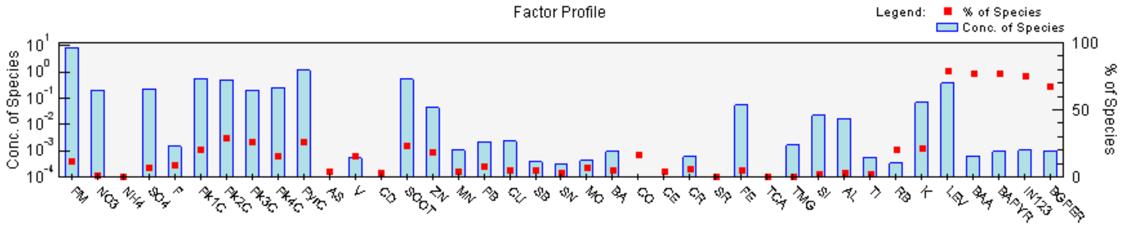
In independent trials, all collected $PM_{2.5}$ and PM_{10} samples were modelled together Sum of PAH selected as independent variable. In any combination PMF yielded factors that split up 2007 data from 2009 data and produce unrealistic PAH fingerprints. This may be explained by measurement differences. Thus the modelling was done for each dataset. Nevertheless the model split individual PAH into different profiles that remained unrealistic. It was concluded that PMF of individual PAH alone, is not possible for the present dataset.

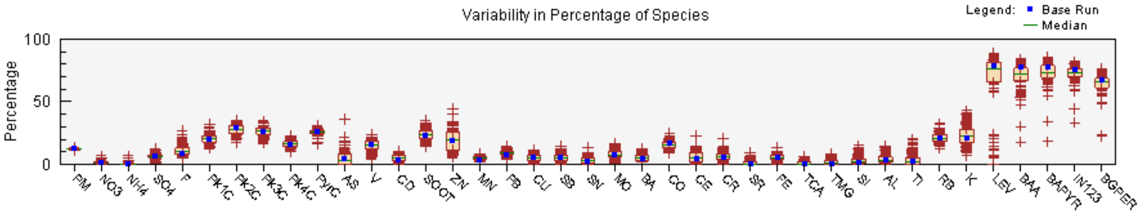
1.2. PMF and CMB results

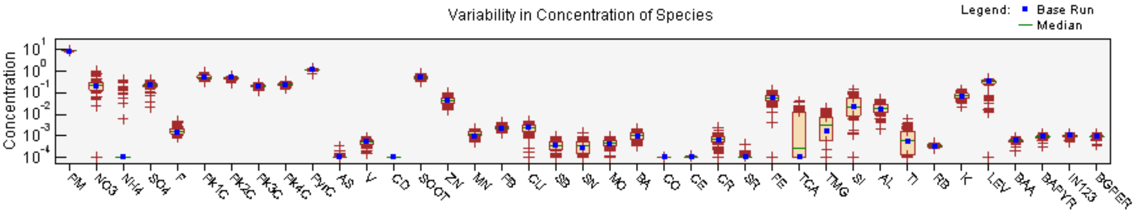
Any discussion of PMF results must start by examining the distribution of species among the different factors. These distributions define the factor profiles, which we compare to actual source profiles in order to link the PMF factors to sources and are depicted in the following. PM_{10} and $PM_{2.5}$ was modelled together. However, information on SCEs for each component was extracted and will be presented under 1.6.

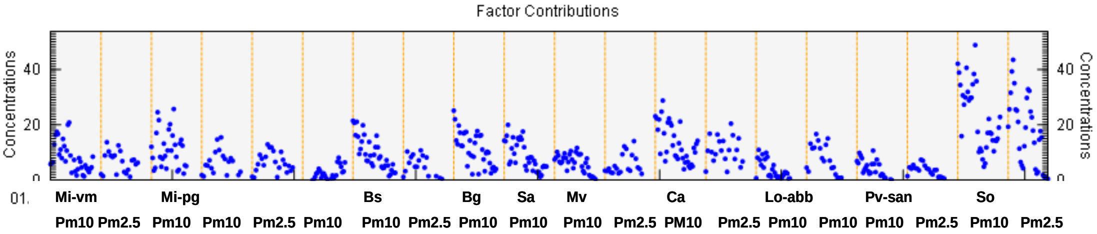
PMF Factor (coded # 4): Biomass/wood burning

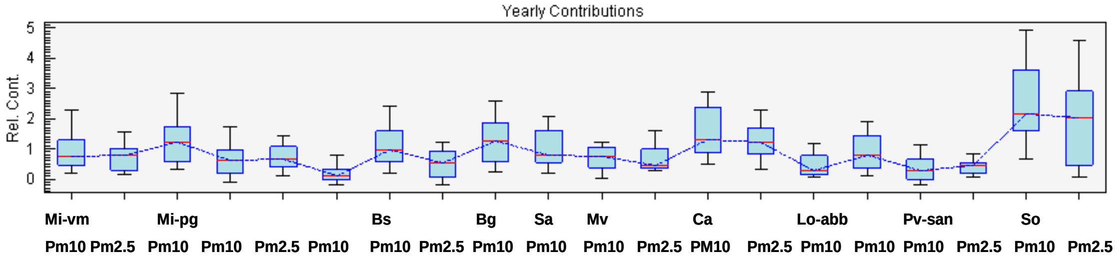
The profile contains 70-80 % of the marker compounds levoglucosan and PAHs, 20% of K and Ru, 20-35 % of the organic carbon fractions and soot. The overall source contribution of biomass/wood burning to PM_{10} and $PM_{2.5}$ is 12.4 %.





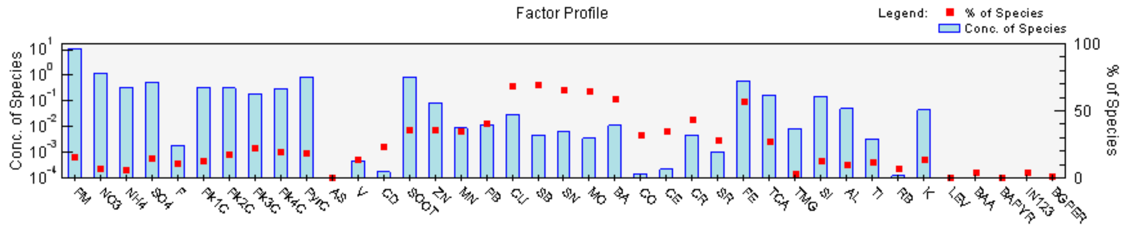


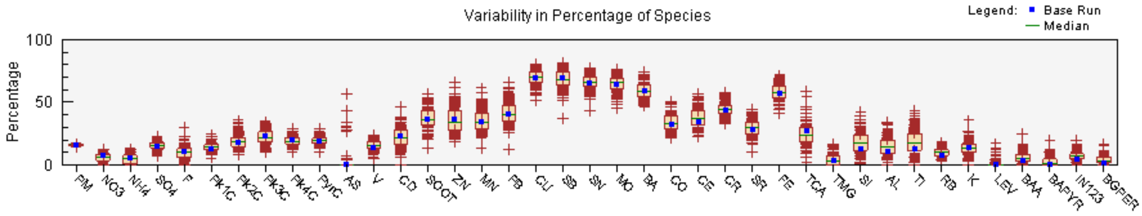


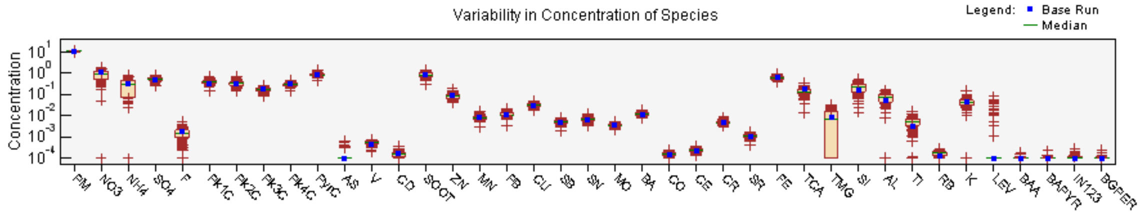


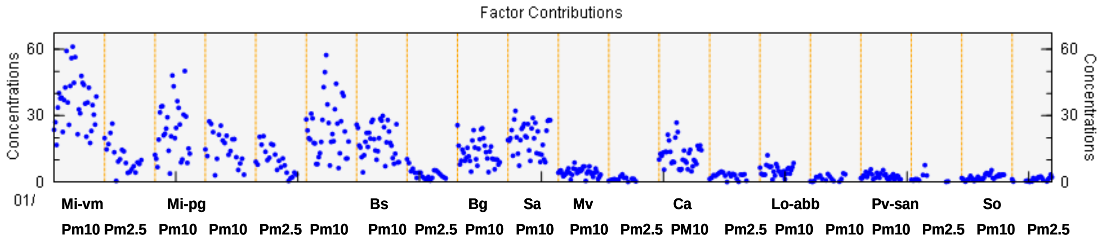
PMF Factor (coded # 3): Traffic (brake and tire-wear, exhaust)

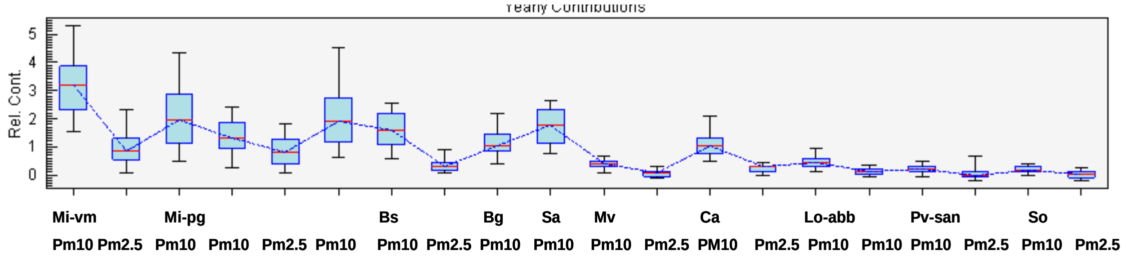
The profile contains brake wear markers (60-70 % of Cu, Sb, Sn, Mo Ba, and Fe, and 30-43% of Co, Ce, and Cr), mixed with tire wear markers and exhaust compounds The overall source contribution of traffic (brake and tire-wear)to PM_{10} and $PM_{2.5}$ is 15.9 %.





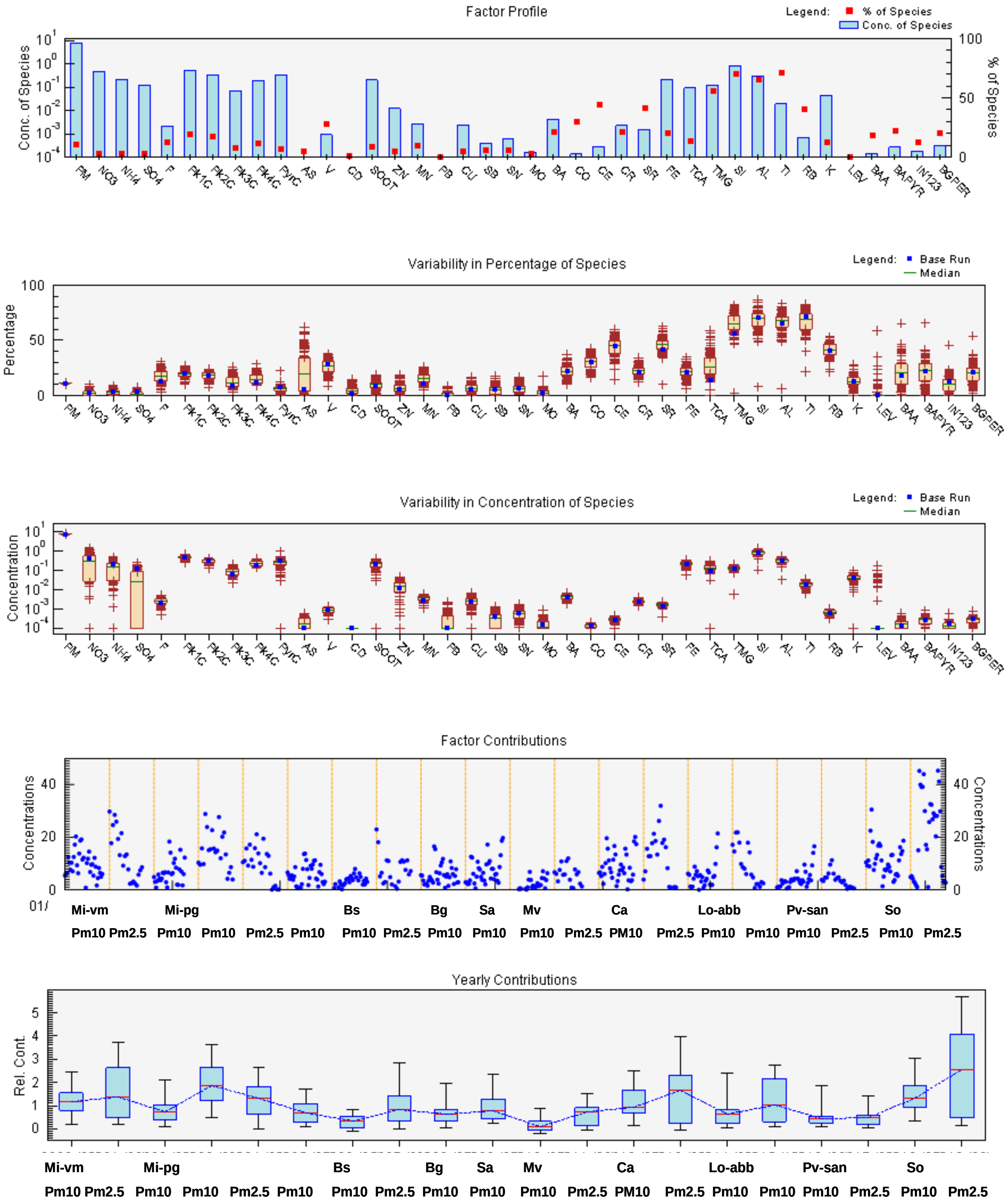






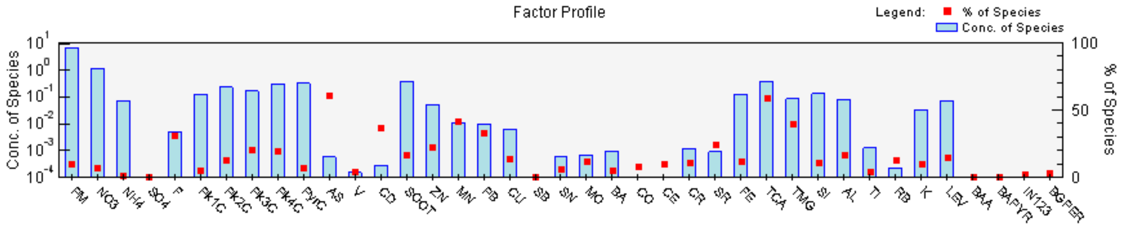
PMF Factor (coded # 1): Road-dust re-suspension (traffic related)

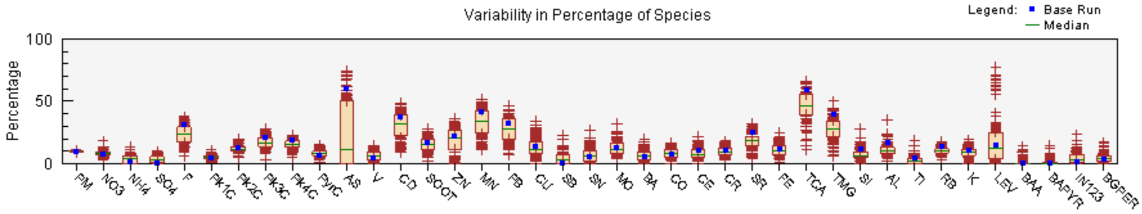
The profile contains road-dust re-suspension markers (60-70 % of Si, Al, Mg, and 15-45 % of Ca, Sr, Ru, and Ce) mixed with vehicle exhaust compounds . The overall source contribution of Soil dust re-suspension (traffic related**)** to PM_{10} and $PM_{2.5}$ is 11.2 %.

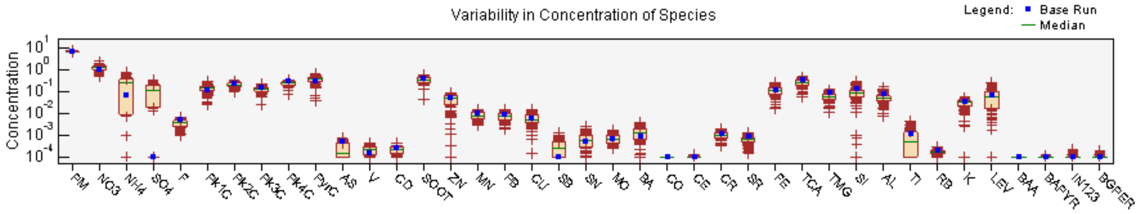


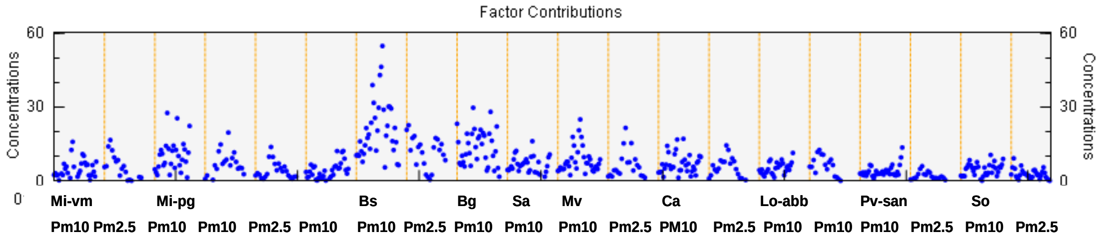
PMF Factor (coded # 2): Re-suspension of calcareous soil-dust (mixed)

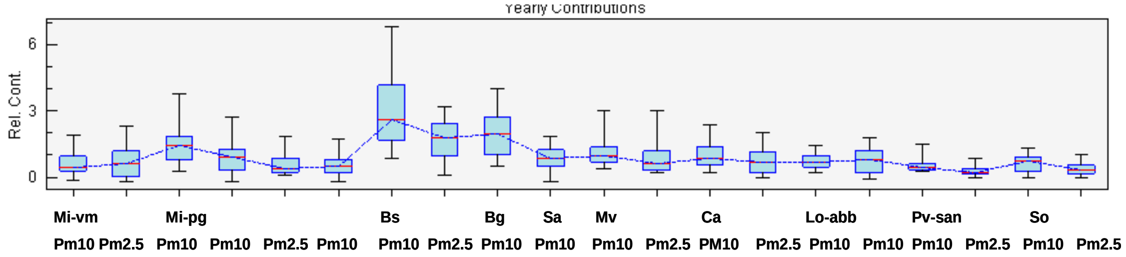
The profile contains soil/dust re-suspension markers (40-60 % Ca and Mg, and 10-20 % of other soil component) mixed with indicator compounds for cement production and related activities, nonferrous metals production, and municipal solid waste incineration (40-60% Cd As, and F together with other heavy metals. The contribution from re-suspension of calcareous soil-dust cannot be separated from the other sources and amount to PM_{10} and $PM_{2.5}$ is 10.0 %. Also, the re-suspension caused by natural factors such as wind cannot be separated from re-suspension caused by traffic.





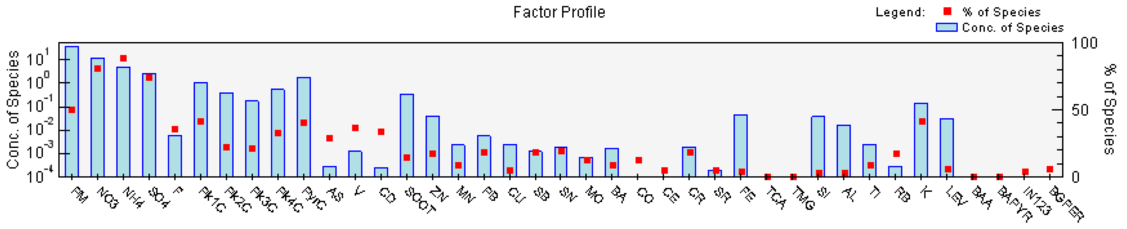


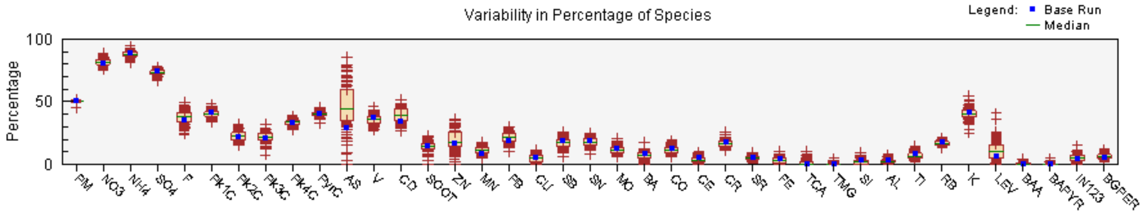


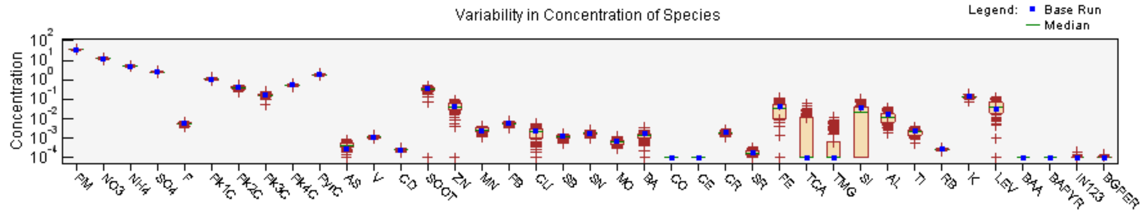


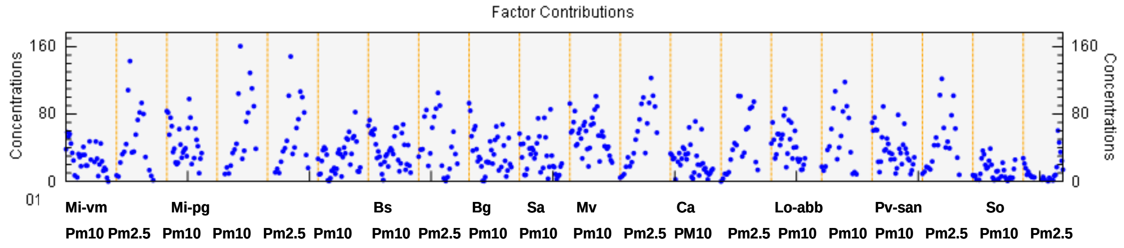
PMF Factor (coded # 5): Secondary, aged aerosol

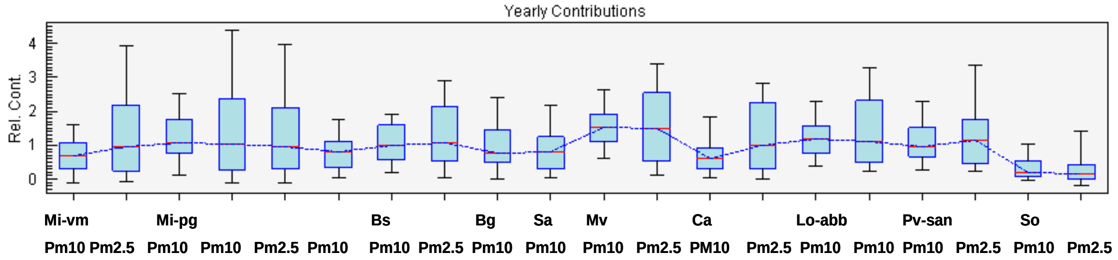
The profile is dominated by secondary, aged aerosol compounds (80-90 % of NO_3^-, SO_4^{--}, and NH_4^+ mixed with organic carbon (42% of the most volatile fraction Pk1). The overall source contribution of secondary, aged aerosol to PM_{10} and $PM_{2.5}$ is 50.5 %. In the profiles a minor contribution from trace elements can be observed, which cannot be considered secondary. However, the mass of these elements are insignificant (<2%) compared to the macro-tracers.





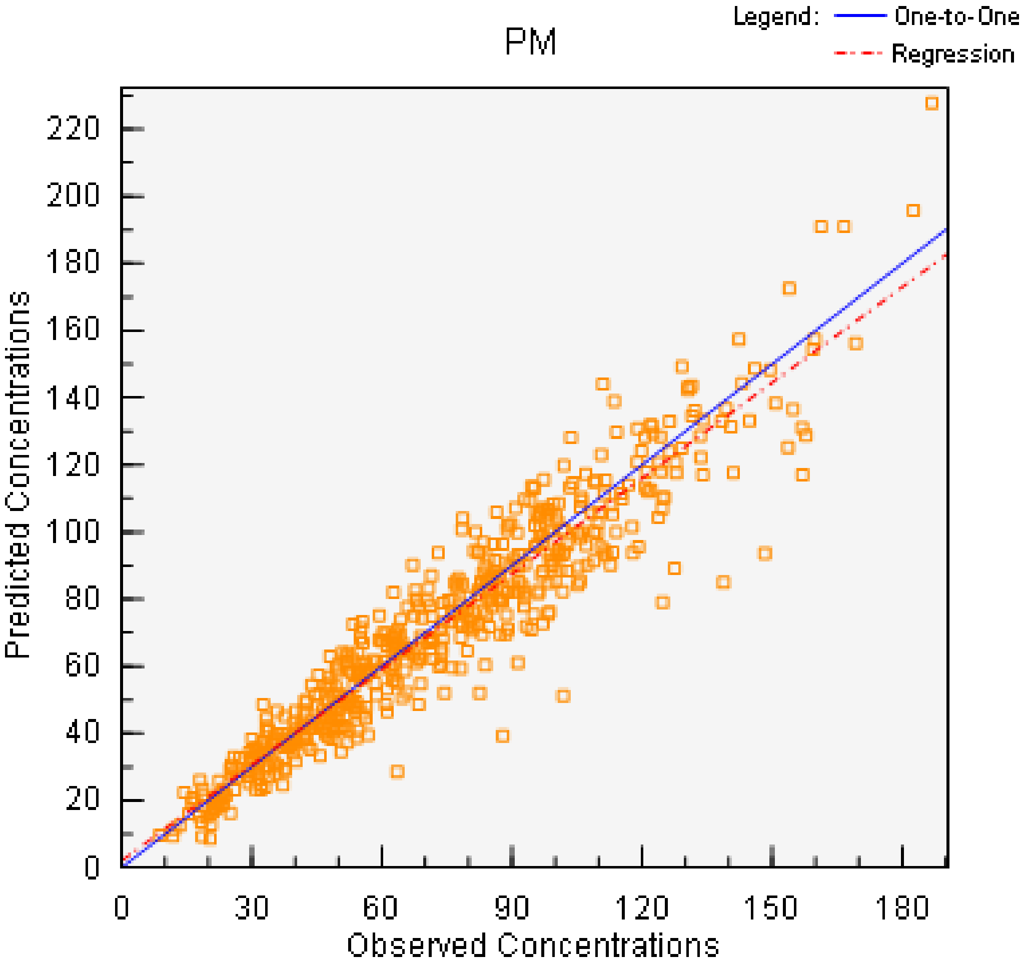






1.3. Receptor model performance

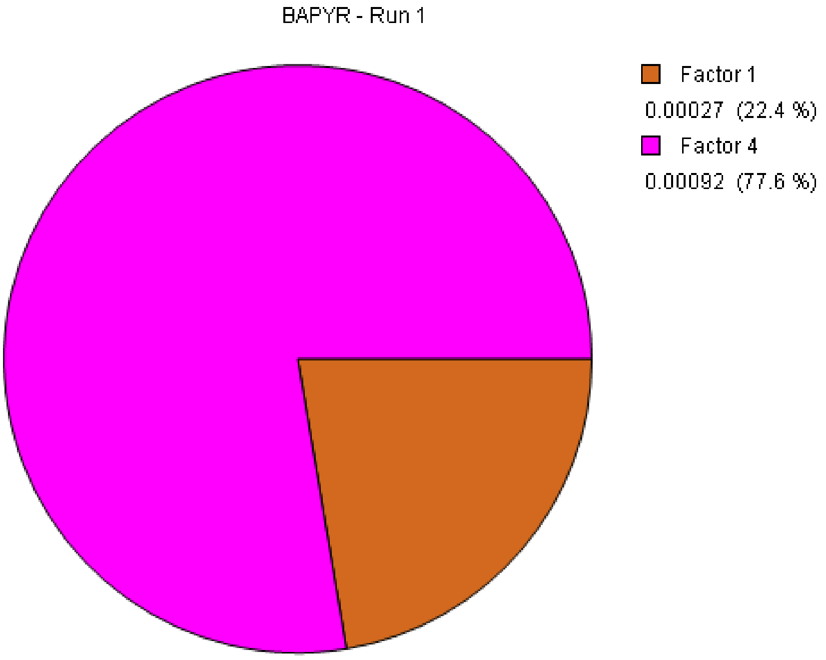
The overall performance of the five-factor positive matrix factorization receptor model was very good and produced predicted concentrations of PM in agreement with the observed observations: Predicted = 2.1(±1.1) + 0.95(±0.01) * Observed; $R^2 = 0.90$.



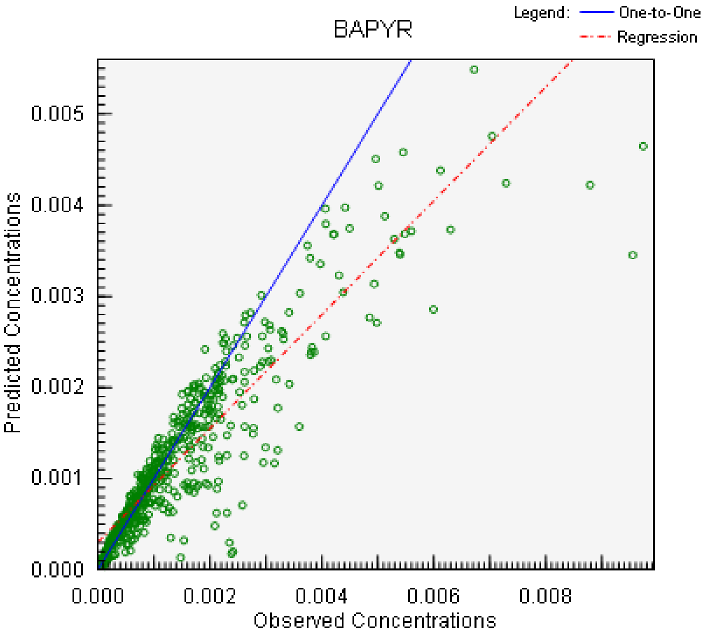
As expected the model performance for individual compounds was not as good as for PM. However, the predicted concentrations of the majority of individual compounds were correlated with the observed concentration with an R^2 above 0.6. Thus, it was possible to derive statistically significant source contribution estimates (SCEs) also for the individual compounds as seen in the following for compounds regulated by the EU Air Quality Directive, and in Appendix 1 for the remaining receptor compounds.

1.4. Single compound SCEs: Compounds regulated by the EU Air Quality Directive

Benzo(a)pyrene. The origin of this carcinogenic compound is attributed to two sources, namely biomass/wood burning (Factor 4, SCE = 77.7%) and traffic related soil dust re-suspension (22.4%).

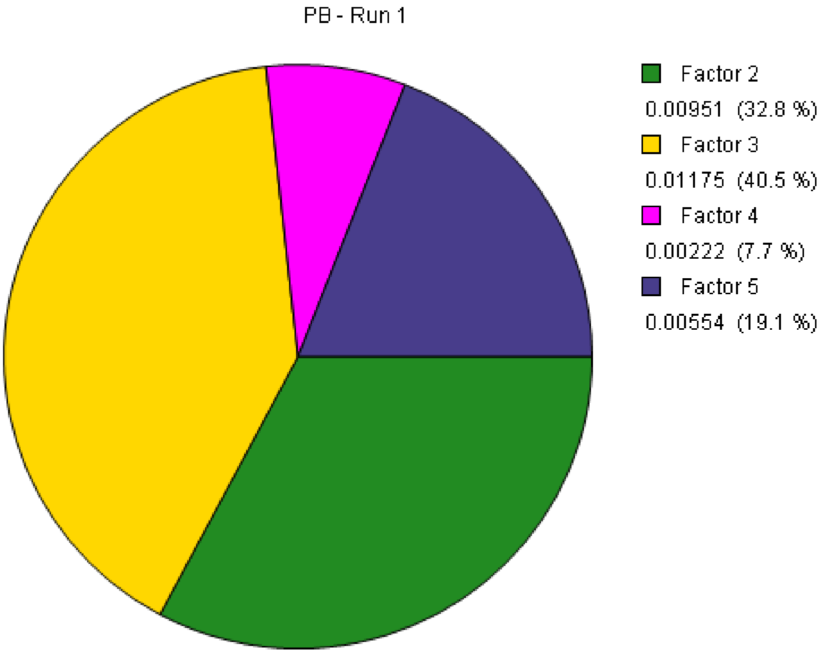


The PMF model has problems to predict the highest concentrations:

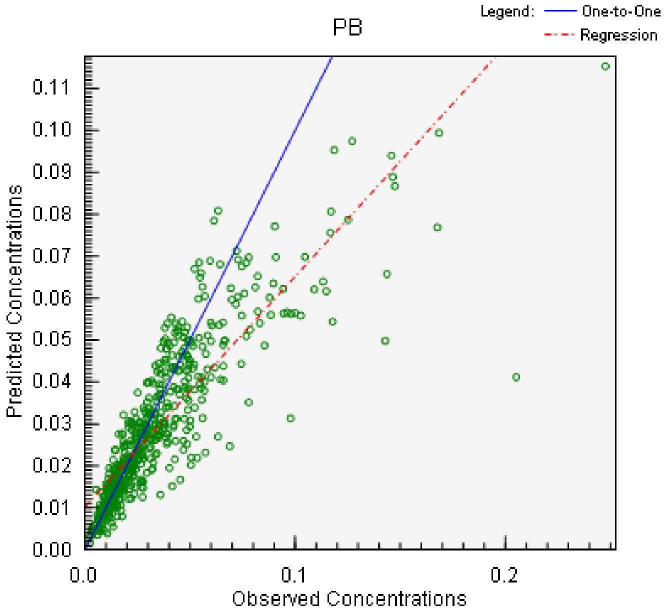


Predicted = 0.0003(±0.00002) + 0.63(±0.03) * Observed; R^2 = 0.82.

Lead. The origin of this toxic heavy metal, also regulated by the EU Hazardous Substances (RoHS) Directive, is attributed to mainly two-three sources, namely traffic (brake and tire wear + exhaust; Factor 3, SCE = 40.5 %), re-suspension of calcareous soil-dust with indication of incineration (Factor 2, SCE = 32.8%), and dispersed regional background sources (Factor 5, SCE = 19.1%).

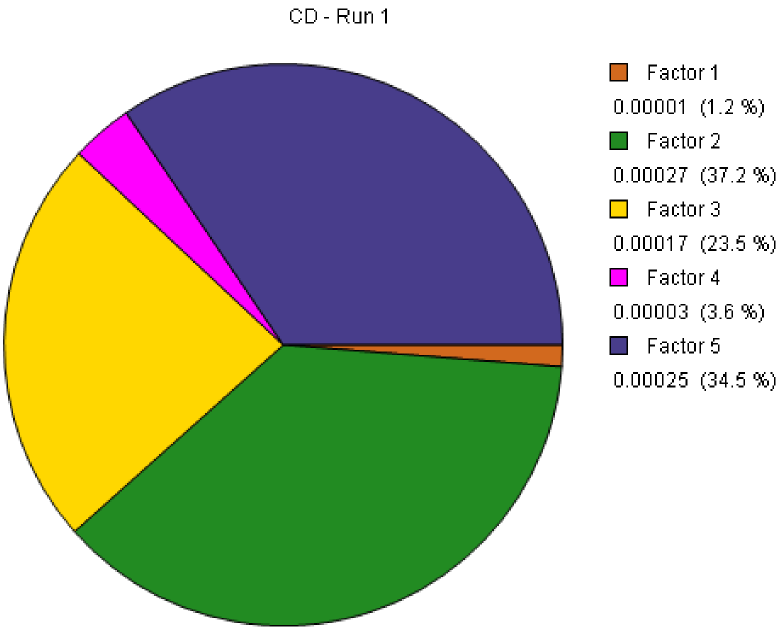


The PMF model has problems to predict the highest concentrations:

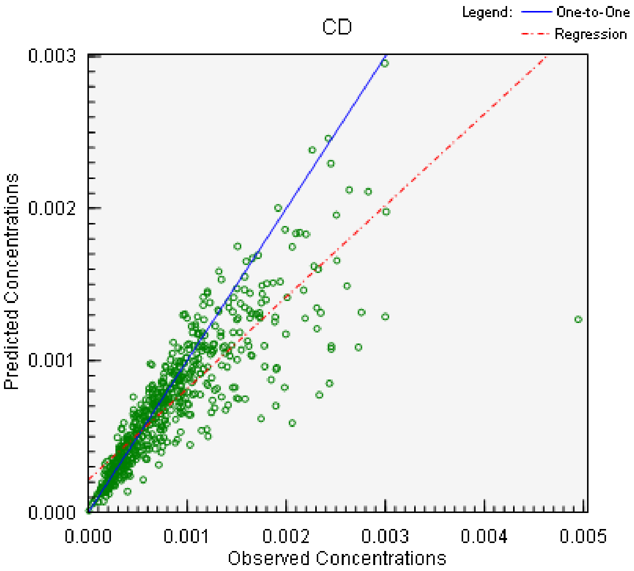


Predicted = 0.01(±0.0006) + 0.55(±0.01) * Observed; R^2 = 0.73.

Cadmium. The origin of this toxic heavy metal, also regulated by the EU Hazardous Substances (RoHS) Directive, is attributed to mainly three sources, namely re-suspension of calcareous soil-dust with indication of cement production and related activities, nonferrous metals production, and municipal solid waste incineration (Factor 2, SCE = 37.2%), dispersed regional background sources (Factor 5, SCE = 34.5.%) and traffic (brake and tire wear + exhaust; Factor 3, SCE = 23.5 %),

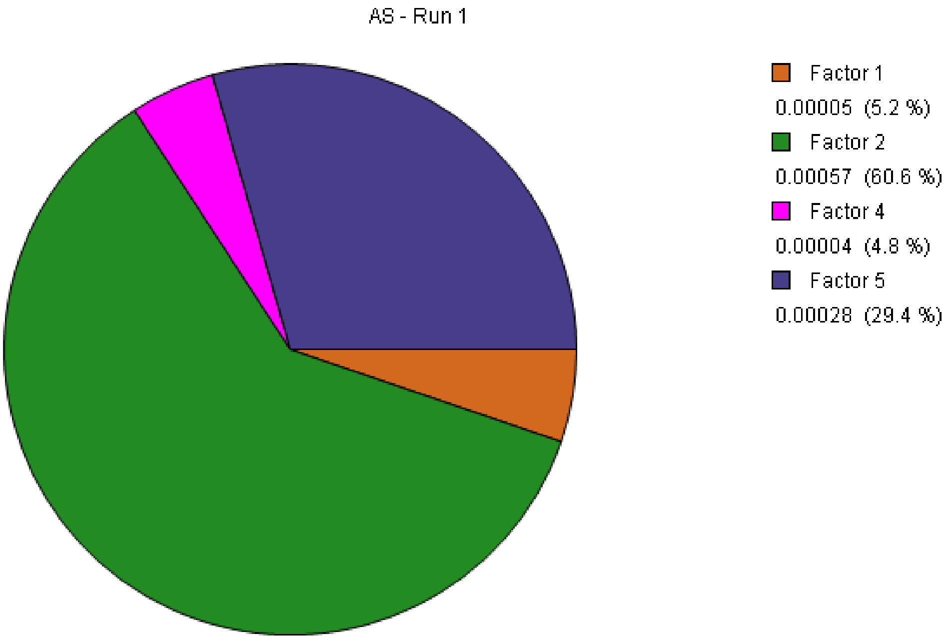


The PMF model has problems to predict the highest concentrations:

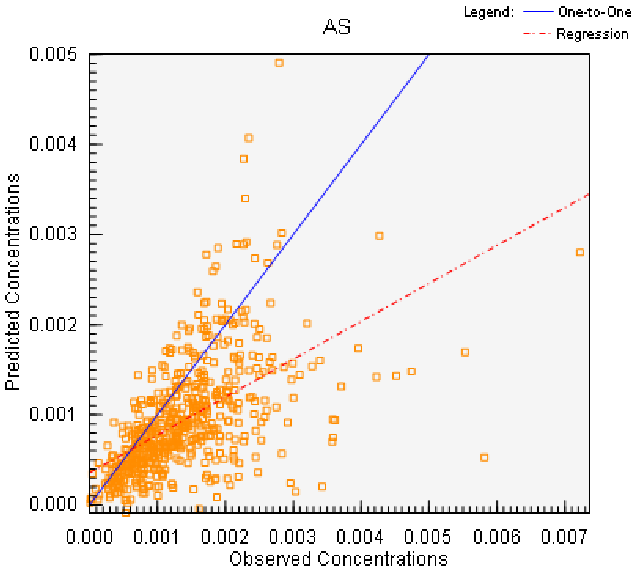


Predicted = 0.0002(±0.00002) + 0.60(±0.02) * Observed; $R^2 = 0.71$.

Arsenic. The origin of this carcinogenic compound is attributed to mainly two sources, namely re-suspension of calcareous soil-dust with indication of cement production and related activities, nonferrous metals production, and municipal solid waste incineration (Factor 2, SCE = 60.6%.8%), and dispersed regional background sources (Factor 5, SCE = 29.4%).



The PMF model has problems to predict the As concentrations:



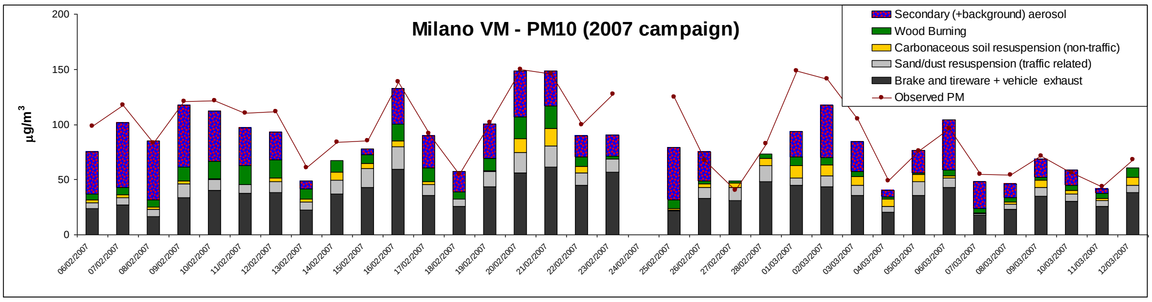
Predicted = 0.0004(±0.00004) + 0.42(±0.03) * Observed; R^2 = 0.30.

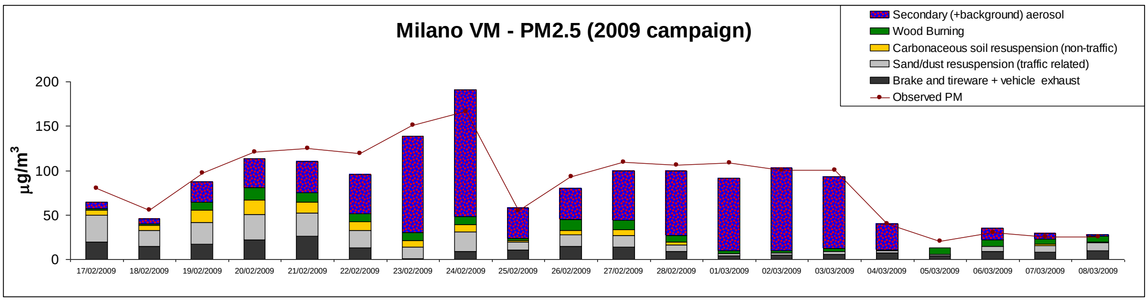
1.5. Source contribution estimates for particulate matter with 24-hour temporal resolution:

The daily variations in source contributions to PM_{10} and $PM_{2.5}$ are shown in the following for all the investigated receptor sites throughout the project. Very good agreements between monitored and modelled particulate matter were obtained.

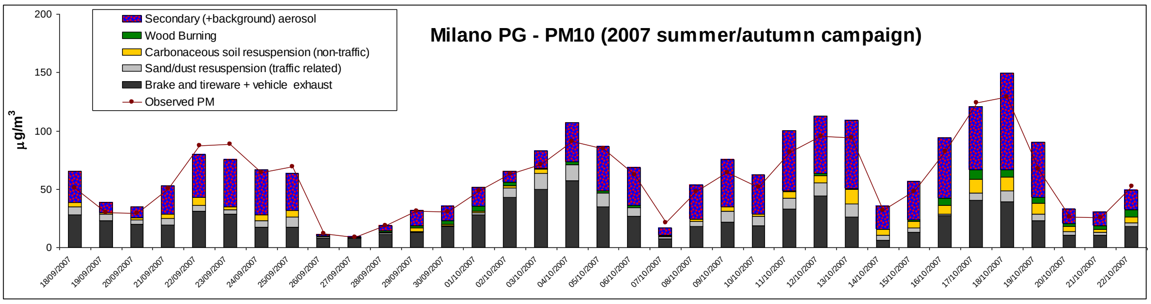
Traffic stations

Brake and tire-wear + vehicle exhaust dominated the PM_{10} source apportionments at the kerb-side station Milano Viale Marche. As expected this course fraction was of a much lesser importance for $PM_{2.5}$. The highest temporal variation was observed for secondary, aged aerosol that approaches zero during episodes of clean air with high wind-speed (Foehn).



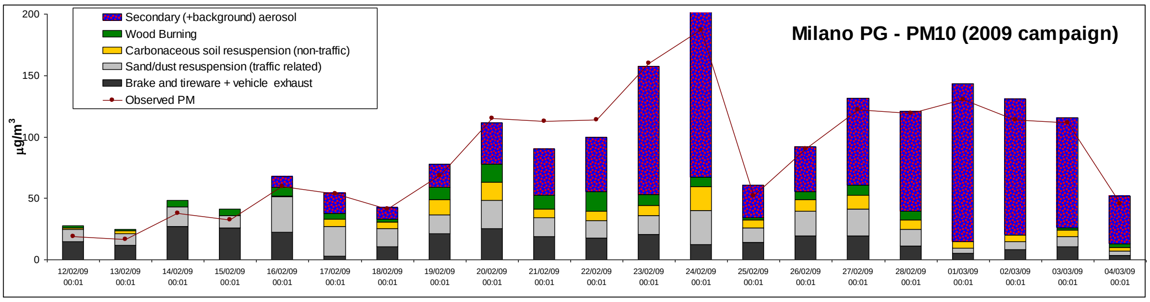


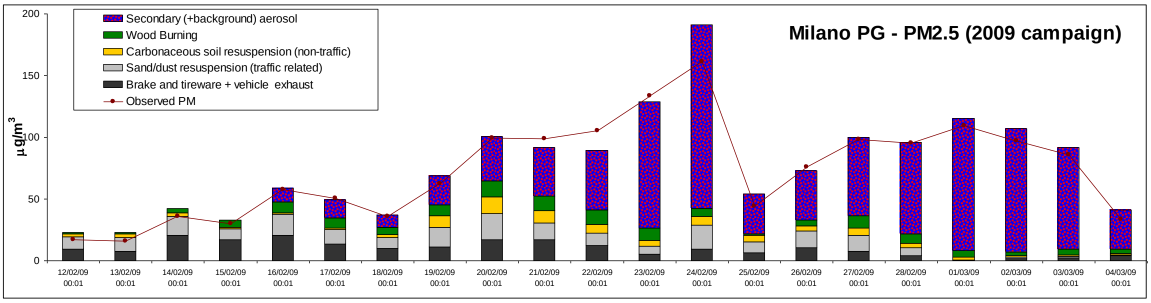
A similar pattern in the daily variation of SCEs was observed for PM_{10} during summer and autumn at the urban background station Milano Politecnico. During prolonged periods of high PM_{10} concentrations, the intensity of source contributions from secondary, aged aerosol increase steadily:



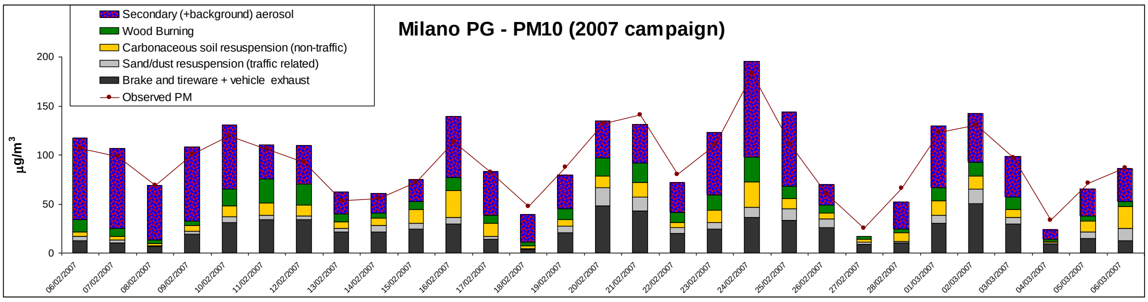
Urban background stations and regional background stations in the Po Plain

The daily variation of SCEs for PM_{10} and $PM_{2.5}$ at the urban background station Milano Politecnico during 2009 provides a text-book example of the role of secondary, aged aerosol for the build-up of episodes with high particulate matter concentrations in the Po Plain. In the beginning of the campaign Foehn conditions prevailed and the PM concentrations were low and derived mainly from local sand/dust re-suspension together with brake and tire-wear + vehicle exhaust. When the meteorological conditions changed to anti-cyclonic with wind speed below 1 m/s the proportion of secondary, aged aerosol increased steadily. By the end of the campaign the PMF factor (coded # 5): secondary, aged aerosol contributed with up to 90% of the particulate matter. Secondary, aged aerosol is known to be prevalent in the accumulation mode of particulate matter, and as expected the observed trends were identical for PM_{10} and $PM_{2.5}$.

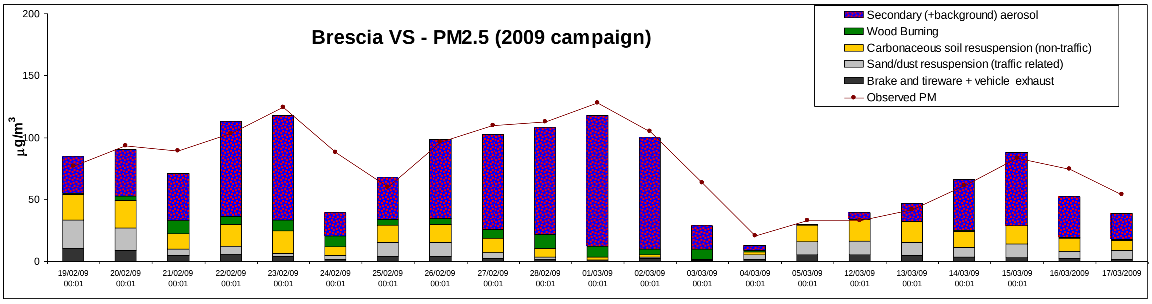


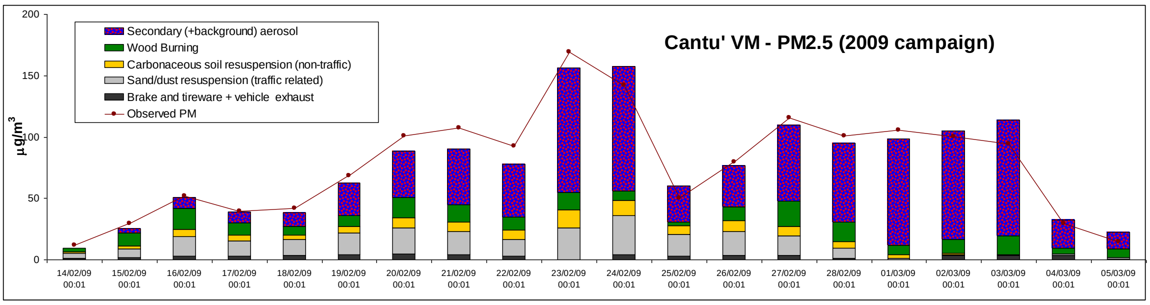


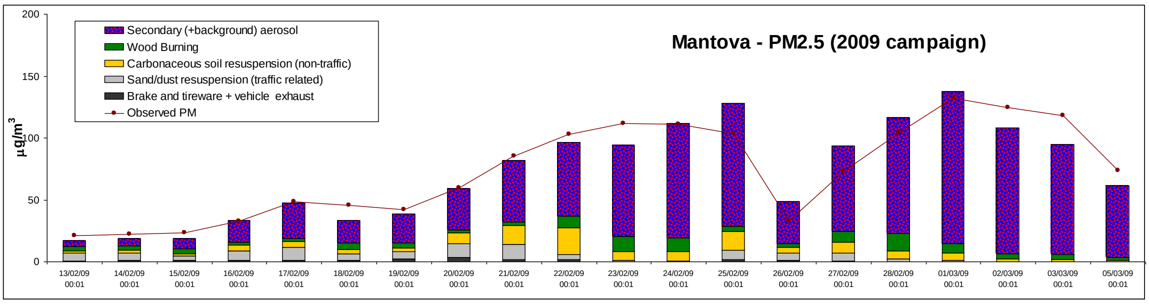
During the 2007 campaign the meteorological conditions were different and characterized by more interruptions of cyclonic conditions. However, the role of secondary, aged aerosol can still be pin-pointed in the build-up periods of PM pollution at the Milan Politecnico station:

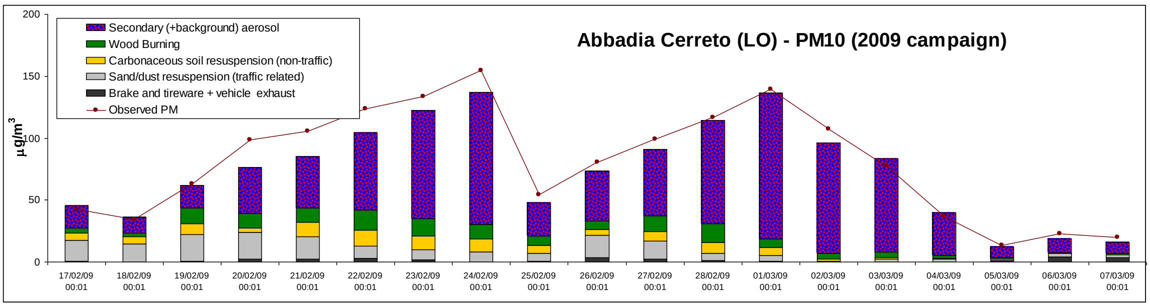


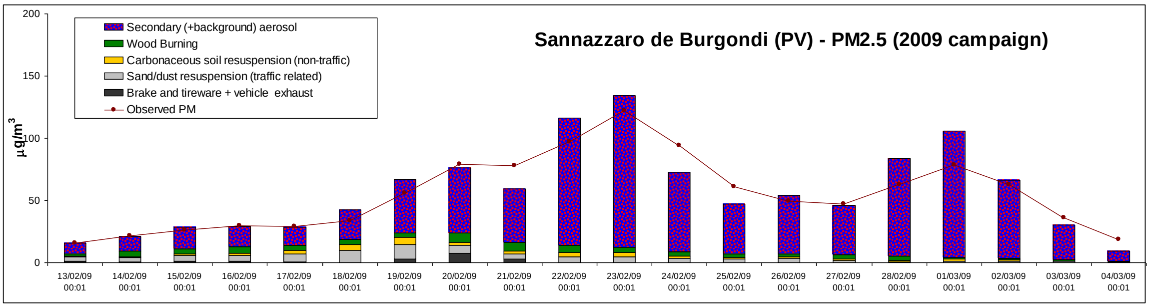
The dynamics in the build-up of the prolonged pollution event during 2009 appears also clearly for the urban and regional background stations in Brescia, Cantu', Mantova, Abbadia cerreto (LO) and Sannazzaro de' Burgondi (PV):



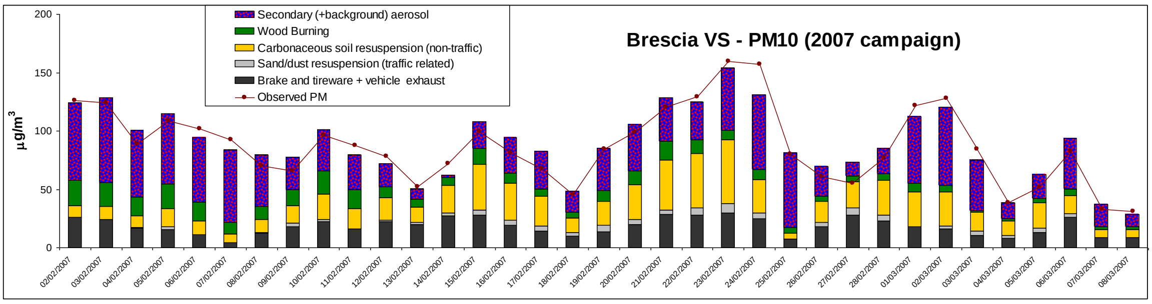


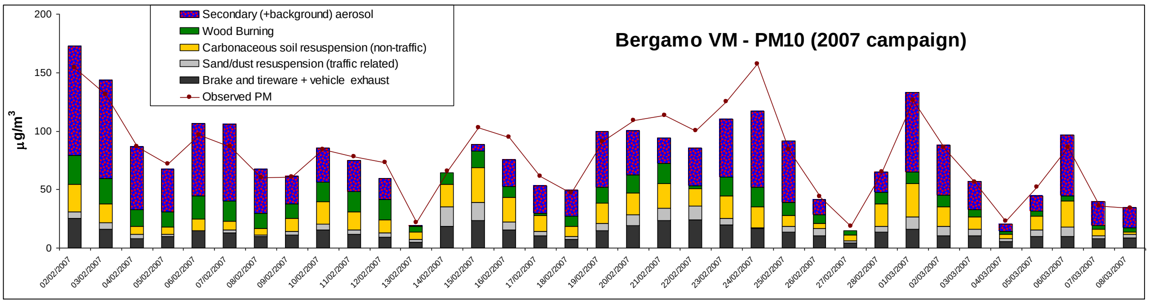


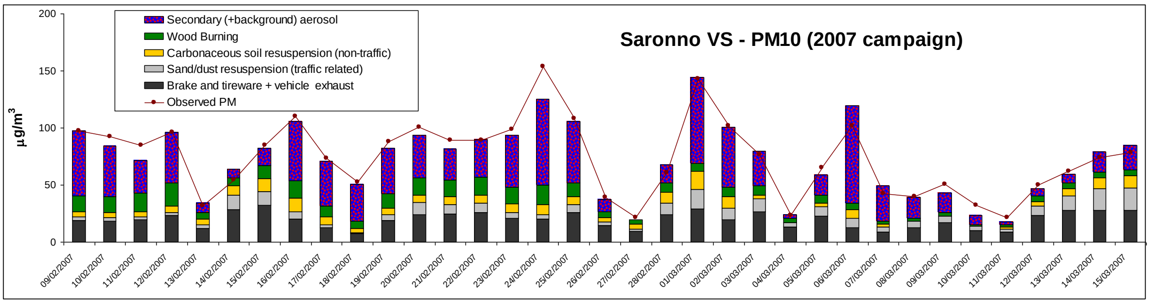


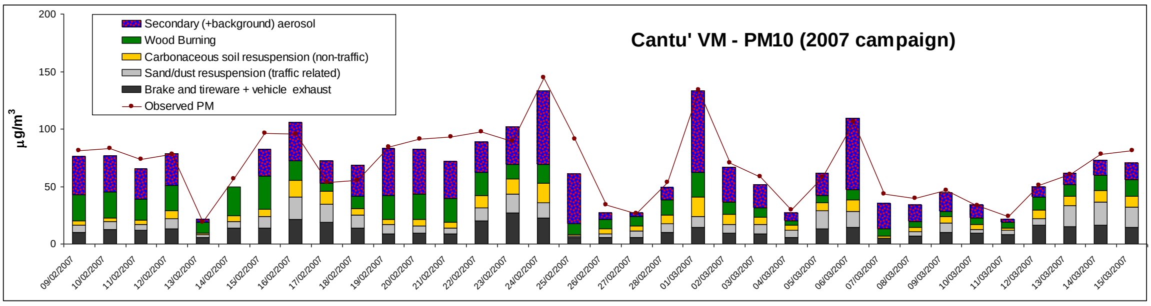


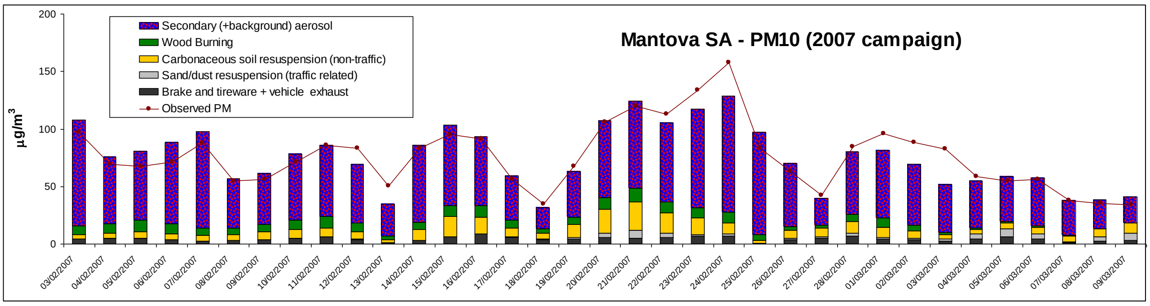
As discussed for Milano Politecnico, the meteorological conditions during the 2007 campaigns in Brescia, Bergamo, Saronno, Cantu', Mantova, Abbadia cerreto (LO) and Sannazzaro de' Burgondi (PV) were different and characterized by more interruptions of cyclonic conditions. However, the dynamics in the build-up of PM_{10} pollution can still be discerned:

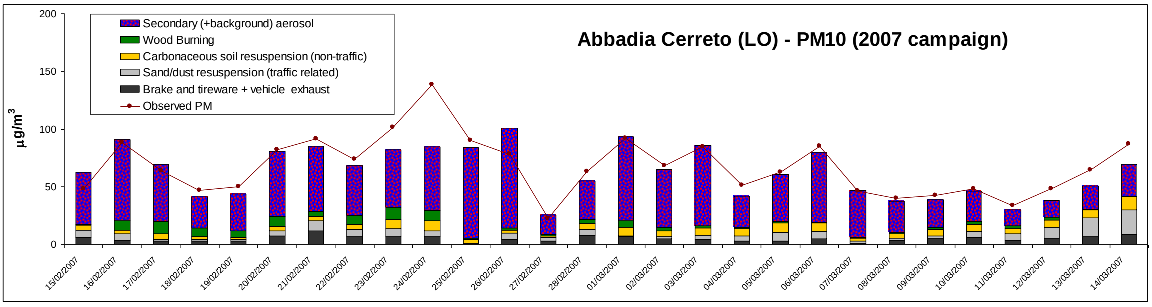


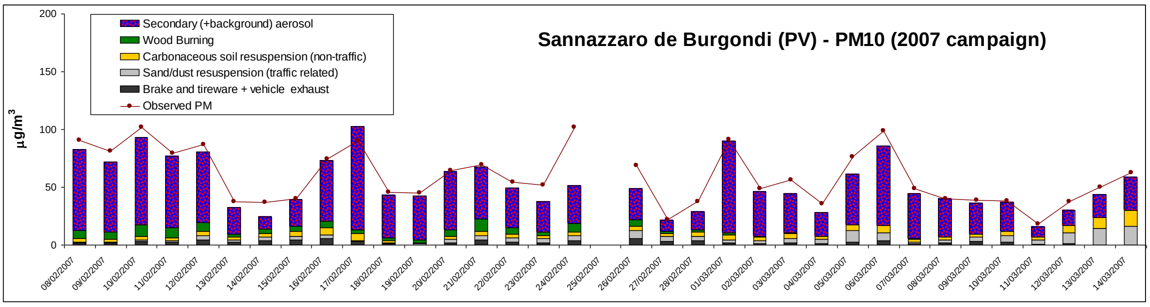






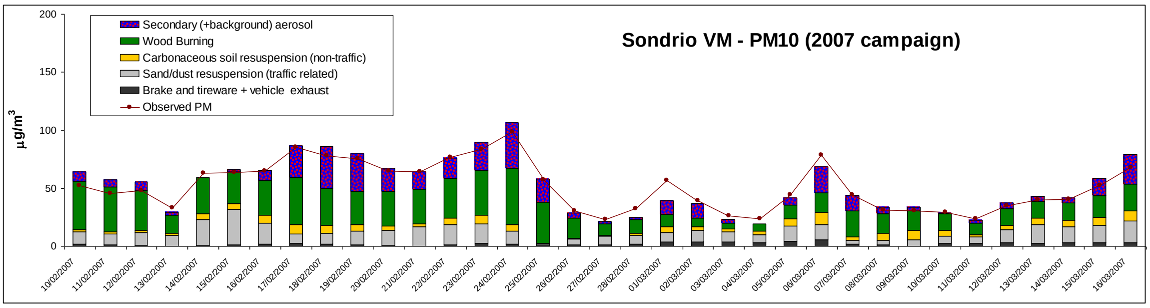


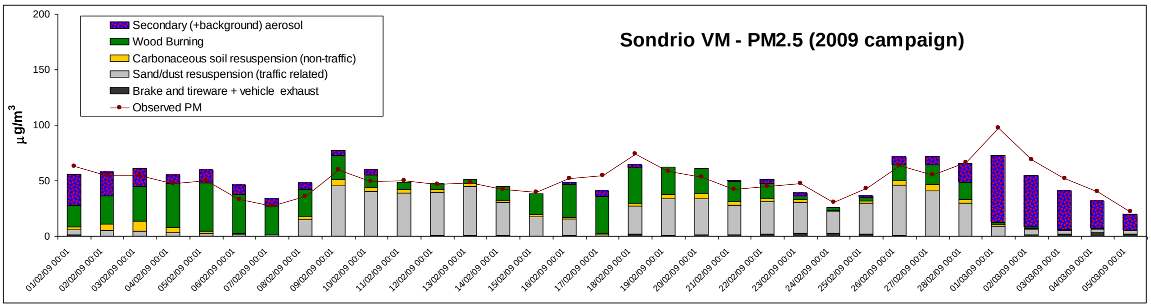




Urban background station in the Valtelline Valley

The dynamics of prolonged PM pollution in Sondrio also demonstrate some impact of secondary, aged aerosol. However, the particulate matter pollution (PM_{10} in 2007 and the $PM_{2.5}$ in 2009) at this station was heavily influenced by wood burning. The dynamics of the wood burning source showed trends similar to secondary, aged aerosol during the build-up phase of episodes.



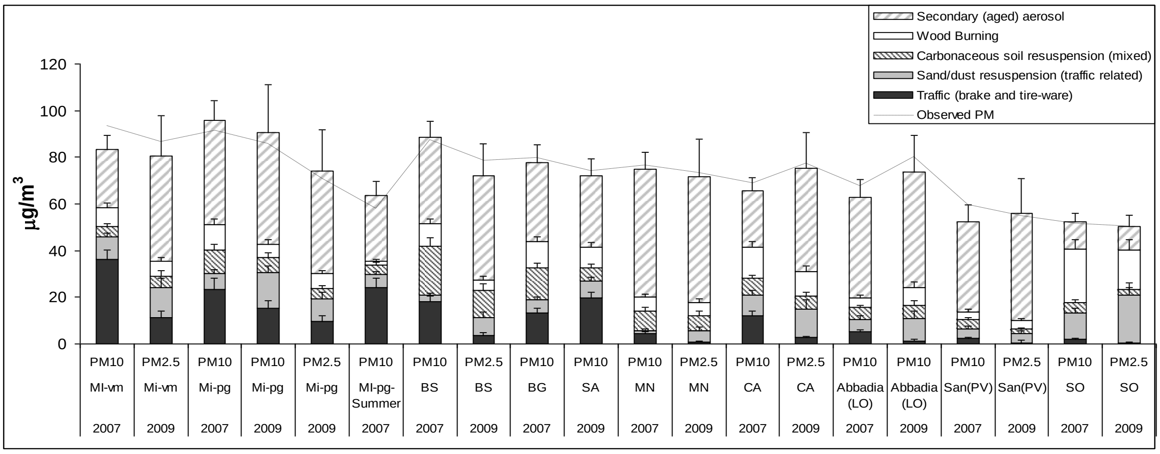


1.6. Source apportionment results as average for the complete sampling period.

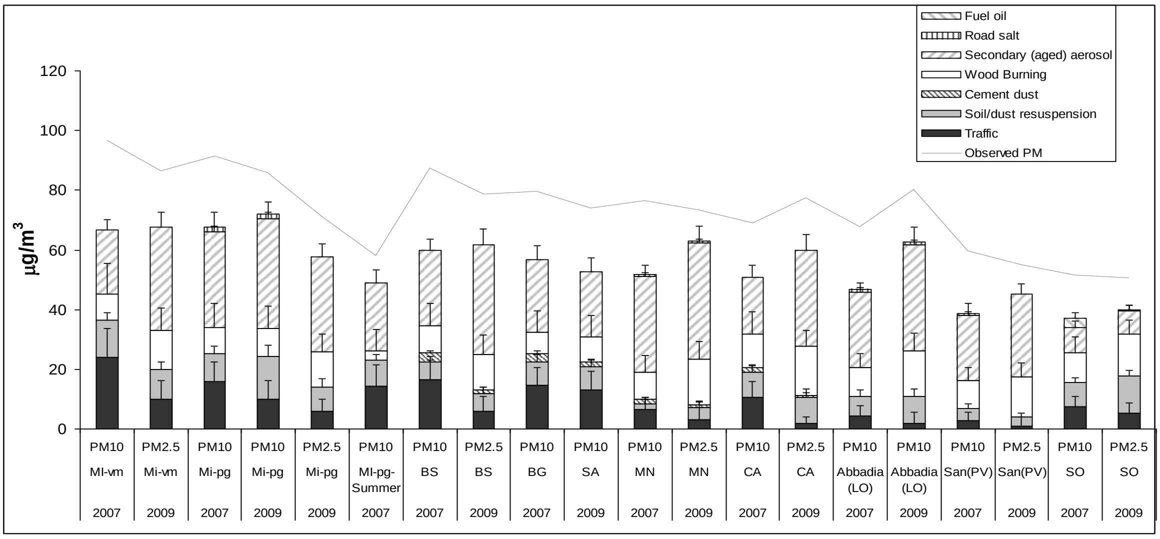
An overview of the source apportionment results averaged for each receptor site and sampling period is given below.

In order for the source apportionment results to be representative for the Lombardy Region it is essential that the PM sampled by JRC correspond to the PM monitored by the air quality authorities. In fact excellent correlations were obtained between the two datasets (ARPA-PM_{10} = - 1.9 µg/m^3 + 0.89 x JRC-$PM_{10,}$ R^2 = 0.94, N=297). Moreover, the PM_{10} concentrations measured by JRC were only slightly higher (13%) than the concentrations reported by ARPA air quality network, which is within the intrinsic uncertainty of receptor modelling.

Good agreements were obtained between PMF and CMB results. A clear difference between the Po Plain stations on one hand and the Valtelline station on the other hand is evident for the influence of secondary, aged aerosol and wood burning. Furthermore a clear influence from traffic is seen not only for the traffic site but also for the urban background stations.

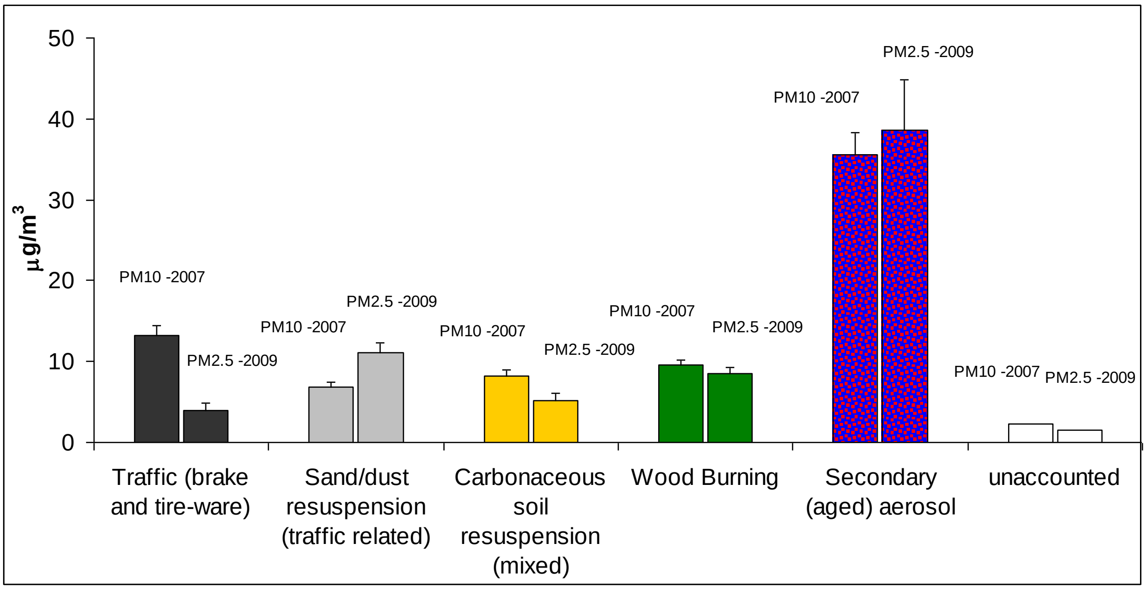


Overview of the PMF source apportionment results for PM averaged for each receptor site and sampling period.

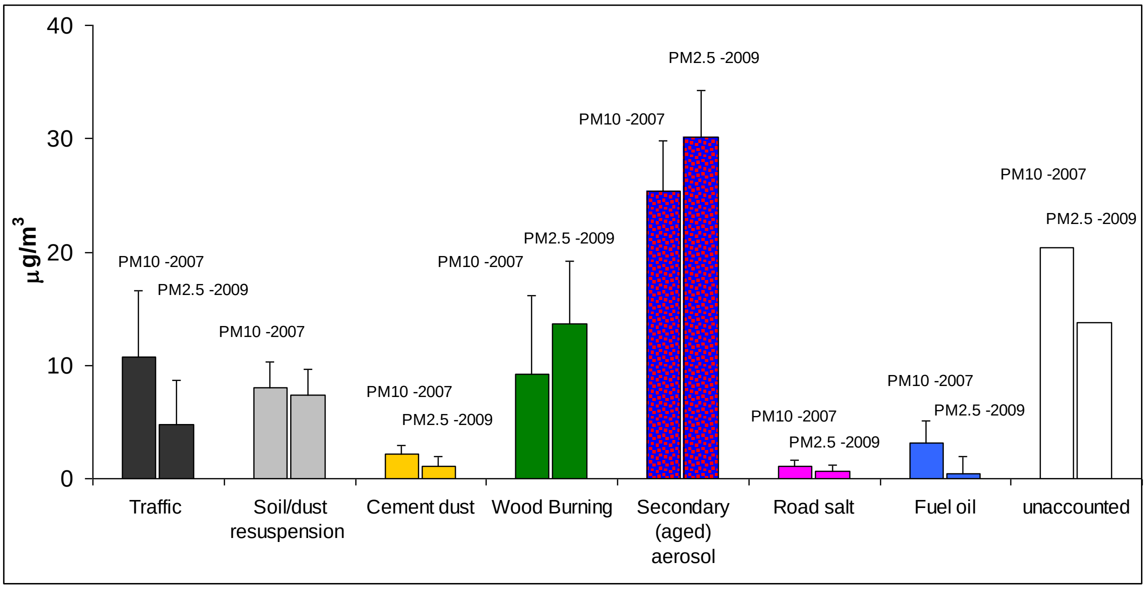


Overview of the CMB source apportionment results for PM averaged for each receptor site and sampling period.

A comparison of the source apportionment results is given below for the PM_{10} measurement campaign in winter 2007 and the $PM_{2.5}$ measurement campaigns in winter 2009. It is evident that the main difference in source apportionment of PM_{10} and $PM_{2.5}$ comes from brake and tire-wear (+ vehicle exhaust), which prevail in the course fraction. The absolute contribution ($\mu g/m^3$) from wood burning is similar for PM_{10} and $PM_{2.5}$ within the 95% confidence limits. The same is the case for secondary, aged aerosol.

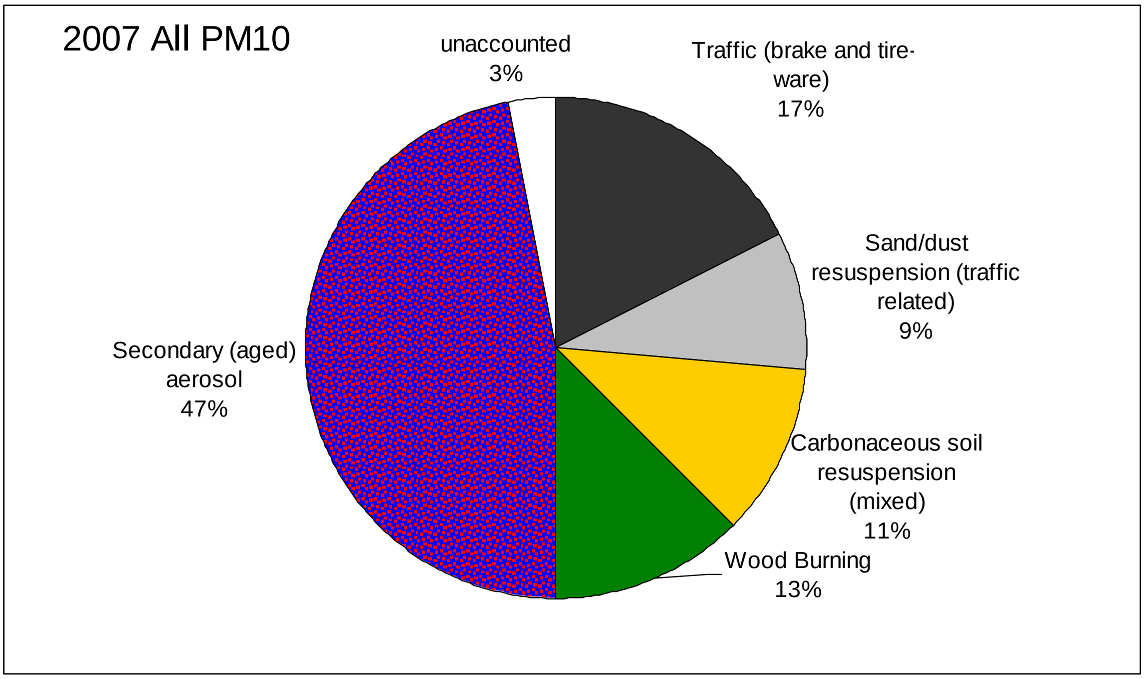


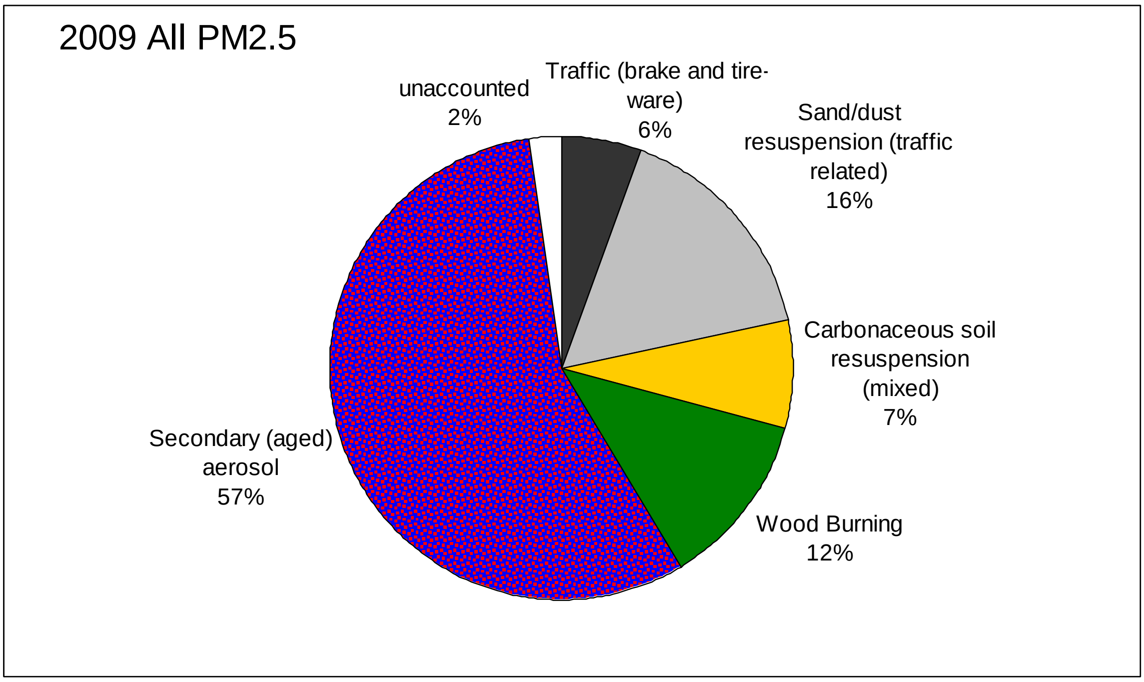
Comparison of the PMF source apportionment results averaged for all receptor sites for the PM_{10} measurement campaign in winter 2007 and the $PM_{2.5}$ measurement campaigns in winter 2009.



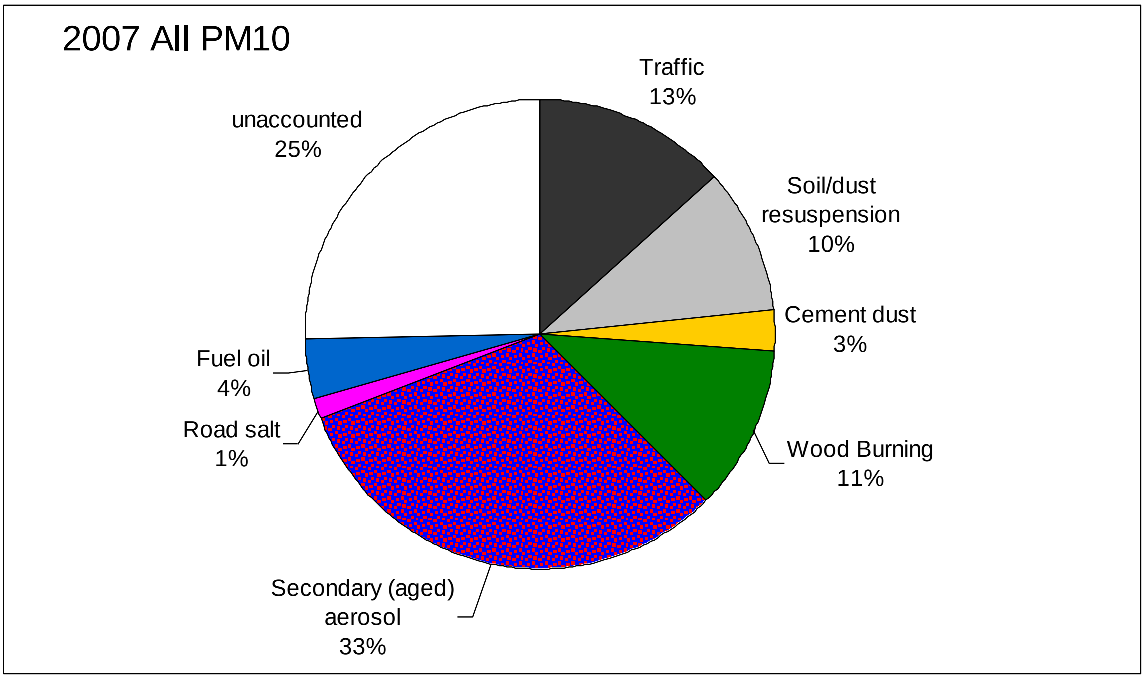
Comparison of the CMB source apportionment results averaged for all receptor site for the PM_{10} measurement campaign in winter 2007 and the $PM_{2.5}$ measurement campaigns in winter 2009.

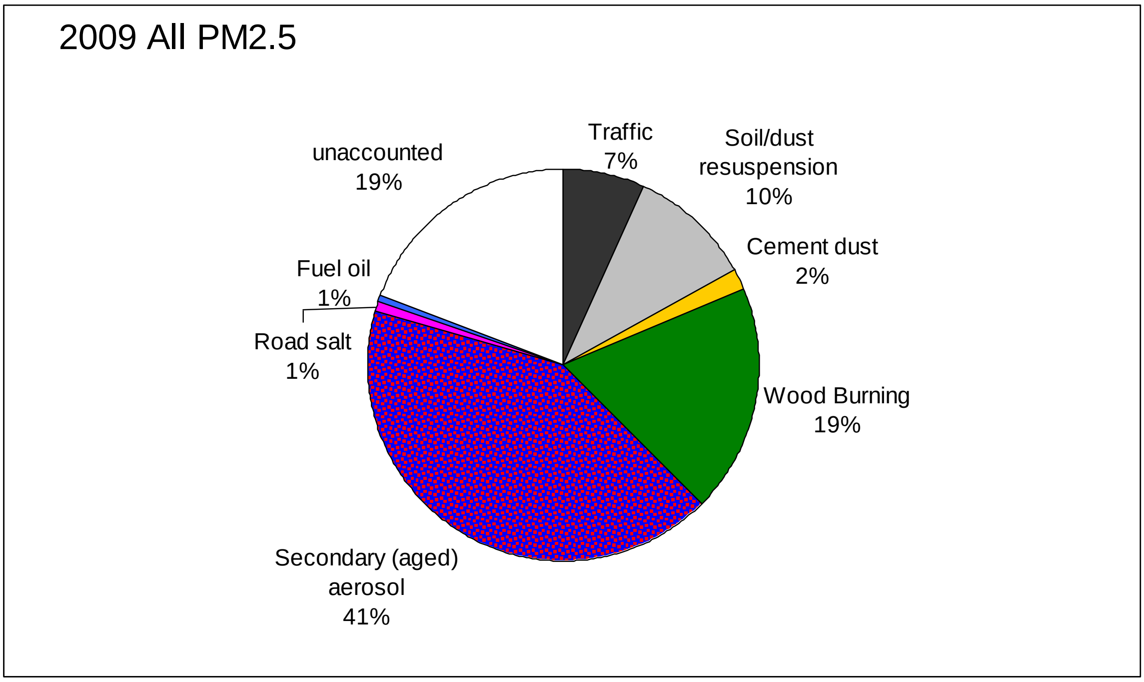
Similar observations can be done for the relative contributions of the various sources as seen below.





Relative (PMF) source contributions for all receptor site for the PM10 measurement campaign in winter 2007 (top) and the PM2.5 measurement campaigns in winter 2009 (bottom).





Relative (CMB) source contributions for all receptor site for the PM_{10} *measurement campaign in winter 2007 (top) and the* $PM_{2.5}$ *measurement campaigns in winter 2009 (bottom).*

2. General conclusions on WP1 activities under the "Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)".

Air pollution in the Po Plain is among the highest of Europe with respect to ambient particulate matter and ozone (see the discussions in Progress Reports I and VI). The EU limit and target values are regularly exceeded as well as the WHO guideline values, and although the Regions of the Po Plain over the past two decades have invested appreciably in air pollution abatement measures, PM_{10} and in particular ozone have not responded with the same significant decreasing trends as CO, SO_2, benzene and to some extent NO_X.

On this background Regione Lombardia and the Joint Research Centre embarked in 2006 on a joint pluriannual research project for air pollution reduction in Lombardy. Work package 1 (WP1) of this project was designed to identify the origin of air pollution in the Region and to apportion sources for ambient particulate matter and ozone.

The efforts spent under WP1 during its five-year duration (2006-2010) have been enormous. Measured on an international scale, this project is one of the largest of its kind. Many thousand samples have been collected from ambient air as well as emission sources and analysed chemically. The obtained measurement data amount to more than thirty thousand data points for PM and more than fifty thousand data points for ozone precursor non-methane hydrocarbons (NMHCs). The obtained data have been used as input to multivariate receptor models, which have yielded source contribution estimates for PM_{10} and $PM_{2.5}$ at ten sites distributed over the Lombardy Region and for ozone precursor NMHCs at 5 sites in the Po Plain and 2 sites in the Valtelline Valley. The sites were mainly located in densely populated areas representing urban background to regional background air quality. To facilitate the comparison of data the sites were designated by ARPA Regione Lombardia within its Air Quality Network. The activities relevant for particulate matter have been focused on winter periods in order to put a figure on the source strength of biomass combustion for residential heating. However, at a selected site also the seasonality of source contributions has been demonstrated. The activities relevant for volatile organic compounds have been focused on summer periods for the apportionment of the impact of the main sources for NMHCs as ozone precursor.

The outcome of the source apportionment activities under the "Contract for the Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)" has been highly successful, which can be explained by a number of factors:

- ✓ An effective planning and management of the source apportionment activities with clear and streamlined objectives and with allocation of dedicated human resources to this work package (The JRC source apportionment team counted nine technicians and scientists),

- ✓ a devoted effort from the source apportionment team during all phases of the project (purchase of equipment, preparation and execution of campaign, quality assurance and control, chemical analysis, modelling, and periodical reporting),
- ✓ a strong collaboration between JRC and ARPA during the planning and execution of measurement campaigns,
- ✓ the investment in state-of-the-art equipment specifically for this project,
- ✓ the outsourcing to specialist laboratories of the physico-chemical characterization of selected key substances (receptor model marker compounds),
- ✓ an open exchange of data and knowledge on receptor modelling between JRC and ARPA scientists throughout the project.

The individual deliverables of WP1 specified in the “Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)” have been described and discussed in details in the Progress Reports from JRC to Regione Lombardia (on a six-month basis). The WP1 activities are summarised in the following and final conclusions are derived.

2.1. Source apportionment of particulate matter

In the period 2007-2009 a large number of sampling campaigns were carried out at receptor sites distributed in Lombardy. The campaigns focused on 24 hours samples of PM_{10} and $PM_{2.5}$ although campaigns were also organised for other fractions of the particulate mater (PM_1) and with higher time resolutions (4 hours).

Details have been described in Progress Reports II and III for PM_{10} and in Progress Reports VI, VII for $PM_{2.5}$ comprising descriptions of the ten receptor sites, analyses of the prevailing meteorological conditions during the sampling campaigns (winter 2006-2007, summer/autumn 2007) the used PM samplers, the installation of equipment at the receptor sites, the sampling, the recollection of samplers and filters, the methods used for gravimetric analysis and physico-chemical analysis of the collected filters.

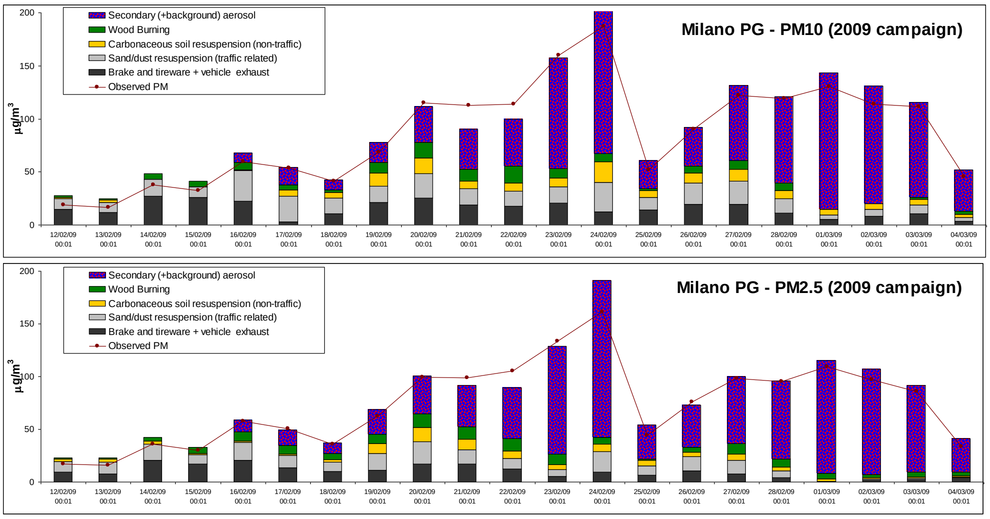
The quality assurance and quality control of the data obtained under the present project were of high priority. Details on the analytical methods and the excellent precision and accuracy of the obtained results for all individual sites have been discussed in Progress Reports IV and V for PM_{10} and in Progress Reports VII and VIII for $PM_{2.5}$, comprising polyaromatic compounds, trace elements, cations and anions, elementary and organic carbon, levoglucosan, and higher alkanes. In order for the source apportionment results to be representative for the Lombardy Region it is essential that the PM sampled by JRC correspond to the PM monitored by the local air quality authorities (ARPA). In fact there were only minor discrepancies between the two data sets. For PM_{10}, the concentrations measured by JRC were 5% to 23% higher than the concentrations reported by ARPA - varying from station to station. This corresponds to an average deviation of less than 13 %, which is in the same order of magnitude as the intrinsic uncertainty of receptor modelling. It was therefore concluded, that for source apportionment purposes the JRC samples are representative of the official air quality data. For $PM_{2.5}$, ARPA monitoring data was only available for a limited number of stations. Thus, only little data was available for comparison, which, however, indicated good agreements.

Discussions of the concentration levels and time evolutions have been included for those compounds (associated with PM_{10}) that are regulated by the EU Air Quality Directives (Pb, Ni, As and Cd and the polyaromatic hydrocarbon benzo(a)pyrene).

The source profiles used for chemical mass balance modelling (CMB) are listed in Appendix 3 of Progress Report V and details are discussed for the sources traffic, wood burning, road-dust re-suspension, cement, road salt, fuel oil combustion, and secondary ammonium sulphate/ ammonium nitrate in Progress Reports V and VII.

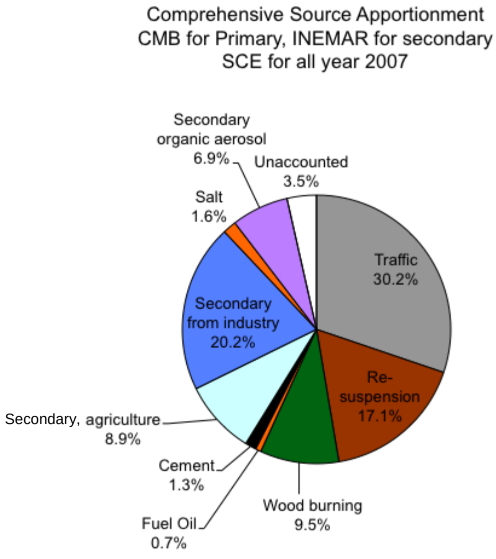
The utilized receptor modelling approach is described in great detail in Progress Reports V, VII and IX. The final results of the source apportionment are presented and discussed in Progress Reports VII and IX for CMB and PMF (positive matrix factorization), respectively. The discussions include descriptions of the estimations of source contributions from secondary, aged aerosol at the ten stations and sensitivity studies for the used receptor models.

CMB and PMF are receptor models working on different principles. CMB de-convolutes the concentrations of chemical compounds measured in ambient PM into source contributions by use of the chemical composition of emission sources. PMF de-convolutes the concentrations of chemical compounds measured in ambient PM into co-varying factors, which needs interpretation by the receptor modeller. Most PMF factors corresponded to individual emission sources, and a few were either mixed (secondary, aged aerosol) or split into two sub-sources (e.g. soil types). However, good agreements were obtained between source apportionment results obtained with PMF and CMB; clear differences were evident between the Po Plain stations and the Valtelline station for the influence of secondary, aged aerosol (highest in the Po Plain) and wood burning (highest at the Valtelline station). The source contribution from traffic was significant not only for the traffic site but also for the urban background stations. PM from all measurement sites contains high concentrations of nitrate and organic carbon. These compounds are the main component of secondary, aged aerosol and the typical build-up of the high winter concentrations of PM in the Po Plain after episodes of clean air was demonstrated to be governed by nitrate and organic carbon. Indeed, the main source for PM was identified to be secondary, aged aerosol, which on average for all stations during the winter campaigns contributed 33-47 % of the PM_{10} mass (2007) and 41-57 % of the $PM_{2.5}$ mass (2009). After the build-up events, the mass of these substances alone, can be sufficient to infringe the 24 h EU Air Quality Limit for PM_{10} of 50 $\mu g/m^3$ (see figure below). Thus, source abatement strategies should be designed to set in against nitrate and organic carbon. Also abatement of ammonia would be beneficial. The main primary source for PM was revealed to be road transport, comprising engine exhaust, brake/tire wear, and re-suspended road dust, which on average for all stations during the winter campaigns contributed 23-26 % of the PM_{10} mass (2007), and 17-22 % of the $PM_{2.5}$ mass (2009). Wood burning was the third most important primary source and contributed on average for all stations during the winter campaigns with 11-13 % of the PM_{10} mass (2007) and 12-19% of the $PM_{2.5}$ mass (2009).



Secondary, aged aerosol is the main component in building up PM pollution after episodes of clean air (winter 2009.

The source apportionment results were slightly different for the Valtelline station (Sondrio), for which wood burning had significantly higher contributions (37-51 % of the PM_{10} mass (2007); 25-43% of the $PM_{2.5}$ mass (2009)) and secondary, aged, aerosol had significantly lower contributions (16-30 % of the PM_{10} mass (2007); 9-29% of the $PM_{2.5}$ mass (2009)).



Estimated source contributions to the annual mean concentration of 44 µg/m^3 PM$_{10}$ in the Lombardy Region, 2007 (ten representative sites).

The extrapolation of the seasonal data obtained for the background station in Milan to all stations in the Po Plain was combined with INEMAR data for gaseous emissions (INventario di EMissioni in ARia - Air Emission Inventory) and indicated, that on a 2007 full year basis the major culprit for PM_{10} pollution in the Po Plain was road transport, which contributed 47±9% of the mass (engine exhaust including secondary contributions from nitrous gases and sulphur dioxide, brake/tire wear, and re-suspended road dust). The contributions from other major sources were secondary, aged aerosol of originating mainly from industry, energy production and residential heating by mainly natural gas (20±3%), wood and biomass burning (10±3%), and secondary aerosol from agriculture (9±3%).

The set objectives for WP1 in the “Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)” were to provide relevant inputs to the Regione Lombardia for the design of abatement strategies in the region with an adequate spatial coverage of the most representative areas of the region. The main conclusion of WP1 is that in order to come to terms with the particulate matter pollution in the Lombardy Region, abatement strategies must be designed that inevitably intervene on road transport and gaseous emissions of NOx from industry and energy production.

The abatement of transport emissions by renewing the vehicle park (Euro 5 for light duty vehicles, Euro 6 for heavy duty vehicles) is essential, but may not be sufficient to reduce the PM pollution below the ambient air EU limits for PM_{10} and $PM_{2.5}$, in as much as such a strategy does not intervene on two significant features of road transport emissions *i.e.* brake/tire wear and traffic related re-suspension of road dust. It is possible that a reduction of the vehicle park (number of vehicles and/or the number of driven kilometres) may be called for.

A strict implementation of the already existing ban in the Po Plain on inefficient wood burning for residential heating can reduce the annual mean concentrations of particulate matter of up to 5 $\mu g/m^3$. The implementation of a ban on biomass/wood burning in the Valtelline Valley would have a higher effect than in the Po Plain and would also be a significant step in abating benzo(a)pyrene, which exceeds the EU limit of 1 ng/m^3 every year.

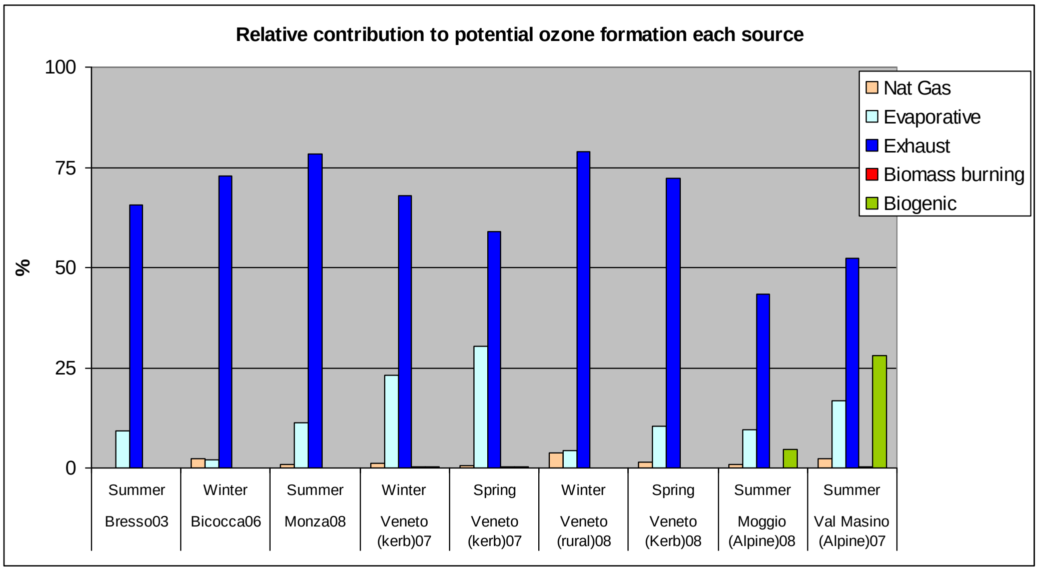
2.2. Source apportionment of ozone precursor non-methane hydrocarbons.

The Ozone Directive 2002/3/EC, which has been in force since 9th September 2003, obliges Member States not only to monitor ozone itself but also its photo-chemically reactive precursors in the air, namely nitrogen oxides and 31 volatile organic compounds (29 non-methane hydrocarbons; NMHCs). One of the aims of NMHC monitoring, as stated in the Ozone Directive, is to obtain data that will increase the understanding of the sources that contribute to tropospheric ozone formation. Under WP1 of the Contract for the Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010) nine NMHC measurement campaigns have been conducted during 2006-2008 and a database (MEGAVOC 2.0) has been set-up for source emission profiles of NMHC based upon JRC measurement from the VELA facilities and upon literature data for non-vehicle emissions. The obtained data has served as input for receptor modelling (chemical mass balance calculations) and the source contributions to tropospheric ozone have been estimated.

Details have been given in Progress Reports II, IV and VI on descriptions of the receptor sites, the analysis of meteorological conditions controlling ozone formation in the Po Valley, the used analytical methodology, the installation of equipment at the receptor sites, the on-line sampling and analysis of NMHCs, the construction of the MEGAVOC 2.0 database, the statistical treatment of data, the utilized receptor modelling approach and the conclusions on direct exhaust emissions versus evaporative emissions. The following conclusions can be derived:

Five significant sources were responsible for approximately 90 % of the NMHCs emissions: *Exhaust* (the sum of diesel, and gasoline exhaust emissions), *Evaporative* (the sum of evaporative vehicle emissions), *Natural Gas* (sum of incompletely combusted natural gas and fugitive emissions of natural gas components from the distribution network - including compressor stations), *Biogenic* (emissions of isoprene and terpenoids from vegetation), and *Biomass burning* (hydrocarbons generated through incomplete combustion of wood for residential heating and agricultural biomass combustion).

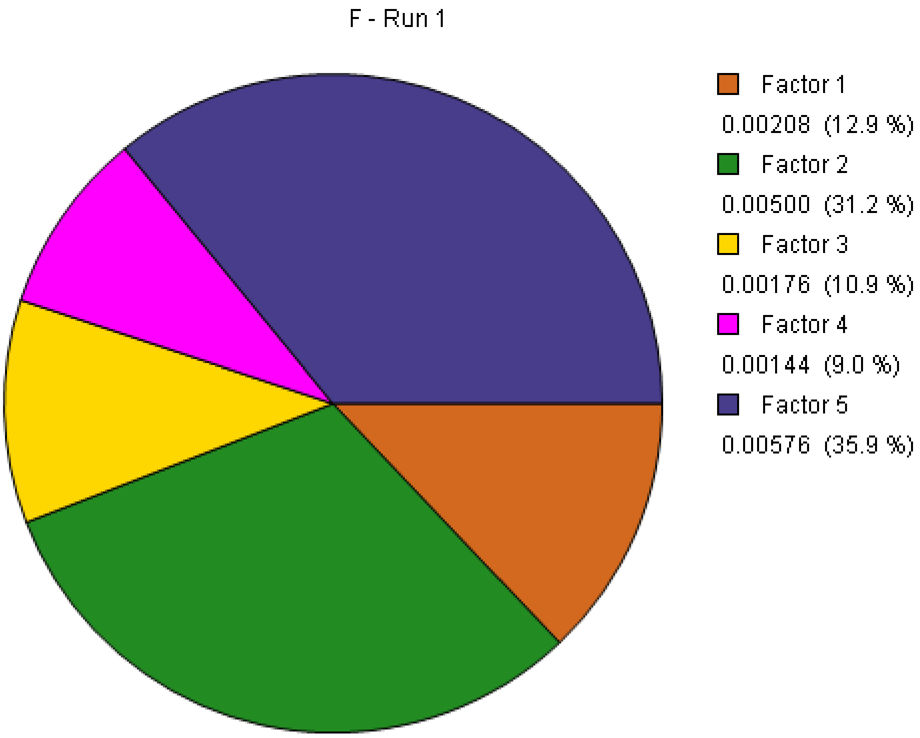
The most significant source for NMHCs was found to be vehicle exhaust, which contributed to the total NMHC concentration from 30-35% at the remote sites to 40-45 % at the traffic sites. The chemical composition of vehicle exhaust consisted of many compounds with a high ozone formation potential. When converted to potential (maximal) ozone concentrations (µg/m^3) using the MIR approach (*W.P.L. Carter. 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manage. Assoc., 44, 881*) for atmospheric conditions in excess of NO$_X$ (which indeed is fulfilled at all moments for all sites with the possible exception of night time values at Val Masino) the source contributions of vehicle exhaust emissions was revealed to be dominating at all the investigated sites (se figure below). This is a significant result for designing a future ozone abatement strategy in the Po Plain.

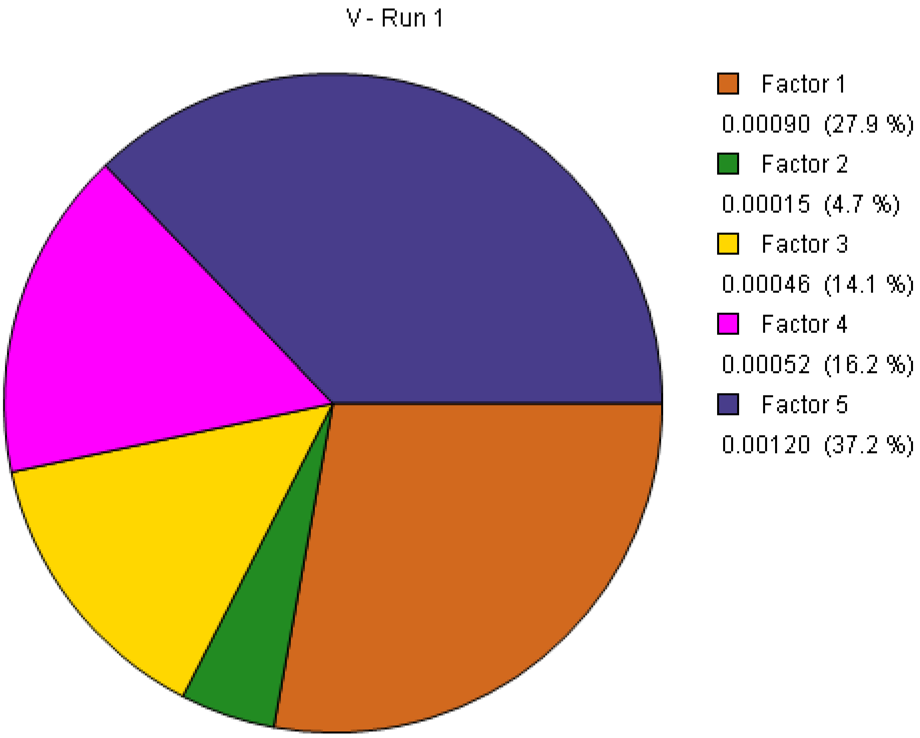


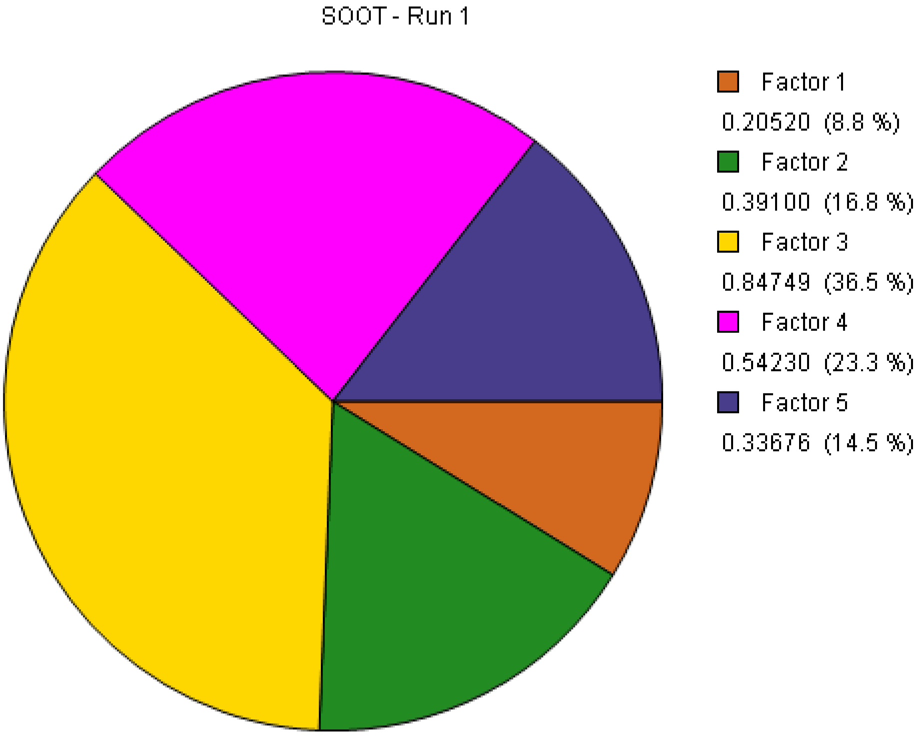
Potential contribution to ozone formation of the five significant NMHC sources.

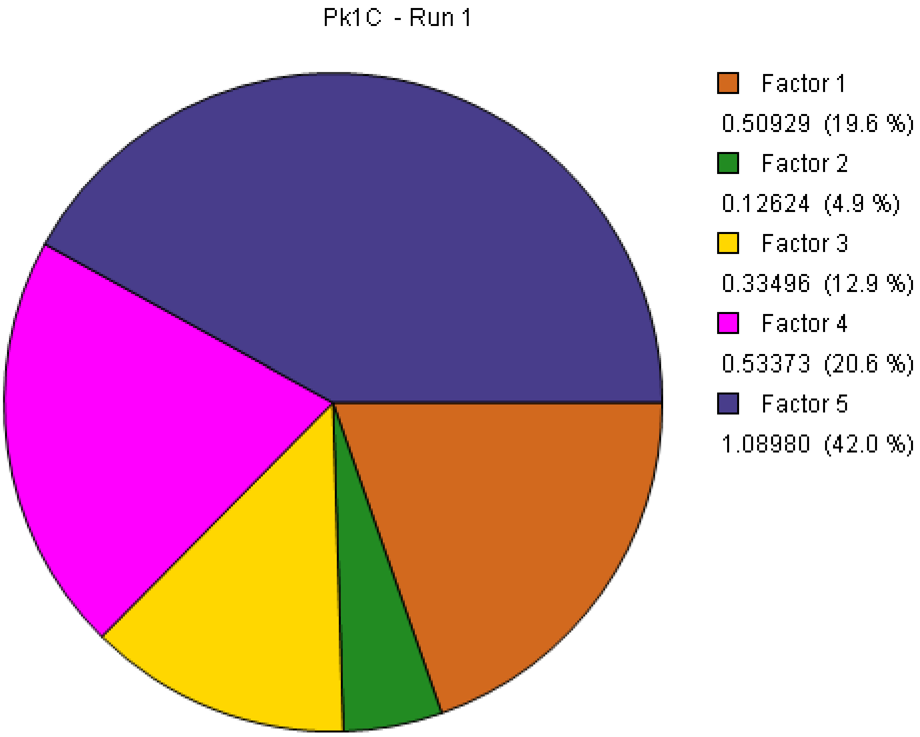
These conclusions complete the obligations laid down in the “Contract for the Collaborative Research Project for Air Pollution Reduction in Lombardia (2006-2010)” regarding Work Package 1: “Identification of air pollution origin: Source apportionment”.

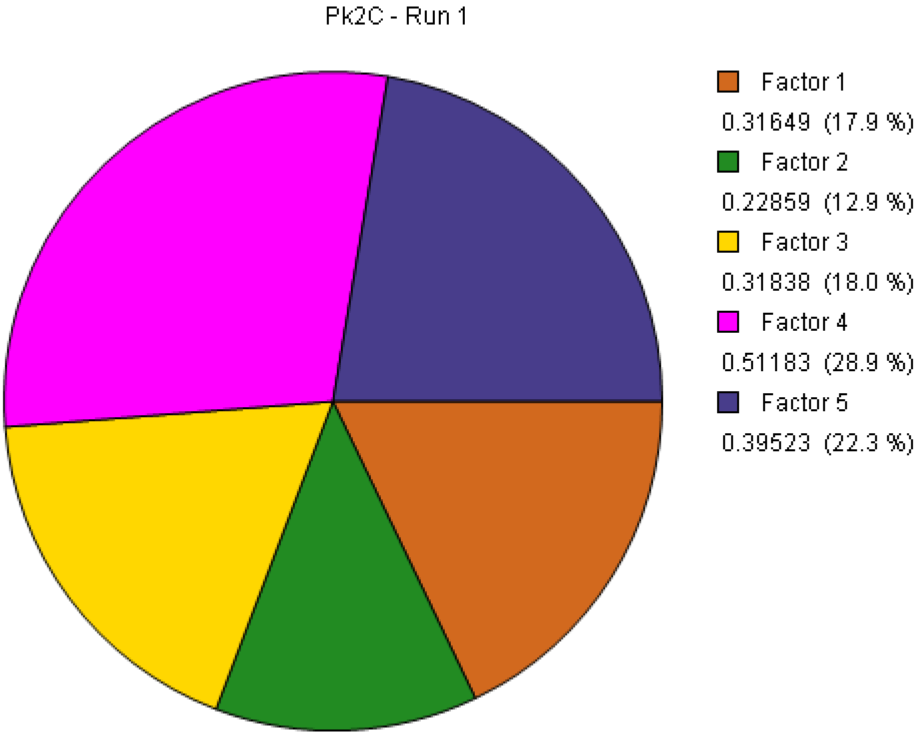
Appendix 1: Source contribution estimates for other receptor compounds

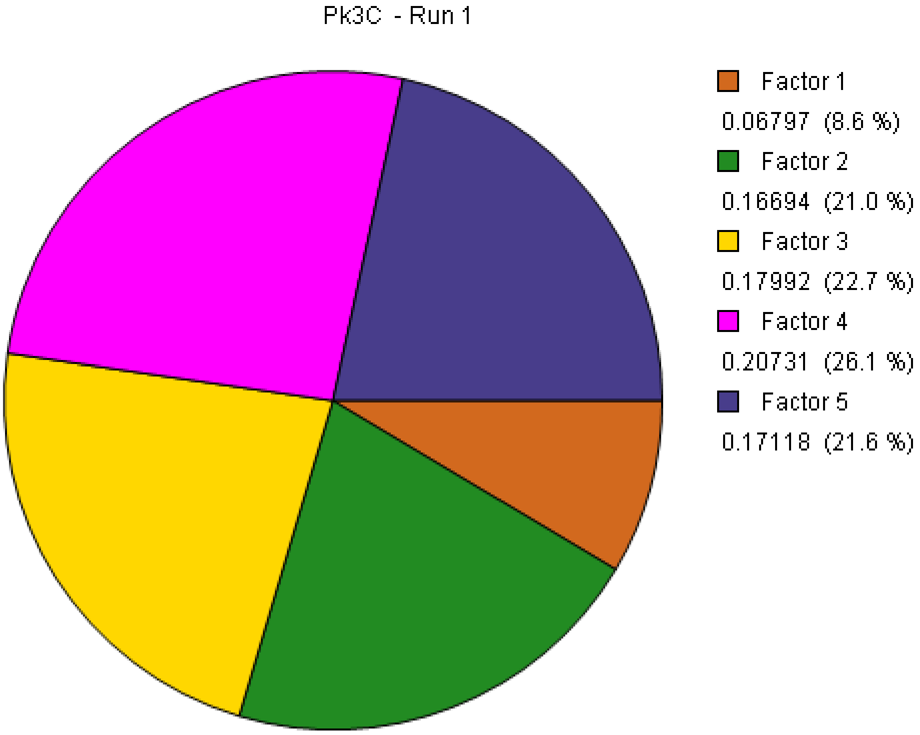


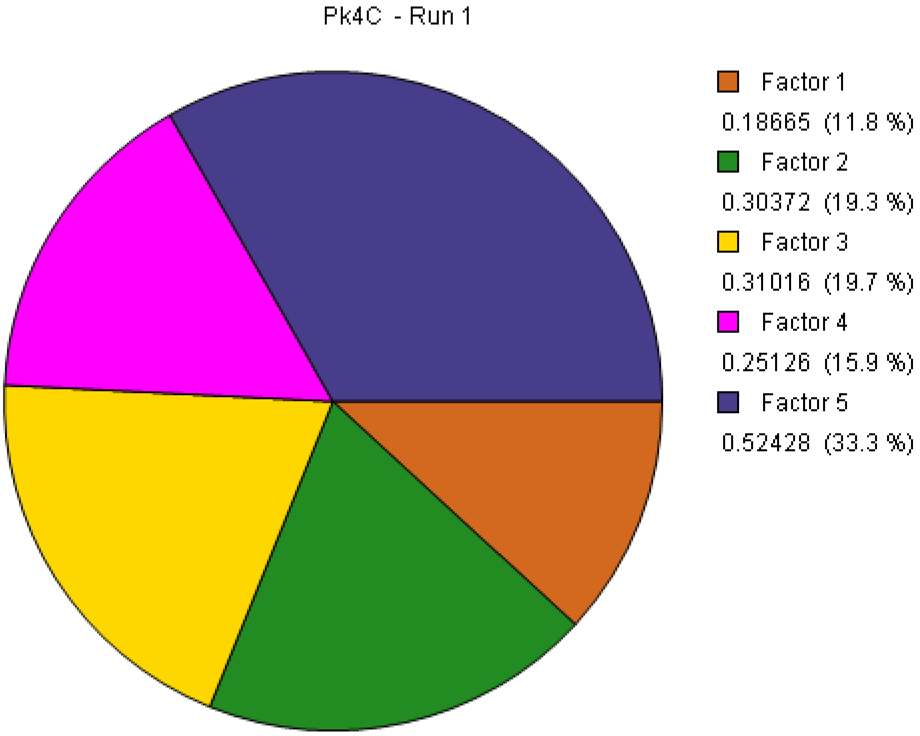


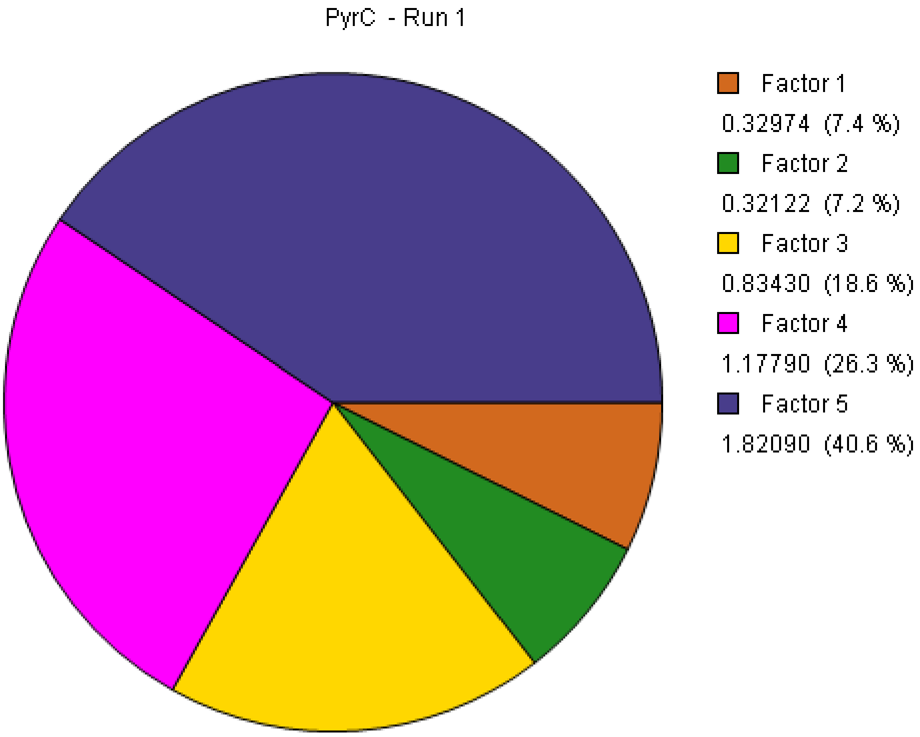

SOOT - Run 1

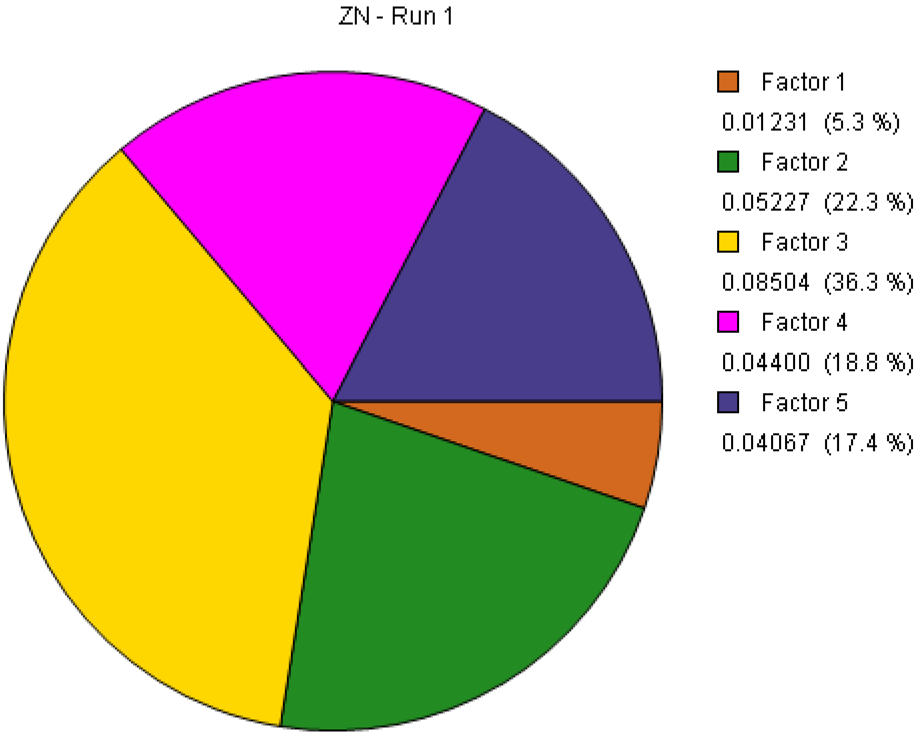

Pk1C - Run 1

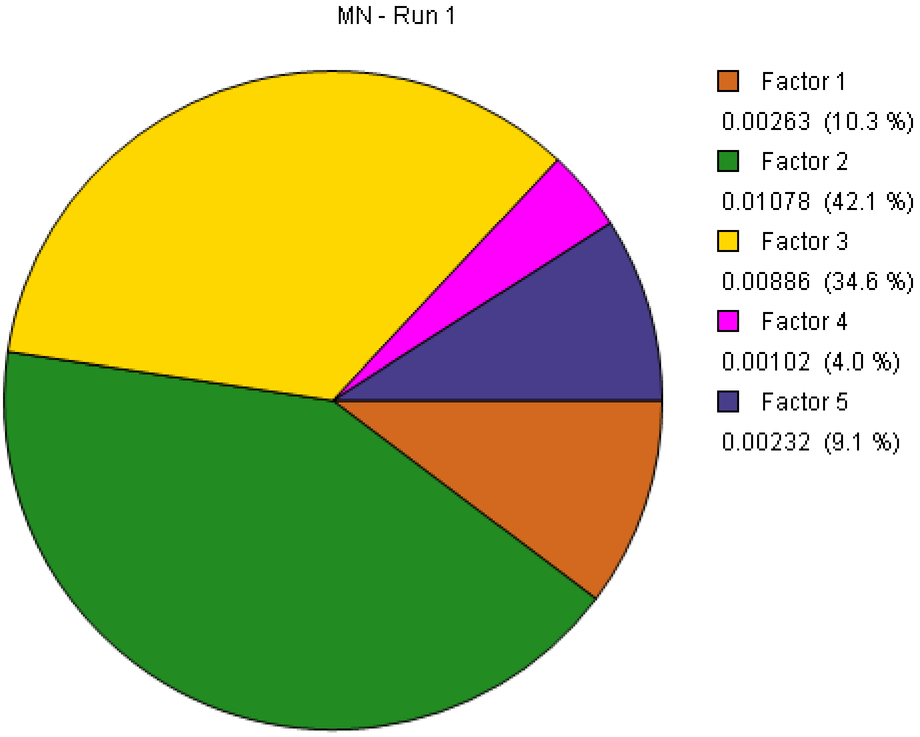

Pk2C - Run 1
Factor 1
0.31649 (17.9 %)
Factor 2
0.22859 (12.9 %)
Factor 3
0.31838 (18.0 %)
Factor 4
0.51183 (28.9 %)
Factor 5
0.39523 (22.3 %)

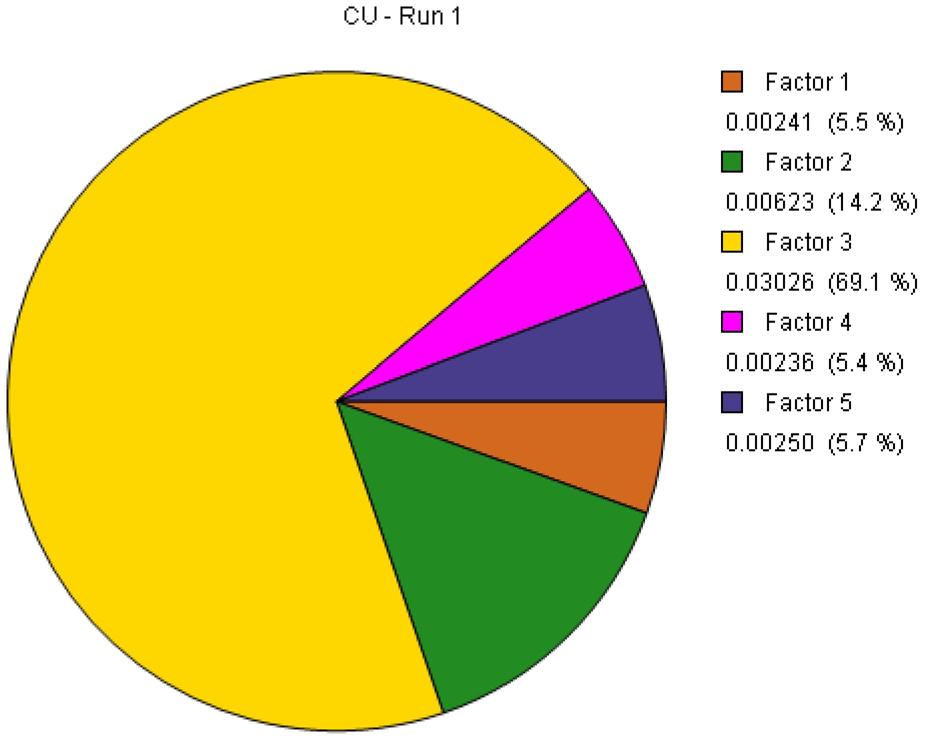

Pk3C - Run 1
Factor 1
0.06797 (8.6 %)
Factor 2
0.16694 (21.0 %)
Factor 3
0.17992 (22.7 %)
Factor 4
0.20731 (26.1 %)
Factor 5
0.17118 (21.6 %)

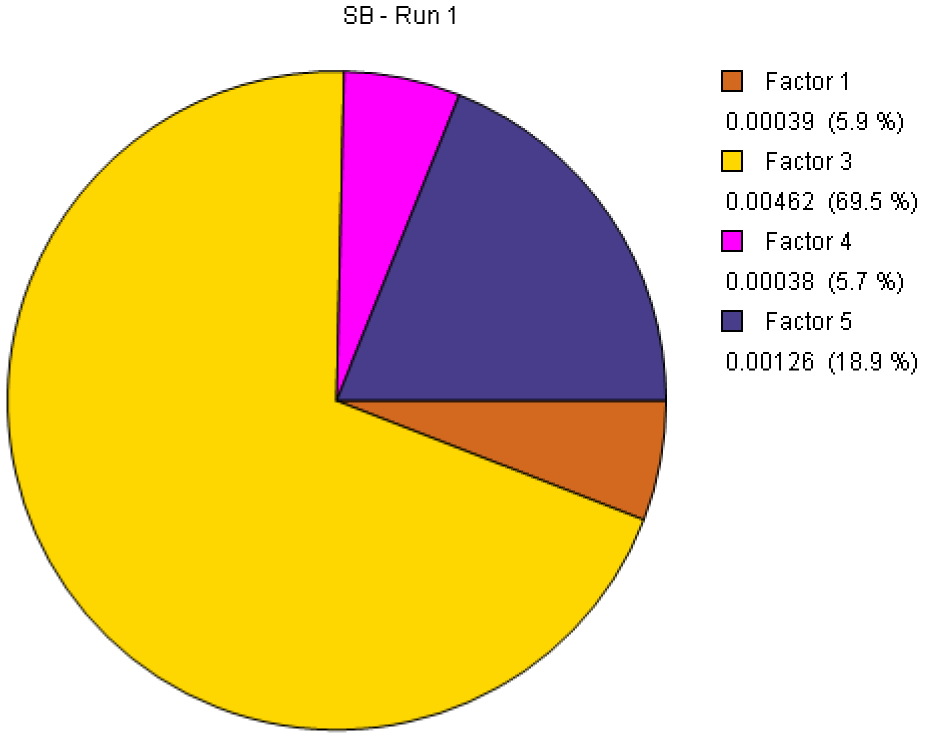

Pk4C - Run 1
Factor 1
0.18665 (11.8 %)
Factor 2
0.30372 (19.3 %)
Factor 3
0.31016 (19.7 %)
Factor 4
0.25126 (15.9 %)
Factor 5
0.52428 (33.3 %)

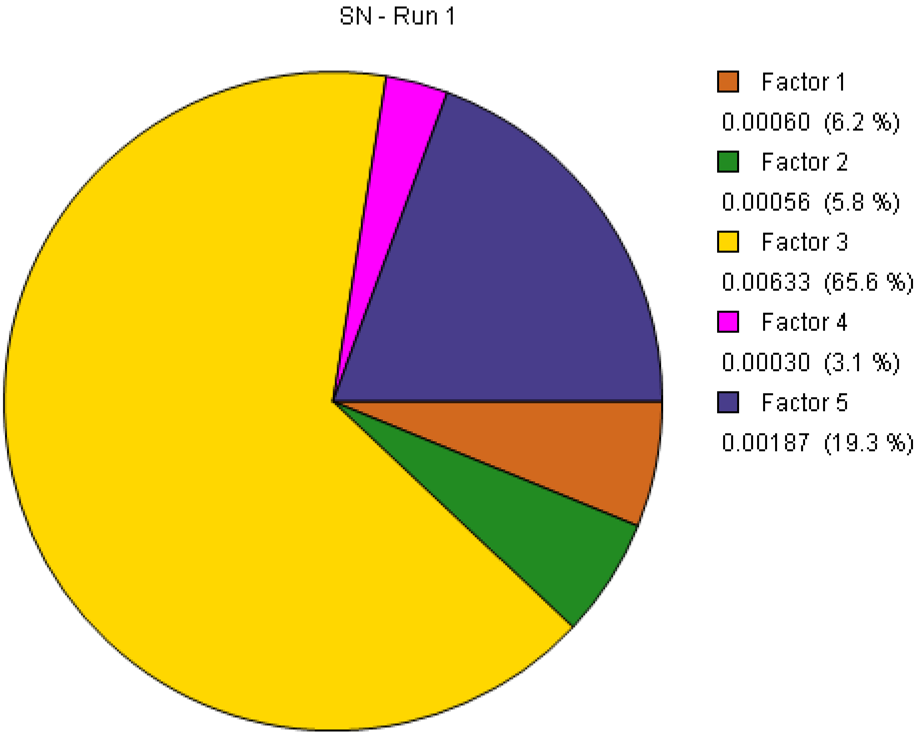

PyrC - Run 1
Factor 1
0.32974 (7.4 %)
Factor 2
0.32122 (7.2 %)
Factor 3
0.83430 (18.6 %)
Factor 4
1.17790 (26.3 %)
Factor 5
1.82090 (40.6 %)

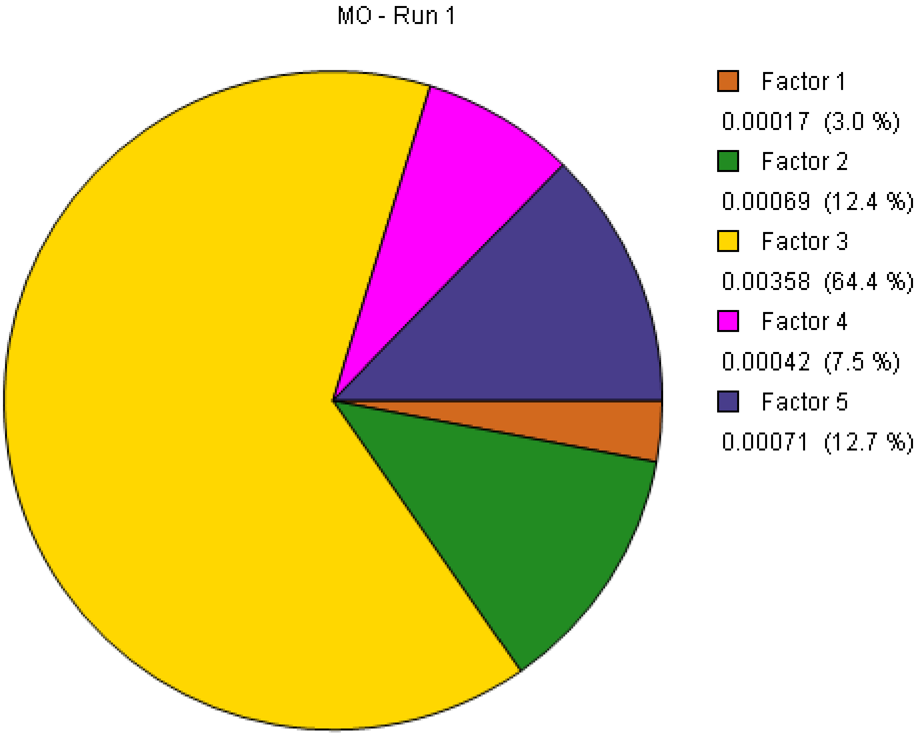

ZN - Run 1
Factor 1
0.01231 (5.3 %)
Factor 2
0.05227 (22.3 %)
Factor 3
0.08504 (36.3 %)
Factor 4
0.04400 (18.8 %)
Factor 5
0.04067 (17.4 %)

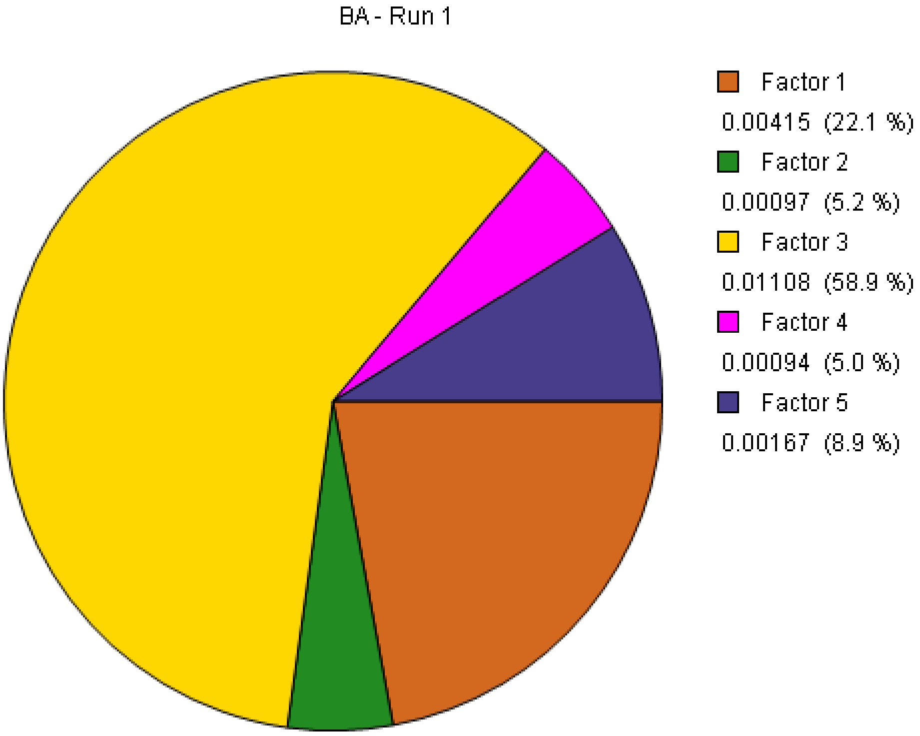

MN - Run 1
Factor 1
0.00263 (10.3 %)
Factor 2
0.01078 (42.1 %)
Factor 3
0.00886 (34.6 %)
Factor 4
0.00102 (4.0 %)
Factor 5
0.00232 (9.1 %)

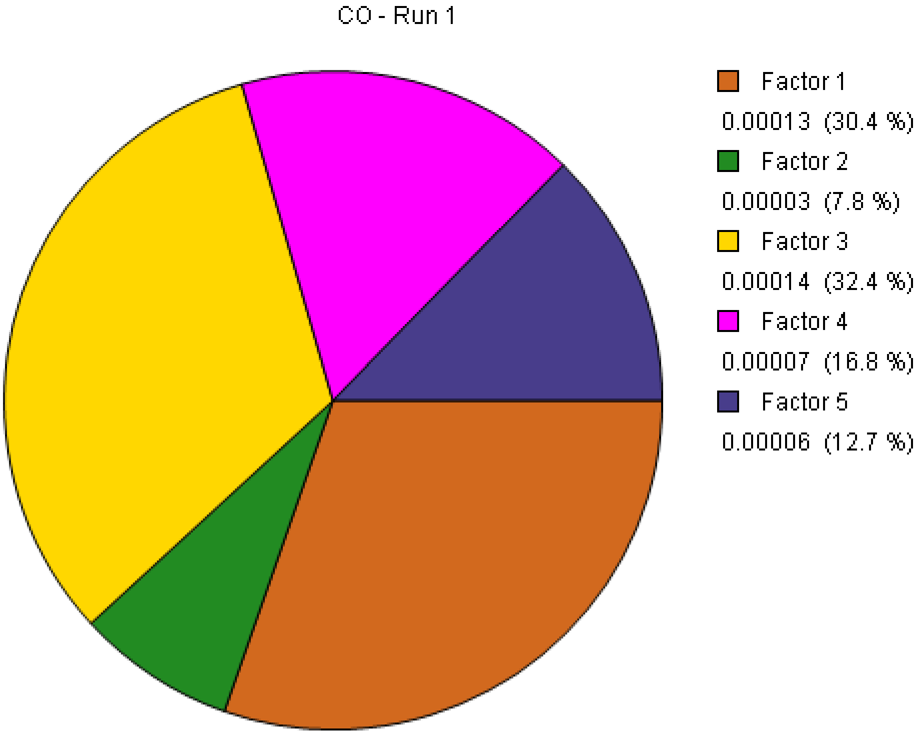

CU - Run 1
Factor 1
0.00241 (5.5 %)
Factor 2
0.00623 (14.2 %)
Factor 3
0.03026 (69.1 %)
Factor 4
0.00236 (5.4 %)
Factor 5
0.00250 (5.7 %)

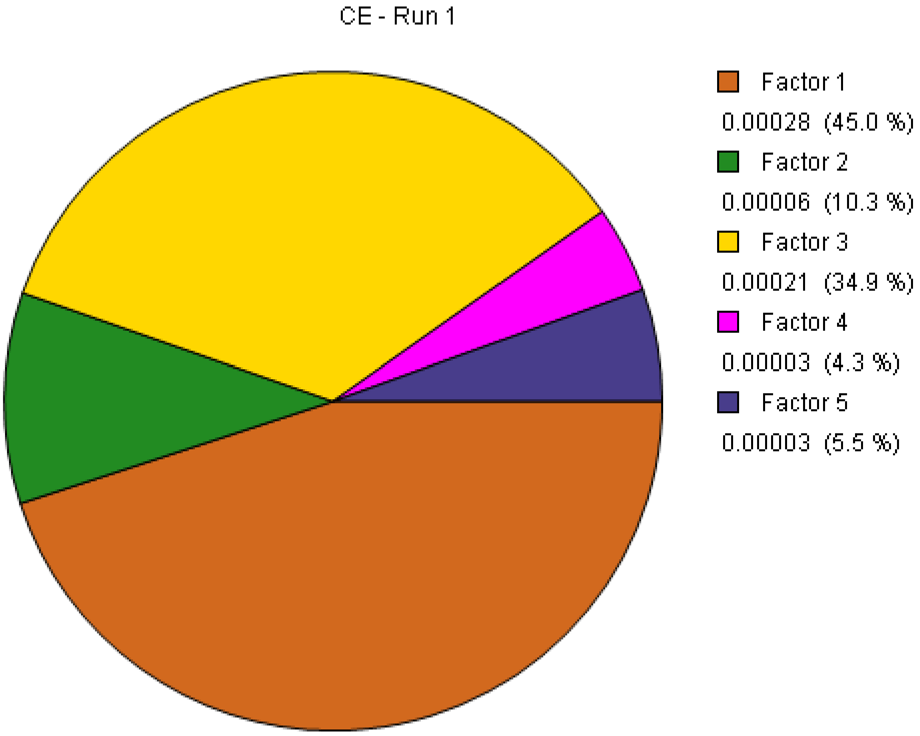

SB - Run 1
Factor 1
0.00039 (5.9 %)
Factor 3
0.00462 (69.5 %)
Factor 4
0.00038 (5.7 %)
Factor 5
0.00126 (18.9 %)

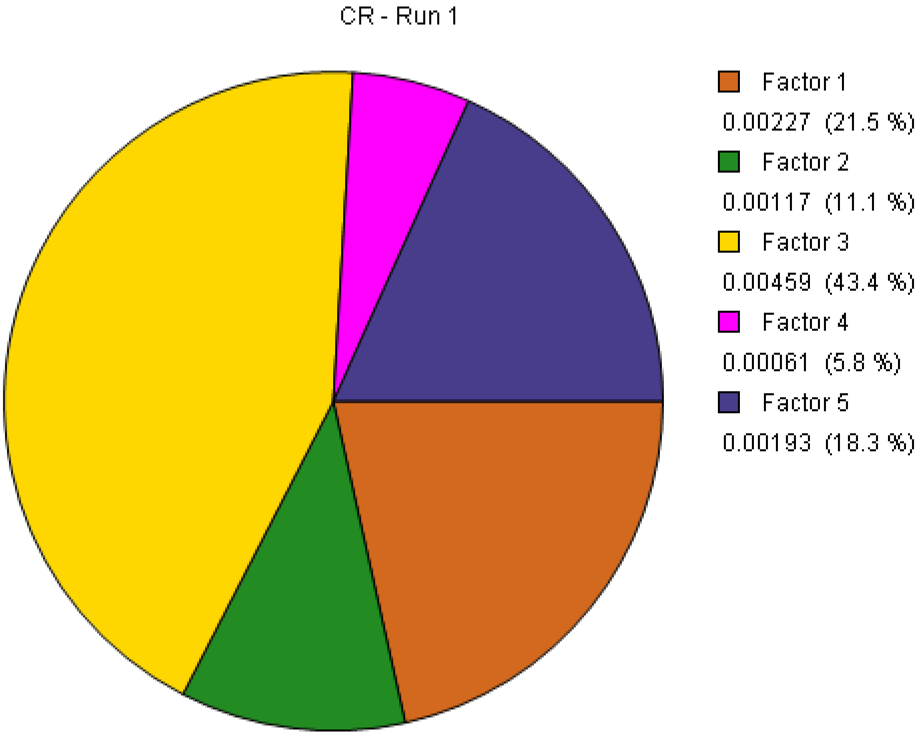

SN - Run 1
Factor 1
0.00060 (6.2 %)
Factor 2
0.00056 (5.8 %)
Factor 3
0.00633 (65.6 %)
Factor 4
0.00030 (3.1 %)
Factor 5
0.00187 (19.3 %)

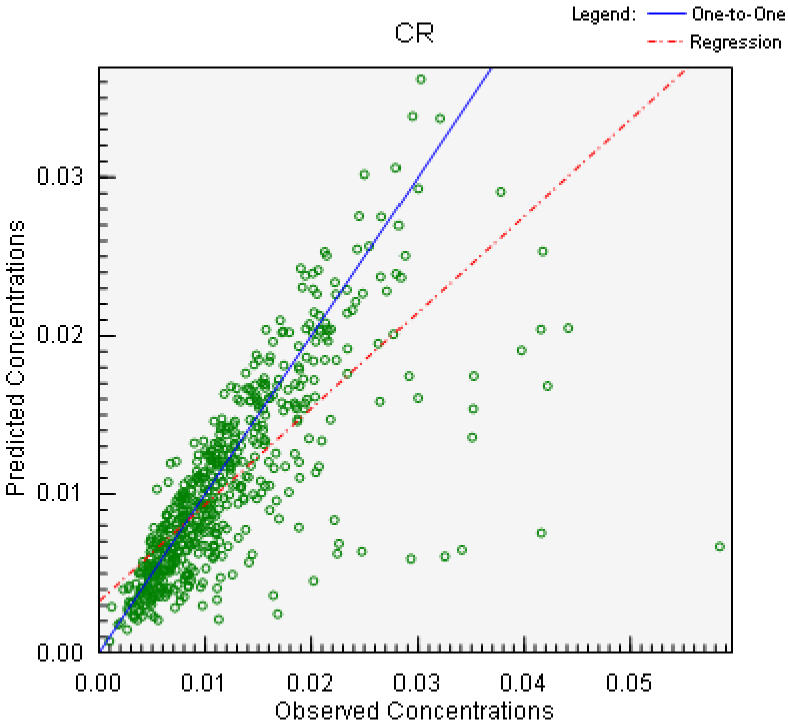

MO - Run 1
Factor 1
0.00017 (3.0 %)
Factor 2
0.00069 (12.4 %)
Factor 3
0.00358 (64.4 %)
Factor 4
0.00042 (7.5 %)
Factor 5
0.00071 (12.7 %)


BA - Run 1
Factor 1
0.00415 (22.1 %)
Factor 2
0.00097 (5.2 %)
Factor 3
0.01108 (58.9 %)
Factor 4
0.00094 (5.0 %)
Factor 5
0.00167 (8.9 %)

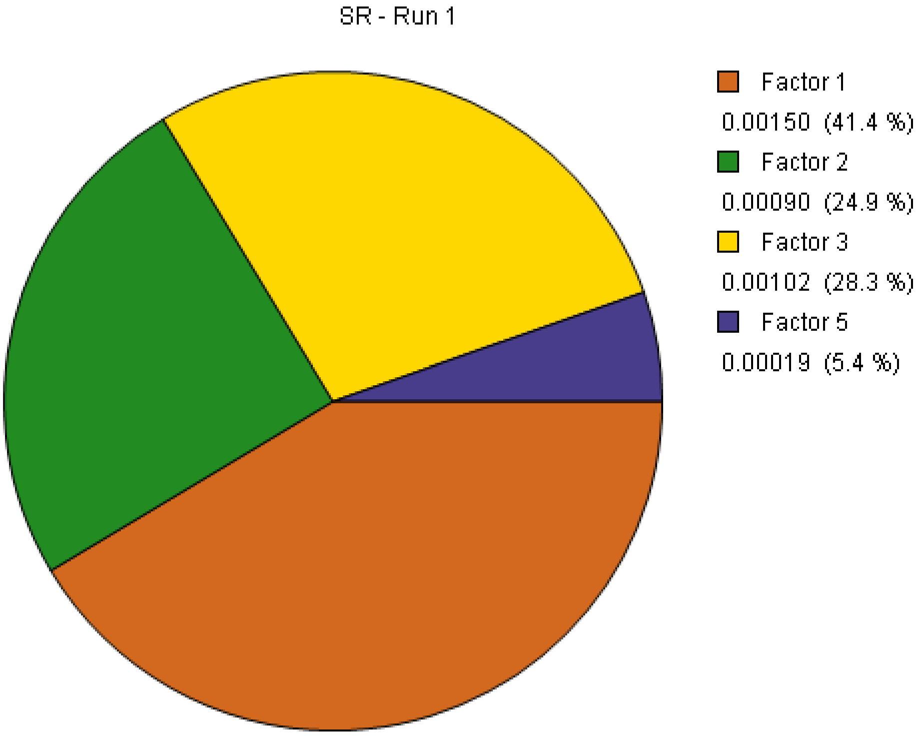

CO - Run 1
Factor 1
0.00013 (30.4 %)
Factor 2
0.00003 (7.8 %)
Factor 3
0.00014 (32.4 %)
Factor 4
0.00007 (16.8 %)
Factor 5
0.00006 (12.7 %)

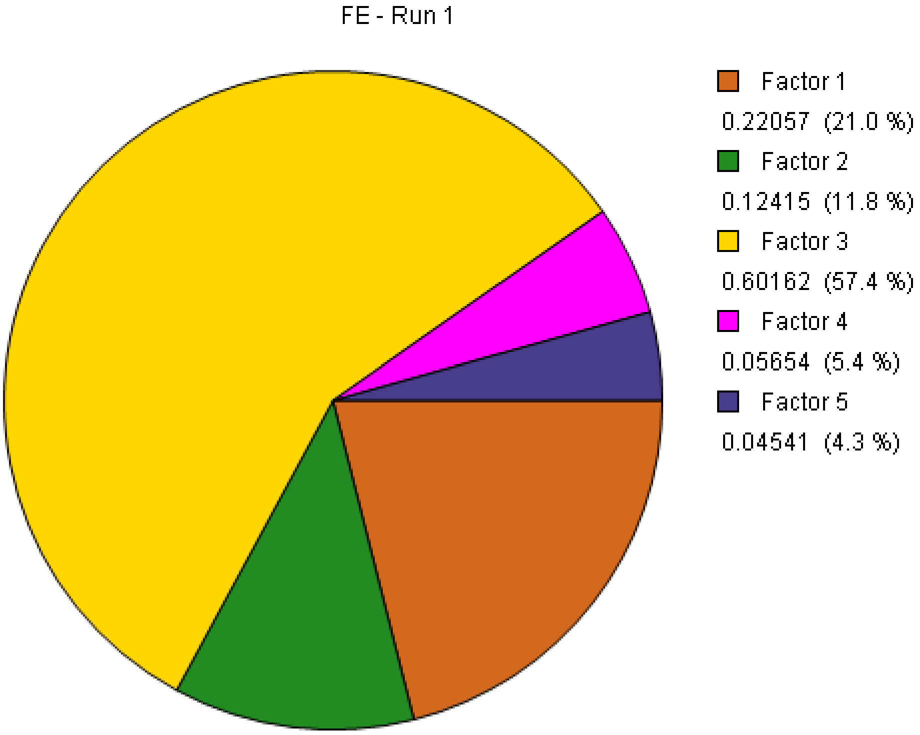

CE - Run 1
Factor 1
0.00028 (45.0 %)
Factor 2
0.00006 (10.3 %)
Factor 3
0.00021 (34.9 %)
Factor 4
0.00003 (4.3 %)
Factor 5
0.00003 (5.5 %)

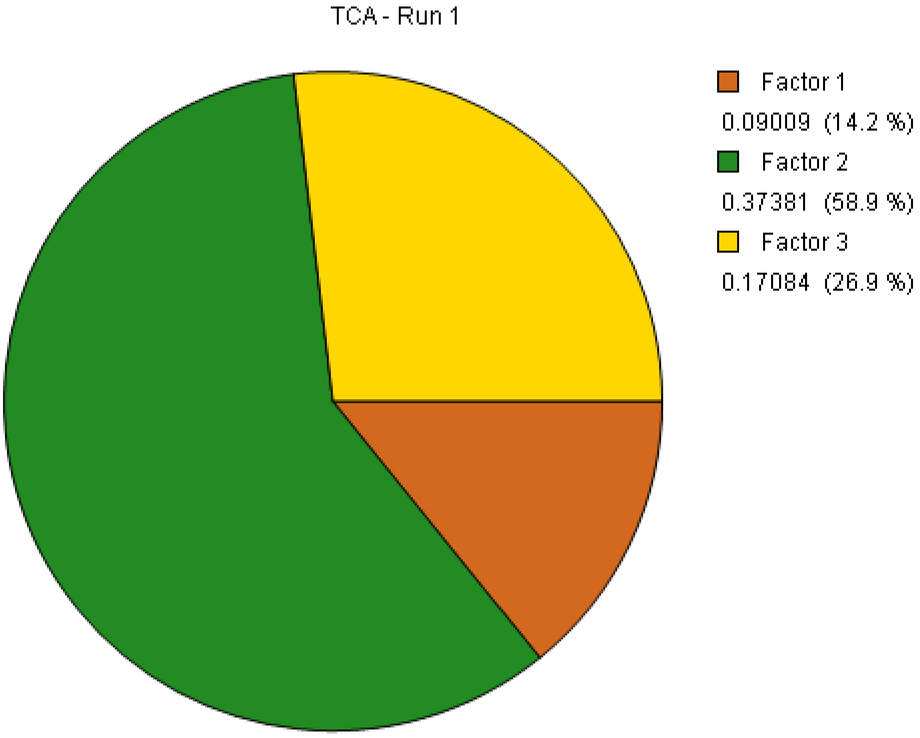


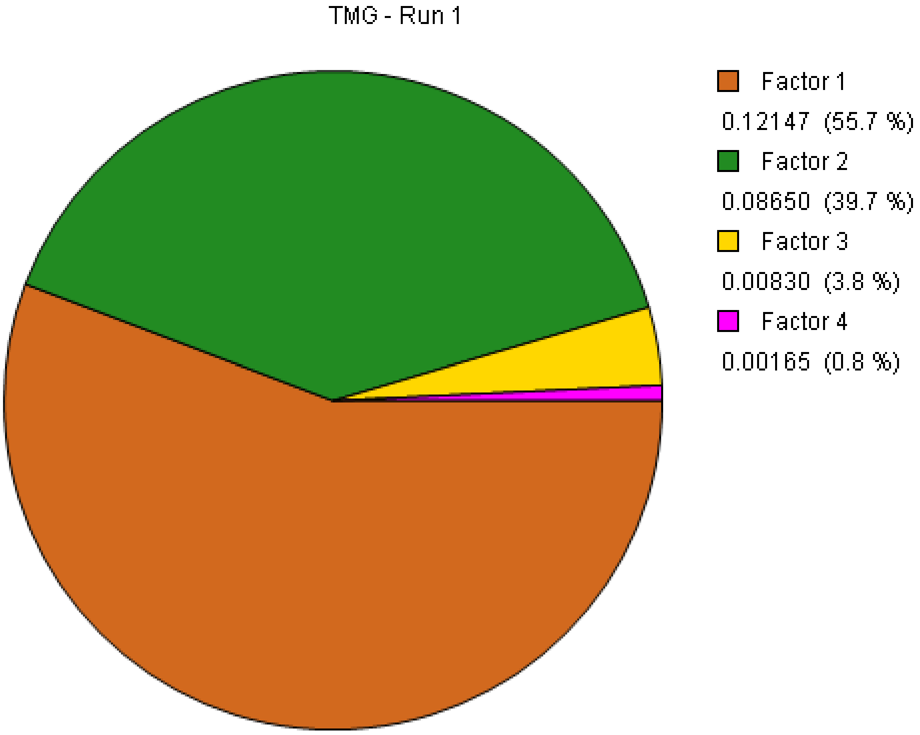


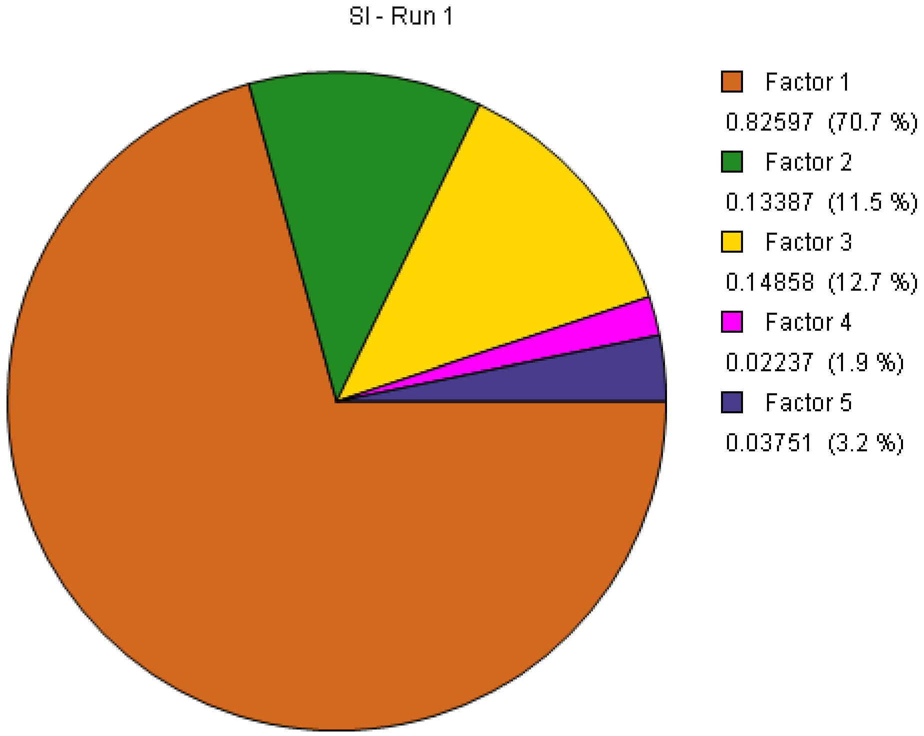
Predicted = 0.00032(±0.00003) + 0.61(±0.02) * Observed; R^2 = 0.55.

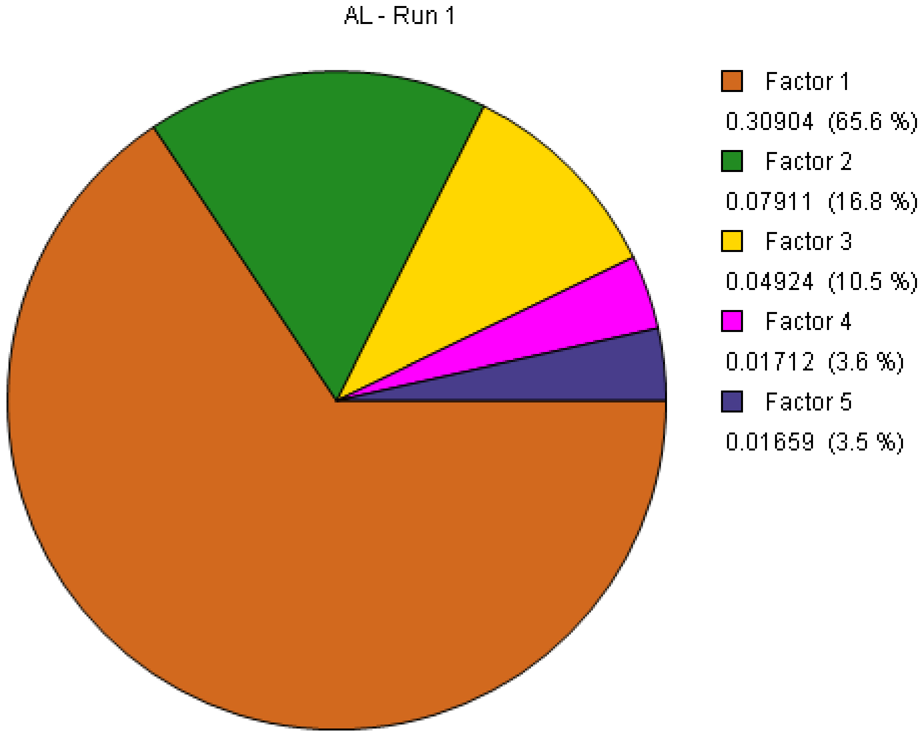

SR - Run 1
Factor 1
0.00150 (41.4 %)
Factor 2
0.00090 (24.9 %)
Factor 3
0.00102 (28.3 %)
Factor 5
0.00019 (5.4 %)

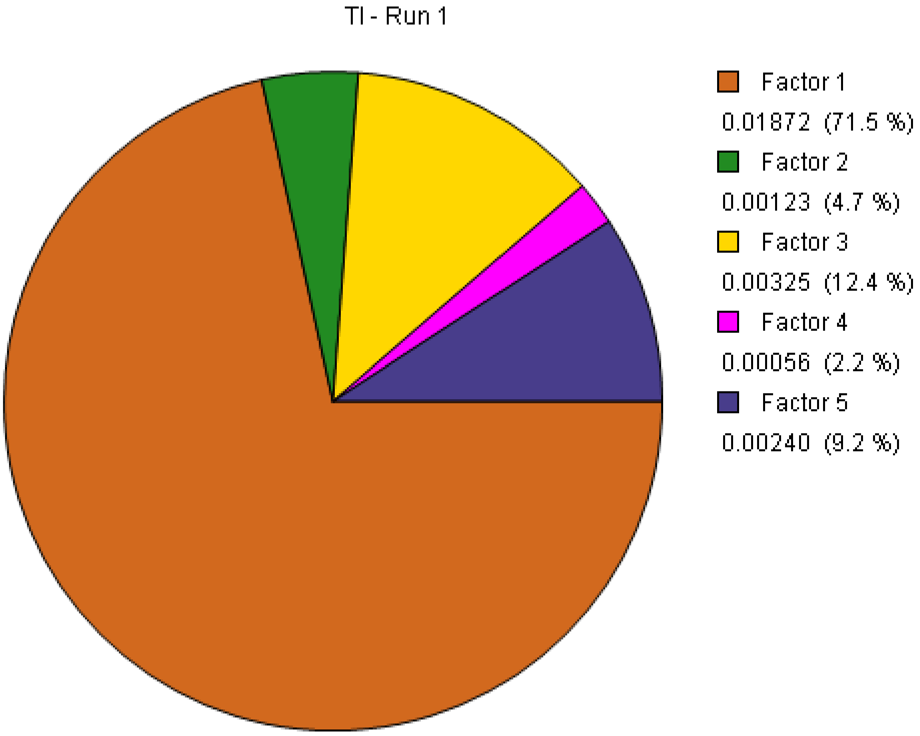

FE - Run 1
Factor 1
0.22057 (21.0 %)
Factor 2
0.12415 (11.8 %)
Factor 3
0.60162 (57.4 %)
Factor 4
0.05654 (5.4 %)
Factor 5
0.04541 (4.3 %)

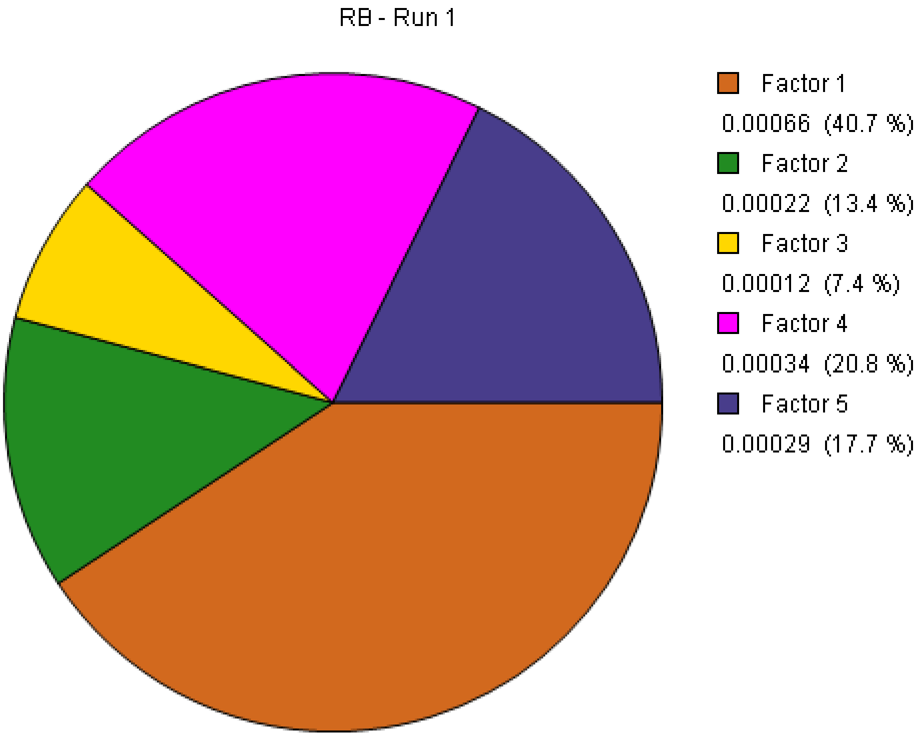

TCA - Run 1
Factor 1
0.09009 (14.2 %)
Factor 2
0.37381 (58.9 %)
Factor 3
0.17084 (26.9 %)

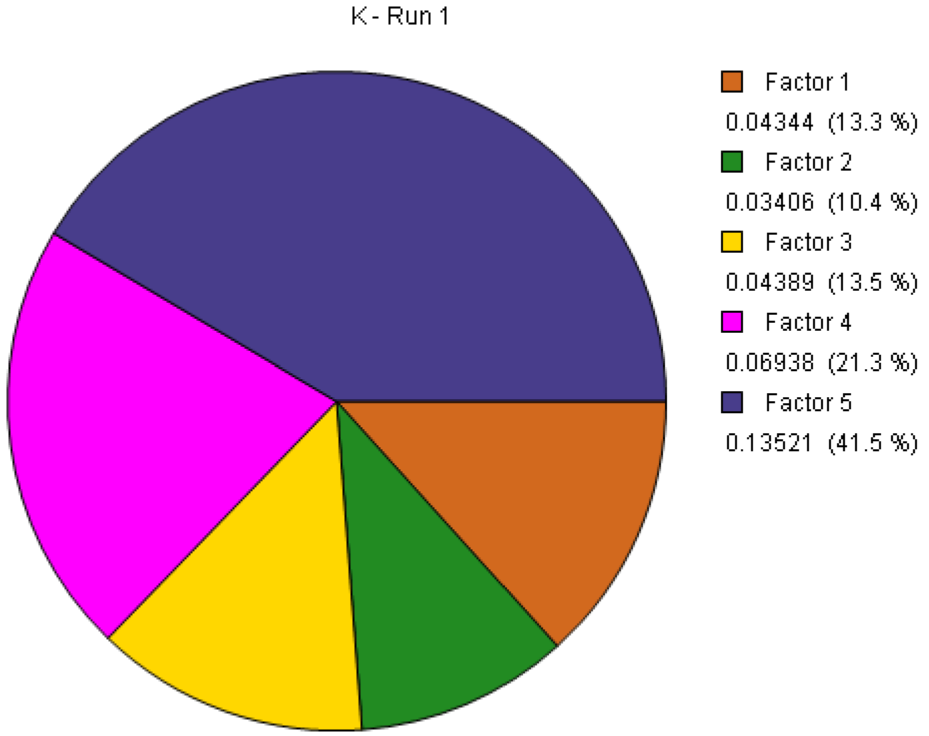

TMG - Run 1
Factor 1
0.12147 (55.7 %)
Factor 2
0.08650 (39.7 %)
Factor 3
0.00830 (3.8 %)
Factor 4
0.00165 (0.8 %)

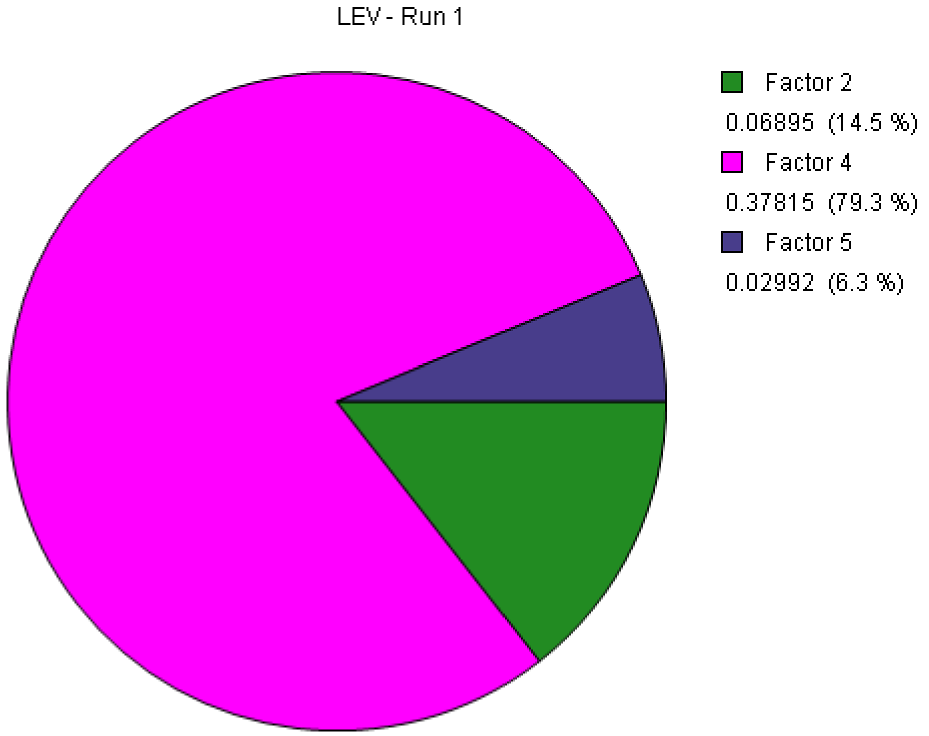

SI - Run 1
Factor 1
0.82597 (70.7 %)
Factor 2
0.13387 (11.5 %)
Factor 3
0.14858 (12.7 %)
Factor 4
0.02237 (1.9 %)
Factor 5
0.03751 (3.2 %)

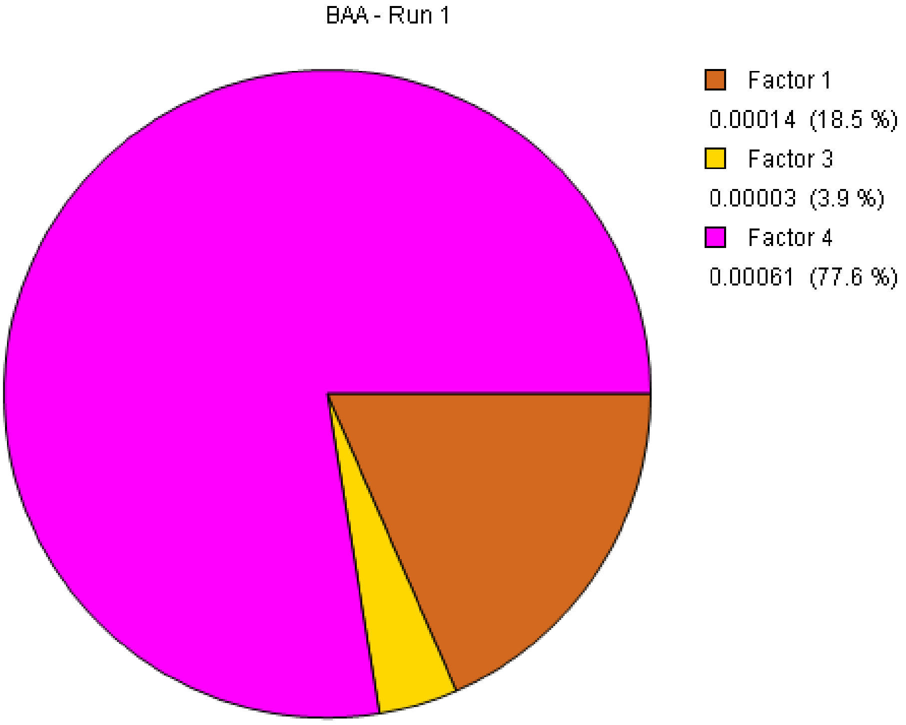

AL - Run 1
Factor 1
0.30904 (65.6 %)
Factor 2
0.07911 (16.8 %)
Factor 3
0.04924 (10.5 %)
Factor 4
0.01712 (3.6 %)
Factor 5
0.01659 (3.5 %)

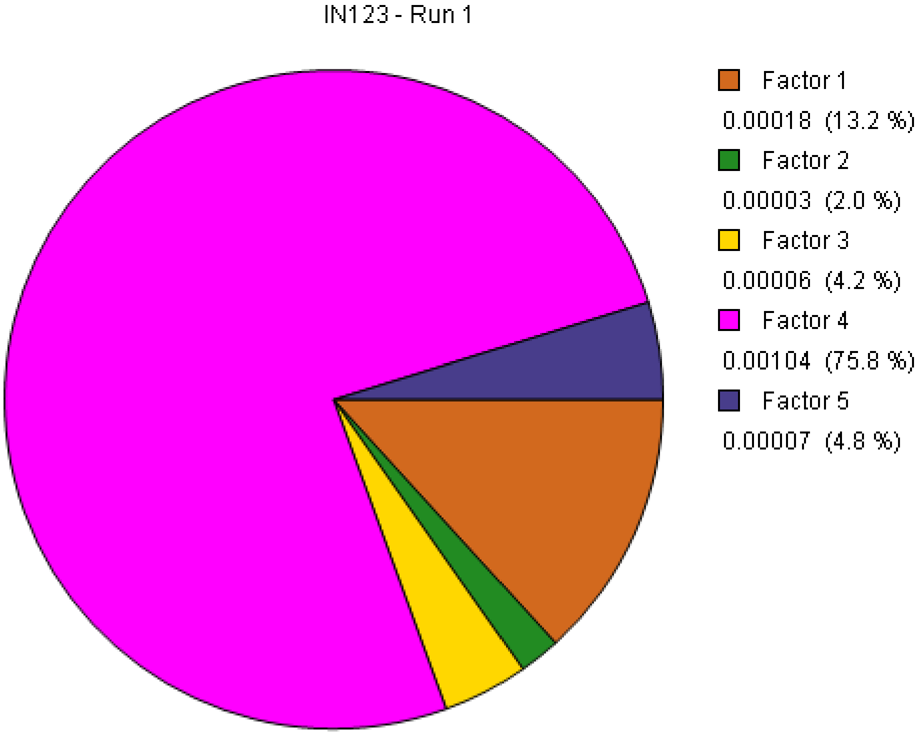

TI - Run 1
Factor 1
0.01872 (71.5 %)
Factor 2
0.00123 (4.7 %)
Factor 3
0.00325 (12.4 %)
Factor 4
0.00056 (2.2 %)
Factor 5
0.00240 (9.2 %)

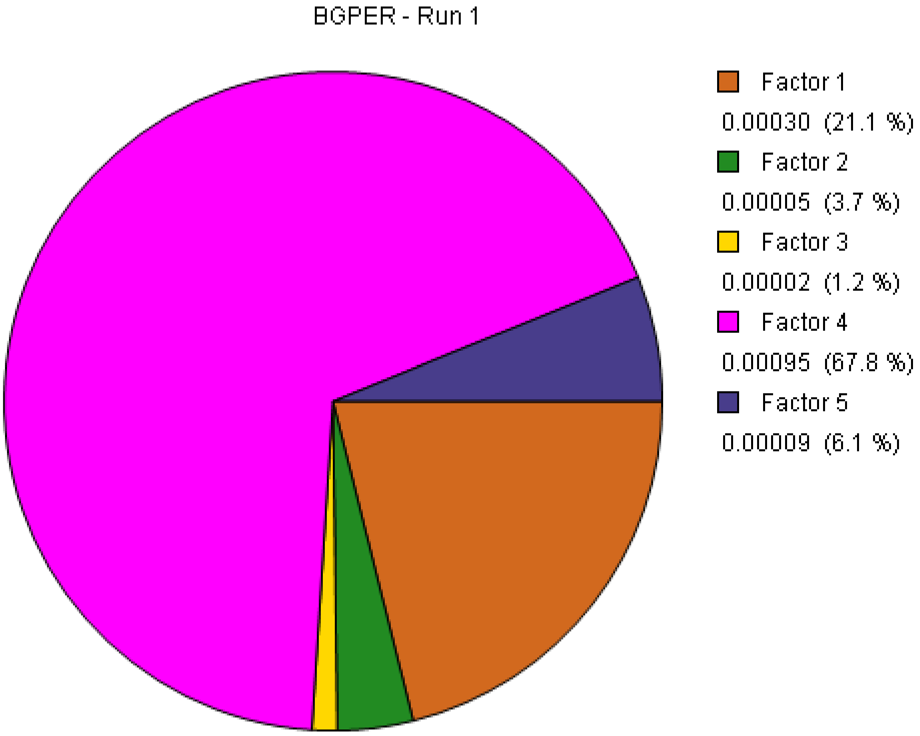

RB - Run 1
Factor 1
0.00066 (40.7 %)
Factor 2
0.00022 (13.4 %)
Factor 3
0.00012 (7.4 %)
Factor 4
0.00034 (20.8 %)
Factor 5
0.00029 (17.7 %)


K - Run 1
Factor 1
0.04344 (13.3 %)
Factor 2
0.03406 (10.4 %)
Factor 3
0.04389 (13.5 %)
Factor 4
0.06938 (21.3 %)
Factor 5
0.13521 (41.5 %)


LEV - Run 1
Factor 2
0.06895 (14.5 %)
Factor 4
0.37815 (79.3 %)
Factor 5
0.02992 (6.3 %)


BAA - Run 1
Factor 1
0.00014 (18.5 %)
Factor 3
0.00003 (3.9 %)
Factor 4
0.00061 (77.6 %)


IN123 - Run 1
Factor 1
0.00018 (13.2 %)
Factor 2
0.00003 (2.0 %)
Factor 3
0.00006 (4.2 %)
Factor 4
0.00104 (75.8 %)
Factor 5
0.00007 (4.8 %)


BGPER - Run 1
Factor 1
0.00030 (21.1 %)
Factor 2
0.00005 (3.7 %)
Factor 3
0.00002 (1.2 %)
Factor 4
0.00095 (67.8 %)
Factor 5
0.00009 (6.1 %)

Appendix 2. Detailed Chemical Mass Balance output data

```
                         Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                                 INPUT FILES:

SITE:          1MI-vm         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                          AD-RL6.csv
                                                                             PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.93                           % MASS      68.9
     CHI SQUARE      0.47                 DEGREES FREEDOM         27


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE    NAME      SCE(µg/m³)     Std Err       Tstat
----------------------------------------------------
YES NH4NO3 AMNITR      17.66685     2.65760     6.64768
YES NH4sul AMSULF       3.72333     0.90358     4.12064
YES NMIXED NM81055      8.82358    10.17488     0.86719
YES REVEHI REVEHI      24.12769     9.67463     2.49391
YES REBITU REBITUM     12.25548     2.45863     4.98467

----------------------------------------------------
                       66.59692

MEASURED CONCENTRATION FOR SIZE: PART
      96.6+-     8.9

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    5 FOR MAX. UNC. = 19.32009  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.74490   2.36473   2.65642   5.49333  12.94877
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    5 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 REBITU
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================
```

```
SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------   -----------
SPECIES      FIT        MEASURED          CALCULATED        MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM         96.60043+- 8.85117  66.59692+- 7.75951   0.69+- 0.10    -2.5
LEV    ULEV   *     0.51928+- 0.15049   0.58397+- 3.26697   1.12+- 6.30     0.0
OC     UOC    *    16.21446+- 4.38980  20.83091+- 3.19526   1.28+- 0.40     0.9
SOOT   USOOT  *     6.69159+- 3.38605   8.24122+- 2.57992   1.23+- 0.73     0.4
NO3    UNO3   *    14.00422+- 1.94493  14.01918+- 1.00319   1.00+- 0.16     0.0
SO4    USO4   *     4.19119+- 0.47301   4.19247+- 0.28709   1.00+- 0.13     0.0
CL     UCL    *     0.77281+- 0.13782   0.12028+- 0.20256   0.16+- 0.26    -2.7
NH4    UNH4   *     4.77484+- 0.72387   4.73036+- 1.81175   0.99+- 0.41     0.0
NA     UNA    *     0.38831+- 0.04095   0.13370+- 0.24590   0.34+- 0.63    -1.0
K      UK     *     0.34133+- 0.05019   0.44171+- 1.06050   1.29+- 3.11     0.1
CA     UCA    *     0.95681+- 0.15951   0.92715+- 0.18487   0.97+- 0.25    -0.1
MG     UMG    *     0.22955+- 0.04262   0.30143+- 1.82346   1.31+- 7.95     0.0
SI     USI    *     1.66460+- 0.54921   1.95770+- 0.25758   1.18+- 0.42     0.5
FE     UFE    *     2.68843+- 0.64919   1.80338+- 0.31904   0.67+- 0.20    -1.2
AL     UAL    *     0.67856+- 0.12833   0.68756+- 0.22159   1.01+- 0.38     0.0
ZN     UZN    *     0.33493+- 0.09500   0.07732+- 0.16376   0.23+- 0.49    -1.4
TI     UTI    *     0.04143+- 0.00980   0.07079+- 0.16311   1.71+- 3.96     0.2
CU     UCU    *     0.12325+- 0.02329   0.10899+- 0.19340   0.88+- 1.58    -0.1
V      UV     *     0.00453+- 0.00087   0.00178+- 0.16291   0.39+-35.96     0.0
MN     UMN    *     0.03681+- 0.00703   0.03642+- 0.16319   0.99+- 4.44     0.0
PB     UPB    *     0.05655+- 0.01289   0.10203+- 0.16321   1.80+- 2.92     0.3
NI     UNI    *     0.01030+- 0.00203   0.00338+- 0.16291   0.33+-15.82     0.0
SR     USR    *     0.00649+- 0.00127   0.00519+- 0.19296   0.80+-29.73     0.0
CR     UCR    *     0.01872+- 0.00366   0.01026+- 0.16293   0.55+- 8.70    -0.1
SB     USB    *     0.02068+- 0.00661   0.04700+- 0.16342   2.27+- 7.93     0.2
SN     USN    *     0.02719+- 0.00563   0.02290+- 0.16303   0.84+- 6.00     0.0
RB     URB    *     0.00183+- 0.00036   0.00289+- 0.16290   1.58+-88.96     0.0
MO     UMO    *     0.01583+- 0.00341   0.00707+- 0.16291   0.45+-10.29    -0.1
AS     UAS    *     0.00196+- 0.00055   0.00228+- 0.19312   1.17+-98.69     0.0
CD     UCD    *     0.00102+- 0.00019   0.00046+- 0.26271   0.46+-*****     0.0
CHRYS  UCHRYS       0.00335+- 0.00197 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU       0.00260+- 0.00065 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU       0.00070+- 0.00019 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR       0.00095+- 0.00020 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *     0.00124+- 0.00026   0.00159+- 0.18056   1.28+-*****     0.0
IN123  UIN123 *     0.00145+- 0.00029   0.00111+- 0.18055   0.77+-*****     0.0
DBAHA  UDBAHA       0.00018+- 0.00005 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *     0.00140+- 0.00029   0.00201+- 0.18056   1.44+-*****     0.0
COR    UCOR         0.00154+- 0.00041 *********+-********  *****+-*****    -1.0
PAH    UPAH         0.01697+- 0.00260 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                                   INPUT FILES:

SITE:          2MI-vm         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2009       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
```

```
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.96                       % MASS      78.4
     CHI SQUARE      0.20             DEGREES FREEDOM        27


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)     Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR      30.46340    3.97661    7.66064
YES NH4sul AMSULF       4.26547    0.84898    5.02422
YES NMIXED NM81055     13.18155    7.46098    1.76673
YES REVEHI REVEHI      10.12174    6.08139    1.66438
YES REBITU REBITUM      9.73768    2.71065    3.59238

----------------------------------------------------
                      67.76984

MEASURED CONCENTRATION FOR SIZE: PART
      86.4+-     8.3

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    5 FOR MAX. UNC. = 17.28639  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.78036   2.53127   3.96952   4.20605   8.72164
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    5 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 REBITU
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT        MEASURED          CALCULATED       MEASURED  UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM        86.43195+- 8.34546  67.76984+- 7.12995   0.78+- 0.11     -1.7
LEV     ULEV   *    0.56103+- 0.15202    0.87240+- 3.41108   1.55+- 6.09      0.1
OC      UOC    *   15.10143+- 4.15815  15.92389+- 1.50015   1.05+- 0.31      0.2
SOOT    USOOT  *    4.06915+- 2.17015    4.35182+- 1.19170   1.07+- 0.64      0.1
```

```
NO3    UNO3   *  22.71875+- 3.59085  24.11933+- 0.49977   1.06+- 0.17     0.4
SO4    USO4   *   3.90495+- 0.49183   3.95308+- 0.30959   1.01+- 0.15     0.1
CL     UCL    *   0.75346+- 0.14078   0.14151+- 0.28733   0.19+- 0.38    -1.9
NH4    UNH4   *   8.67415+- 1.44951   7.57647+- 0.80609   0.87+- 0.17    -0.7
NA     UNA    *   0.21084+- 0.03176   0.11354+- 0.28911   0.54+- 1.37    -0.3
K      UK     *   0.37010+- 0.05415   0.55005+- 0.56732   1.49+- 1.55     0.3
CA     UCA    *   0.58539+- 0.09257   0.71765+- 0.28686   1.23+- 0.53     0.4
MG     UMG    *   0.27204+- 0.04482   0.23241+- 0.81251   0.85+- 2.99     0.0
SI     USI    *   1.54926+- 0.51935   1.52662+- 0.30323   0.99+- 0.38     0.0
FE     UFE    *   1.08005+- 0.26694   0.95839+- 0.30714   0.89+- 0.36    -0.3
AL     UAL    *   0.62234+- 0.11904   0.54188+- 0.28849   0.87+- 0.49    -0.3
ZN     UZN    *   0.27735+- 0.08004   0.05094+- 0.27719   0.18+- 1.00    -0.8
TI     UTI    *   0.04369+- 0.01084   0.05299+- 0.27665   1.21+- 6.34     0.0
CU     UCU    *   0.04679+- 0.00855   0.04995+- 0.28004   1.07+- 5.99     0.0
V      UV     *   0.00313+- 0.00063   0.00119+- 0.27657   0.38+-88.34     0.0
MN     UMN    *   0.02369+- 0.00446   0.02449+- 0.27661   1.03+-11.68     0.0
PB     UPB    *   0.02398+- 0.00528   0.04450+- 0.27660   1.86+-11.54     0.1
NI     UNI    *   0.00827+- 0.00154   0.00235+- 0.27657   0.28+-33.44     0.0
SR     USR    *   0.00497+- 0.00109   0.00399+- 0.27996   0.80+-56.34     0.0
CR     UCR    *   0.01190+- 0.00232   0.00520+- 0.27657   0.44+-23.24     0.0
SB     USB    *   0.00883+- 0.00279   0.01987+- 0.27662   2.25+-31.35     0.0
SN     USN    *   0.01397+- 0.00285   0.01581+- 0.27666   1.13+-19.81     0.0
RB     URB    *   0.00194+- 0.00041   0.00254+- 0.27657   1.31+-*****     0.0
MO     UMO    *   0.00547+- 0.00112   0.00312+- 0.27657   0.57+-50.53     0.0
AS     UAS    *   0.00137+- 0.00038   0.00112+- 0.27997   0.82+-*****     0.0
CD     UCD    *   0.00091+- 0.00018   0.00044+- 0.28977   0.48+-*****     0.0
CHRYS  UCHRYS     0.00253+- 0.00142 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00179+- 0.00037 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00106+- 0.00023 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00125+- 0.00019 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00162+- 0.00026   0.00167+- 0.30761   1.03+-*****     0.0
IN123  UIN123 *   0.00108+- 0.00016   0.00083+- 0.30761   0.77+-*****     0.0
DBAHA  UDBAHA     0.00065+- 0.00010 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00172+- 0.00027   0.00220+- 0.30762   1.28+-*****     0.0
COR    UCOR       0.00036+- 0.00008 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01169+- 0.00215 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1MI-pg         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.92                      % MASS      73.8
     CHI SQUARE      0.38             DEGREES FREEDOM        26
```

```
SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     26.65312    5.17021    5.15513
YES NH4sul AMSULF      5.35272    1.41386    3.78588
YES SeaSal SALT        1.57993    0.53427    2.95717
YES NMIXED NM81055     8.66616    8.10173    1.06967
YES REVEHI REVEHI     16.03848    6.55060    2.44840
YES RESOIL RESOILCA    9.23899    2.43555    3.79338

----------------------------------------------------
                      67.52940

MEASURED CONCENTRATION FOR SIZE: PART
      91.4+-     8.5

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =   6 FOR MAX. UNC. = 18.28973  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.52301   1.36373   2.34182   4.24643   5.17095   9.54503
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED      MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       91.44866+- 8.50151  67.52940+- 8.09170   0.74+- 0.11    -2.0
LEV    ULEV   *   0.67046+- 0.16051   0.57355+- 3.30575   0.86+- 4.93     0.0
OC     UOC    *  14.33300+- 3.90667  15.19559+- 2.15456   1.06+- 0.33     0.2
SOOT   USOOT  *   4.23262+- 2.19480   5.69238+- 1.74204   1.34+- 0.81     0.5
NO3    UNO3   *  20.44643+- 4.57312  21.10125+- 0.70243   1.03+- 0.23     0.1
SO4    USO4   *   5.01821+- 0.97593   5.06075+- 0.29557   1.01+- 0.20     0.0
CL     UCL    *   1.04018+- 0.22502   0.96957+- 0.27222   0.93+- 0.33    -0.2
NH4    UNH4   *   7.64707+- 1.91943   7.05186+- 1.22437   0.92+- 0.28    -0.3
NA     UNA    *   0.48088+- 0.07153   0.58876+- 0.27497   1.22+- 0.60     0.4
K      UK     *   0.53077+- 0.10566   0.43376+- 0.74743   0.82+- 1.42    -0.1
CA     UCA    *   1.08254+- 0.13694   0.35090+- 0.24860   0.32+- 0.23    -2.6
MG     UMG    *   0.24039+- 0.03481   0.20797+- 1.23083   0.87+- 5.12     0.0
SI     USI    *   1.42215+- 0.39058   1.53181+- 0.31238   1.08+- 0.37     0.2
```

```
FE     UFE    *   1.35579+- 0.29435   1.24448+- 0.29958   0.92+- 0.30    -0.3
AL     UAL    *   0.49535+- 0.07441   0.68560+- 0.27280   1.38+- 0.59     0.7
ZN     UZN    *   0.42146+- 0.11008   0.04761+- 0.24599   0.11+- 0.58    -1.4
TI     UTI    *   0.03338+- 0.00706   0.04816+- 0.24562   1.44+- 7.37     0.1
CU     UCU    *   0.07992+- 0.01132   0.07009+- 0.25519   0.88+- 3.20     0.0
V      UV     *   0.00495+- 0.00070   0.00141+- 0.24559   0.28+-49.62     0.0
MN     UMN    *   0.04369+- 0.00613   0.02838+- 0.24568   0.65+- 5.62    -0.1
PB     UPB    *   0.06333+- 0.01143   0.06667+- 0.24568   1.05+- 3.88     0.0
NI     UNI    *   0.01209+- 0.00183   0.00248+- 0.24559   0.21+-20.31     0.0
SR     USR    *   0.00472+- 0.00078   0.00276+- 0.25460   0.59+-53.99     0.0
CR     UCR    *   0.01702+- 0.00252   0.00699+- 0.24560   0.41+-14.43     0.0
SB     USB    *   0.01551+- 0.00453   0.03349+- 0.24576   2.16+-15.86     0.1
SN     USN    *   0.02020+- 0.00344   0.01651+- 0.24565   0.82+-12.16     0.0
RB     URB    *   0.00192+- 0.00030   0.00264+- 0.24515   1.38+-*****     0.0
MO     UMO    *   0.00967+- 0.00166   0.00469+- 0.24559   0.49+-25.39     0.0
AS     UAS    *   0.00239+- 0.00062   0.00172+- 0.25508   0.72+-*****     0.0
CD     UCD    *   0.00137+- 0.00018   0.00025+- 0.28122   0.18+-*****     0.0
CHRYS  UCHRYS     0.00243+- 0.00146 *********+-********* *****+-*****    -1.0
BBFLU  UBBFLU     0.00318+- 0.00070 *********+-********* *****+-*****    -1.0
BKFLU  UBKFLU     0.00094+- 0.00023 *********+-********* *****+-*****    -1.0
BEPYR  UBEPYR     0.00138+- 0.00022 *********+-********* *****+-*****    -1.0
BAPYR  UBAPYR *   0.00137+- 0.00023   0.00135+- 0.27232   0.98+-*****     0.0
IN123  UIN123 *   0.00193+- 0.00030   0.00084+- 0.27231   0.44+-*****     0.0
DBAHA  UDBAHA     0.00029+- 0.00005 *********+-********* *****+-*****    -1.0
BGPER  UBGPER *   0.00217+- 0.00037   0.00174+- 0.27232   0.80+-*****     0.0
COR    UCOR       0.00231+- 0.00050 *********+-********* *****+-*****    -1.0
PAH    UPAH       0.02071+- 0.00437 *********+-********* *****+-*****    -1.0
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          21MI-pg        BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2009       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.97                   % MASS      84.0
     CHI SQUARE      0.18           DEGREES FREEDOM       26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     32.21029    4.44093    7.25305
YES NH4sul AMSULF      4.78692    0.91412    5.23665
YES SeaSal SALT        1.47665    0.55346    2.66805
```

```
YES NMIXED NM81055     9.25386    7.54090    1.22716
YES REVEHI REVEHI     10.08548    6.06748    1.66222
YES RESOIL RESOILCA   14.24445    3.65638    3.89578

----------------------------------------------------
                      72.05766

MEASURED CONCENTRATION FOR SIZE: PART
      85.8+-     8.4

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 17.16046  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.54200   0.85708   3.29960   3.92580   4.44138   8.99216
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                             CALCULATED    RESIDUAL
                                                             ----------  -----------
SPECIES      FIT        MEASURED          CALCULATED          MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM       85.80228+- 8.38916  72.05766+- 7.39910   0.84+- 0.12    -1.2
LEV     ULEV   *   0.53768+- 0.13169   0.61245+- 3.71094   1.14+- 6.91     0.0
OC      UOC    *  13.70544+- 3.74203  12.77030+- 1.42649   0.93+- 0.27    -0.2
SOOT    USOOT  *   2.43060+- 1.35990   3.94324+- 1.15075   1.62+- 1.02     0.8
NO3     UNO3   *  25.07643+- 4.17482  25.48911+- 0.50746   1.02+- 0.17     0.1
SO4     USO4   *   4.34497+- 0.55278   4.35762+- 0.31623   1.00+- 0.15     0.0
CL      UCL    *   1.01683+- 0.18343   0.91314+- 0.30946   0.90+- 0.34    -0.3
NH4     UNH4   *   8.32340+- 1.46841   8.07807+- 0.80933   0.97+- 0.20    -0.1
NA      UNA    *   0.43452+- 0.04163   0.58271+- 0.30640   1.34+- 0.72     0.5
K       UK     *   0.40027+- 0.05613   0.52209+- 0.54898   1.30+- 1.38     0.2
CA      UCA    *   0.72070+- 0.09541   0.44413+- 0.29673   0.62+- 0.42    -0.9
MG      UMG    *   0.38380+- 0.05368   0.26621+- 0.81345   0.69+- 2.12    -0.1
SI      USI    *   2.24339+- 0.84522   2.28852+- 0.39390   1.02+- 0.42     0.0
FE      UFE    *   1.77761+- 0.49406   1.13901+- 0.31417   0.64+- 0.25    -1.1
AL      UAL    *   0.78140+- 0.18020   1.03258+- 0.32409   1.32+- 0.51     0.7
ZN      UZN    *   0.35896+- 0.11730   0.03744+- 0.29353   0.10+- 0.82    -1.0
TI      UTI    *   0.05573+- 0.01450   0.06755+- 0.29327   1.21+- 5.27     0.0
CU      UCU    *   0.07312+- 0.01719   0.04575+- 0.29645   0.63+- 4.06    -0.1
V       UV     *   0.00463+- 0.00105   0.00180+- 0.29322   0.39+-63.38     0.0
MN      UMN    *   0.03335+- 0.00795   0.02835+- 0.29326   0.85+- 8.80     0.0
PB      UPB    *   0.02951+- 0.00750   0.04323+- 0.29325   1.46+- 9.94     0.0
NI      UNI    *   0.00864+- 0.00209   0.00269+- 0.29322   0.31+-33.95     0.0
```

```
SR     USR    *   0.00539+- 0.00135   0.00324+- 0.29607   0.60+-54.89     0.0
CR     UCR    *   0.01777+- 0.00461   0.00570+- 0.29322   0.32+-16.50     0.0
SB     USB    *   0.01219+- 0.00444   0.02330+- 0.29331   1.91+-24.07     0.0
SN     USN    *   0.01893+- 0.00472   0.01294+- 0.29326   0.68+-15.49     0.0
RB     URB    *   0.00200+- 0.00048   0.00305+- 0.29290   1.53+-*****     0.0
MO     UMO    *   0.00692+- 0.00178   0.00314+- 0.29322   0.45+-42.34     0.0
AS     UAS    *   0.00171+- 0.00049   0.00147+- 0.29640   0.86+-*****     0.0
CD     UCD    *   0.00113+- 0.00029   0.00034+- 0.30561   0.30+-*****     0.0
CHRYS  UCHRYS     0.00252+- 0.00149 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00199+- 0.00040 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00126+- 0.00027 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00092+- 0.00013 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00116+- 0.00018   0.00125+- 0.32598   1.08+-*****     0.0
IN123  UIN123 *   0.00149+- 0.00021   0.00068+- 0.32598   0.45+-*****     0.0
DBAHA  UDBAHA     0.00089+- 0.00013 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00155+- 0.00024   0.00163+- 0.32598   1.06+-*****     0.0
COR    UCOR       0.00018+- 0.00004 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01197+- 0.00267 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------



                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          2MI-pg         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2009       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.96                   % MASS      81.5
     CHI SQUARE      0.25          DEGREES FREEDOM        27


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     27.51669    3.51627    7.82553
YES NH4sul AMSULF      4.30825    0.68827    6.25955
YES NMIXED NM81055    11.89240    5.77357    2.05980
YES RESOIL RESOILCA    8.20419    2.75836    2.97430
YES RETUNN RETUNNL     5.87356    4.06335    1.44550

----------------------------------------------------
                      57.79509

MEASURED CONCENTRATION FOR SIZE: PART
      70.9+-     7.4
```

```
                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    5 FOR MAX. UNC. = 14.18772  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.67225   2.36060   3.27405   3.51643   6.41735
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    5 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 RESOIL  1.0000 RETUNN
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                              CALCULATED    RESIDUAL
                                                              ----------   -----------
SPECIES      FIT       MEASURED            CALCULATED          MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM        70.93860+- 7.43823  57.79509+- 6.09010   0.81+- 0.12     -1.4
LEV     ULEV   *    0.40106+- 0.08949   0.78708+- 2.98976   1.96+- 7.47      0.1
OC      UOC    *   12.57380+- 3.43961  12.08792+- 1.66674   0.96+- 0.29     -0.1
SOOT    USOOT  *    1.95885+- 1.04871   3.16773+- 1.32388   1.62+- 1.10      0.7
NO3     UNO3   *   20.75760+- 3.33193  21.91631+- 0.25346   1.06+- 0.17      0.3
SO4     USO4   *    3.54845+- 0.42210   3.58322+- 0.26895   1.01+- 0.14      0.1
CL      UCL    *    0.65988+- 0.12121   0.10493+- 0.25669   0.16+- 0.39     -2.0
NH4     UNH4   *    7.63898+- 1.29396   6.96370+- 0.25113   0.91+- 0.16     -0.5
NA      UNA    *    0.18235+- 0.01763   0.09471+- 0.25645   0.52+- 1.41     -0.3
K       UK     *    0.33964+- 0.04855   0.52002+- 0.32999   1.53+- 1.00      0.5
CA      UCA    *    0.46239+- 0.06151   0.38482+- 0.25482   0.83+- 0.56     -0.3
MG      UMG    *    0.19113+- 0.02851   0.16484+- 0.25115   0.86+- 1.32     -0.1
SI      USI    *    1.42293+- 0.55999   1.39665+- 0.29126   0.98+- 0.44      0.0
FE      UFE    *    0.95951+- 0.28295   0.71943+- 0.25425   0.75+- 0.35     -0.6
AL      UAL    *    0.49562+- 0.12164   0.61439+- 0.26111   1.24+- 0.61      0.4
ZN      UZN    *    0.29395+- 0.09871   0.03014+- 0.25111   0.10+- 0.85     -1.0
TI      UTI    *    0.04086+- 0.01183   0.04519+- 0.25062   1.11+- 6.14      0.0
CU      UCU    *    0.03806+- 0.00947   0.02212+- 0.25063   0.58+- 6.59     -0.1
V       UV     *    0.00349+- 0.00087   0.00137+- 0.25060   0.39+-71.84      0.0
MN      UMN    *    0.02322+- 0.00562   0.01787+- 0.25061   0.77+-10.80      0.0
PB      UPB    *    0.02563+- 0.00686   0.01360+- 0.25060   0.53+- 9.78      0.0
NI      UNI    *    0.00860+- 0.00230   0.00180+- 0.25060   0.21+-29.14      0.0
SR      USR    *    0.00399+- 0.00103   0.00156+- 0.25060   0.39+-62.81      0.0
CR      UCR    *    0.01339+- 0.00428   0.00338+- 0.25060   0.25+-18.72      0.0
SB      USB    *    0.00856+- 0.00320   0.00221+- 0.25654   0.26+-29.98      0.0
SN      USN    *    0.01418+- 0.00367   0.00752+- 0.25067   0.53+-17.67      0.0
RB      URB    *    0.00165+- 0.00042   0.00223+- 0.25060   1.36+-*****      0.0
MO      UMO    *    0.00486+- 0.00130   0.00021+- 0.28827   0.04+-59.35      0.0
AS      UAS    *    0.00148+- 0.00044   0.00041+- 0.28827   0.28+-*****      0.0
CD      UCD    *    0.00101+- 0.00027   0.00027+- 0.28827   0.27+-*****      0.0
CHRYS   UCHRYS      0.00172+- 0.00101 *********+-********  *****+-*****     -1.0
BBFLU   UBBFLU      0.00195+- 0.00039 *********+-********  *****+-*****     -1.0
BKFLU   UBKFLU      0.00123+- 0.00026 *********+-********  *****+-*****     -1.0
```

```
BEPYR  UBEPYR     0.00107+- 0.00015 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00122+- 0.00018   0.00142+- 0.27853   1.16+-*****     0.0
IN123  UIN123 *   0.00100+- 0.00014   0.00064+- 0.27852   0.64+-*****     0.0
DBAHA  UDBAHA     0.00071+- 0.00011 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00182+- 0.00027   0.00188+- 0.27853   1.03+-*****     0.0
COR    UCOR       0.00018+- 0.00004 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01091+- 0.00215 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------



                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          sMI-pg         BRITT & LUECKE:          No
SAMPLE DATE:   Sep 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.90                       % MASS      84.3
     CHI SQUARE      0.45                DEGREES FREEDOM      27


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     19.46532    3.28496    5.92558
YES NH4sul AMSULF      3.40704    0.91229    3.73462
YES NMIXED NM81055     3.07716    7.40465    0.41557
YES REVEHI REVEHI     14.29402    7.15644    1.99736
YES REBITU REBITUM     8.71463    2.03994    4.27201

----------------------------------------------------
                      48.95816

MEASURED CONCENTRATION FOR SIZE: PART
      58.1+-     6.6

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    5 FOR MAX. UNC. = 11.61905  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.83308   1.97240   3.28254   3.70263   9.63116
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    5 FOR MIN. PROJ. =   0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
```

```
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 REBITU
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM          58.09525+- 6.55902  48.95816+- 6.00876   0.84+- 0.14     -1.0
LEV    ULEV   *      0.20218+- 0.08412   0.20366+- 2.59203   1.01+-12.83      0.0
OC     UOC    *      9.28441+- 3.08804  11.09057+- 1.88953   1.19+- 0.45      0.5
SOOT   USOOT  *      3.28254+- 1.92599   4.69791+- 1.52929   1.43+- 0.96      0.6
NO3    UNO3   *     14.55486+- 2.80129  15.40045+- 0.61280   1.06+- 0.21      0.3
SO4    USO4   *      3.28283+- 0.57973   3.33597+- 0.22410   1.02+- 0.19      0.1
CL     UCL    *      0.46817+- 0.10839   0.05531+- 0.19071   0.12+- 0.41     -1.9
NH4    UNH4   *      5.99872+- 1.18120   5.01088+- 1.08368   0.84+- 0.24     -0.6
NA     UNA    *      0.35902+- 0.06727   0.08180+- 0.20920   0.23+- 0.58     -1.3
K      UK     *      0.37357+- 0.08101   0.20944+- 0.64133   0.56+- 1.72     -0.3
CA     UCA    *      0.65681+- 0.11309   0.63278+- 0.18727   0.96+- 0.33     -0.1
MG     UMG    *      0.16939+- 0.03083   0.20952+- 1.09106   1.24+- 6.45      0.0
SI     USI    *      1.21580+- 0.41545   1.37328+- 0.21986   1.13+- 0.43      0.3
FE     UFE    *      2.04997+- 0.58235   1.12789+- 0.24413   0.55+- 0.20     -1.5
AL     UAL    *      0.42347+- 0.08183   0.48119+- 0.20129   1.14+- 0.52      0.3
ZN     UZN    *      0.45833+- 0.12594   0.04472+- 0.17814   0.10+- 0.39     -1.9
TI     UTI    *      0.03250+- 0.00735   0.04878+- 0.17805   1.50+- 5.49      0.1
CU     UCU    *      0.08199+- 0.01392   0.06480+- 0.18836   0.79+- 2.30     -0.1
V      UV     *      0.00271+- 0.00048   0.00119+- 0.17796   0.44+-65.55      0.0
MN     UMN    *      0.02977+- 0.00491   0.02149+- 0.17805   0.72+- 5.98      0.0
PB     UPB    *      0.04575+- 0.00986   0.06084+- 0.17805   1.33+- 3.90      0.1
NI     UNI    *      0.01367+- 0.00375   0.00208+- 0.17796   0.15+-13.02     -0.1
SR     USR    *      0.00362+- 0.00073   0.00348+- 0.18821   0.96+-52.00      0.0
CR     UCR    *      0.01674+- 0.00333   0.00625+- 0.17796   0.37+-10.63     -0.1
SB     USB    *      0.01402+- 0.00433   0.02787+- 0.17812   1.99+-12.72      0.1
SN     USN    *      0.01836+- 0.00389   0.01236+- 0.17798   0.67+- 9.69      0.0
RB     URB    *      0.00108+- 0.00022   0.00162+- 0.17796   1.51+-*****      0.0
MO     UMO    *      0.00946+- 0.00183   0.00422+- 0.17796   0.45+-18.80      0.0
AS     UAS    *      0.00202+- 0.00065   0.00138+- 0.18827   0.68+-92.99      0.0
CD     UCD    *      0.00098+- 0.00020   0.00030+- 0.21582   0.30+-*****      0.0
CHRYS  UCHRYS        0.00105+- 0.00067 *********+-********  *****+-*****     -1.0
BBFLU  UBBFLU        0.00079+- 0.00025 *********+-********  *****+-*****     -1.0
BKFLU  UBKFLU        0.00024+- 0.00008 *********+-********  *****+-*****     -1.0
BEPYR  UBEPYR        0.00033+- 0.00008 *********+-********  *****+-*****     -1.0
BAPYR  UBAPYR *      0.00041+- 0.00011   0.00071+- 0.19762   1.74+-*****      0.0
IN123  UIN123 *      0.00049+- 0.00013   0.00057+- 0.19761   1.18+-*****      0.0
DBAHA  UDBAHA        0.00012+- 0.00003 *********+-********  *****+-*****     -1.0
BGPER  UBGPER *      0.00048+- 0.00012   0.00088+- 0.19762   1.84+-*****      0.0
COR    UCOR          0.00154+- 0.00049 *********+-********  *****+-*****     -1.0
PAH    UPAH          0.00542+- 0.00101 *********+-********  *****+-*****     -1.0
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1BS-vs         BRITT & LUECKE:         No
SAMPLE DATE:   Feb 2009       SOURCE ELIMINATION:     Yes
DURATION:      24             BEST FIT:               No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.94                        % MASS      68.7
     CHI SQUARE      0.44                DEGREES FREEDOM       26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(μg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     21.19037    2.76142    7.67372
YES NH4sul AMSULF      4.20288    1.00111    4.19820
YES NREALW NREALLWO    9.08926    7.57631    1.19970
YES REVEHI REVEHI     16.61781    6.53390    2.54332
YES RESOIL RESOILCA    5.76043    2.03232    2.83441
YES N19    CEMENT      3.11340    0.76806    4.05359

----------------------------------------------------
                      59.97415

MEASURED CONCENTRATION FOR SIZE: PART
      87.2+-     8.2

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 17.44865  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.72081   0.94585   1.99394   2.76093   4.36816   9.01924
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NREALW  1.0000 REVEHI  1.0000 RESOIL
1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================
```

```
SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       87.24325+- 8.23816  59.97415+- 6.68005   0.69+- 0.10    -2.6
LEV    ULEV   *   0.89730+- 0.22441   0.89016+- 2.85784   0.99+- 3.19     0.0
OC     UOC    *  14.87823+- 3.98313  16.90259+- 3.01727   1.14+- 0.37     0.4
SOOT   USOOT  *   3.86485+- 1.98593   6.03991+- 1.99736   1.56+- 0.95     0.8
NO3    UNO3   *  16.58183+- 2.24716  16.79930+- 0.70985   1.01+- 0.14     0.1
SO4    USO4   *   4.49697+- 0.42884   4.52253+- 0.55362   1.01+- 0.16     0.0
CL     UCL    *   1.06730+- 0.18249   0.44834+- 0.22236   0.42+- 0.22    -2.2
NH4    UNH4   *   5.96358+- 0.83619   5.62992+- 1.25804   0.94+- 0.25    -0.2
NA     UNA    *   0.35875+- 0.03287   0.12039+- 0.23714   0.34+- 0.66    -1.0
K      UK     *   0.46068+- 0.05952   0.63156+- 1.03569   1.37+- 2.26     0.2
CA     UCA    *   1.27342+- 0.19599   1.46456+- 0.22330   1.15+- 0.25     0.6
MG     UMG    *   0.35178+- 0.06032   0.10827+- 1.26476   0.31+- 3.60    -0.2
SI     USI    *   1.05984+- 0.30901   1.06908+- 0.24333   1.01+- 0.37     0.0
FE     UFE    *   1.55791+- 0.35496   1.15002+- 0.26298   0.74+- 0.24    -0.9
AL     UAL    *   0.46396+- 0.07922   0.50145+- 0.22097   1.08+- 0.51     0.2
ZN     UZN    *   0.51837+- 0.14193   0.05838+- 0.20051   0.11+- 0.39    -1.9
TI     UTI    *   0.02069+- 0.00517   0.03601+- 0.19480   1.74+- 9.42     0.1
CU     UCU    *   0.09521+- 0.01888   0.07230+- 0.20761   0.76+- 2.19    -0.1
V      UV     *   0.00322+- 0.00065   0.00127+- 0.19478   0.40+-60.43     0.0
MN     UMN    *   0.06952+- 0.01048   0.03068+- 0.19643   0.44+- 2.83    -0.2
PB     UPB    *   0.08300+- 0.01653   0.06949+- 0.19490   0.84+- 2.35    -0.1
NI     UNI    *   0.01078+- 0.00195   0.00223+- 0.19478   0.21+-18.07     0.0
SR     USR    *   0.00480+- 0.00089   0.00276+- 0.20739   0.57+-43.22     0.0
CR     UCR    *   0.01446+- 0.00249   0.00680+- 0.19479   0.47+-13.47     0.0
SB     USB    *   0.00887+- 0.00269   0.03372+- 0.19500   3.80+-22.01     0.1
SN     USN    *   0.01385+- 0.00266   0.01560+- 0.19488   1.13+-14.07     0.0
RB     URB    *   0.00178+- 0.00032   0.00454+- 0.19481   2.54+-*****     0.0
MO     UMO    *   0.00847+- 0.00150   0.00479+- 0.19478   0.57+-23.00     0.0
AS     UAS    *   0.00172+- 0.00046   0.00166+- 0.20747   0.97+-*****     0.0
CD     UCD    *   0.00163+- 0.00030   0.00020+- 0.24102   0.13+-*****     0.0
CHRYS  UCHRYS     0.00194+- 0.00120 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00269+- 0.00059 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00074+- 0.00017 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00095+- 0.00016 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00118+- 0.00020   0.00139+- 0.21603   1.17+-*****     0.0
IN123  UIN123 *   0.00142+- 0.00023   0.00070+- 0.21603   0.50+-*****     0.0
DBAHA  UDBAHA     0.00016+- 0.00003 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00141+- 0.00025   0.00178+- 0.21603   1.26+-*****     0.0
COR    UCOR       0.00132+- 0.00029 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01494+- 0.00229 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------



                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          2BS-vs         BRITT & LUECKE:          No
SAMPLE DATE:   feb 2009       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
```

```
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.98                          % MASS      78.6
     CHI SQUARE      0.07                DEGREES FREEDOM         26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     33.83187    3.97238    8.51678
YES NH4sul AMSULF      3.14787    1.09131    2.88450
YES NREALW NREALLWO   11.61140    6.76172    1.71723
YES REVEHI REVEHI      5.87504    5.13751    1.14356
YES RESOIL RESOILCA    5.81627    2.34856    2.47653
YES N19    CEMENT      1.52295    0.88221    1.72630

----------------------------------------------------
                      61.80540

MEASURED CONCENTRATION FOR SIZE: PART
      78.6+-     7.7

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 15.72816  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.82907   1.05805   2.25733   3.56978   3.98188   7.73813
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NREALW  1.0000 REVEHI  1.0000 RESOIL
1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED        MEASURED  UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM       78.64082+- 7.72580  61.80540+- 6.72636   0.79+- 0.12    -1.6
LEV     ULEV   *   0.29686+- 0.06720   1.13716+- 3.57178   3.83+-12.06     0.2
OC      UOC    *  12.78956+- 3.36851  12.59735+- 2.77800   0.98+- 0.34     0.0
```

```
SOOT   USOOT  *   2.61693+- 1.35253   3.01666+- 1.36535   1.15+- 0.79     0.2
NO3    UNO3   *  26.86264+- 3.94516  26.77033+- 0.39161   1.00+- 0.15     0.0
SO4    USO4   *   3.11377+- 0.36429   3.10891+- 0.70090   1.00+- 0.25     0.0
CL     UCL    *   0.56234+- 0.10724   0.28969+- 0.31959   0.52+- 0.58    -0.8
NH4    UNH4   *   7.96217+- 1.22394   8.00146+- 0.53530   1.00+- 0.17     0.0
NA     UNA    *   0.12427+- 0.01268   0.10032+- 0.31569   0.81+- 2.54    -0.1
K      UK     *   0.35478+- 0.05185   0.71890+- 1.00732   2.03+- 2.85     0.4
CA     UCA    *   0.73309+- 0.10469   0.81234+- 0.32597   1.11+- 0.47     0.2
MG     UMG    *   0.30859+- 0.04493   0.09602+- 0.53719   0.31+- 1.74    -0.4
SI     USI    *   1.00221+- 0.28112   0.99025+- 0.32477   0.99+- 0.43     0.0
FE     UFE    *   0.61946+- 0.14086   0.57277+- 0.31171   0.92+- 0.55    -0.1
AL     UAL    *   0.43835+- 0.06595   0.46542+- 0.31173   1.06+- 0.73     0.1
ZN     UZN    *   0.32851+- 0.08191   0.04137+- 0.31085   0.13+- 0.95    -0.9
TI     UTI    *   0.03425+- 0.00691   0.03014+- 0.30502   0.88+- 8.91     0.0
CU     UCU    *   0.03772+- 0.00502   0.02769+- 0.30609   0.73+- 8.11     0.0
V      UV     *   0.00256+- 0.00039   0.00092+- 0.30501   0.36+-*****     0.0
MN     UMN    *   0.03350+- 0.00449   0.02332+- 0.30663   0.70+- 9.15     0.0
PB     UPB    *   0.03018+- 0.00530   0.02549+- 0.30502   0.84+-10.11     0.0
NI     UNI    *   0.00686+- 0.00109   0.00159+- 0.30501   0.23+-44.48     0.0
SR     USR    *   0.00333+- 0.00057   0.00181+- 0.30605   0.54+-92.01     0.0
CR     UCR    *   0.00855+- 0.00135   0.00315+- 0.30501   0.37+-35.69     0.0
SB     USB    *   0.00470+- 0.00156   0.01295+- 0.30503   2.76+-64.94     0.0
SN     USN    *   0.00645+- 0.00111   0.00939+- 0.30509   1.46+-47.27     0.0
RB     URB    *   0.00152+- 0.00024   0.00381+- 0.30504   2.50+-*****     0.0
MO     UMO    *   0.00372+- 0.00065   0.00179+- 0.30501   0.48+-81.94     0.0
AS     UAS    *   0.00129+- 0.00031   0.00079+- 0.30605   0.61+-*****     0.0
CD     UCD    *   0.00101+- 0.00013   0.00022+- 0.30911   0.21+-*****     0.0
CHRYS  UCHRYS     0.00178+- 0.00101 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00180+- 0.00036 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00118+- 0.00025 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00104+- 0.00014 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00125+- 0.00018   0.00135+- 0.33978   1.08+-*****     0.0
IN123  UIN123 *   0.00074+- 0.00011   0.00040+- 0.33978   0.54+-*****     0.0
DBAHA  UDBAHA     0.00088+- 0.00013 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00197+- 0.00031   0.00179+- 0.33978   0.91+-*****     0.0
COR    UCOR       0.00016+- 0.00004 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01080+- 0.00210 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1BG-vs         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.96                       % MASS      71.3
     CHI SQUARE      0.21             DEGREES FREEDOM         26
```

```
SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(μg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     20.97279    3.68813    5.68657
YES NH4sul AMSULF      3.27302    1.09779    2.98146
YES NREALW NREALLWO    7.14866    6.98986    1.02272
YES REVEHI REVEHI     14.52111    6.03554    2.40593
YES RESOIL RESOILCA    7.95645    2.35675    3.37602
YES N19    CEMENT      2.83391    0.77813    3.64193

----------------------------------------------------
                      56.70593

MEASURED CONCENTRATION FOR SIZE: PART
      79.5+-     7.8

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 15.90692  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.73108   1.04870   2.28764   3.68459   4.14229   8.28558
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NREALW  1.0000 REVEHI  1.0000 RESOIL
1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       79.53458+- 7.83838  56.70593+- 6.89674   0.71+- 0.11     -2.2
LEV    ULEV   *   0.65201+- 0.17677   0.70010+- 2.74216   1.07+- 4.22      0.0
OC     UOC    *  13.40903+- 4.02155  14.42285+- 2.51774   1.08+- 0.37      0.2
SOOT   USOOT  *   3.76288+- 2.05869   5.20285+- 1.71199   1.38+- 0.88      0.5
NO3    UNO3   *  16.55774+- 3.26586  16.61864+- 0.62615   1.00+- 0.20      0.0
SO4    USO4   *   3.64934+- 0.63408   3.65382+- 0.45459   1.00+- 0.21      0.0
CL     UCL    *   0.65998+- 0.13488   0.39684+- 0.21107   0.60+- 0.34     -1.1
NH4    UNH4   *   5.38534+- 1.13303   5.33379+- 1.10270   0.99+- 0.29      0.0
NA     UNA    *   0.33042+- 0.05766   0.12180+- 0.22458   0.37+- 0.68     -0.9
K      UK     *   0.38058+- 0.07064   0.55578+- 0.86625   1.46+- 2.29      0.2
CA     UCA    *   1.27533+- 0.21776   1.39014+- 0.21210   1.09+- 0.25      0.4
MG     UMG    *   0.24525+- 0.04525   0.13428+- 1.10862   0.55+- 4.52     -0.1
```

```
SI     USI    *  1.39051+- 0.42887   1.39302+- 0.25473   1.00+- 0.36     0.0
FE     UFE    *  1.34700+- 0.31543   1.12769+- 0.24606   0.84+- 0.27    -0.5
AL     UAL    *  0.60859+- 0.10904   0.64588+- 0.21859   1.06+- 0.41     0.2
ZN     UZN    *  0.42239+- 0.11142   0.05004+- 0.19464   0.12+- 0.46    -1.7
TI     UTI    *  0.01860+- 0.00442   0.04432+- 0.19101   2.38+-10.28     0.1
CU     UCU    *  0.05261+- 0.00885   0.06332+- 0.20103   1.20+- 3.83     0.1
V      UV     *  0.00377+- 0.00066   0.00143+- 0.19098   0.38+-50.63     0.0
MN     UMN    *  0.03792+- 0.00614   0.02890+- 0.19204   0.76+- 5.07     0.0
PB     UPB    *  0.04641+- 0.00910   0.06115+- 0.19108   1.32+- 4.13     0.1
NI     UNI    *  0.00913+- 0.00188   0.00225+- 0.19098   0.25+-20.91     0.0
SR     USR    *  0.00490+- 0.00098   0.00286+- 0.20087   0.58+-40.98     0.0
CR     UCR    *  0.01135+- 0.00202   0.00635+- 0.19099   0.56+-16.83     0.0
SB     USB    *  0.00855+- 0.00253   0.03024+- 0.19116   3.54+-22.37     0.1
SN     USN    *  0.01175+- 0.00220   0.01335+- 0.19105   1.14+-16.26     0.0
RB     URB    *  0.00158+- 0.00030   0.00423+- 0.19100   2.67+-*****     0.0
MO     UMO    *  0.00758+- 0.00144   0.00424+- 0.19098   0.56+-25.19     0.0
AS     UAS    *  0.00132+- 0.00035   0.00157+- 0.20093   1.20+-*****     0.0
CD     UCD    *  0.00096+- 0.00018   0.00022+- 0.22773   0.23+-*****     0.0
CHRYS  UCHRYS    0.00426+- 0.00258 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU    0.00300+- 0.00066 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU    0.00082+- 0.00019 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR    0.00140+- 0.00024 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *  0.00135+- 0.00023   0.00113+- 0.21227   0.84+-*****     0.0
IN123  UIN123 *  0.00188+- 0.00032   0.00060+- 0.21227   0.32+-*****     0.0
DBAHA  UDBAHA    0.00023+- 0.00004 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *  0.00217+- 0.00039   0.00144+- 0.21227   0.67+-97.79     0.0
COR    UCOR      0.00230+- 0.00053 *********+-********  *****+-*****    -1.0
PAH    UPAH      0.02130+- 0.00337 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                        OPTIONS:                           INPUT FILES:

SITE:          1Saron          BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007        SOURCE ELIMINATION:      Yes
DURATION:      24              BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                    AD-RL6.csv
                                                                       PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.90                     % MASS      71.1
     CHI SQUARE      0.39            DEGREES FREEDOM        26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE    NAME      SCE(µg/m³)     Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     18.77285     3.47803     5.39755
YES NH4sul AMSULF      3.00293     1.18107     2.54255
```

```
YES NREALW NREALLWO    8.50584    7.30530    1.16434
YES REVEHI REVEHI     12.95619    6.28225    2.06235
YES RESOIL RESOILCA    8.06013    2.39599    3.36401
YES N19    CEMENT      1.32199    0.62603    2.11171

----------------------------------------------------
                      52.61993

MEASURED CONCENTRATION FOR SIZE: PART
      74.0+-     7.5

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =   6 FOR MAX. UNC. = 14.80274  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.58622   1.13024   2.36118   3.47608   4.08338   8.74672
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NREALW  1.0000 REVEHI  1.0000 RESOIL
1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  ------------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       74.01371+- 7.49052  52.61993+- 6.81269   0.71+- 0.12    -2.1
LEV    ULEV   *   0.94752+- 0.26892   0.83302+- 2.49632   0.88+- 2.65     0.0
OC     UOC    *  13.15501+- 4.12464  14.19592+- 2.58504   1.08+- 0.39     0.2
SOOT   USOOT  *   2.64288+- 1.45033   4.85535+- 1.63044   1.84+- 1.18     1.0
NO3    UNO3   *  14.59776+- 3.07271  14.88130+- 0.55935   1.02+- 0.22     0.1
SO4    USO4   *   3.23011+- 0.68202   3.25817+- 0.50621   1.01+- 0.26     0.0
CL     UCL    *   0.61862+- 0.15312   0.24297+- 0.19352   0.39+- 0.33    -1.5
NH4    UNH4   *   5.03037+- 1.13904   4.78407+- 0.98404   0.95+- 0.29    -0.2
NA     UNA    *   0.41166+- 0.07037   0.11020+- 0.20386   0.27+- 0.50    -1.4
K      UK     *   0.39908+- 0.06430   0.58787+- 0.89393   1.47+- 2.25     0.2
CA     UCA    *   0.70461+- 0.13786   0.80796+- 0.19251   1.15+- 0.35     0.4
MG     UMG    *   0.18434+- 0.04066   0.13240+- 0.98932   0.72+- 5.37    -0.1
SI     USI    *   1.38522+- 0.49163   1.36339+- 0.23791   0.98+- 0.39     0.0
FE     UFE    *   1.80055+- 0.46823   1.03888+- 0.22030   0.58+- 0.19    -1.5
AL     UAL    *   0.53348+- 0.11978   0.62508+- 0.19867   1.17+- 0.46     0.4
ZN     UZN    *   0.33483+- 0.09219   0.04943+- 0.17674   0.15+- 0.53    -1.4
TI     UTI    *   0.02378+- 0.00586   0.04262+- 0.17112   1.79+- 7.21     0.1
CU     UCU    *   0.07372+- 0.01332   0.05699+- 0.18003   0.77+- 2.45    -0.1
V      UV     *   0.00406+- 0.00081   0.00131+- 0.17108   0.32+-42.14     0.0
MN     UMN    *   0.03595+- 0.00682   0.02857+- 0.17270   0.79+- 4.81     0.0
PB     UPB    *   0.03920+- 0.00864   0.05440+- 0.17117   1.39+- 4.38     0.1
```

```
NI     UNI     *   0.01674+- 0.00340   0.00218+- 0.17108   0.13+-10.22    -0.1
SR     USR     *   0.00403+- 0.00090   0.00226+- 0.17987   0.56+-44.62     0.0
CR     UCR     *   0.01573+- 0.00304   0.00581+- 0.17109   0.37+-10.87    -0.1
SB     USB     *   0.00798+- 0.00258   0.02723+- 0.17125   3.41+-21.49     0.1
SN     USN     *   0.01197+- 0.00263   0.01288+- 0.17118   1.08+-14.30     0.0
RB     URB     *   0.00185+- 0.00039   0.00370+- 0.17111   2.00+-92.46     0.0
MO     UMO     *   0.00972+- 0.00200   0.00381+- 0.17108   0.39+-17.59     0.0
AS     UAS     *   0.00124+- 0.00038   0.00144+- 0.17992   1.16+-*****     0.0
CD     UCD     *   0.00099+- 0.00020   0.00022+- 0.20376   0.23+-*****     0.0
CHRYS  UCHRYS      0.00329+- 0.00194 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU      0.00287+- 0.00068 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU      0.00079+- 0.00020 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR      0.00089+- 0.00017 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *    0.00118+- 0.00023   0.00122+- 0.19012   1.03+-*****     0.0
IN123  UIN123 *    0.00147+- 0.00028   0.00057+- 0.19012   0.39+-*****     0.0
DBAHA  UDBAHA      0.00018+- 0.00004 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *    0.00118+- 0.00024   0.00158+- 0.19012   1.34+-*****     0.0
COR    UCOR        0.00101+- 0.00024 *********+-********  *****+-*****    -1.0
PAH    UPAH        0.01572+- 0.00245 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1MN-sa         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.99                      % MASS      68.0
     CHI SQUARE      0.08             DEGREES FREEDOM        25


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE    NAME     SCE(µg/m³)    Std Err       Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     26.17072    3.11088    8.41265
YES NH4sul AMSULF      5.70154    0.83793    6.80431
YES SeaSal SALT        0.90717    0.45156    2.00897
YES NMIXED NM81055     9.15824    5.42461    1.68828
YES REVEHI REVEHI      6.52449    3.96975    1.64355
YES RESOIL RESOILCA    2.01688    1.57380    1.28153
YES N19    CEMENT      1.39898    0.69035    2.02647

----------------------------------------------------
                      51.87802
```

```
MEASURED CONCENTRATION FOR SIZE: PART
      76.3+-     7.6

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =   7 FOR MAX. UNC. = 15.26745  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.42303   0.67057   0.81517   1.54401   2.70159   3.11237   6.16926
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   7 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL  1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE          Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  ------------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       76.33723+- 7.56684  51.87802+- 5.20962   0.68+- 0.10    -2.7
LEV    ULEV   *   0.46677+- 0.11981   0.60612+- 2.78660   1.30+- 5.98     0.0
OC     UOC    *  10.75226+- 2.97864  10.28277+- 0.99284   0.96+- 0.28    -0.1
SOOT   USOOT  *   1.96661+- 1.14198   2.83397+- 0.79353   1.44+- 0.93     0.6
NO3    UNO3   *  19.98514+- 2.84080  20.70828+- 0.36129   1.04+- 0.15     0.3
SO4    USO4   *   4.87901+- 0.54183   4.92163+- 0.26024   1.01+- 0.12     0.1
CL     UCL    *   0.78531+- 0.13517   0.74388+- 0.25202   0.95+- 0.36    -0.1
NH4    UNH4   *   7.57273+- 1.12997   7.05345+- 0.54475   0.93+- 0.16    -0.4
NA     UNA    *   0.28408+- 0.02466   0.34075+- 0.24728   1.20+- 0.88     0.2
K      UK     *   0.39695+- 0.05943   0.37355+- 0.40520   0.94+- 1.03    -0.1
CA     UCA    *   0.65694+- 0.08708   0.66603+- 0.24548   1.01+- 0.40     0.0
MG     UMG    *   0.14514+- 0.02156   0.07572+- 0.54701   0.52+- 3.77    -0.1
SI     USI    *   0.36055+- 0.11545   0.39903+- 0.24828   1.11+- 0.77     0.1
FE     UFE    *   0.62734+- 0.14059   0.44824+- 0.25174   0.71+- 0.43    -0.6
AL     UAL    *   0.18034+- 0.03229   0.18862+- 0.24514   1.05+- 1.37     0.0
ZN     UZN    *   0.25104+- 0.06873   0.02696+- 0.24225   0.11+- 0.97    -0.9
TI     UTI    *   0.01138+- 0.00280   0.01399+- 0.24192   1.23+-21.27     0.0
CU     UCU    *   0.02136+- 0.00315   0.02959+- 0.24357   1.39+-11.40     0.0
V      UV     *   0.00321+- 0.00053   0.00048+- 0.24192   0.15+-75.40     0.0
MN     UMN    *   0.02078+- 0.00303   0.01352+- 0.24194   0.65+-11.64     0.0
PB     UPB    *   0.02764+- 0.00540   0.02745+- 0.24193   0.99+- 8.76     0.0
NI     UNI    *   0.00902+- 0.00154   0.00109+- 0.24192   0.12+-26.82     0.0
SR     USR    *   0.00220+- 0.00039   0.00169+- 0.24338   0.77+-*****     0.0
CR     UCR    *   0.01379+- 0.00238   0.00275+- 0.24192   0.20+-17.54     0.0
SB     USB    *   0.00503+- 0.00153   0.01320+- 0.24194   2.63+-48.13     0.0
SN     USN    *   0.00692+- 0.00129   0.01015+- 0.24197   1.47+-34.97     0.0
RB     URB    *   0.00115+- 0.00021   0.00210+- 0.24177   1.83+-*****     0.0
MO     UMO    *   0.00516+- 0.00092   0.00190+- 0.24192   0.37+-46.87     0.0
AS     UAS    *   0.00176+- 0.00044   0.00068+- 0.24354   0.38+-*****     0.0
```

```
CD     UCD    *   0.00096+- 0.00015   0.00015+- 0.24825   0.15+-*****     0.0
CHRYS  UCHRYS     0.00200+- 0.00116 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00202+- 0.00043 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00055+- 0.00013 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00074+- 0.00012 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00065+- 0.00011   0.00115+- 0.26800   1.76+-*****     0.0
IN123  UIN123 *   0.00097+- 0.00016   0.00056+- 0.26800   0.58+-*****     0.0
DBAHA  UDBAHA     0.00011+- 0.00002 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00095+- 0.00018   0.00151+- 0.26800   1.59+-*****     0.0
COR    UCOR       0.00087+- 0.00019 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01062+- 0.00151 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          2MN-sa         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                    AD-RL6.csv
                                                                       PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE       0.99                     % MASS       85.9
     CHI SQUARE       0.04            DEGREES FREEDOM         25


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME      SCE(µg/m³)     Std Err       Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     34.76234    4.75706    7.30752
YES NH4sul AMSULF      4.36459    0.86127    5.06763
YES SeaSal SALT        0.64528    0.56468    1.14274
YES NMIXED NM81055    15.10180    6.10624    2.47318
YES REVEHI REVEHI      3.01108    4.19167    0.71835
YES RESOIL RESOILCA    4.03797    2.16020    1.86926
YES N19    CEMENT      1.13364    0.88704    1.27800

----------------------------------------------------
                      63.05669

MEASURED CONCENTRATION FOR SIZE: PART
      73.4+-     7.5

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    7 FOR MAX. UNC. = 14.67308  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
```

```
--------------------------------------------------------------------------------
 0.52764   0.79772   0.90248   2.09794   2.90488   4.75661   6.84146
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   7 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL  1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE          Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                                CALCULATED    RESIDUAL
                                                                ----------  ------------
SPECIES      FIT        MEASURED          CALCULATED          MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM       73.36542+- 7.53306  63.05669+- 6.73775   0.86+- 0.13    -1.0
LEV     ULEV   *   0.42677+- 0.10926   0.99948+- 3.57893   2.34+- 8.41     0.2
OC      UOC    *  12.90302+- 3.46807  12.54248+- 0.88359   0.97+- 0.27    -0.1
SOOT    USOOT  *   2.11247+- 1.13528   2.30565+- 0.67315   1.09+- 0.67     0.1
NO3     UNO3   *  26.51159+- 4.69047  27.51172+- 0.33982   1.04+- 0.18     0.2
SO4     USO4   *   3.80534+- 0.51001   3.82795+- 0.33739   1.01+- 0.16     0.0
CL      UCL    *   0.71227+- 0.14396   0.61810+- 0.32477   0.87+- 0.49    -0.3
NH4     UNH4   *   8.98352+- 1.60264   8.52299+- 0.38766   0.95+- 0.17    -0.3
NA      UNA    *   0.14295+- 0.01801   0.28399+- 0.31692   1.99+- 2.23     0.4
K       UK     *   0.52706+- 0.08360   0.58566+- 0.43592   1.11+- 0.85     0.1
CA      UCA    *   0.59816+- 0.09806   0.61628+- 0.31977   1.03+- 0.56     0.1
MG      UMG    *   0.18783+- 0.03338   0.09218+- 0.38796   0.49+- 2.07    -0.2
SI      USI    *   0.72411+- 0.21425   0.70321+- 0.32448   0.97+- 0.53    -0.1
FE      UFE    *   0.38898+- 0.09827   0.34973+- 0.31687   0.90+- 0.85    -0.1
AL      UAL    *   0.28447+- 0.04857   0.32932+- 0.31742   1.16+- 1.13     0.1
ZN      UZN    *   0.21958+- 0.05868   0.02814+- 0.31555   0.13+- 1.44    -0.6
TI      UTI    *   0.02374+- 0.00537   0.02165+- 0.31489   0.91+-13.27     0.0
CU      UCU    *   0.01739+- 0.00291   0.01632+- 0.31519   0.94+-18.12     0.0
V       UV     *   0.00328+- 0.00056   0.00060+- 0.31489   0.18+-95.92     0.0
MN      UMN    *   0.02133+- 0.00358   0.01577+- 0.31491   0.74+-14.76     0.0
PB      UPB    *   0.02016+- 0.00435   0.01356+- 0.31489   0.67+-15.62     0.0
NI      UNI    *   0.00567+- 0.00098   0.00134+- 0.31489   0.24+-55.54     0.0
SR      USR    *   0.00209+- 0.00040   0.00185+- 0.31509   0.88+-*****     0.0
CR      UCR    *   0.00688+- 0.00119   0.00196+- 0.31489   0.29+-45.76     0.0
SB      USB    *   0.00300+- 0.00096   0.00696+- 0.31489   2.32+-*****     0.0
SN      USN    *   0.00473+- 0.00097   0.01145+- 0.31498   2.42+-66.59     0.0
RB      URB    *   0.00129+- 0.00024   0.00265+- 0.31483   2.05+-*****     0.0
MO      UMO    *   0.00285+- 0.00062   0.00098+- 0.31489   0.35+-*****     0.0
AS      UAS    *   0.00112+- 0.00029   0.00051+- 0.31515   0.45+-*****     0.0
CD      UCD    *   0.00063+- 0.00011   0.00024+- 0.31594   0.39+-*****     0.0
CHRYS   UCHRYS     0.00167+- 0.00094 *********+-********  *****+-*****    -1.0
BBFLU   UBBFLU     0.00265+- 0.00053 *********+-********  *****+-*****    -1.0
BKFLU   UBKFLU     0.00148+- 0.00032 *********+-********  *****+-*****    -1.0
BEPYR   UBEPYR     0.00144+- 0.00021 *********+-********  *****+-*****    -1.0
BAPYR   UBAPYR *   0.00148+- 0.00022   0.00168+- 0.35042   1.14+-*****     0.0
IN123   UIN123 *   0.00099+- 0.00014   0.00067+- 0.35041   0.68+-*****     0.0
DBAHA   UDBAHA     0.00046+- 0.00007 *********+-********  *****+-*****    -1.0
```

```
BGPER  UBGPER *   0.00090+- 0.00014   0.00225+- 0.35042   2.51+-*****     0.0
COR    UCOR       0.00027+- 0.00006 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.01606+- 0.00315 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------



                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1Cantu         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                    AD-RL6.csv
                                                                       PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.92                      % MASS      73.6
     CHI SQUARE      0.31               DEGREES FREEDOM      26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     16.78031    3.07601    5.45522
YES NH4sul AMSULF      2.26802    0.90690    2.50084
YES NMIXED NM81055    11.23511    7.56497    1.48515
YES REVEHI REVEHI     10.51916    5.47302    1.92200
YES RESOIL RESOILCA    8.56755    2.35745    3.63425
YES N19    CEMENT      1.35178    0.61311    2.20481

----------------------------------------------------
                      50.72192

MEASURED CONCENTRATION FOR SIZE: PART
      68.9+-     7.2

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 13.77591  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.57370   0.85429   2.29691   3.07319   4.04947   8.43937
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 RESOIL
1.0000 N19
```

```
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       68.87956+- 7.16272  50.72192+- 6.94397   0.74+- 0.13    -1.8
LEV    ULEV   *   1.39810+- 0.39853   0.74357+- 2.20722   0.53+- 1.59    -0.3
OC     UOC    *  13.20451+- 4.68353  14.30729+- 1.48883   1.08+- 0.40     0.2
SOOT   USOOT  *   2.86051+- 1.78448   4.25323+- 1.18596   1.49+- 1.02     0.7
NO3    UNO3   *  13.15204+- 2.81073  13.31730+- 0.45817   1.01+- 0.22     0.1
SO4    USO4   *   2.56178+- 0.60415   2.57284+- 0.20224   1.00+- 0.25     0.0
CL     UCL    *   0.63159+- 0.25745   0.25677+- 0.16861   0.41+- 0.31    -1.2
NH4    UNH4   *   4.29268+- 0.91511   4.17985+- 0.80141   0.97+- 0.28    -0.1
NA     UNA    *   0.35888+- 0.12906   0.11434+- 0.17428   0.32+- 0.50    -1.1
K      UK     *   0.46503+- 0.11136   0.52476+- 0.51792   1.13+- 1.15     0.1
CA     UCA    *   0.76112+- 0.16391   0.82367+- 0.16089   1.08+- 0.31     0.3
MG     UMG    *   0.21840+- 0.05067   0.13687+- 0.80566   0.63+- 3.69    -0.1
SI     USI    *   1.51374+- 0.52403   1.44323+- 0.22631   0.95+- 0.36    -0.1
FE     UFE    *   1.22342+- 0.34287   0.93575+- 0.19004   0.76+- 0.26    -0.7
AL     UAL    *   0.58272+- 0.12631   0.65908+- 0.17944   1.13+- 0.39     0.3
ZN     UZN    *   0.48377+- 0.15962   0.03989+- 0.15305   0.08+- 0.32    -2.0
TI     UTI    *   0.03473+- 0.00988   0.04451+- 0.15226   1.28+- 4.40     0.1
CU     UCU    *   0.04576+- 0.01043   0.04747+- 0.15889   1.04+- 3.48     0.0
V      UV     *   0.00325+- 0.00088   0.00129+- 0.15222   0.40+-46.83     0.0
MN     UMN    *   0.02413+- 0.00600   0.02471+- 0.15229   1.02+- 6.32     0.0
PB     UPB    *   0.03740+- 0.00978   0.04464+- 0.15228   1.19+- 4.08     0.0
NI     UNI    *   0.01241+- 0.00292   0.00219+- 0.15222   0.18+-12.26    -0.1
SR     USR    *   0.00394+- 0.00093   0.00249+- 0.15875   0.63+-40.29     0.0
CR     UCR    *   0.01249+- 0.00340   0.00511+- 0.15222   0.41+-12.18     0.0
SB     USB    *   0.00797+- 0.00278   0.02267+- 0.15235   2.84+-19.14     0.1
SN     USN    *   0.00966+- 0.00237   0.01432+- 0.15234   1.48+-15.77     0.0
RB     URB    *   0.00181+- 0.00044   0.00322+- 0.15222   1.78+-83.91     0.0
MO     UMO    *   0.00732+- 0.00198   0.00316+- 0.15222   0.43+-20.80     0.0
AS     UAS    *   0.00106+- 0.00032   0.00129+- 0.15879   1.21+-*****     0.0
CD     UCD    *   0.00071+- 0.00019   0.00028+- 0.17676   0.40+-*****     0.0
CHRYS  UCHRYS     0.00378+- 0.00222 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00375+- 0.00100 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00106+- 0.00030 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00125+- 0.00028 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR *   0.00177+- 0.00038   0.00148+- 0.16934   0.84+-95.74     0.0
IN123  UIN123 *   0.00197+- 0.00045   0.00077+- 0.16933   0.39+-85.89     0.0
DBAHA  UDBAHA     0.00025+- 0.00006 *********+-********  *****+-*****    -1.0
BGPER  UBGPER *   0.00190+- 0.00044   0.00193+- 0.16934   1.02+-89.14     0.0
COR    UCOR       0.00151+- 0.00039 *********+-********  *****+-*****    -1.0
PAH    UPAH       0.02107+- 0.00310 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                      Chemical Mass Balance Version EPA-CMB8.2
                             Report Date: 02/09/2010
```

```
SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          2Cantu         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2009       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.97                        % MASS      77.4
     CHI SQUARE      0.14                DEGREES FREEDOM       26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME      SCE(µg/m³)     Std Err        Tstat
----------------------------------------------------
YES NH4NO3 AMNITR      28.30014     4.58573    6.17135
YES NH4sul AMSULF       3.80836     0.87166    4.36908
YES NMIXED NM81055     16.40338     5.25977    3.11865
YES RESOIL RESOILCA     8.78794     2.75564    3.18907
YES TRAFCI TRAFCITY     1.82488     2.14505    0.85074
YES N19    CEMENT       0.70921     0.72172    0.98268

----------------------------------------------------
                       59.83392

MEASURED CONCENTRATION FOR SIZE: PART
      77.3+-     7.8

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 15.46879  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.67226   0.86411   1.74753   2.85559   4.58624   5.35995
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 RESOIL  1.0000 TRAFCI
1.0000 N19
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE          Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
```

```
                                                        ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED        MEASURED   UNCERTAINTY
----------------------------------------------------------------------------------

PM     UPM        77.34397+- 7.83589  59.83392+- 6.88259   0.77+- 0.12    -1.7
LEV    ULEV    *   0.66620+- 0.15657   1.08563+- 3.04794   1.63+- 4.59     0.1
OC     UOC     *  14.40394+- 3.85520  13.02863+- 0.86246   0.90+- 0.25    -0.3
SOOT   USOOT   *   1.54189+- 0.84478   2.06956+- 0.63310   1.34+- 0.84     0.5
NO3    UNO3    *  20.95665+- 4.36853  22.41953+- 0.26975   1.07+- 0.22     0.3
SO4    USO4    *   3.25915+- 0.56480   3.30014+- 0.28694   1.01+- 0.20     0.1
CL     UCL     *   0.57287+- 0.12322   0.22373+- 0.26808   0.39+- 0.48    -1.2
NH4    UNH4    *   7.84553+- 1.67803   7.01585+- 0.29158   0.89+- 0.19    -0.5
NA     UNA     *   0.15592+- 0.01857   0.11474+- 0.26000   0.74+- 1.67    -0.2
K      UK      *   0.42273+- 0.07564   0.67874+- 0.39958   1.61+- 0.99     0.6
CA     UCA     *   0.48116+- 0.07909   0.56441+- 0.26362   1.17+- 0.58     0.3
MG     UMG     *   0.23461+- 0.04240   0.13327+- 0.29178   0.57+- 1.25    -0.3
SI     USI     *   1.48124+- 0.50530   1.43941+- 0.30248   0.97+- 0.39    -0.1
FE     UFE     *   0.69795+- 0.16751   0.63453+- 0.25967   0.91+- 0.43    -0.2
AL     UAL     *   0.62973+- 0.11675   0.66024+- 0.26867   1.05+- 0.47     0.1
ZN     UZN     *   0.27513+- 0.07441   0.03222+- 0.25764   0.12+- 0.94    -0.9
TI     UTI     *   0.04769+- 0.01133   0.04200+- 0.25671   0.88+- 5.39     0.0
CU     UCU     *   0.02319+- 0.00377   0.02417+- 0.25688   1.04+-11.08     0.0
V      UV      *   0.00299+- 0.00052   0.00108+- 0.25669   0.36+-85.82     0.0
MN     UMN     *   0.01970+- 0.00346   0.02112+- 0.25671   1.07+-13.04     0.0
PB     UPB     *   0.02424+- 0.00502   0.00940+- 0.25669   0.39+-10.59    -0.1
NI     UNI     *   0.00968+- 0.00173   0.00192+- 0.25669   0.20+-26.53     0.0
SR     USR     *   0.00375+- 0.00077   0.00216+- 0.25681   0.58+-68.41     0.0
CR     UCR     *   0.01046+- 0.00191   0.00372+- 0.25669   0.36+-24.55     0.0
SB     USB     *   0.00532+- 0.00181   0.00594+- 0.25671   1.12+-48.24     0.0
SN     USN     *   0.00679+- 0.00132   0.01156+- 0.25683   1.70+-37.85     0.0
RB     URB     *   0.00223+- 0.00040   0.00310+- 0.25669   1.39+-*****     0.0
MO     UMO     *   0.00387+- 0.00074   0.00083+- 0.25669   0.21+-66.33     0.0
AS     UAS     *   0.00113+- 0.00030   0.00062+- 0.25681   0.54+-*****     0.0
CD     UCD     *   0.00072+- 0.00012   0.00034+- 0.25716   0.47+-*****     0.0
CHRYS  UCHRYS      0.00250+- 0.00143 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU      0.00266+- 0.00051 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU      0.00160+- 0.00032 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR      0.00148+- 0.00020 *********+-********  *****+-*****    -1.0
BAPYR  UBAPYR  *   0.00233+- 0.00032   0.00179+- 0.28557   0.77+-*****     0.0
IN123  UIN123  *   0.00154+- 0.00021   0.00069+- 0.28556   0.45+-*****     0.0
DBAHA  UDBAHA      0.00097+- 0.00014 *********+-********  *****+-*****    -1.0
BGPER  UBGPER  *   0.00210+- 0.00031   0.00240+- 0.28557   1.15+-*****     0.0
COR    UCOR        0.00033+- 0.00008 *********+-********  *****+-*****    -1.0
PAH    UPAH        0.01548+- 0.00266 *********+-********  *****+-*****    -1.0
----------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                               Report Date: 02/09/2010

SAMPLE:                        OPTIONS:                            INPUT FILES:

SITE:          1Abb-LO         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007        SOURCE ELIMINATION:      Yes
DURATION:      24              BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                    AD-RL6.csv
                                                                       PR-RL5.csv
```

```
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.97                          % MASS      69.2
     CHI SQUARE      0.18                 DEGREES FREEDOM        26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME      SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     20.62397    2.61030    7.90099
YES NH4sul AMSULF      4.44246    0.69511    6.39104
YES SeaSal SALT        1.21337    0.37565    3.23004
YES NMIXED NM81055     9.61738    4.72628    2.03487
YES REVEHI REVEHI      4.32714    3.38977    1.27653
YES RESOIL RESOILCA    6.66898    2.01680    3.30671

----------------------------------------------------
                      46.89329

MEASURED CONCENTRATION FOR SIZE: PART
      67.8+-     7.0

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =   6 FOR MAX. UNC. = 13.55384  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.36888   0.66736   1.85778   2.49722   2.61503   5.31285
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  ------------
SPECIES      FIT        MEASURED          CALCULATED      MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM       67.76921+- 7.03605  46.89329+- 4.70332   0.69+- 0.10    -2.5
LEV     ULEV   *   0.41913+- 0.11971   0.63651+- 2.28130   1.52+- 5.46     0.1
OC      UOC    *   9.73247+- 2.80341   9.38347+- 0.75560   0.96+- 0.29    -0.1
SOOT    USOOT  *   1.82813+- 1.02923   2.20569+- 0.59087   1.21+- 0.75     0.3
NO3     UNO3   *  15.50733+- 2.38850  16.33058+- 0.26138   1.05+- 0.16     0.3
```

```
SO4     USO4    *   3.73443+- 0.45349   3.78193+- 0.20854   1.01+- 0.14      0.1
CL      UCL     *   0.68000+- 0.13012   0.76349+- 0.20653   1.12+- 0.37      0.3
NH4     UNH4    *   6.13256+- 0.98288   5.54097+- 0.37586   0.90+- 0.16     -0.6
NA      UNA     *   0.55863+- 0.08105   0.44842+- 0.19523   0.80+- 0.37     -0.5
K       UK      *   0.35658+- 0.06122   0.42187+- 0.31766   1.18+- 0.91      0.2
CA      UCA     *   0.44616+- 0.08075   0.23252+- 0.19379   0.52+- 0.44     -1.0
MG      UMG     *   0.12344+- 0.02423   0.14638+- 0.37731   1.19+- 3.07      0.1
SI      USI     *   1.06104+- 0.40819   1.07960+- 0.22713   1.02+- 0.45      0.0
FE      UFE     *   0.55282+- 0.14335   0.51681+- 0.19701   0.93+- 0.43     -0.1
AL      UAL     *   0.39707+- 0.08699   0.48940+- 0.20116   1.23+- 0.57      0.4
ZN      UZN     *   0.37162+- 0.10769   0.02383+- 0.19119   0.06+- 0.51     -1.6
TI      UTI     *   0.02094+- 0.00565   0.03199+- 0.19076   1.53+- 9.12      0.1
CU      UCU     *   0.02221+- 0.00389   0.02090+- 0.19168   0.94+- 8.63      0.0
V       UV      *   0.00291+- 0.00064   0.00084+- 0.19074   0.29+-65.51      0.0
MN      UMN     *   0.01963+- 0.00365   0.01600+- 0.19076   0.82+- 9.72      0.0
PB      UPB     *   0.02137+- 0.00482   0.01878+- 0.19075   0.88+- 8.93      0.0
NI      UNI     *   0.00754+- 0.00156   0.00146+- 0.19074   0.19+-25.29      0.0
SR      USR     *   0.00268+- 0.00056   0.00186+- 0.19130   0.70+-71.48      0.0
CR      UCR     *   0.00689+- 0.00139   0.00264+- 0.19074   0.38+-27.70      0.0
SB      USB     *   0.00468+- 0.00149   0.01017+- 0.19077   2.17+-40.74      0.0
SN      USN     *   0.00595+- 0.00128   0.00904+- 0.19080   1.52+-32.07      0.0
RB      URB     *   0.00125+- 0.00027   0.00194+- 0.19040   1.55+-*****      0.0
MO      UMO     *   0.00386+- 0.00079   0.00138+- 0.19074   0.36+-49.37      0.0
AS      UAS     *   0.00129+- 0.00037   0.00068+- 0.19164   0.53+-*****      0.0
CD      UCD     *   0.00078+- 0.00017   0.00022+- 0.19429   0.28+-*****      0.0
CHRYS   UCHRYS      0.00161+- 0.00099 *********+-********  *****+-*****     -1.0
BBFLU   UBBFLU      0.00193+- 0.00048 *********+-********  *****+-*****     -1.0
BKFLU   UBKFLU      0.00052+- 0.00014 *********+-********  *****+-*****     -1.0
BEPYR   UBEPYR      0.00062+- 0.00013 *********+-********  *****+-*****     -1.0
BAPYR   UBAPYR  *   0.00050+- 0.00011   0.00114+- 0.21133   2.27+-*****      0.0
IN123   UIN123  *   0.00112+- 0.00022   0.00051+- 0.21132   0.45+-*****      0.0
DBAHA   UDBAHA      0.00016+- 0.00004 *********+-********  *****+-*****     -1.0
BGPER   UBGPER  *   0.00072+- 0.00017   0.00151+- 0.21133   2.10+-*****      0.0
COR     UCOR        0.00049+- 0.00013 *********+-********  *****+-*****     -1.0
PAH     UPAH        0.00914+- 0.00173 *********+-********  *****+-*****     -1.0
--------------------------------------------------------------------------------


                   Chemical Mass Balance Version EPA-CMB8.2
                            Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                               INPUT FILES:

SITE:          2Abb-LO        BRITT & LUECKE:         No
SAMPLE DATE:   feb 2007       SOURCE ELIMINATION:     Yes
DURATION:      24             BEST FIT:               No
START HOUR:    0
SIZE:          PART                                                       AD-RL6.csv
                                                                          PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE       0.97                       % MASS       78.2
     CHI SQUARE       0.14               DEGREES FREEDOM        26
```

```
SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     31.29307    4.77551    6.55282
YES NH4sul AMSULF      4.50790    0.91137    4.94631
YES SeaSal SALT        0.90904    0.51826    1.75402
YES NMIXED NM81055    15.04243    5.93711    2.53363
YES REVEHI REVEHI      1.92209    3.71939    0.51677
YES RESOIL RESOILCA    9.06815    2.50595    3.61864

----------------------------------------------------
                      62.74268

MEASURED CONCENTRATION FOR SIZE: PART
      80.2+-     8.0

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 16.04197  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.51000   0.88657   2.27655   2.78875   4.77540   6.51593
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM        80.20985+- 8.01529  62.74268+- 6.79799   0.78+- 0.12     -1.7
LEV    ULEV   *   0.53671+- 0.12934   0.99555+- 3.33535   1.85+- 6.23      0.1
OC     UOC    *  12.63825+- 3.53745  11.98062+- 0.81604   0.95+- 0.27     -0.2
SOOT   USOOT  *   1.63140+- 0.89427   1.97078+- 0.61044   1.21+- 0.76      0.3
NO3    UNO3   *  23.30020+- 4.57487  24.77413+- 0.29697   1.06+- 0.21      0.3
SO4    USO4   *   3.75195+- 0.58317   3.79273+- 0.30770   1.01+- 0.18      0.1
CL     UCL    *   0.73797+- 0.16334   0.63977+- 0.29680   0.87+- 0.45     -0.3
NH4    UNH4   *   8.62499+- 1.72164   7.81966+- 0.31936   0.91+- 0.18     -0.5
NA     UNA    *   0.23773+- 0.04573   0.38349+- 0.28732   1.61+- 1.25      0.5
K      UK     *   0.49705+- 0.09358   0.62906+- 0.40168   1.27+- 0.84      0.3
CA     UCA    *   0.70010+- 0.10522   0.29715+- 0.28947   0.42+- 0.42     -1.3
MG     UMG    *   0.23144+- 0.03685   0.16783+- 0.31951   0.73+- 1.39     -0.2
SI     USI    *   1.41452+- 0.41890   1.45396+- 0.32862   1.03+- 0.38      0.1
FE     UFE    *   0.57613+- 0.13519   0.49437+- 0.28630   0.86+- 0.54     -0.3
```

```
AL      UAL     *   0.52298+- 0.08267   0.66261+- 0.29595   1.27+- 0.60      0.5
ZN      UZN     *   0.25881+- 0.07132   0.02681+- 0.28516   0.10+- 1.10     -0.8
TI      UTI     *   0.03220+- 0.00693   0.04200+- 0.28446   1.30+- 8.84      0.0
CU      UCU     *   0.01885+- 0.00276   0.01221+- 0.28460   0.65+-15.10      0.0
V       UV      *   0.00332+- 0.00049   0.00104+- 0.28444   0.31+-85.76      0.0
MN      UMN     *   0.01939+- 0.00282   0.01938+- 0.28446   1.00+-14.67      0.0
PB      UPB     *   0.01419+- 0.00304   0.00951+- 0.28444   0.67+-20.04      0.0
NI      UNI     *   0.00535+- 0.00094   0.00181+- 0.28444   0.34+-53.20      0.0
SR      USR     *   0.00391+- 0.00072   0.00218+- 0.28443   0.56+-72.82      0.0
CR      UCR     *   0.00972+- 0.00150   0.00229+- 0.28444   0.24+-29.25      0.0
SB      USB     *   0.00347+- 0.00110   0.00617+- 0.28446   1.78+-81.89      0.0
SN      USN     *   0.00565+- 0.00102   0.01079+- 0.28454   1.91+-50.37      0.0
RB      URB     *   0.00158+- 0.00026   0.00267+- 0.28431   1.69+-*****      0.0
MO      UMO     *   0.00277+- 0.00053   0.00078+- 0.28444   0.28+-*****      0.0
AS      UAS     *   0.00119+- 0.00030   0.00062+- 0.28456   0.52+-*****      0.0
CD      UCD     *   0.00059+- 0.00008   0.00032+- 0.28491   0.54+-*****      0.0
CHRYS   UCHRYS      0.00181+- 0.00116 *********+-********  *****+-*****     -1.0
BBFLU   UBBFLU      0.00207+- 0.00043 *********+-********  *****+-*****     -1.0
BKFLU   UBKFLU      0.00125+- 0.00028 *********+-********  *****+-*****     -1.0
BEPYR   UBEPYR      0.00101+- 0.00015 *********+-********  *****+-*****     -1.0
BAPYR   UBAPYR  *   0.00112+- 0.00018   0.00165+- 0.31630   1.46+-*****      0.0
IN123   UIN123  *   0.00261+- 0.00036   0.00063+- 0.31629   0.24+-*****      0.0
DBAHA   UDBAHA      0.00088+- 0.00013 *********+-********  *****+-*****     -1.0
BGPER   UBGPER  *   0.00123+- 0.00020   0.00221+- 0.31631   1.79+-*****      0.0
COR     UCOR        0.00021+- 0.00006 *********+-********  *****+-*****     -1.0
PAH     UPAH        0.01200+- 0.00313 *********+-********  *****+-*****     -1.0
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1San-PV        BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.97                      % MASS       63.1
     CHI SQUARE      0.12             DEGREES FREEDOM         26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE    NAME     SCE(µg/m³)    Std Err       Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     17.58190    3.00870    5.84369
YES NH4sul AMSULF      4.08182    0.95589    4.27015
YES SeaSal SALT        0.73332    0.37585    1.95113
YES NMIXED NM81055     9.44575    4.29883    2.19728
```

```
YES REVEHI REVEHI      2.81255    2.71275    1.03679
YES RESOIL RESOILCA    4.09953    1.43355    2.85970

----------------------------------------------------
                      38.75487

MEASURED CONCENTRATION FOR SIZE: PART
      61.4+-     6.7

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 12.28604  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.37071   0.93529   1.36111   2.09290   3.01082   4.65739
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 SeaSal  1.0000 NMIXED  1.0000 REVEHI
1.0000 RESOIL
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------   -----------
SPECIES      FIT       MEASURED          CALCULATED       MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM      UPM         61.43022+- 6.66904  38.75487+- 4.66271   0.63+- 0.10    -2.8
LEV     ULEV   *     0.39133+- 0.10513   0.62515+- 1.90090   1.60+- 4.88     0.1
OC      UOC    *     8.29590+- 2.79310   8.26796+- 0.60580   1.00+- 0.34     0.0
SOOT    USOOT  *     1.36155+- 0.82213   1.72315+- 0.46280   1.27+- 0.84     0.4
NO3     UNO3   *    13.07807+- 2.78819  13.92414+- 0.20091   1.06+- 0.23     0.3
SO4     USO4   *     3.32111+- 0.68348   3.39349+- 0.18062   1.02+- 0.22     0.1
CL      UCL    *     0.50539+- 0.19417   0.49319+- 0.17368   0.98+- 0.51     0.0
NH4     UNH4   *     5.36170+- 1.14337   4.80277+- 0.26654   0.90+- 0.20    -0.5
NA      UNA    *     0.26546+- 0.08753   0.28269+- 0.16579   1.06+- 0.72     0.1
K       UK     *     0.40970+- 0.07517   0.37427+- 0.26497   0.91+- 0.67    -0.1
CA      UCA    *     0.28642+- 0.04936   0.15759+- 0.16637   0.55+- 0.59    -0.7
MG      UMG    *     0.11385+- 0.02216   0.09145+- 0.26725   0.80+- 2.35    -0.1
SI      USI    *     0.65096+- 0.23300   0.67096+- 0.18040   1.03+- 0.46     0.1
FE      UFE    *     0.39707+- 0.10023   0.32877+- 0.16638   0.83+- 0.47    -0.4
AL      UAL    *     0.23970+- 0.05070   0.30538+- 0.16796   1.27+- 0.75     0.4
ZN      UZN    *     0.26502+- 0.07361   0.01972+- 0.16371   0.07+- 0.62    -1.4
TI      UTI    *     0.01242+- 0.00334   0.02009+- 0.16322   1.62+-13.14     0.0
CU      UCU    *     0.01463+- 0.00258   0.01424+- 0.16368   0.97+-11.19     0.0
V       UV     *     0.00301+- 0.00061   0.00052+- 0.16321   0.17+-54.17     0.0
MN      UMN    *     0.01181+- 0.00216   0.01203+- 0.16322   1.02+-13.83     0.0
PB      UPB    *     0.01978+- 0.00430   0.01227+- 0.16321   0.62+- 8.25     0.0
NI      UNI    *     0.00924+- 0.00174   0.00106+- 0.16321   0.11+-17.66    -0.1
SR      USR    *     0.00216+- 0.00046   0.00126+- 0.16351   0.59+-75.79     0.0
```

```
CR      UCR     *   0.00646+- 0.00124   0.00175+- 0.16321   0.27+-25.28     0.0
SB      USB     *   0.00317+- 0.00109   0.00656+- 0.16322   2.07+-51.44     0.0
SN      USN     *   0.00472+- 0.00099   0.00783+- 0.16328   1.66+-34.61     0.0
RB      URB     *   0.00101+- 0.00021   0.00155+- 0.16306   1.54+-*****     0.0
MO      UMO     *   0.00190+- 0.00045   0.00090+- 0.16321   0.48+-86.04     0.0
AS      UAS     *   0.00094+- 0.00025   0.00045+- 0.16365   0.48+-*****     0.0
CD      UCD     *   0.00042+- 0.00007   0.00017+- 0.16497   0.41+-*****     0.0
CHRYS   UCHRYS      0.00130+- 0.00081 *********+-********  *****+-*****    -1.0
BBFLU   UBBFLU      0.00183+- 0.00044 *********+-********  *****+-*****    -1.0
BKFLU   UBKFLU      0.00047+- 0.00013 *********+-********  *****+-*****    -1.0
BEPYR   UBEPYR      0.00056+- 0.00011 *********+-********  *****+-*****    -1.0
BAPYR   UBAPYR *    0.00038+- 0.00008   0.00108+- 0.18065   2.80+-*****     0.0
IN123   UIN123 *    0.00062+- 0.00012   0.00045+- 0.18065   0.72+-*****     0.0
DBAHA   UDBAHA      0.00011+- 0.00002 *********+-********  *****+-*****    -1.0
BGPER   UBGPER *    0.00073+- 0.00015   0.00144+- 0.18065   1.96+-*****     0.0
COR     UCOR        0.00178+- 0.00049 *********+-********  *****+-*****    -1.0
PAH     UPAH        0.00915+- 0.00150 *********+-********  *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:           2San-PV       BRITT & LUECKE:         No
SAMPLE DATE:    Feb 2009      SOURCE ELIMINATION:     Yes
DURATION:       24            BEST FIT:               No
START HOUR:     0
SIZE:           PART                                                  AD-RL6.csv
                                                                      PR-RL5.csv

Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE       0.99                   % MASS       82.5
     CHI SQUARE       0.06          DEGREES FREEDOM         27


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME      SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR     23.40656    2.63435    8.88514
YES NH4sul AMSULF      4.53735    0.56027    8.09848
YES NMIXED NM81055    13.37684    4.63558    2.88569
YES REVEHI REVEHI      1.02285    2.94087    0.34781
YES REBITU REBITUM     2.96532    1.41235    2.09956

----------------------------------------------------
                      45.30893

MEASURED CONCENTRATION FOR SIZE: PART
      54.9+-     6.4

                   Eligible Space Collinearity Display
```

```
================================================================================
ELIGIBLE SPACE DIM. =   5 FOR MAX. UNC. = 10.98439  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.53504   1.34902   2.18594   2.63527   5.05536
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   5 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 REBITU
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------  -----------
SPECIES      FIT        MEASURED          CALCULATED       MEASURED  UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       54.92195+- 6.36685  45.30893+- 4.52498   0.82+- 0.13    -1.2
LEV    ULEV   *   0.41548+- 0.11031   0.88532+- 2.44736   2.13+- 5.92     0.2
OC     UOC    *  10.49988+- 2.87697  10.15192+- 0.68935   0.97+- 0.27    -0.1
SOOT   USOOT  *   1.41402+- 0.79982   1.54785+- 0.50568   1.09+- 0.72     0.1
NO3    UNO3   *  17.42047+- 2.45350  18.53378+- 0.22091   1.06+- 0.15     0.5
SO4    USO4   *   3.62298+- 0.32008   3.66209+- 0.23859   1.01+- 0.11     0.1
CL     UCL    *   0.23854+- 0.04386   0.12271+- 0.22389   0.51+- 0.94    -0.5
NH4    UNH4   *   6.87799+- 0.99834   6.15714+- 0.22885   0.90+- 0.13    -0.7
NA     UNA    *   0.10211+- 0.00860   0.06032+- 0.21638   0.59+- 2.12    -0.2
K      UK     *   0.39106+- 0.05003   0.47189+- 0.32606   1.21+- 0.85     0.2
CA     UCA    *   0.15523+- 0.02440   0.24586+- 0.22022   1.58+- 1.44     0.4
MG     UMG    *   0.09437+- 0.01420   0.07315+- 0.22925   0.78+- 2.43    -0.1
SI     USI    *   0.49660+- 0.13424   0.47325+- 0.21839   0.95+- 0.51    -0.1
FE     UFE    *   0.22409+- 0.06230   0.19059+- 0.21678   0.85+- 1.00    -0.1
AL     UAL    *   0.19195+- 0.03197   0.17377+- 0.21585   0.91+- 1.13    -0.1
ZN     UZN    *   0.13633+- 0.03617   0.02384+- 0.21567   0.17+- 1.58    -0.5
TI     UTI    *   0.01226+- 0.00285   0.01621+- 0.21493   1.32+-17.53     0.0
CU     UCU    *   0.00828+- 0.00142   0.00857+- 0.21500   1.04+-25.98     0.0
V      UV     *   0.00349+- 0.00056   0.00032+- 0.21492   0.09+-61.58     0.0
MN     UMN    *   0.00682+- 0.00120   0.01109+- 0.21493   1.62+-31.50     0.0
PB     UPB    *   0.01227+- 0.00272   0.00545+- 0.21492   0.44+-17.52     0.0
NI     UNI    *   0.00490+- 0.00086   0.00098+- 0.21492   0.20+-43.85     0.0
SR     USR    *   0.00148+- 0.00027   0.00145+- 0.21496   0.98+-*****     0.0
CR     UCR    *   0.00488+- 0.00090   0.00108+- 0.21492   0.22+-44.08     0.0
SB     USB    *   0.00294+- 0.00093   0.00211+- 0.21492   0.72+-73.03     0.0
SN     USN    *   0.00363+- 0.00075   0.00917+- 0.21503   2.52+-59.22     0.0
RB     URB    *   0.00098+- 0.00018   0.00162+- 0.21492   1.65+-*****     0.0
MO     UMO    *   0.00140+- 0.00034   0.00041+- 0.21492   0.30+-*****     0.0
AS     UAS    *   0.00091+- 0.00023   0.00022+- 0.21496   0.25+-*****     0.0
CD     UCD    *   0.00044+- 0.00006   0.00024+- 0.21509   0.54+-*****     0.0
CHRYS  UCHRYS     0.00126+- 0.00077 *********+-********  *****+-*****    -1.0
BBFLU  UBBFLU     0.00167+- 0.00038 *********+-********  *****+-*****    -1.0
BKFLU  UBKFLU     0.00102+- 0.00025 *********+-********  *****+-*****    -1.0
BEPYR  UBEPYR     0.00080+- 0.00012 *********+-********  *****+-*****    -1.0
```

```
BAPYR  UBAPYR *   0.00059+- 0.00009   0.00145+- 0.23843   2.46+-*****     0.0
IN123  UIN123 *   0.00052+- 0.00008   0.00054+- 0.23842   1.04+-*****     0.0
DBAHA  UDBAHA     0.00025+- 0.00004 *********+-******** *****+-*****    -1.0
BGPER  UBGPER *   0.00072+- 0.00013   0.00194+- 0.23844   2.72+-*****     0.0
COR    UCOR       0.00014+- 0.00003 *********+-******** *****+-*****    -1.0
PAH    UPAH       0.00697+- 0.00177 *********+-******** *****+-*****    -1.0
--------------------------------------------------------------------------------


                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          1SO-vm         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                   AD-RL6.csv
                                                                      PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.95                      % MASS      72.2
     CHI SQUARE      0.23              DEGREES FREEDOM       26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err       Tstat
----------------------------------------------------
YES NH4NO3 AMNITR      7.26942    1.23237    5.89872
YES NH4sul AMSULF      1.13625    0.85505    1.32887
YES NREALW NREALLWO   10.10382    5.15815    1.95881
YES REVEHI REVEHI      7.42282    3.53953    2.09712
YES RESOIL RESOILCA    8.02939    1.56035    5.14589
YES New8V  NFUEL2      3.17761    1.92358    1.65192

----------------------------------------------------
                      37.13931

MEASURED CONCENTRATION FOR SIZE: PART
      51.5+-     6.1

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =   6 FOR MAX. UNC. = 10.29103  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.76110   1.16834   1.43624   1.91239   2.96865   5.57156
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =   6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE    PROJ. SOURCE
```

```
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NREALW  1.0000 REVEHI  1.0000 RESOIL
1.0000 New8V
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================

SPECIES CONCENTRATIONS:
                                                             CALCULATED    RESIDUAL
                                                             ----------   -----------
SPECIES       FIT       MEASURED          CALCULATED          MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       51.45517+- 6.05522  37.13931+- 4.53212   0.72+- 0.12     -1.9
LEV    ULEV   *   1.05514+- 0.28632   0.98952+- 1.49033   0.94+- 1.44      0.0
OC     UOC    * 11.49307+- 3.23488  12.86519+- 2.50972   1.12+- 0.38      0.3
SOOT   USOOT  *   2.34183+- 1.24633   3.35189+- 1.29271   1.43+- 0.94      0.6
NO3    UNO3   *   6.18641+- 0.95016   6.38677+- 0.31448   1.03+- 0.17      0.2
SO4    USO4   *   1.85106+- 0.24372   1.94939+- 0.55520   1.05+- 0.33      0.2
CL     UCL    *   0.23435+- 0.04444   0.14600+- 0.10883   0.62+- 0.48     -0.8
NH4    UNH4   *   2.19685+- 0.36212   1.86437+- 0.55937   0.85+- 0.29     -0.5
NA     UNA    *   0.24869+- 0.03411   0.28024+- 0.10719   1.13+- 0.46      0.3
K      UK     *   0.35571+- 0.05288   0.63564+- 0.86929   1.79+- 2.46      0.3
CA     UCA    *   0.45451+- 0.07519   0.31623+- 0.11815   0.70+- 0.28     -1.0
MG     UMG    *   0.29375+- 0.05169   0.14292+- 0.56244   0.49+- 1.92     -0.3
SI     USI    *   1.23647+- 0.38205   1.30489+- 0.16546   1.06+- 0.35      0.2
FE     UFE    *   0.85533+- 0.20023   0.73577+- 0.10489   0.86+- 0.24     -0.5
AL     UAL    *   0.55598+- 0.09668   0.60650+- 0.10706   1.09+- 0.27      0.4
ZN     UZN    *   0.25467+- 0.08035   0.06093+- 0.08435   0.24+- 0.34     -1.7
TI     UTI    *   0.02366+- 0.00539   0.03884+- 0.06628   1.64+- 2.83      0.2
CU     UCU    *   0.02115+- 0.00370   0.03408+- 0.07364   1.61+- 3.49      0.2
V      UV     *   0.00499+- 0.00085   0.00624+- 0.06621   1.25+-13.26      0.0
MN     UMN    *   0.01469+- 0.00270   0.02504+- 0.07168   1.70+- 4.89      0.1
PB     UPB    *   0.01824+- 0.00456   0.03185+- 0.06628   1.75+- 3.66      0.2
NI     UNI    *   0.00860+- 0.00164   0.00627+- 0.06621   0.73+- 7.70      0.0
SR     USR    *   0.00278+- 0.00057   0.00198+- 0.07345   0.71+-26.42      0.0
CR     UCR    *   0.00822+- 0.00179   0.00427+- 0.06621   0.52+- 8.06     -0.1
SB     USB    *   0.00277+- 0.00092   0.01675+- 0.06639   6.04+-24.04      0.2
SN     USN    *   0.00341+- 0.00082   0.00990+- 0.06650   2.90+-19.51      0.1
RB     URB    *   0.00192+- 0.00036   0.00314+- 0.06630   1.64+-34.53      0.0
MO     UMO    *   0.00366+- 0.00092   0.00227+- 0.06620   0.62+-18.10      0.0
AS     UAS    *   0.00073+- 0.00020   0.00107+- 0.07349   1.46+-*****      0.0
CD     UCD    *   0.00033+- 0.00006   0.00034+- 0.09167   1.02+-*****      0.0
CHRYS  UCHRYS     0.00625+- 0.00375 *********+-********  *****+-*****     -1.3
BBFLU  UBBFLU     0.00544+- 0.00127 *********+-********  *****+-*****     -1.3
BKFLU  UBKFLU     0.00157+- 0.00040 *********+-********  *****+-*****     -1.3
BEPYR  UBEPYR     0.00248+- 0.00046 *********+-********  *****+-*****     -1.3
BAPYR  UBAPYR *   0.00299+- 0.00056   0.00133+- 0.07358   0.45+-24.63      0.0
IN123  UIN123 *   0.00324+- 0.00060   0.00057+- 0.07358   0.17+-22.73      0.0
DBAHA  UDBAHA     0.00040+- 0.00008 *********+-********  *****+-*****     -1.3
BGPER  UBGPER *   0.00328+- 0.00068   0.00184+- 0.07359   0.56+-22.41      0.0
COR    UCOR       0.00264+- 0.00064 *********+-********  *****+-*****     -1.3
PAH    UPAH       0.03323+- 0.00568 *********+-********  *****+-*****     -1.3
--------------------------------------------------------------------------------
```

```
                     Chemical Mass Balance Version EPA-CMB8.2
                              Report Date: 02/09/2010

SAMPLE:                       OPTIONS:                           INPUT FILES:

SITE:          2SO-vm         BRITT & LUECKE:          No
SAMPLE DATE:   Feb 2007       SOURCE ELIMINATION:      Yes
DURATION:      24             BEST FIT:                No
START HOUR:    0
SIZE:          PART                                                    AD-RL6.csv
                                                                       PR-RL5.csv
Species Array: 1
Sources Array: 1

FITTING STATISTICS:

       R SQUARE      0.96                       % MASS      79.0
     CHI SQUARE      0.25               DEGREES FREEDOM       26


SOURCE CONTRIBUTION ESTIMATES:

SOURCE
EST CODE   NAME     SCE(µg/m³)    Std Err      Tstat
----------------------------------------------------
YES NH4NO3 AMNITR      6.79019    1.31508    5.16332
YES NH4sul AMSULF      1.07427    0.48048    2.23582
YES NMIXED NM81055    13.87894    4.86329    2.85382
YES REVEHI REVEHI      5.37909    3.44104    1.56322
YES RESOIL RESOILCA   12.38242    2.01173    6.15510
YES New8V  NFUEL2      0.39119    1.51824    0.25766

----------------------------------------------------
                      39.89610

MEASURED CONCENTRATION FOR SIZE: PART
      50.5+-     5.9

                   Eligible Space Collinearity Display
================================================================================
ELIGIBLE SPACE DIM. =    6 FOR MAX. UNC. = 10.09605  (20.% OF TOTAL MEAS. MASS)

1 / Singular Value
--------------------------------------------------------------------------------
 0.34409   1.24604   1.42047   1.88584   2.97113   5.26612
--------------------------------------------------------------------------------

NUMBER ESTIMABLE SOURCES =    6 FOR MIN. PROJ. =  0.95
 PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
--------------------------------------------------------------------------------
1.0000 NH4NO3  1.0000 NH4sul  1.0000 NMIXED  1.0000 REVEHI  1.0000 RESOIL
1.0000 New8V
--------------------------------------------------------------------------------

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE         Std Err
--------------------------------------------------------------------------------
================================================================================
```

```
SPECIES CONCENTRATIONS:
                                                         CALCULATED    RESIDUAL
                                                         ----------   -----------
SPECIES      FIT      MEASURED          CALCULATED         MEASURED   UNCERTAINTY
--------------------------------------------------------------------------------

PM     UPM       50.48025+- 5.93828  39.89610+- 4.38912   0.79+- 0.13      -1.4
LEV    ULEV   *   0.88997+- 0.24467   0.91855+- 1.58718   1.03+- 1.81       0.0
OC     UOC    *  12.18883+- 3.40518  13.37652+- 0.97392   1.10+- 0.32       0.3
SOOT   USOOT  *   3.28056+- 1.80777   2.92872+- 0.73633   0.89+- 0.54      -0.2
NO3    UNO3   *   5.42765+- 1.13110   5.51005+- 0.23114   1.02+- 0.22       0.1
SO4    USO4   *   1.40122+- 0.22534   1.40690+- 0.13370   1.00+- 0.19       0.0
CL     UCL    *   0.24510+- 0.04401   0.13212+- 0.09314   0.54+- 0.39      -1.1
NH4    UNH4   *   1.83309+- 0.42039   1.75372+- 0.40746   0.96+- 0.31      -0.1
NA     UNA    *   0.12661+- 0.01369   0.14898+- 0.08658   1.18+- 0.70       0.3
K      UK     *   0.49952+- 0.07299   0.62981+- 0.34643   1.26+- 0.72       0.4
CA     UCA    *   0.32784+- 0.05036   0.38424+- 0.08285   1.17+- 0.31       0.6
MG     UMG    *   0.42148+- 0.06590   0.18472+- 0.40985   0.44+- 0.97      -0.6
SI     USI    *   2.23362+- 0.65643   1.98572+- 0.23368   0.89+- 0.28      -0.4
FE     UFE    *   0.83714+- 0.18984   0.81547+- 0.09024   0.97+- 0.25      -0.1
AL     UAL    *   0.92838+- 0.14278   0.90188+- 0.12994   0.97+- 0.20      -0.1
ZN     UZN    *   0.19878+- 0.05123   0.03580+- 0.06470   0.18+- 0.33      -2.0
TI     UTI    *   0.06624+- 0.01367   0.05786+- 0.06207   0.87+- 0.95      -0.1
CU     UCU    *   0.01731+- 0.00251   0.02681+- 0.06623   1.55+- 3.83       0.1
V      UV     *   0.00450+- 0.00068   0.00212+- 0.06187   0.47+-13.74       0.0
MN     UMN    *   0.01747+- 0.00250   0.02505+- 0.06199   1.43+- 3.56       0.1
PB     UPB    *   0.01119+- 0.00239   0.02402+- 0.06191   2.15+- 5.55       0.2
NI     UNI    *   0.00907+- 0.00139   0.00291+- 0.06188   0.32+- 6.83      -0.1
SR     USR    *   0.00421+- 0.00076   0.00246+- 0.06603   0.59+-15.69       0.0
CR     UCR    *   0.01058+- 0.00159   0.00396+- 0.06188   0.37+- 5.85      -0.1
SB     USB    *   0.00253+- 0.00081   0.01376+- 0.06209   5.43+-24.56       0.2
SN     USN    *   0.00342+- 0.00068   0.01253+- 0.06228   3.66+-18.22       0.1
RB     URB    *   0.00329+- 0.00049   0.00308+- 0.06188   0.94+-18.80       0.0
MO     UMO    *   0.00212+- 0.00043   0.00180+- 0.06186   0.85+-29.20       0.0
AS     UAS    *   0.00081+- 0.00020   0.00104+- 0.06604   1.29+-81.50       0.0
CD     UCD    *   0.00030+- 0.00004   0.00038+- 0.07706   1.26+-*****       0.0
CHRYS  UCHRYS     0.00483+- 0.00284 *********+-********  *****+-*****      -1.0
BBFLU  UBBFLU     0.00483+- 0.00096 *********+-********  *****+-*****      -1.0
BKFLU  UBKFLU     0.00348+- 0.00074 *********+-********  *****+-*****      -1.0
BEPYR  UBEPYR     0.00248+- 0.00036 *********+-********  *****+-*****      -1.0
BAPYR  UBAPYR *   0.00433+- 0.00066   0.00163+- 0.06879   0.38+-15.89       0.0
IN123  UIN123 *   0.00290+- 0.00043   0.00072+- 0.06876   0.25+-23.67       0.0
DBAHA  UDBAHA     0.00238+- 0.00038 *********+-********  *****+-*****      -1.0
BGPER  UBGPER *   0.00265+- 0.00042   0.00218+- 0.06881   0.82+-25.96       0.0
COR    UCOR       0.00067+- 0.00016 *********+-********  *****+-*****      -1.0
PAH    UPAH       0.02856+- 0.00441 *********+-********  *****+-*****      -1.0
--------------------------------------------------------------------------------
```

WP2

Transport Emissions Abatement Technological options

(WP2 Leader: Giorgio Martini)

Final Report – 31/10/2010

WP2

Transport Emission Abatement Technological Options

Deliverables:

- IX.2.1.Progress Report on HDV and Bus Testing

Deliverable IX.2.1. Final Report on HDV and Bus Testing

INTRODUCTION

The present report covers the period from March 2010 to September 2010.

During this semester the JRC has continued the experimental activity having the objective of assessing the emissions of different heavy duty vehicles and the effectiveness of different emission abatement measures by means of measurements carried out both in the laboratory and in real world conditions.

In particular emission tests have been performed on a garbage collection truck equipped with a retrofit device consisting in a particulate filter.

The truck was homologated according to the Euro II standards and was fitted with a particulate filter about one year before the testing described in the report. The added value of the tests carried out on this truck is the possibility to check the effectiveness of the filter in reducing particulate emissions after having been in operation for about one year.

In addition, the report summarizes all the testing work on heavy duty vehicles carried out in the framework of the Regione Lombardia project.

1 SUMMARY AND CONCLUSIONS

In the framework of the Regione Lombardia project the JRC has tested several heavy duty vehicles with the objective of assessing pollutant emissions of trucks and buses of different technology when operated either on-road in real-world conditions or on a chassis dynamometer reproducing driving patterns similar to the real ones.

The following table provides an overview of the vehicles and the range of technology tested:

Vehicles	Fuel	Testing place
Urban bus "Euro 0"	Diesel	VELA 7 Laboratory
Urban bus "Euro II"	Diesel	VELA 7 Laboratory
Urban bus "Euro II"	Diesel	On-road
Urban bus "Euro III"	Diesel	On-road
Truck "Euro III"	Diesel	VELA 7 Laboratory
Garbage collection truck "Euro V EEV"	CNG	VELA 7 laboratory
Garbage collection truck "Euro V"	Diesel+25% biodiesel	On-road
Garbage collection truck "Euro V EEV"	CNG	On-road + VELA 7 laboratory
Garbage collection truck "Euro II" with retrofit DPF	Diesel Diesel+25% biodiesel	VELA 7 laboratory
Tractor "Euro V"	Diesel	VELA 7 laboratory
Tractor "Euro V"	Diesel	VELA 7 laboratory
Road sweeper with retrofit DPF	Diesel	On-road

The experimental work has been designed to address the following main issues:

- Emission performances of heavy duty vehicles of different technology tested in the laboratory in conditions simulating the real-world operation
- Emission performances of heavy duty vehicles of different technology in real-world operation tested on-road by using portable emissions measurement systems (PEMS)
- Comparison of laboratory and on-road emission data
- Effect of biodiesel on the emissions of heavy duty vehicles
- Effect of retrofit Diesel Particulate Filters (DPF) on particulate emissions

The main findings of this experimental work main conclusion can be summarized as follows:

- Real world emissions of diesel heavy duty vehicles may differ from the type approval emission data to a very large extent. There are several factors that can explain this behaviour:
  - As far as heavy duty vehicles are concerned, only the engine has to be certified for emissions. Then the engine can be installed on very different vehicles with a very different final use (for example, the same engine can be installed in garbage collection trucks, in long-haul trucks and in urban buses, which are operated in extremely different conditions).
  - The legislative test cycle has been developed to cover "average" operating conditions. Of course this implies that extreme operating conditions, like for example very low speeds and frequent stops typical of urban buses, are not covered by the test cycle.
  - Very often the manufacturers optimize pollutant emissions over the test cycle while outside the operating area covered by the test cycle other parameters are optimized (typically fuel consumption).

  All these factors results in high pollutant emissions when the vehicle is operated in conditions far from those of the certification test cycle.
  As a consequence, the emissions of heavy duty vehicles homologated according to the most recent Euro emission standards very often exhibit emission levels in real world driving condition not much lower than vehicle homologated according to older standards. This is especially true for NOx emissions while other pollutants have been effectively reduced. This implies that the introduction of the more and more stringent emission standards (Euro II, III, IV, V) over the last two decades may have resulted in limited reduction of total NOx emissions and consequently limited improvements in terms of NOx ambient levels compared to the expected benefits.
  As an example, the tests carried out by the JRC have clearly shown that an Euro III urban bus may have NOx emissions very close to those of a Euro II bus although, with the introduction of Euro III, the relevant emission standard was reduced by almost 30 % and new test cycles were adopted.
  Even vehicles homologated according to the Euro V standards may have NOx emissions at levels typical of Euro II-Euro III vehicles. This is mainly due to the fact that the after-treatment device used to reduce NOx emissions, the Selective Catalytic Reduction system (SCR), works effectively only when the temperature of the exhaust is above 250 °C. Since the certification test cycles prescribed by the Euro V standards are executed with a fully warmed engine, the SCR system is very effective in reducing NOx emissions in the type approval test. However, when the real world driving conditions are very far from those of the legislative test cycle, like for example the driving patterns typical of urban buses and garbage collection trucks, the SCR system may even not wok at all.
  Moreover, since there is an inverse correlation between NOx emissions and fuel consumption, the fact that NOx emissions can be controlled with the SCR system, at least over the legislative cycle, allowed the manufacturers to

calibrate the engine for higher engine out NOx emissions in order to improve the fuel economy. For this reason Euro IV and V vehicles generally show better fuel economy than Euro III vehicles but, as a consequence, when the SCR system does not work properly NOx emission can be very high as demonstrated by the on road measurements carried out on a Euro V garbage collection truck.

Another important aspect related to test cycles is the fact that standard cycles do not adequately cover extreme operating conditions like those of garbage collection trucks and urban buses, characterized by very low average speeds and frequent starts/stops.
The JRC has compared the emissions measured over the FIGE driving cycle, which the legislative transient test is based on, with emission measured on-road, both for garbage collection trucks and urban buses. The results clearly showed that the on-road emissions are much higher for a number of reasons. For example, in the case of garbage collection trucks the engine is also operated during garbage collection to move the blade. The exhaust gas emitted during this operation is not accounted for in the laboratory test. Furthermore, the frequent idling periods and the accelerations/decelerations typical of the urban driving are not adequately represented in the FIGE cycle.

- Primary particulate emissions are instead very effectively reduced, also in real world driving conditions, by diesel particulate filters. The tests carried out by the JRC and the experience with filters in many other countries have demonstrated that this technology is very robust and that emissions of solid particles are reduced to very low level, comparable with the background levels. During regeneration process particle emissions may increase by more than one order of magnitude but in any case the emission levels remain well below those typical of vehicles not equipped with a DPF. However, some DPFs technology that uses the reaction between NO2 and carbon to regenerate the filter may lead to an increase of NO2 emissions. In general an oxidation catalyst located before the DPF is used to convert NO to NO2. A widespread use of filter based on this technology may lead to increased NO2 emissions from traffic and, as a consequence, higher NO2 ambient levels. The tests performed at the JRC (described in this report) have shown that there are filter technologies able to reduce particulate emissions with a very high efficiency without increasing NO2 emissions.

- Several studies published in the last years have clearly demonstrated that the effect of fuel quality on emissions is greatly reduced and almost negligible when vehicles are equipped with very effective after-treatment devices. For example, particulate emissions of a diesel vehicle equipped with a particulate filter will be affected to a very limited extent by fuel quality.
  One of the conclusions that can be drawn is that biofuels cannot be considered any more as an option to reduce pollutant emissions. On the contrary biofuels can even be a problem for the very sophisticated emission control devices of modern engines and may even increase some pollutants.

The tests carried out at the JRC on a Euro II garbage collection truck running on a diesel fuel containing 25% biodiesel have shown that while particulate emissions are reduced up to 20%, NOx emissions increase up to10% compared to a standard diesel fuel. These results are fully in line with the literature data. Since this garbage collection truck was retrofitted with a DPF reducing particulate emissions with an efficiency higher than 90%, it is clear that it does not make any sense to use fuel with high biodiesel content in this truck.

As a consequence, the only potential benefit linked to the use of biofuels is the reduced greenhouse gas emissions when considering the well-to-wheels balance.

As well known, the European Directive on the promotion of renewable fuels[1] set the objective of 10% coverage of the transport fuel market with renewable fuels by 2020 and biofuels are considered one of the most important options to achieve this target.

From the above consideration it is probably better to use blends containing low levels of biodiesel (max 5-10%) rather than blends with high biodiesel content or even neat biodiesel. This would guarantee the same benefits in terms of CO2 savings without the potential problems associated with the use of high biodiesel contents.

A 7% maximum content of biodiesel is also requested by the vehicle manufacturers since high level of biodiesel in the fuel can create problems to the engine especially when this is designed to be equipped with a DPF. In fact biodiesel leads to an increased dilution of the lubricant.

Nevertheless fuel quality may still play a significant role in reducing particulate emissions in old vehicles.

The main options to reformulate the fuel in order to reduce particulate emissions are:

- Using metal additives (Iron, Cerium) which promote the oxidation of the soot. However, in this case the additive will generate ash that will be emitted in the ambient with consequences for human health that are not well known.
- Using oxygenated components (ethers, alcohols, …) that locally modify the air/fuel ratio reducing the formation of particulate in the combustion chamber.
- Using water/diesel fuel emulsions. These modified fuels have an important effect on particulate emissions but the presence of water can create serious problems to the engine. In any case this is a solution that can be implemented only for old technology vehicles.

The main differences between a retrofit programme (for example based on the installation of particulate filters) and the introduction of a reformulated fuel are the magnitude of the effects on emissions and the time required to obtain

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[1] DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC

the maximum benefits. It is well known that the positive effects on emissions of after-treatment devices or other technology based improvements are much higher than the effects of a reformulated fuel. For example, the maximum reduction of particulate emissions that can be obtained with a reformulated fuel is typically around 30-40% while a particulate filter may have a reduction efficiency higher than 99%!!
However, while once a reformulated fuel has been introduced in the market all the vehicles on the road will show reduced emissions, with a technology based programme the actual benefits depend on the ratio of vehicles equipped with the new technology.

- The JRC has tested a few Euro V EEV garbage collection trucks running on compressed natural gas (CNG) both in the laboratory and in real world driving conditions. The measured emission levels have been compared with those of a Euro V diesel truck. The results can be summarized as follow:
  - Particulate emissions of the CNG truck were much lower than those of the diesel truck. This is valid in general unless diesel vehicles are equipped with a particulate filter; in this case their particulate emissions are very likely to be lower or at least at the same level than CNG vehicles.
  - The CNG vehicle exhibited much lower NOx emissions.
  - The CNG vehicle emitted more CO and HC than the diesel vehicle. However, it has to be taken into account that there is an important difference between the quality of hydrocarbons emitted by the diesel vehicle and those emitted by the CNG engine. In the latter case typically more than 90% of the unburned hydrocarbons consists of methane which is not toxic and is a very stable gas. HC emitted by diesel engines consists of a very complex mixture of compounds including potentially dangerous species like poly-aromatics.
  - The CO2 emissions of the CNG engine were higher than the diesel engine confirming that diesel engines are still the most efficient ones.

These results can be explained considering that the CNG engine adopts the Otto cycle and is equipped with a three way catalyst (TWC). The three way catalyst is very efficient in reducing NOx, HC and CO emissions but for the maximum efficiency a strict control of the air/fuel ratio is required. This ratio has to be as close as possible to the stoichiometric value. However, the catalyst is not effective in oxidizing methane as for other hydrocarbons since methane is a very stable gas. This is a very well know issue and for this reason the catalysts of CNG passenger cars are in general more active (higher precious metal load) than the catalysts of the same models running only on gasoline.

Tests on passenger cars carried out at the JRC have shown that gasoline models have in general on-road emissions quite in line with those measured over the legislative cycle while for diesel models on-road emissions are very often much higher. The good on-road performance of gasoline models can be explained with the high efficiency of the three way catalyst in most of the real world operating conditions. On the contrary, to control pollutant emissions diesel vehicles rely on other systems of which the efficiency is very dependent on the operating conditions. As soon as the operating conditions deviate from those covered by the legislative test cycle, emissions may increase significantly as described above.

Other tests carried out by the JRC have shown that there may be a very important difference between the emissions of CNG heavy duty vehicles even if certified according to the same emission standard (Euro V EEV).
In particular, two brand new garbage collection trucks from different manufacturers but with very similar characteristics (inertia, superstructure,…) were tested on the Autodromo of Monza track simulating both the real world driving conditions and the garbage collection.

The results obtained are summarized in the following table:

	CO2 (g/km)	**CO (g/km)**	**NOx (g/km)**	**HC (g/km)**
Vehicle 1	**2202**	**1.66**	**3.50**	**0.55**
Vehicle 2	**3168**	**1.01**	**13.63**	**6.99**

The difference in terms of NOx and CO2 emissions is very important and cannot be easily explained as beyond the fact that both the engines were certified as Euro V EEV and spark ignited, the combustion strategy and the after-treatment technology is not known in detail. The fact that both the engines were certified as Euro V EEV, further confirms that real world emissions may be very different from those measured over the legislative cycle.

In theory, natural gas vehicles should exhibit lower CO2 emissions due to the lower carbon content of the fuel. However, since the natural gas vehicles in general adopt the Otto cycle and a stoichiometric combustion in order to maximize the efficiency of the three way catalyst, the overall CO2 emissions of CNG engines may be higher when compared to diesel engines. In fact the diesel combustion cycle is still the most efficient one.

For example, as far as CO2 emissions are concerned, the two trucks tested in real world driving conditions by the JRC exhibited the following emission levels:

Vehicle	CO2 Emissions (g/km)	Fuel consumption (kg/km)
Euro V EEV CNG	3634	1.3
Euro V Diesel	2460	0.8

The Well-to-Tank CO2 emissions for diesel fuel and CNG (including production, distribution and, for natural gas, compression) are estimated to be:

	g CO2 / MJoule	g CO2 / kg fuel
Diesel Fuel	14.2	612
CNG	5.5*	248*

* Average values referred to EU mix (JRC/EUCAR/CONCAWE WTW Study)

It is therefore clear that in this specific case the Well-to-Wheels balance is in favour of the diesel engine:

Vehicle	WTT CO2 g/km	TTW CO2 g/km	Well-to-Wheels CO2 g/km
Euro V EEV CNG	330	3634	3964
Euro V Diesel	490	2460	2950

Of course the Well-to-Wheels balance presented in the previous table is strictly referred to the two trucks tested by the JRC. As shown before there can be a very large difference in CO2 emissions of CNG heavy duty vehicles depending on the engine technology and calibration.

Moreover, the CO2 emission values shown above do not include methane emissions. Methane is a greenhouse gas with global warming potential (GWP) higher than CO2. Considering CO2 as baseline (GWP=1), the GWP of methane is:

	Time horizon		
	20 years	100 years	500 years
Methane	72	25	7.6

(2007 IPCC Fourth Assessment Report)

It is therefore clear that methane emissions should be added to those of CO2 to correctly estimate the impact of diesel vehicles and CNG vehicles in terms of GHG emissions.

For example, the Well-to-Tank CO2 equivalent emissions for CNG become 8.7 g/MJoule if methane emissions are included. In fact methane emissions associated with methane production, transport and compression are estimated to be around 0.13 g/MJoule. Using the 100 years time horizon GWP value the contribution of methane expressed in CO2 equivalent is therefore 3.2 g/MJoule that added to 5.5 g CO2/MJoule gives 8.7 g CO2 eq / MJoule.

Of course also the Tank-to-Wheel GHG emissions are affected. In fact in general about 90% of unburned hydrocarbons emitted by CNG vehicles consists of methane. For the vehicle tested, emissions of methane converted to CO2 equivalent emissions represent about 1-2% of the actual CO2 emission.

Conclusions

- There is no ideal solution to minimize pollutant emissions from heavy duty vehicles. First of all there is a very important difference between minimizing pollutant emissions dangerous for human health and minimizing greenhouse gas emissions (GHG). In fact the ideal solution to minimize CO2 emissions, which means minimizing fuel consumption or using non-fossil fuels, very often does not correspond to the ideal solution to minimize pollutant emissions. For example, diesel engines are the most efficient ones but they have much higher emissions than petrol engines fitted with a three way catalyst. In addition, most of the measures taken to curb emissions from diesel engines reduce their efficiency to a certain extent. Viceversa, calibrating the engine for the best fuel economy means increasing pollutant emissions.
  Furthermore, also the overall well-to-wheel balance has to be taken into account: Electric vehicles have clearly zero Tank-to-Wheel GHG and pollutant emissions but the Well-to-Tank emissions may be even higher than those of a current diesel vehicle depending on the process used to generate the electric power.

- Heavy duty vehicles of the current generation equipped with SCR systems and DPF, combine the excellent fuel economy and low NOx emissions only when the operating conditions are close to those covered by the legislative test cycles. In particular, Euro V diesel trucks have relatively low NOx emissions only when the vehicle is operated at high loads/speeds resulting in exhaust temperatures high enough to enable the proper functioning of SCR systems. In other words, heavy duty diesel vehicles still represent the best option for the on-road transport of goods and passengers over long distances and in driving conditions typical of highways. Future heavy duty vehicles combining diesel engines with the hybrid technology will improve further this situation.

- For heavy duty vehicles operated in urban areas and with very specific driving patterns (e.g garbage collection trucks, urban buses,…) it is very difficult to identify the best solution that guarantees the lowest environmental impact since, as discussed above, actual emissions of heavy duty vehicles are very dependent on engine operating conditions and on the engine calibration.
  In general compressed natural gas may represent a good option to reduce pollutant emissions in urban areas. Despite the low loads and speeds typical of city driving conditions, the three way catalyst fitted to CNG Otto engines may guarantee lower NOx emissions than diesel vehicles. As far as primary particulate emissions are concerned, there is no benefit in using CNG rather than diesel vehicles if the latter are equipped with a diesel particulate filter. However, the on-road tests carried out by the JRC on two very similar CNG trucks manufactured by different companies showed impressive difference in terms of NOx and CO2 emissions.
  As far as diesel vehicles are concerned, the model tested by the JRC showed in general very high real world NOx emissions. However, there are currently on the market heavy duty diesel vehicles using other technologies than SCR to reduce

NOx emissions and these might have better performances in urban driving conditions than the vehicles tested by the JRC.
In addition, a new generation of diesel vehicles incorporating hybrid technology is being now introduced in the market and they could represent another interesting option for commercial and industrial vehicles used in urban driving conditions.

The ideal approach to identify the best vehicle for a given application would require a thorough assessment of the operating conditions and a dedicated testing programme to compare different vehicle technologies. However the study should be repeated every time a new technology is introduced on the market since this could change completely the conclusions.
A viable option and a recommended practice to be implemented by those companies running large vehicle fleets in urban areas could be the introduction of an evaluation criteria based on actual emission performances in the selection procedure of new vehicles. The candidate vehicles could be easily and quickly tested in real world driving and operating conditions by means of portable emissions measurement system.
Some companies, like for example the company in charge of garbage collection in Milan (AMSA), have already implemented such practice.

- Retrofitting existing vehicles with particulate filters is an effective measure to reduce primary particulate emissions from heavy duty vehicles. Care should be taken in order to promote filters with a high efficiency that do not increase remarkably NO2 emissions.
  However particulate filters do not affect total NOx emissions and retrofit pollutants for this pollutant should be developed. If the retrofit systems for NOx emissions will be based on the SCR technology they will be largely ineffective in urban driving conditions unless specific devices are developed for these conditions.

- The possibility to reduce significantly pollutant emissions using reformulated or modified fuels is limited to vehicles featuring old technology engines. Vehicles equipped with very modern engines fitted with efficient after-treatment devices are almost insensitive to fuel quality.

2 EFFECT OF A RETROFIT DIESEL PARTICULATE FILTER (DPF) ON THE EMISSIONS OF A GARBAGE COLLECTION TRUCK

The Joint Research Centre (JRC) has conducted an experimental activity having the objective of assessing the particulate and gaseous emissions of a heavy duty garbage collection vehicle with and without a Diesel Particulate Filter (DPF) retrofit system.

In particular emission tests have been performed on the truck with two different fuels, over two driving cycles:

- Over the FIGE cycle
- Over the called “AMSA” cycle, derived by real-life operating conditions representative of the garbage collection truck driving pattern.

A big amount of data has been generated in these experimental activities and these data are still being processed and analyzed. The most important data obtained are shown in the following chapters.

3 EXPERIMENTAL WORK

3.1 Vehicle – DPF system

The truck has been manufactured by IVECO [http://web.iveco.com/Pages/welcome.html]. The company "Azienda Milanese Servizi Ambientali" (AMSA) [http://www.amsa.it/gruppo/cms/amsa/] uses the vehicle for collecting urban waste. Some of the diesel trucks used by the company have been retrofitted with DPF systems. The tested vehicle was one of the vehicles retrofitted and it was equipped with such a retrofit system one year before being tested at the JRC Vehicles Emission Laboratory (VELA 7).

The DPF retrofit system model installed on the vehicle is manufactured by Pirelli, with the commercial name Feelpure^{TM} [Pirelli & C. Eco Technology S. p. A., Products: FeelpureTM, DPF system, http://www.pirelliecotechnology.com/web/products/feelpure/default.page]. The system combines the Silicon Carbide (SiC) filter monolith to collect the solid particles of the diesel exhaust, called soot. The regeneration technology of the filter is based on the use of a specific catalyzing additive called Fuel Born Catalyst (FBC). The filter monolith is made of a honeycomb structure through which the exhaust gases are filtered. The DPF is located in a stainless steel silencer, replacing the original one of the vehicle. The dimensions and the basic characteristics of the filter are presented in Table 1.

Table 1 – Geometric properties of the filter.

Property	Value
Diameter [mm]	279.4
Length [mm]	355.6
Volume [lt]	22.8
Cells Per Square Inch [cpsi]	90

Fig. 1 shows a schematic figure of the installed DPF system. The filter cartridge is dimensioned on the basis of the engine characteristics, taking into account the displacement, power and emissions level of it. It has been designed to be easily removable from the muffler to allow the necessary periodic cleaning of the accumulated ash. The manufactures suggests carrying it out once a year or, in any case, based on the real running time of the vehicle.

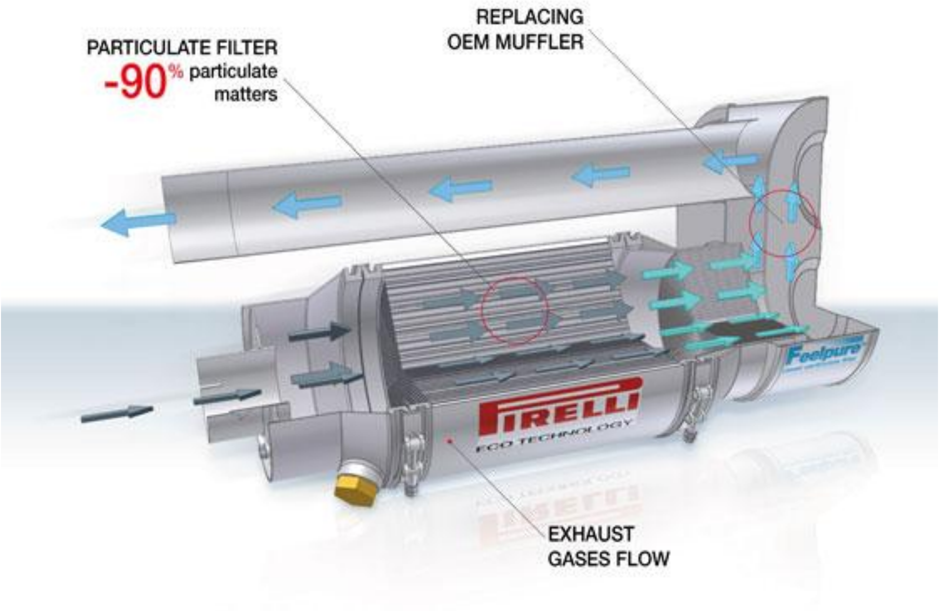

Fig. 1 – Pirelli Feelpure™ Diesel Particulate Filter retrofit system [http://www.pirelliecotechnology.com/web/products/feelpure/default.page].

The system is equipped with an Electronic Control Unit (ECU) which monitors the level of the pressure drop in the exhaust along the DPF. The CPU regulates the dosing of the additive (via a metering 12/24V pump) and stores the operational parameters of the system. A tank is installed on the vehicle to contain the necessary additive for activating the regeneration of the filter. This iron-based additive is dissolved into the diesel fuel, reducing the ignition temperature of the trapped carbon in the filter to 300°C, instead of the normal of 600°C. According to the manufacturer of the retrofit system the FBC consumption is about 1.5 l every 1000 l of diesel fuel consumption by the engine.

The vehicle was an IVECO MAGIRUS model 260E27 of the year 1999. The engine has a capacity of 7790 cm^3 and a power of 200 kW. It was certified for the Euro II emission standards.

When the vehicle arrived in JRC the fuel additive tank was empty and the wiring of one pressure drop sensor was cut. Before testing the vehicle, the additive tank was refilled and the destroyed pressure drop wiring was replaced.

However, the fact that the additive tank was empty and that the pressure sensor was not working implies that for a certain period that cannot be estimated on the basis of the information provided, the DPF system worked in conditions which it is not designed for. In particular, the regeneration process should be less efficient leading to accumulation of soot in the filter. This is a very severe working condition because once the regeneration process starts spontaneously, for example during highway driving to go back to the AMSA’s central depot, very high temperature might be reached in the filter due to the combustion of large amount of soot. After initiating of the regeneration process, the combination of excessive soot loading and low flow rate (while driving for instance after the motorway and before reaching to the depot), may accelerate the combustion of soot in the filter. Excessive quantities of thermal energy would be released, leading to temperature in the filter that could exceed the melting point of the material. This “uncontrolled” regeneration may lead to filter failure (melting or cracking).

3.2 Fuels

The vehicle has been tested on two fuels. The Fuel 1 (F1) is used by AMSA. It is a mixture composed by 75% of commercial diesel fuel and by 25% of biodiesel. The second fuel (F2) is the commercial diesel fuel without biodiesel.

3.3 Test cycles

In the tests carried out in the VELA 7 laboratory two different driving cycles have been used. The first one, the FIGE cycle, was used in the past to derive the European Transient Cycle (ETC) for the type approval of the heavy duty engines. The cycle is shown in Fig. 2. Different driving conditions are represented by three parts of the FIGE cycle, including urban, rural and motorway driving. The duration of the entire cycle is 1800s and the duration of each part is 600s.

- Part one represents city driving with a maximum speed of 50 km/h, frequent starts, stops and idling.

- Part two is rural driving starting with a steep acceleration segment. The average speed is about 72 km/h.

- Part three is motorway driving with average speed of about 88 km/h.

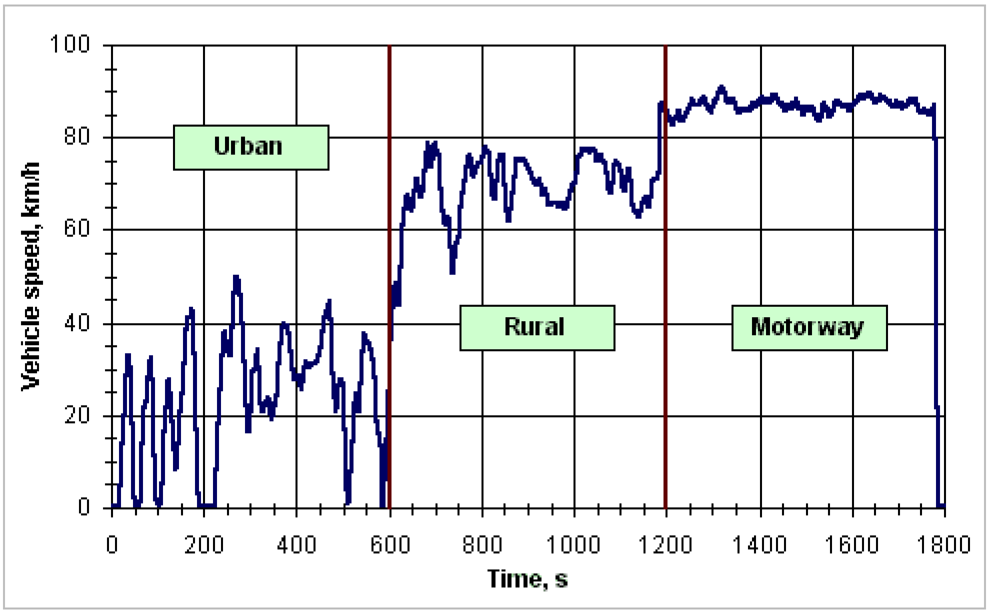

Fig. 2 – FIGE transient cycle.

Since the tested truck had maximum speed of 80 km/h, the part 2 and 3 of the cycle were modified above 50 km/h, in order not to exceed the maximum speed of the vehicle. Fig. 3 shows the original and the modified FIGE cycle. The latter was used to test the garbage collection truck of this study. The speed of 50 km/h was selected in order not to affect the urban part of the cycle, which remained the same with the original one.

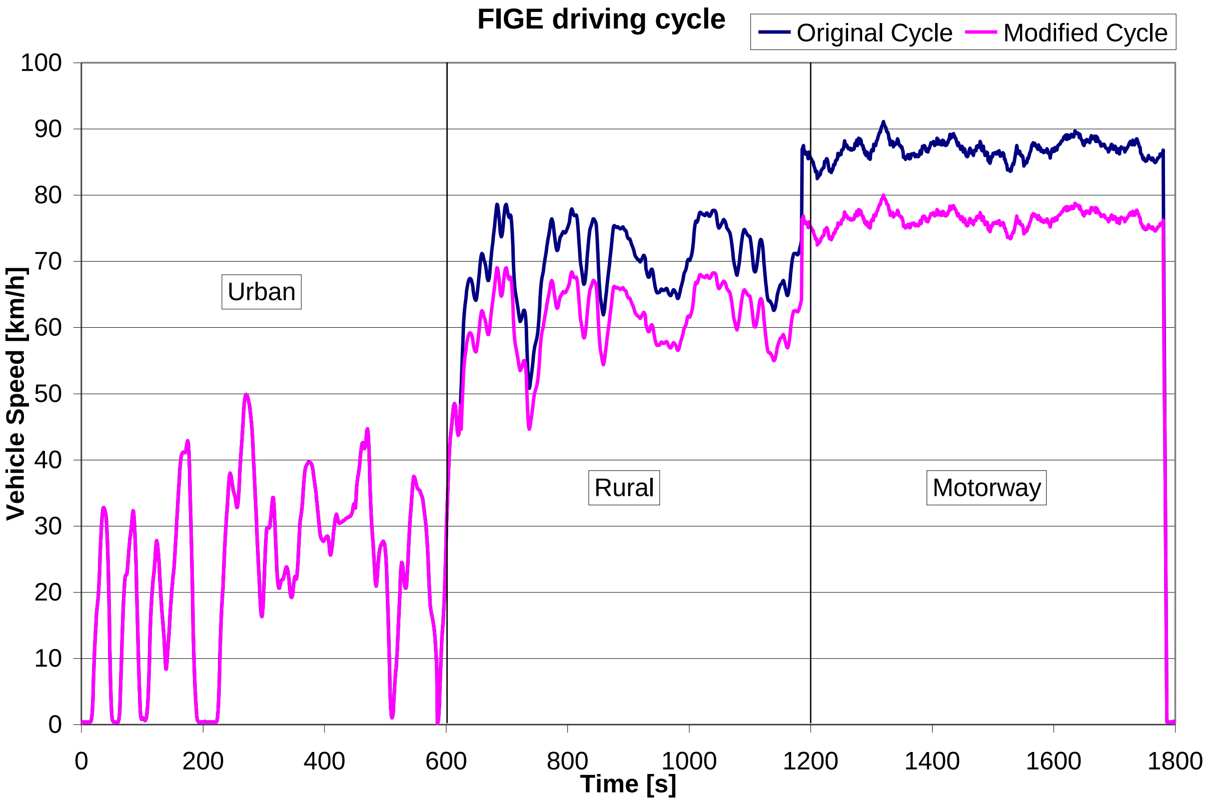

Fig. 3 – Original and modified FIGE transient cycle.

The second driving cycle over which the truck was tested had been derived by data collected monitoring the garbage collection truck speed during typical real-life operating conditions [European Commission, Joint Research Centre, Institute for Environment and Sustainability, "WP2 Transport Emissions Abatement, Technological Options" VI Intermediate Report, 30/04/2009]. The cycle is shown in Fig. 4. It also consists of three parts.

- Part one represents the phase when the truck initiates from the AMSA depot and is driven via the motorway to the area where the garbage have to be collected.
- Part two is the phase when the truck collects the garbage, representing an urban driving pattern with low vehicle speed, idling and frequent start-stop.
- Part three represents the phase when the truck returns to the depot, or to the place where the garbage are deposited, resembling to the part one, with motorway driving pattern.

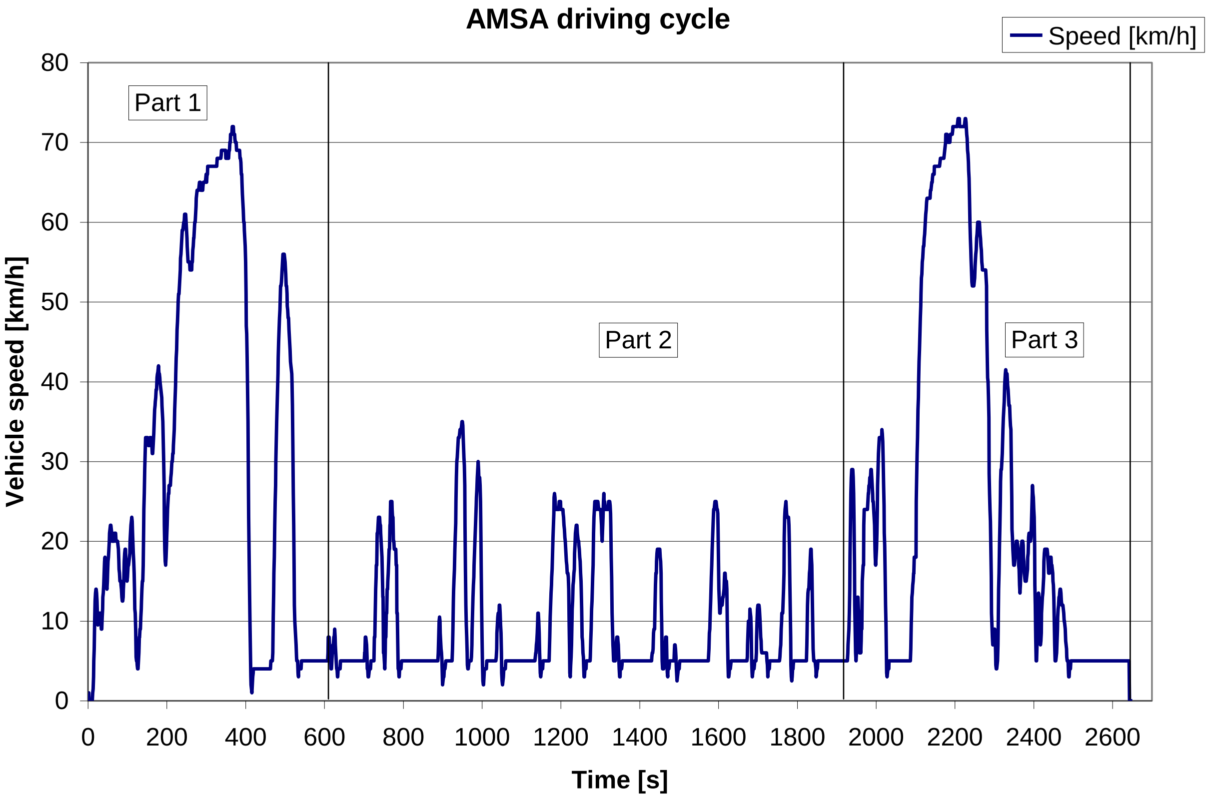

Fig. 4 – Real-life operating condition AMSA driving cycle.

3.4 *Instrumentation for measuring the emissions*

The gaseous and particle emissions of the truck have been measured using the emission test facility VELA 7. VELA is equipped with advanced instrumentation for the quantitative and qualitative measurement of polluting and climatically relevant emissions.

The system consists of a ***total dilution tunnel*** and an ***analysis system*** of the exhaust gases.

The dilution tunnel, which has a total throughput of 150 m^3/min, permits to dilute the exhaust gases of the vehicle with appropriately pre-treated air. This is done for two reasons: first, in order to avoid the condensation of the contained water vapour which would influence the measurements of the other contained substances and secondly, to simulate the processes which in fact happen, once the exhaust gases are released to the atmosphere in real life. This second aspect is of fundamental importance for measuring the *particulate emissions*, because the processes of seeding, condensation and aggregation of the exhausted particles happen in fact after the emission from the vehicle into the atmosphere and determine the chemo-physical character of the final exhaust products.

The analysis system of the VELA7 lab consists of analysers, which are capable of continuously monitoring the gaseous pollutants, with a time resolution of one second. Moreover, part of the diluted exhaust is stored in bags, where after the completion of the test, the exhaust of each three parts of the cycles is analysed.

The gaseous pollutants which are measured are the following:

- Total unburned Hydrocarbons (HC)
- Nitrogen Oxides (NO_x)
- Carbon monoxide (CO)
- Carbon dioxide (CO_2)

In addition to regulated emissions, it was possible to measure also unregulated emissions with the aid of the FTIR (Fourier Transform InfraRed) system, also available in VELA 7. The “Multicomponent Exhaust Gas Measurement System FTIR-based” is on-line capable of ppm to ppb sensitivity for multiple gas species. In this report the NO_x, NO and NO_2 species measurements are analyzed.

Particulate matter (PM) is measured gravimetrically, using standard filters as prescribed by current legislation. A sample of the diluted exhaust gas is conducted through such a filter and the difference between its weight measurements before and after the test gives the overall final result. Additionally, by using advanced laser technology, it is possible to count the total number of particles (PN) emitted by the vehicle and also their size distribution.

4 TEST RESULTS OVER THE FIGE CYCLE

The gaseous and particle emissions of the truck have been measured using the emission test facility VELA 7 over the FIGE driving cycle. The tests were performed with cold and hot start. The vehicle apart from the DPF retrofit system, was not equipped with any exhaust after-treatment system such as Diesel Oxidation Catalyst (DOC) for oxidations of CO and HC gaseous emissions, or Selective Catalytic Reduction (SCR) for reduction of NO_x emissions.

In the following figures the gaseous emission bag values for CO, HC, NO_x and CO_2, and the PM, PN emissions are presented and discussed.

4.1 PM – PN over the FIGE

Table 2 presents the PM mass emissions measurement results over the FIGE driving cycle. Each part of the cycle has been analysed separately. Moreover, the results of each diesel fuel are presented, as well as the percentage decrease of PM emissions when measuring the truck with the DPF retrofit system of Pirelli. The vehicle emits the maximum quantity of PM while driving over the first part of the cycle. The frequent accelerations over this first urban part of the cycle causes increased engine load, resulting in increased PM emissions. The DPF removes effectively the majority of the PM emissions during the first part of the cycle, corresponding to a percentage decrease of almost 90%, regardless the used fuel or the type of the cycle (cold-hot).

The PM emissions without DPF decrease while the truck is driven over the rural and motorway part of the cycle. The steady pattern of driving and the mild accelerations result at lower PM emissions. In this case the filter also removes effectively the PM. Due to the lower PM emissions without DPF, the potential effectiveness of the filter decreases. The filtration efficiency decreases, remaining between 70-82% over the part 2 and 3 of the driving cycle.

Table 2 – PM emissions over the FIGE cycle (cold-hot).

	Phase 1 (F1)	Phase 2 (F1)	Phase 3 (F1)	Phase 1 (F2)	Phase 2 (F2)	Phase 3 (F2)
PM without DPF (cold) [mg/km]	255	117	103	303	139	113
PM with DPF (cold) [mg/km]	36	25	20	32	27	20
Percentage decrease [%]	85.9	78.6	80.2	89.5	80.5	76.0
PM without DPF (hot) [mg/km]	218	116	98	289	136	111
PM with DPF (hot) [mg/km]	24	21	20	33	34	33
Percentage decrease [%]	89.1	82.0	79.7	88.4	74.7	70.6

Fig. 5 shows the same results in bar-chart format for FIGE cycle. Comparing the PM emission values without DPF for Fuel 1 and 2 of each (cold or hot) cycle, it can be noticed that the emissions are lower when the Fuel 1 is used. This fuel, as it has already mentioned, is a mixture of commercial diesel and biodiesel (75-25%). The use of biodiesel decreases the PM emissions over the three pars of the cycle from 9% to 25%. The minimum decrease of 9% has been measured over the cold motorway part of the cycle, while the maximum one of 20% over the hot urban part of the cycle.

To conclude the analysis of PM emissions a comparison between cold and hot cycle should be mentioned. The cold start mainly affects the first urban part of the cycle. The engine has already reached its regular operation temperature when the second rural part of the cycle initiates. The PM emissions over the urban part increase by 17% for when the engine starts cold Fuel 1 and by 5% when the commercial diesel Fuel 2 is used. The increase of PM emissions during the cold start is larger with the mixture biodiesel/diesel fuel (F1) than with the diesel without biodiesel F2. This can be explained by the higher boiling point of the biodiesel which evaporates less promptly that the diesel fuel.

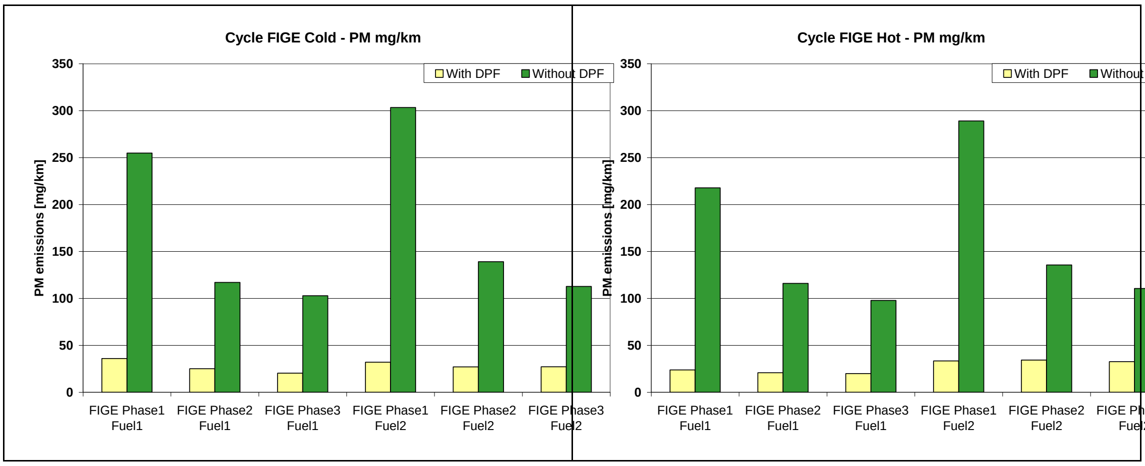

Fig. 5 – PM emissions over the FIGE driving cycle (cold-hot) for both tested fuels.

Table 3 presents the respective results for PN emissions over the FIGE cycle. In this case the decrease of PN is around 97.5% when the DPF is used, regardless the fuel, the part of the cycle and the temperature of the engine before test (cold-hot cycle).

Table 3 – PN emissions over the FIGE cycle (cold-hot).

	Phase 1 (F1)	Phase 2 (F1)	Phase 3 (F1)	Phase 1 (F2)	Phase 2 (F2)	Phase 3 (F2)
PN without DPF (cold) [#/km]	2.2e14	1.1e14	1.1e14	2.4e14	1.2e14	1.1e14
PN with DPF (cold) [#/km]	7.0e12	3.1e12	2.4e12	6.5e12	3.3e12	2.7e12
Percentage decrease [%]	96.8	97.3	97.7	97.2	97.2	97.6
PN without DPF (hot) [#/km]	2.2e14	1.2e14	1.1e14	2.3e14	1.3e14	1.2e14
PN with DPF (hot) [#/km]	6.4e12	3.0e12	2.3e12	7.0e12	3.6e12	3.0e12
Percentage decrease [%]	97.1	97.5	97.8	97.0	97.2	97.5

Fig. 6 shows the PN emission results in bar-chart format. The main conclusion is again the increased emissions over the first urban part of the cycle (without DPF), where the vehicle accelerates often. The deviation of emission values between cold-hot cycle and Fuel 1-Fuel 2 is small.

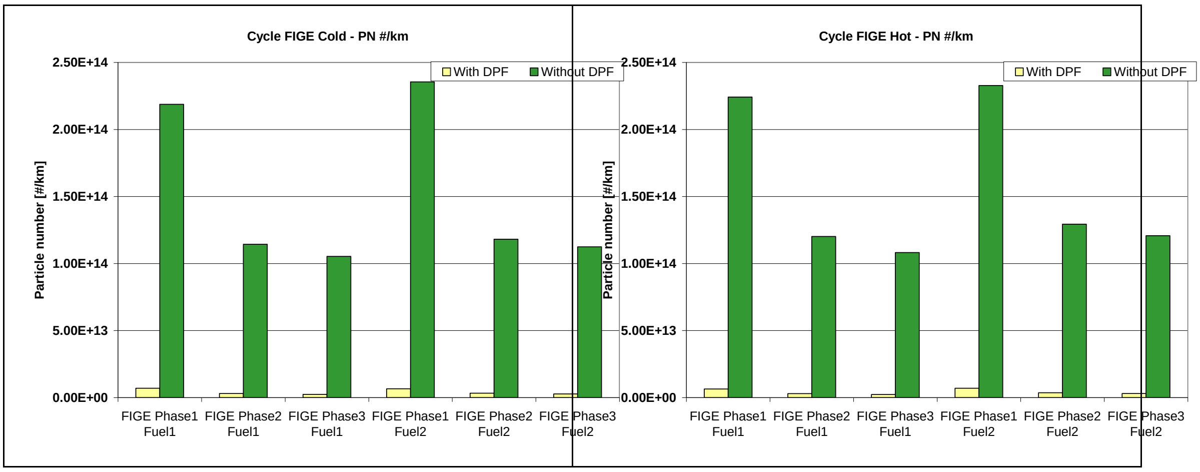

Fig. 6 – PN emissions over the FIGE driving cycle (cold-hot) for both tested fuels.

4.2 Gaseous emissions over the FIGE

Fig. 7 shows the CO and HC bag emission values over the FIGE driving cycle for the above mentioned configurations. The main characteristic is that the emissions are not affected to a great extent when the truck is tested with the DPF. The reason is that the after-treatment system consists only of an uncatalyzed DPF. The regeneration is promoted with the aid of a FBC system, without affecting the gaseous emission performance of the filter. Moreover during measurement no regeneration event took place.

One other interesting aspect is the influence of the use of biodiesel on gaseous emissions. When the Fuel 1 is used (25% biodiesel) CO emissions without DPF decrease by 4-12%, compared to the emissions obtained with Fuel 2 without biodiesel. The same trend is also valid for total HC. In this case, when the F1 is used, the decrease in HC emissions is up to 14% over the cold cycle, without DPF.

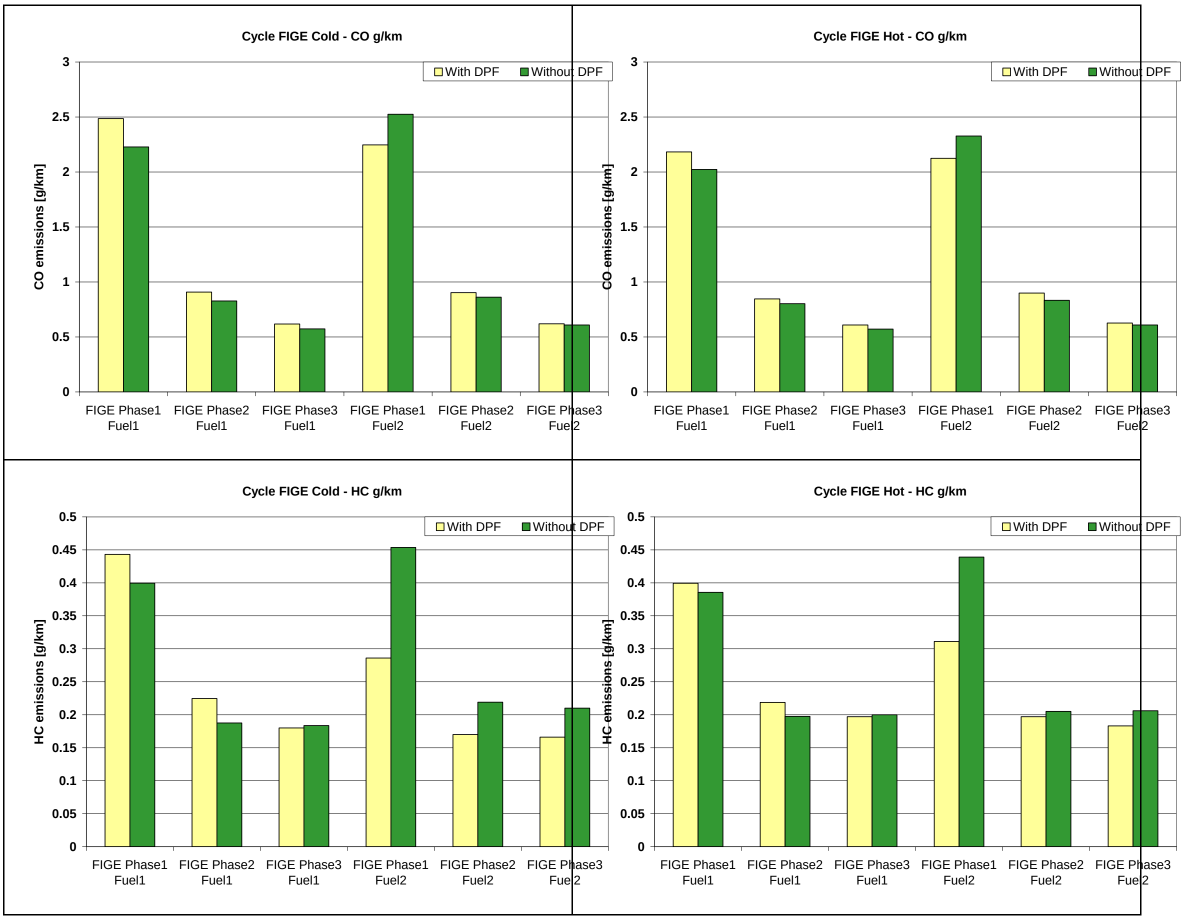

Fig. 7 – CO and HC emissions over the FIGE driving cycle (cold-hot) for both tested fuels.

Fig. 8 shows the results for CO_2 emission values. In this case the emissions are also not affected by the presence of the DPF exhaust after-treatment system. Gaseous emissions are increased (in terms of g/km) over the first urban part of the cycle, due to the frequent accelerations and increased engine load. The difference between cold and hot start measurement results are small, as there is not a catalyzed exhaust after-treatment devise to promote CO and HC oxidation when sufficient warming of its substrate would take place. In general, the emissions are slightly increased over the cold cycle (for the same fuel) comparing to the hot cycle results. This difference could by attributed to increased friction and incomplete combustion when the engine starts cold.

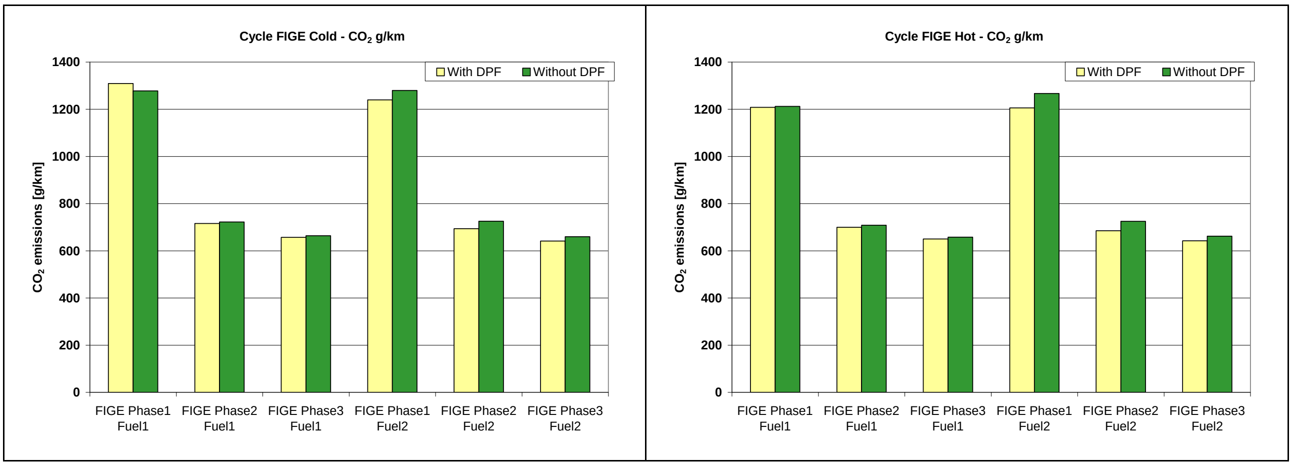

Fig. 8 – CO_2 emissions over the FIGE driving cycle (cold-hot) for both tested fuels.

Fig. 9 shows the FTIR NO_x, NO and NO_2 results over the same cycle for both fuels, with and without DPF. The scale has been kept common for the three emissions in order easily compare the results. Diesel exhaust NO_x composition of diesel engine exhaust is usually 95%-5% NO-NO_2. The NO_2 percentage is increased up to 35% when a DOC or a catalyzed DPF is presented in the exhaust after-treatment configuration [Alvarez R., Weilenmann M., Favez J-Y., “Evidence of increased mass fraction of NO2 within real-world NOx emissions of modern light duty – derived from a reliable online measuring method”, Atmospheric Environment, 42, pp. 4699-4707, 2008]. In this case the Pt based catalyst promotes the oxidation of NO to NO_2. The latter is used upstream the DPF to promote soot regeneration at lower temperatures than the regeneration with O_2 [Kandylas I.P., Haralampous O.A., Koltsakis G.C., “Diesel soot oxidation with NO2: Engine experiments and simulations”, Industrial and Engineering Chemistry Research, 41 (22), pp. 5372-5384, 2002].

In these tests NO_x emissions (bag values) are reduced to a certain extent (from about 3% to 10%) when the DPF is present in the exhaust system. This reduction is also seen with the emission values measured with the FTIR system. As it has already mentioned, apart from the uncatalyzed DPF, no NO_x after-treatment device was installed on the truck. This reduction could be caused by increased internal exhaust gas recirculation due to increased backpressure levels in the exhaust manifold, rather than by reactions in the exhaust system. According to the measured NO and NO_2 emissions with the FTIR system, with and without DPF, NO_x reduction is attributed mainly to the NO_2 reduction (89.5%), rather than to the NO reduction, which is only around 2.7%.

Regarding the influence of biodiesel on NO_x emissions, contrary to what observed in the case of CO and HC, NO_x emissions increase up to 10% when the test is conducted over the cold cycle with Fuel 1 (mixture of diesel and 25% biodiesel). These findings are in good agreement with the US Environmental Protection Agency (EPA) report [“A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions”, U.S. Environmental Protection Agency, Draft Technical Report EPA420-P-02-001, October 2002, http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf], where a comprehensive analysis has been conducted of the emission impacts of biodiesel using publicly available data.

Fig. 9 – NO$_x$, NO and NO$_2$ emissions over the FIGE driving cycle (cold-hot) for both tested fuels.

5 TEST RESULTS OVER THE AMSA CYCLE

In this section the results for PM and gaseous emissions measured over the AMSA driving cycle are presented. The PN was not measured over this cycle. As for previous reported FIGE cycle results, the measurements have been conducted using two fuels (F1 and F2), using both cold and hot driving cycles.

5.1 PM over the AMSA

Table 4 presents the PM results in terms of mg/km for both fuels, two configurations (with and without DPF retrofit system) and over the cold/hot AMSA cycle. In this case, when the results without DPF are examined, the PM mass is highest over the second part of the cycle, while the collection of the garbage takes place. When the commercial diesel Fuel 2 is used the emissions are not affected by the engine temperature at the start of the test (cold/hot cycle). On the contrary, using the mixture of diesel and biodiesel (Fuel 1), the emissions without DPF measured over the first part of the cycle decrease by almost 28% when the test is carried out with a warmed up engine. The percentage decrease of PM when tested with DPF ranges from 71% to 85.5% for F1 and from 78% to 88% for F2.

Table 4 – PM emissions over the AMSA cycle (cold-hot).

	Phase 1 (F1)	Phase 2 (F1)	Phase 3 (F1)	Phase 1 (F2)	Phase 2 (F2)	Phase 3 (F2)
PM without DPF (cold) [mg/km]	248	262	179	253	314	204
PM with DPF (cold) [mg/km]	36	50	45	33	45	45
Percentage decrease [%]	85.5	80.8	74.6	87.1	85.6	77.7
PM without DPF (hot) [mg/km]	180	240	168	256	314	202
PM with DPF (hot) [mg/km]	39	48	49	31	43	43
Percentage decrease [%]	78.1	80.0	70.7	87.9	86.2	78.8

Fig. 10 shows the above mentioned results in bar-chart format. The PM emission values with DPF do not change (for the same part of the cycle) when a different fuel or a hot cycle is used for the test. The influence of the use of biodiesel is also valid over the AMSA driving cycles, where the PM emissions without DPF decrease from 2% to 30% when the Fuel 1 is used.

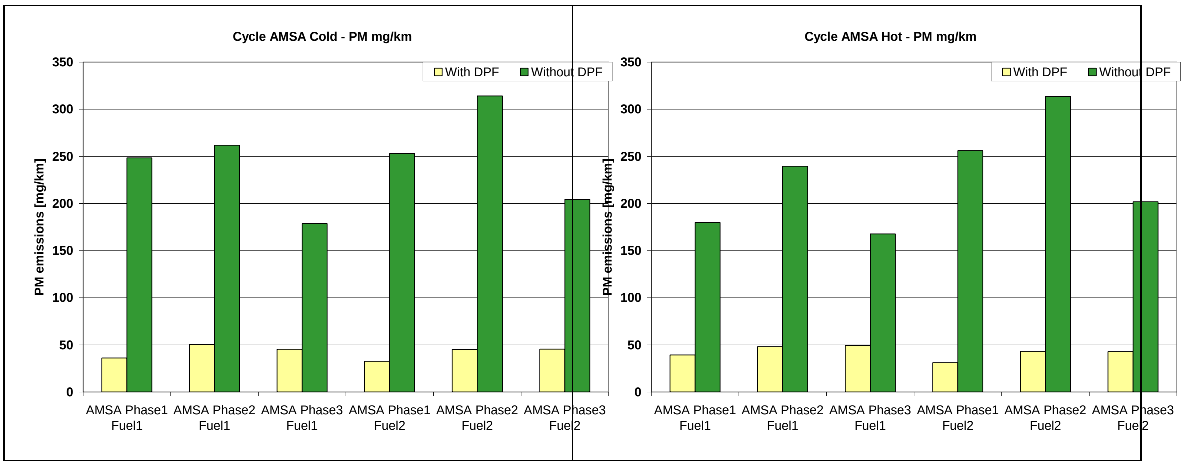

Fig. 10 – PM emissions over the AMSA driving cycle (cold-hot) for both tested fuels.

5.2 Gaseous emissions over the AMSA

In this paragraph the gaseous emissions with and without DPF measured over the AMSA driving cycle are presented. As reported for the previous FIGE results, the non catalyzed DPF does not promote the CO and HC oxidation. The emissions do not change significantly when the DPF retrofit system is used. Emissions are increased over the second part of the cycle, while driving at urban part and collecting the garbage, with alternative acceleration and idling phases.

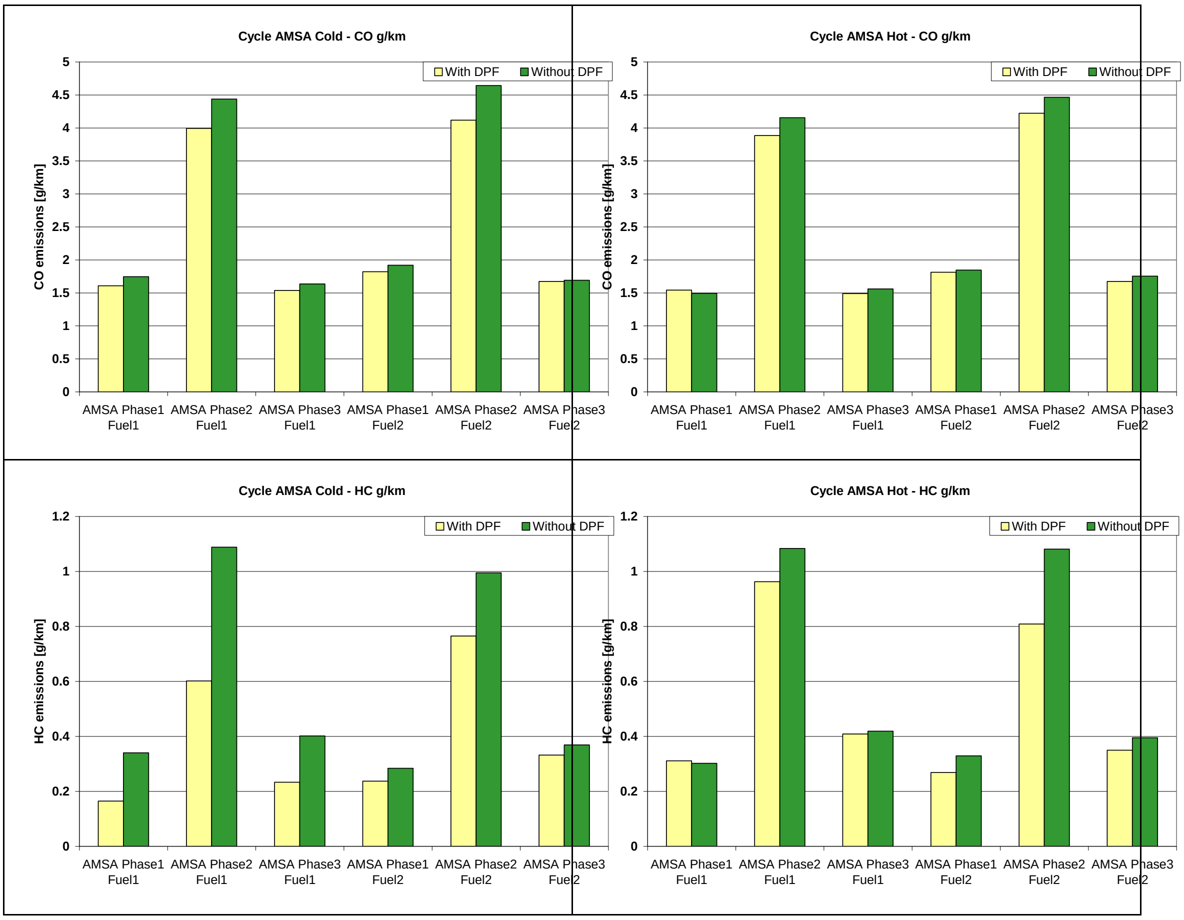

Fig. 11 – CO and HC emissions over the AMSA driving cycle (cold-hot) for both tested fuels.

Fig. 12 shows the FTIR NO_x, NO and NO_2 emission values in terms of g/km, over the AMSA driving cycle for both fuels, with and without DPF. As previous, the scale is common for all the pollutants. The emissions are increased as previously reported over the second part of the cycle, while driving in urban conditions. Again the NO_x emissions decrease (average decrease 11.5%) when DPF is installed, while NO emissions decrease by 6.3% and NO_2 emissions decrease by 69%. The NO/NO_2 ratio is 90/10% of the total NO_x, consequently, NO/NO2 participate to the NO_x reduction from 50/50% respectively.

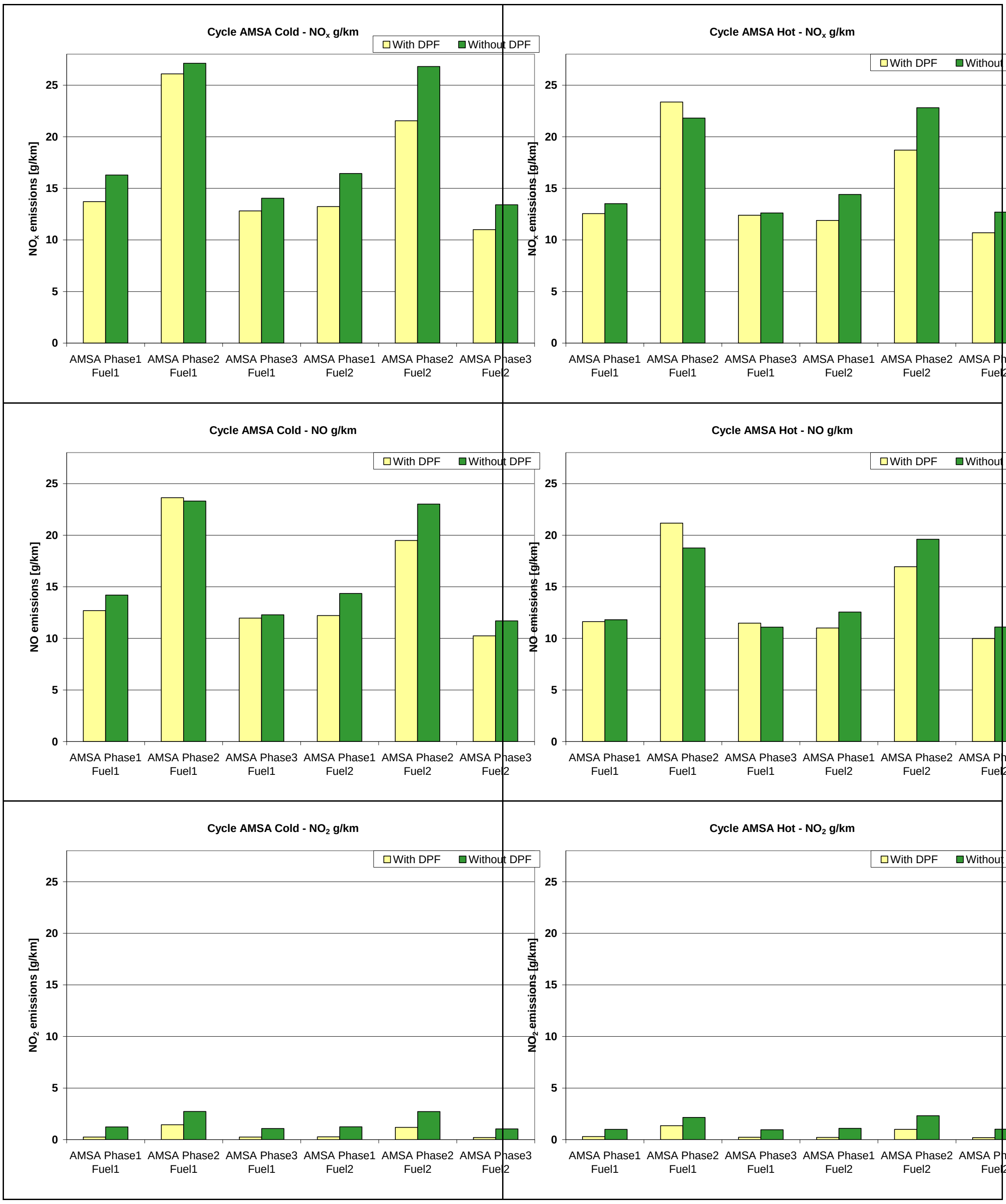

Fig. 12 – NO_x, NO and NO_2 emissions over the AMSA driving cycle (cold-hot) for both tested fuels.

6 CONCLUSIONS

This report presented results of a measuring campaign of JRC concerning a Euro II garbage collector heavy duty truck with and without DPF retrofit after-treatment system. The particulate and gaseous emission performance was presented and discussed. The tests were conducted over the FIGE driving cycle for heavy duty vehicles, and over the “AMSA” cycle, derived from real-life operating conditions typical of a garbage collector truck use. Two set of measurements were analysed over cold and hot driving cycles. Moreover, two diesel fuels were used, the commercial diesel, and a mixture of 75-25% diesel-biodiesel.

The PM emissions decrease from 70% to 90% when the DPF retrofit system is used. The respective decrease for PN reaches 97%. The gaseous performance is not affected by the DPF system, as neither the filter was catalyzed, nor a DOC/SCR was used to promote reduction of CO, HC, NO_x.

NO_x emissions where slightly decreased when the retrofit not catalyzed DPF system was installed in the exhaust after-treatment. The reduction was probably due to increased internal exhaust recirculation caused by the increased backpressure in the exhaust system before the DPF, rather than chemical reactions. Both NO and NO_2 reduction contribute to NO_x reduction emissions. The NO_2 decrease is between 70% and 89%.

The difference between cold and hot cycle results was small, as the uncatalyzed DPF after-treatment system was not affected by the temperature. The emissions were slightly increased over the cold cycle due to the in-cylinder increased friction and incomplete combustion phenomena.

Finally, the emission performance was evaluated using two different fuels. When the mixture of diesel and biodiesel fuel was used the PM, CO and HC emissions tended to decrease, while the NO_x emissions tended to increase. These findings are in agreement with previously reported results of various researchers concerning the influence of the use of biodiesel on emissions.

WP3

Air Quality Monitoring

(WP3 Leader: Claudio Belis)

Deliverables:

WP3

Quality Control of PM Measurements in the Air Quality Monitoring Network of Regione Lombardia

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DELIVERABLE IX 3.1: FINAL REPORT OF WP3 ON QUALITY CONTROL OF PM MEASUREMENTS IN THE REGIONE LOMBARDIA AIR QUALITY MONITORING NETWORK

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Summary

The present report summarizes the QA/QC programme for PM carried out in the framework of WP3. The performance of automatic analyzers present in the monitoring network of ARPA (OPSIS SM200, TEOM FDMS, ENVIRONNEMENT MP101, and FAI SWAM) was evaluated by comparing them with the gravimetric method using Leckel SEQ47/50 samplers as reference.

Data collected in 9 monitoring campaigns at 7 sites showed in general good consistency with the exception of 2 sites where the deviation from the reference or the spread of data were relevant.

The uncertainty at the limit value was checked only for instruments for which there were enough data points to do a suitable for statistical analysis (OPSIS SM200 and TEOM FDMS). In the test both analyzers presented an expanded uncertainty at the limit value below 25%., which is considered acceptable within the international community. In OPSIS SM200 the slope of the regression curve against the reference analyzers was significantly different from 1.

In the second part of the report are presented the results of a pilot study carried out in the city of Varese aiming at developing a methodology to estimate the representativeness of a monitoring station. Levels of $PM_{2.5}$ were measured simultaneously in 16 temporary sites for a whole working day (8 hours). The representativeness of a monitoring station was estimated using a geostatistical approach relying on the relationship between the variance and the distance of the monitoring sites. The highest concentrations of $PM_{2.5}$ were observed in the south-western part of the domain. The distance of representativeness is comparable with the size of the domain (3x3 km) indicating that a single monitoring site located in its centre should be suitable to represent the whole area. More field work would be necessary to evaluate if these conclusions could be extended to longer time windows and different atmospheric conditions

1. Introduction

The levels of air pollutants in Regione Lombardia are measured by ARPA (Agenzia Regionale per la Protezione Ambientale della Lombardia), the technical body in charge of air quality monitoring. Regione Lombardia, and JRC have collaborated in the field of QA/QC of air quality measurements since the nineties. The activity of this work package continued the long tradition of collaboration in this field between both institutions.

The aims of WP3 were:

a) To perform activity of Quality Control of the PM measurements in the Air quality monitoring network of Regione Lombardia as a complement of the QA/QC already implemented by ARPA

b) To support the strategic development of the new technologies for air quality measurement in Regione Lombardia according to the most up to date measurement technologies including a study on the spatial representativeness of a monitoring station.

For that purpose, a limited number of monitoring stations located in representative sites have been selected in collaboration with ARPA for parallel QA/QC measuring campaigns of particulate matter in ambient air. During these surveys the measurements obtained with a variety of automatic instruments operated by ARPA in its monitoring network were compared with those obtained by ERLAP (European Reference Laboratory for Air Pollution) using reference PM samplers in compliance with the reference method (EN 12341) and other methods.

To compare PM_{10} datasets the ratio between the tested and the reference instrumentation was used and their consistency was evaluated using various statistics [1].

To study the spatial representativeness of a monitoring station the area surrounding the site of Via Copelli (Varese) was selected. Sixteen reference samplers for $PM_{2.5}$ were deployed contemporary for one day in an arrangement especially designed to measure the spatial variability of this pollutant.

2. Description of the Activity

The reference methods for PM concentration in ambient air in the European Union are gravimetric methods (EN 12341 and EN 14907). These methods are somewhat labour-intensive and require several days in order to get the final value for the PM mass concentration.

On the other hand, on-line monitoring systems provide mass concentration values that are available immediately after the end of the measurement and commonly with higher time resolution. However, these instruments are usually based on operation principles different from the reference method, either on tapered element oscillating microbalances (TEOM) or on beta-ray attenuation, among others.

All filter based methods for measuring the suspended particulate mass are subject to positive and negative artefacts than cannot be avoid and are difficult to identify. A review of most common sampling artefacts is given in Annex 1.

Data obtained with automatic monitors can be considered comparable to the reference methods provided equivalence to the reference method has been demonstrated. Deviations from the reference method may, for example, derive from the sampling air heating (typically 30-50 ºC) in order to avoid interferences with humidity during sampling. On the contrary, exposing the sample to a temperature higher than ambient air may cause loss of semi-volatile compounds.

3. Methodology

3.1 Data collection

For the measurement of particulate matter no primary metrological standards or reference materials exist for establishing the traceability of PM_{10} and $PM_{2.5}$ measurements to SI units. The uncertainty of any candidate method therefore has to be determined with reference to a PM reference sampler as specified in EN 12341 [2] for PM_{10}, assuming these ‘reference samplers’ to be unbiased with respect to the applied particle-size convention.

In order to evaluate the on-line instrumentation performance criteria were used (see below).

The evaluation was carried out on PM_{10} data available from the QA/QC campaigns performed during this project in the framework of WP3 (Table 1).

Table 1. Parallel measurements of PM_{10} (and other size fractions not reported) carried out during this project in the framework of WP3 (the number of instruments is in parenthesis).

Site	Time (start)	Instrumentation	
		JRC	**ARPA**
Limito di Pioltello (not used)	4-24 Jul 2006	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	TEOM-FDMS
Monza (not used)	29 Jan-11 Feb 2007	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Milan P. Giuriati	26 Sep-9 Oct 2007	(1) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Bergamo	14-27 Nov 2007	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	ENVIRONNEMENT MP101MC
Monza	19 Nov-2 Dec 2007	(1) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Busto Arsizio	7-13 Dec 2007	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	ENVIRONNEMENT MP101M
Milan P. Giuriati	12-25 Jan 2008	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Milan P. Giuriati	10-28 Sep 2008	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Merate	28 Nov-11 Dec 2008	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	FAI SWAM
Brescia	23 Jan-5 Feb 2009	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	OPSIS SM200
Limito di Pioltello	16 Jun-16 Jul 2009	(2) Leckel SEQ 47/50: $\mathbf{PM_{10}}$	TEOM-FDMS

Gravimetric PM_{10} mass fraction was selected since deploying two identical reference samplers made it possible to calculate the between sampler uncertainty (u_{bs}). A detailed description of the instrumentation used in the campaigns is provided in Annex 2.
The first monitoring campaign in Limito di Pioltello has been excluded from this analysis since the FDMS module of the continuous analyzer TEOM of ARPA presented a malfunctioning (1st Intermediate Report deliverable 3.3.1 page 6). In order to check the effectiveness of the remediation measures the campaign was repeated in 2009 (7th Intermediate Report). Also data collected in the second campaign in Monza could not be taken into account for this analysis. In this campaign the reference samplers and the

automatic analyzer worked at different time frames (one starting at midnight and the other starting at noon) therefore it was not possible to compare them directly (2nd Intermediate Report pages 113-115). In addition, the presence of a construction site in the close vicinity of the samplers disturbed the experiment. Parallel measurements with only one reference sampler were carried out in this site later on, between November 19th and December 2nd 2007, to check the comparability of the samplers.

In Annex 3 are reported the 24 h PM_{10} averages of the sampling campaigns used in the evaluation of the analyzers.

3.2 Data evaluation for the assessment of automatic analyzers

In this study has been evaluated only the uncertainty deriving from the field tests. For the evaluation of the uncertainty due to the lack of comparability between automatic samplers and the reference sampler it was assumed that their relationship could be described with a linear equation.

The collected data were validated and outlier tests were carried out.

The reference value for each 24h period was calculated as the mean of two reference samplers Leckel SEQ47/50.

Between sampler uncertainty (u_{bs}) for reference samplers was calculated using equation (1)

$$u_{bs}^2 = \frac{\sum_{i=1}^{n}(y_{i,1} - y_{i,2})^2}{2n} \qquad (1)$$

Where $y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a 24 h period i and n is the number of data pairs.

Between sampler uncertainties < 2.0 µg/m^3 indicate that the performance of the reference sampler is suitable for comparison with non reference samplers. In the datasets used for this exercise u_{bs} ranged between 0.6 and 1.7 µg/m^3.

In total, four types of automatic analyzers have been tested: OPSIS SM200, TEOM FDMS, ENVIRONNEMENT MP101, and FAI SWAM. A description of the instrumentation is given in Annex 2. However, the estimation of the uncertainty at the limit value was performed only on OPSIS SM200 and TEOM FDMS, the instruments with enough valid data pairs for statistical treatment (≥30).

In order to have a better representation of a variety of environmental conditions (PM composition and concentration, humidity, temperature, wind speed) the database used for each kind of automatic analyzer was constructed merging data from different sampling campaigns.

For the purposes of the test carried out in this exercise 30 data pairs were considered enough to check the comparability.

The regression curve for each automatic analyzer against the reference was calculated using orthogonal regression. According to the Guide, if the slope of the regression curve is significantly different from 1 or the intercept is significantly different from 0, data from the analyzer (equivalent method) need to be corrected with the parameters of the regression between the reference and the analyzer.

The uncertainty in the measurements of the automatic analyzers U_{CR} was calculated as a function of PM concentration x_i according to equation (2):

$$u_{CR}^2 = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \qquad 2$$

Where RSS is the sum of residuals of the regression curve, $u(x_i)$ is the uncertainty of the reference method and the parameters of the regression curve are a and b.

The combined uncertainty of the analyzers $W_{c,CM}$ at the limit value (50 µg/m^3) was calculated with equation (3):

$$W_{c,CM}^2(y_i) = \frac{u_{CR}^2(y_i)}{y_i^2} \qquad 3$$

According to common practice (GUM approach) the combined uncertainty was multiplied by a coverage factor (2) to calculate the expanded uncertainty W_{CM}. In order to evaluate the performance of the instruments we compared the relative expanded uncertainty with 25%, that is the maximum uncertainty allowed at the limit value in the Annex 1 of Directive 2008/50/CE [3].

Graphs and validation were performed using RIVM spreadsheet v2.8 (Beijk, 2011)

4. Intercomparison campaigns

4.1. Data consistency

In order to compare the results of the different sampling campaigns the raw PM_{10} concentrations measured by automatic analysers were “normalized” dividing them by the average of the measurements provided by the two reference samplers (Figure 1). The ratios are equal to the unity when the candidate and the reference have the same value. In the present analysis only OPSIS SM 200 is considered for the Milano Giuriati site, since the TEOM FDMS was not set up to measure absolute values of PM. The values measured in Milano Giuriati in Sep-Oct 2007 with the OPSIS SM200 and those observed in Busto Arsizio in December of the same year with ENVIRONNEMENT were those with the highest spread of data. The last one was also the one with the highest deviation from the unity. Values obtained with FAI SWAM were those with the lowest spread.

Figure 1. Plot of normalized PM_{10} measurements obtained as the ratio between candidate and the average of reference samplers.

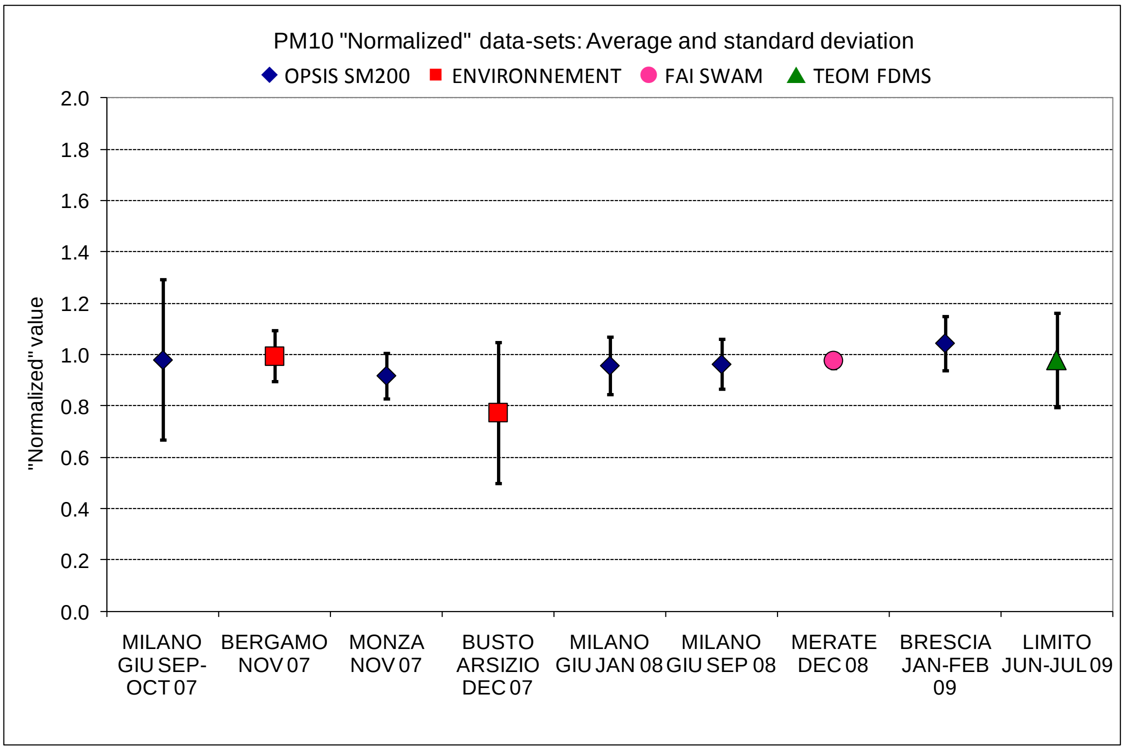


Figure 2. Mandel's *h* statistics to check between dataset consistency. The green line represents 5% significance level and the red one 1% significance level.

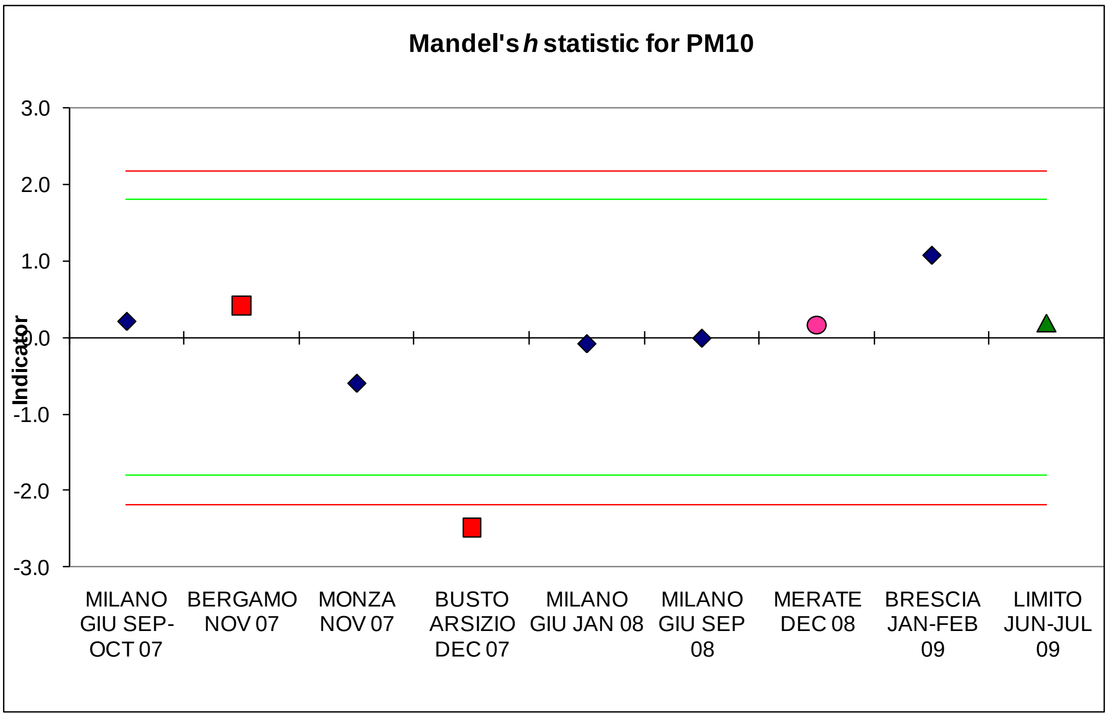
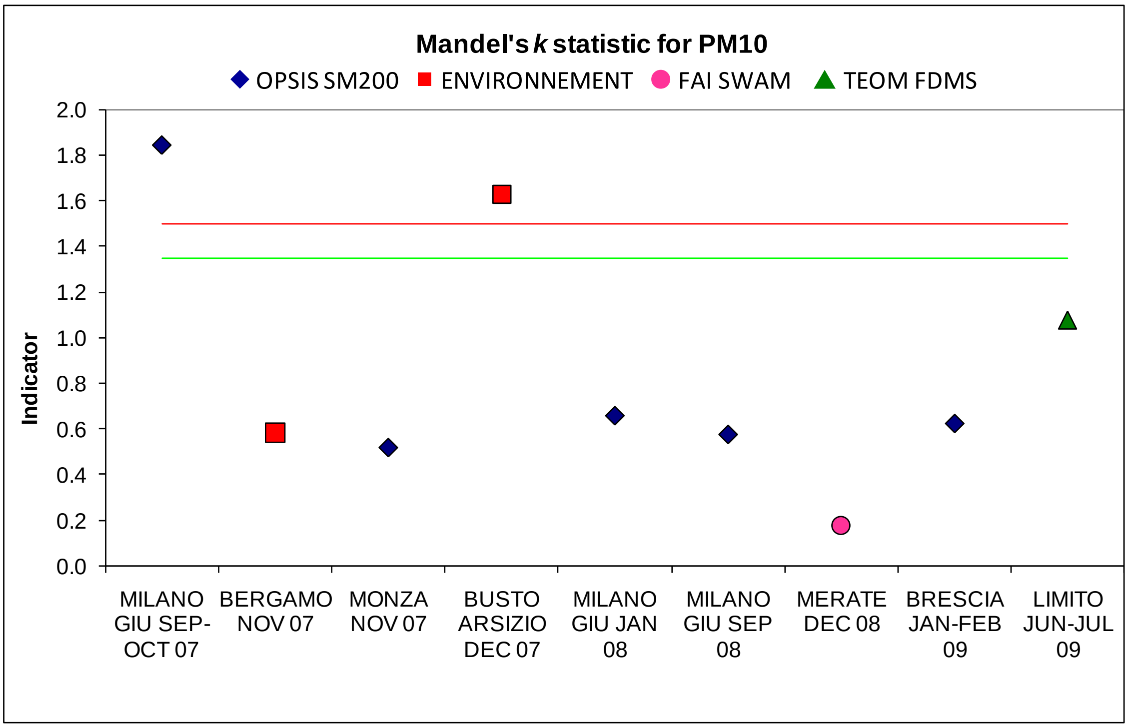


Figure 3. Mandel's *k* statistics for within dataset consistency. The green line represents 5% significance level and the red one 1% significance level.



The performance of ENVIRONNMENT changed among different campaigns. It presented a good performance in Bergamo but results in Busto Arsizio were poor. To a lower extent also OPSIS SM200 presented variations: in some cases the average of the ratios was below unity and in one case it was above.

Mandel test is a visual test of consistency [4]. It includes two statistics: *h* for between dataset consistency and *k* for within dataset consistency. According to Mandel's *h* test there is a good comparability between the results of the different campaigns since the majority of the values fall between zero and the 5% significance level (Figure 2). The only exception is the campaign in Busto Arsizio that was already identified as atypical in Figure 1. This was due to the non adequate performance of the instrument used (ENVIRONNEMENT 101 version M) what is likely associated with the lack of a system to keep the sampling probe in thermal equilibrium with the ambient air. For this instrument however additional number of data pairs would help to draw more robust conclusions.

There is also a good agreement between this figure and the Mandel's *k* for within dataset consistency. The campaigns of Milano Giuriati 2007 and Busto Arsizio, those with the highest spread, are both significant at 1% critical level.

Excluding the Busto Arsizio campaign, which can be considered as an outlier, the average ratios between the measurements from the monitoring network and those from the reference samplers fall between 0.92 and 1.05 (Figure 1). These results are within an acceptable uncertainty range .

4.2. *Assessment of automatic analyzers*

In table 2 are reported the statistical parameters used for the evaluation of the comparability between the reference samplers and the automatic analyzers. As standard procedure we report only campaigns in which two reference samplers were deployed (9 out of 11). In a limited number of campaigns only one reference sampler was deployed and in one case two reference PM_{10} samplers were available only for part of the campaign. Considering that u_{bs} of the reference sampler is well below the critical value of 2 µg/m^3 and that its value is rather stable (taking into account data collected in more than 20 measuring campaigns) we have reported calculations including these data.

The test of significance on the parameters of the regression line for automatic analyzers uncorrected data (i.e. data as provided by ARPA) indicates that slope is significant for OPSIS SM200 (Table 2, Figure 4).

The uncertainty at the limit value of uncorrected data is close to 23 % for both OPSIS SM 200 and TEOM FDMS and hence of acceptable quality.

Table 2. Orthogonal regression parameters for the intercomparison between reference method *versus* automatic analyzers (uncorrected data).

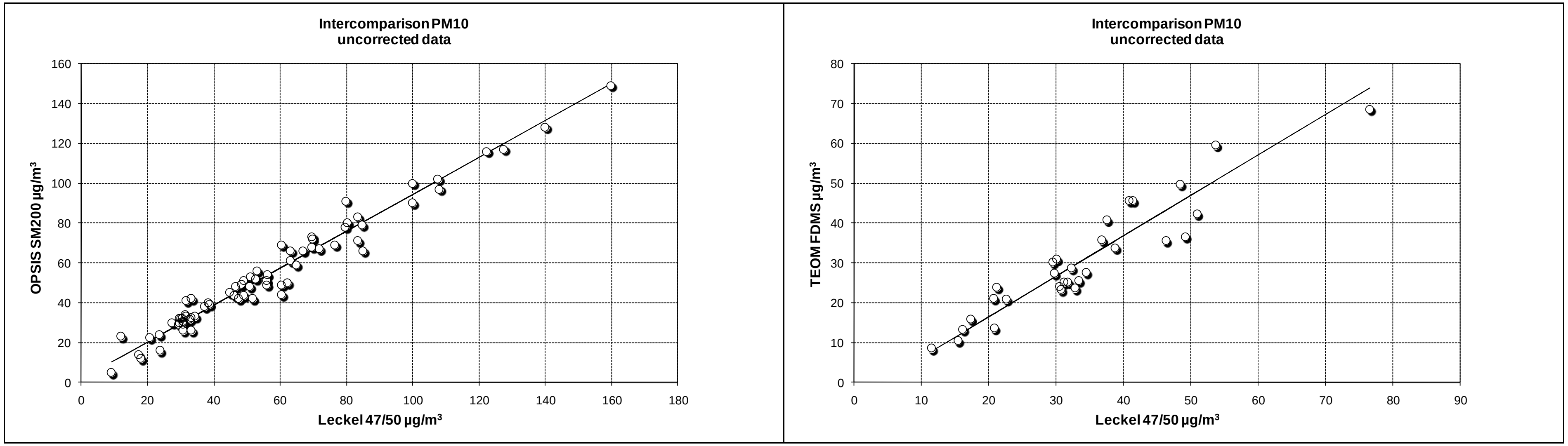
JRC	ARPA	b	u(b)	significant	a	u(a)	significant	u_{cr}	$W_{c,CM}$	W_{CM}	u_{bs}	Site	period	n
Leckel SEQ47/50	OPSIS SM 200	0.93	0.02	yes	1.80	1.33	no	5.67	11.34	**22.68**	0.76	Brescia Milan Giuriati Milan Giuriati Milan Giuriati Monza	Jan-Feb 09 Jan 08 Sep 08 Sep-Oct 07 Nov-Dec 07	71
Leckel SEQ47/50	TEOM-FDMS	1.02	0.07	no	-3.86	2.42	no	5.77	11.53	**23.06**	0.63	Limito di Pioltello Milan Giuriati	Jun-Jul 09 Sep 08	30

a and **b** are the intercept and slope, respectively, calculated from orthogonal regression.
u(a) (µg/m³) and **u(b)** are the standard uncertainties of the slope and intercept, respectively, calculated as the square root of their variances.
$\mathbf{u_{bs}}$ (µg/m³) is the uncertainty between samplers used by JRC (Leckel SEQ47/50)
$\mathbf{u_{cr}}$ (µg/m³) is the combined uncertainty between ARPA and JRC samplers.
n is the number of samples
$\mathbf{W_{c,CM}}$ (%) is the relative uncertainty calculated at a level of PM_{10} = 50 µg/m³
$\mathbf{W_{CM}}$ (%) is the expanded uncertainty

Expanded uncertainty criteria: $\mathbf{W_{CM}}$ **(%)** = **25%**
The between sampler/instrument uncertainty $\mathbf{u_{bs}}$ for the standard method is ≤ 2 µg/m³.

Conditions for the acceptance of a full dataset of values from a candidate instrument with respect the reference instrument is that:
- the slope **b** is insignificantly from 1, that is: $|b-1| \leq 2u(b)$
- the intercept **a** is insignificantly different from 0 that is: $|a| \leq 2u(a)$

Figure 4. Scatter plot of PM_{10} measurements obtained with reference method and automatic analyzers (equivalent method). Regression parameters are reported in table 2.



4.3. *Investigation on field blanks*

Field blanks are filters that are conditioned, weighed, transported and stored in the sampler but are not used for collecting PM. Since field blank undergo almost the same treatment than sampled filters, their mass change during the filter handling can be used as an indirect estimation of the influence of storage and transport on the sampled filter mass. However, since field blanks are not exposed to the sampling air flow that may either remove or deposit material on the filter, they're not appropriate to evaluate sampling artefacts in sampled filters (a more detailed discussion on PM sampling artefacts is available in Annex 1). For that reason, the PM_{10} reference method does not consider the subtraction of the field blanks mass change from the measured PM_{10} mass. Although not mandatory for PM_{10}, field blanks were used to monitor the influence of filter handling conditions (storage and transport) on the filter mass. In table 3 are reported the average field blank mass change (hereon field blanks) in every sampling campaign.

Table 3. Average field blank mass change in each monitoring campaign

site	Milan Giuriati	Bergamo	Monza	Busto Arsizio	Milan Giuriati	Milan Giuriati	Merate	Brescia	Limito di Pioltello
period	Sep-Oct 07	Nov-07	Nov-07	Dec 07	Jan 08	Sep-08	Nov-Dec 08	Jan-Feb 09	Jun-Jul 09
average (µg)	116.0	39.9	118.5	84.6	38.5	70.3	29.9	50.9	39.0

The observed field blanks expressed in mass concentration equivalent range from 0.7 to 2.1 µg/m^3, which on average corresponds to 1-3% of the PM mean observed concentrations. Although the reference method does not admit subtracting field blanks from the PM_{10} mass, an investigation aiming at evaluating what could be the effect of sample handling on the comparison between automated analyzers and reference samplers reported in the previous chapter was carried out.

Only for demonstration purposes average field blanks were subtracted from JRC measurements. Subsequently the regression curve of automatic measurements were calculated against both JRC reported values according to EN12341 (Figure 5, Table 4) and JRC values minus field blanks (Figure 6, Table 5).

Figure 5. Regression automatic analyzers (CM) vs JRC reference samplers (RM) values according to EN12341. The red lines indicate 99% confidence interval.

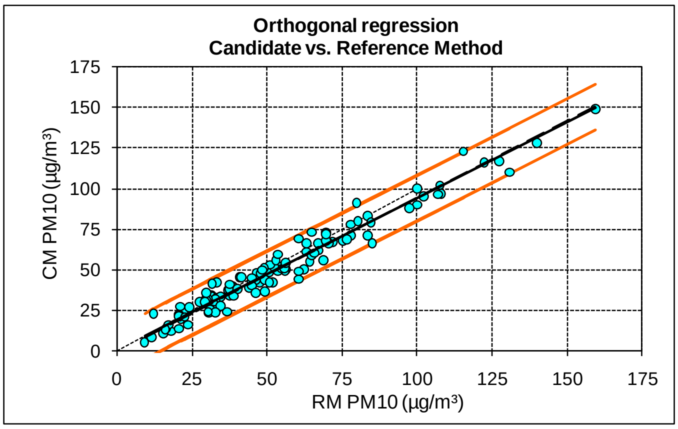


Table 4. Parameters of the regression automatic analyzers vs JRC reference samplers values according to EN12341

Number of data pairs	125	
Mean AUTOMATIC (candidate)	48.2	µg/m³
Mean REFERENCE	50.8	µg/m³
Slope b	**0.94**	**significant**
Uncertainty of b	0.02	
Intercept a	**0.24**	µg/m³
Uncertainty of a	0.99	µg/m³
R^2	0.96	

Figure 6. Regression automatic analyzers (CM) vs JRC reference samplers (RM) subtracting field blanks. The red lines indicate 99% confidence interval.

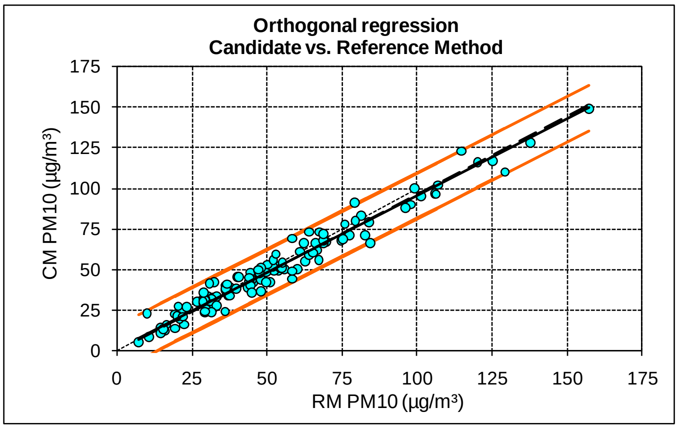


Table 5.. Parameters of the regression ARPA vs JRC values subtracting field blanks

Number of data pairs	125	n
Mean AUTOMATIC (candidate)	48.2	µg/m³
Mean REFERENCE	49.6	µg/m³
Slope b	**0.94**	**significant**
Uncertainty of b	0.02	
Intercept a	**1.18**	µg/m³
Uncertainty of a	0.97	µg/m³
R^2	0.96	

Comparing the regression curves reveals that subtracting blanks from JRC values has no relevant effect on the comparison between automatic analyzers and reference samplers. It could be observed no influence on the regression slope, which in both cases is 0.94 and is statistically significant ($p<0.05$). There is a slight increase in the intercept (0.94 μg/m^3) which is comparable with its uncertainty (0.94-0.97 μg/m^3).

5. Representativeness of a monitoring station

5.1 Introduction

The whole variability of PM concentration cannot be captured with the limited number of monitoring sites available. Consequently, interpolated contour maps include important uncertainty that can lead to misinterpretation of geographic patterns and consequently to ineffective abatement strategies. In order to produce more robust spatial representation of pollutants concentrations it is essential to evaluate what is the extent of the area of representativeness of monitoring sites.

In the context of this study the representativeness of a monitoring site is defined as the distance after which the PM levels measured in different sites are no more correlated. This definition corresponds to the so called “range” of a variogram (Figure 7).

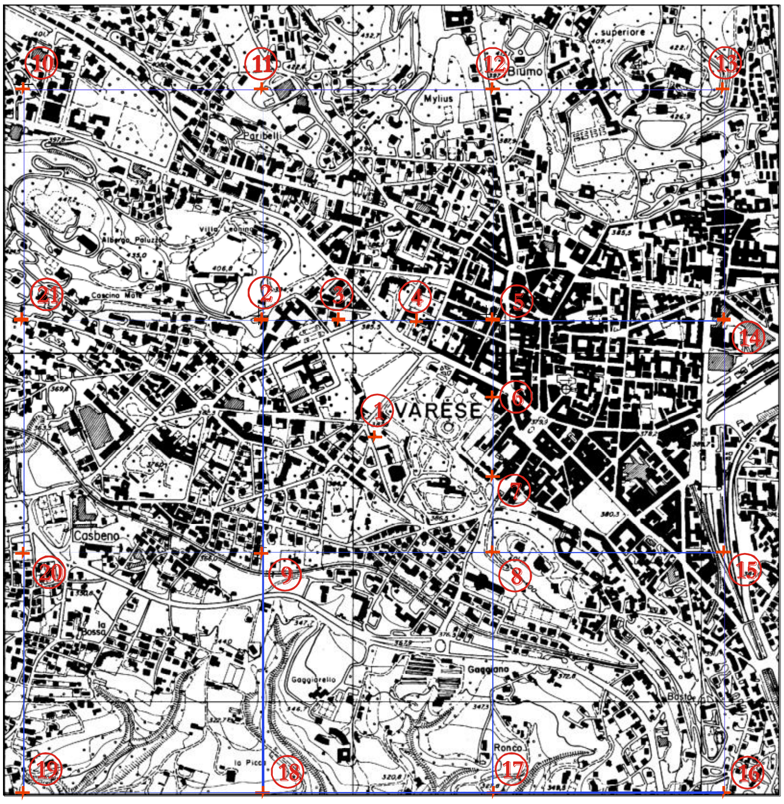
Figure 7. The range of a variogram is used as an indicator of the representativeness of a fixed station

According to this methodology the representativeness is not only a property of the monitoring station but depends on the characteristics of the selected domain.

In this section are presented the results of the field campaign carried out on 10th of February 2010 in the city of Varese with the aim of evaluating a methodology to estimate the representativeness of $PM_{2.5}$ concentrations measured in a fixed monitored station applying a geostatistical approach.

The experimental design was conceived so as the spatial correlation of $PM_{2.5}$ concentrations at increasing distances ranging from hundred meters to few kilometres could be measured (Figure 8). In order to obtain an homogeneous spatial representation 16 temporary sites were arranged on a 2 x 2 km^2 grid with the fixed monitoring station in its centre [8] . Were selected for the study only sites with homogeneous features (urban back ground) close to the grid nodes. The only site which differs from the others is the one in via Trolli (code 20) which is located less than 25 m from a crossroad. However, the values collected in this location were not higher than those of the neighbour sites (see below).

Figure 8. Theoretical sampling grid designed around the fixed monitoring station in Varese (site 1). The actual monitoring sites where located as close as possible to their expected position in the map.



The fixed station chosen for the study is a traffic-oriented monitoring station of ARPA located in Via Copelli nearby a park called Giardini Estensi. This station was selected because is the closest to the city centre and is therefore suitable to be placed at the centre of a domain that includes most of the urban area of the city.

For the field work was selected a day with meteorological conditions favourable for the accumulation of $PM_{2.5}$ at the ground level: low ventilation, night temperatures close or below to zero and strong thermal inversion at the ground level.

5.2 $PM_{2.5}$ concentrations

$PM_{2.5}$ concentrations were measured in compliance with standard EN 14907 [4] using reference gravimetric samplers Derenda LVS 3.2 with $PM_{2.5}$ inlet and collecting particulate matter on 47 mm Teflon® filters. Before sampling, filters were conditioned for 48 hours in a climatic room at 20ºC (±1ºC) and 50% (±3%) relative humidity. Filters were weighed twice before sampling within a time range of 24 hours and weighted again after the campaign with the same procedure.

Table 6. $PM_{2.5}$ mass concentration for 8 hours samples collected on February 10th in 16 temporary sites of Varese.

Site	Code	Temporary site	$PM_{2.5}$(μg/m³)
1	1	Via Copelli, 11 **(JRC mobile station)**	36
2	2	Vicolo Luigi Russolo	31
3	4	Via Staurenghi 17	31
4	5	Piazza S. Giovanni Bosco, 3	30
5	6	Giardini estensi	29
6	7	Via San Francesco d'Assisi, 15	35
7	8	Via Carlo Frattini, 1	48
8	9	Via Mulazzo 35 - Varese/Casbeno	59
9	10	Via F.lli Bandiera, 8	41
10	12	Viale Aggugiari, 63	33
11	13	Villa Ponti	29
12	15	Scalo merci FF.SS. stazione FS Varese	34
13	16	Via Donatello, 1	33
14	19	Via Filippo Corridoni, 89	46
15	20	Via E. Trolli, 5	41
16	21	Via Campigli, 43	43

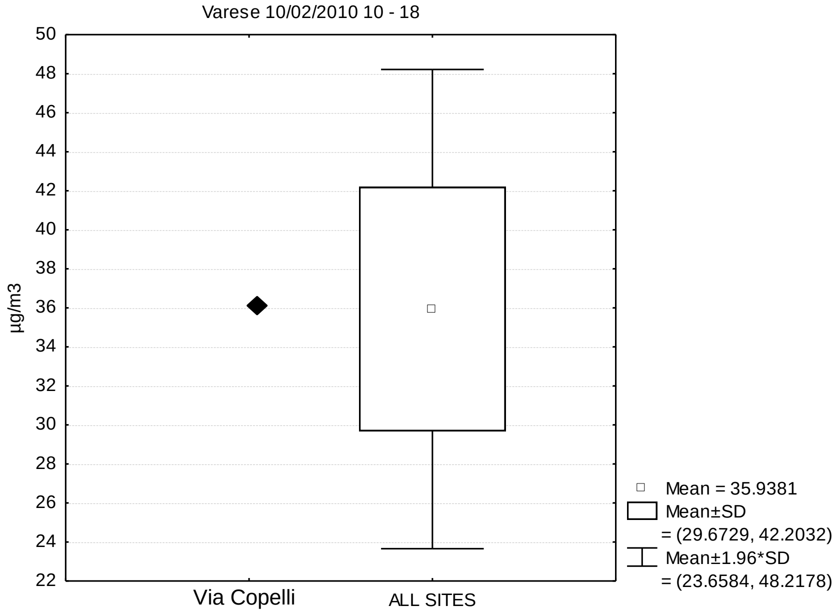
Concentrations of $PM_{2.5}$ in the temporary sampling sites around the monitoring station in via Copelli for a whole working day (~ 8 hours) from 10:00 AM to 6:00 PM on 10th of February, 2010.

In addition to the temporary sites, the JRC mobile laboratory was placed at few meters apart from the monitoring station and was equipped with Derenda LVS 3.2, TEOM FDMS $PM_{2.5}$ analyzer, optical particle counter, and meteorological probes for monitoring of temperature, humidity and wind speed.

ARPA Department of Varese (Ms Elena Bravetti) provided invaluable support to get access to the sites and to the electric power points.

$PM_{2.5}$ 8 hour mass concentrations measured with the gravimetric method in 16 sites are reported in table 6. Levels ranged from 29 µg/m³, in the park Giardini Estensi located at the centre of Varese, to 59 µg/m³ in the temporary sampling site located in via Mulazzo, which was influenced by local sources: pizzeria and unpaved parking. This value was identified as outlier using Grubbs test (z=2.61 critical z= 2.55).

Figure 9. Statistical distribution of 8 hour $PM_{2.5}$ concentrations in all sites in Varese compared to those observed in via Copelli (full symbol).



The 8 h average observed in via Copelli (36.0 µg/m³) coincided with the average of the measured 8 hour $PM_{2.5}$ concentrations in all the stations in the study, outlier excluded (35.9 µg/m³). The last is a preliminary indication that although it is a traffic station the concentrations in via Copelli are representative of the whole studied area.

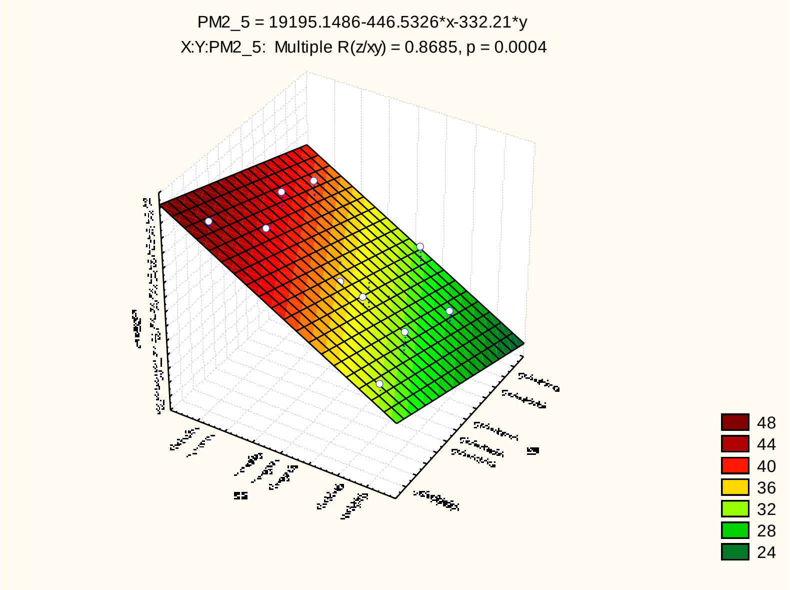
5.3 Geostastistical analysis

The three dimensional matrix of data points $PM_{2.5}(X,Y)_i$ representing the level for $PM_{2.5}$ mass concentration at site *i* which latitude and longitude are X and Y, respectively, can be described using the expression

$$PM_{2.5}(X,Y)_i = \tilde{T}(X,Y) + \varepsilon(X,Y) \qquad (4)$$

Where $\tilde{T}(X,Y)$ is the plane that represents the general spatial trend of $PM_{2.5}$ mass concentrations and $\varepsilon(X,Y)$ are the residuals between the sampled values and the values predicted by the trend (Figure 10).

Figure 10. Example of spatial representation of $PM_{2.5}$ trend and residuals on a grid. (multiple R= 0.86; p=0.004)

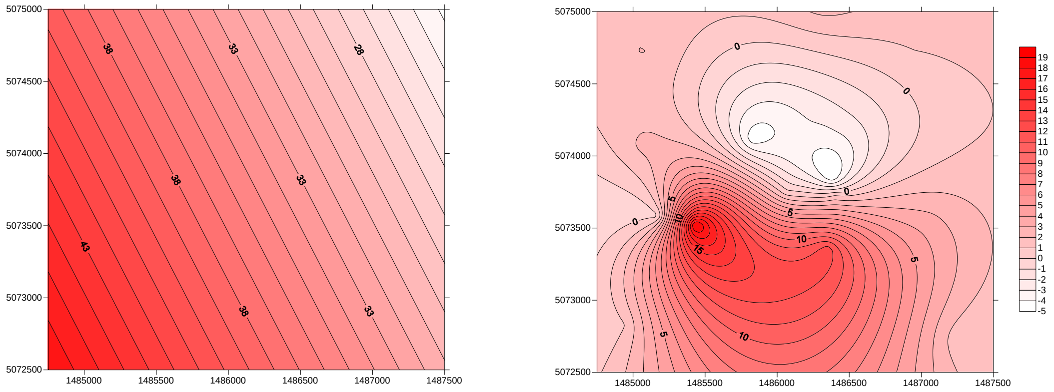


The application of this approach implies a number of assumptions:

- the sampled values are representative of the measured value at the location.
- the locations at which values are estimated, are part of a physically continuous and homogeneous "surface" of potential samples
- the values at the chosen locations are related to each other in a way which is dependent on their distance.

In Figure 11 are reported the surfaces representing the observed trend (a) and the observed residuals (b) in $PM_{2.5}$ concentrations in the city of Varese.

Figure 11. **(a)**, Trend $\tilde{T}(X,Y)$ $PM_{2.5}$ during the campaign of Varese. **(b)**, residuals $\varepsilon(X,Y)$ between sampled and predicted values for $PM_{2.5}$ concentration (units are in µg/m^3; coordinates: Gauss-Boaga).



(a) **(b)**

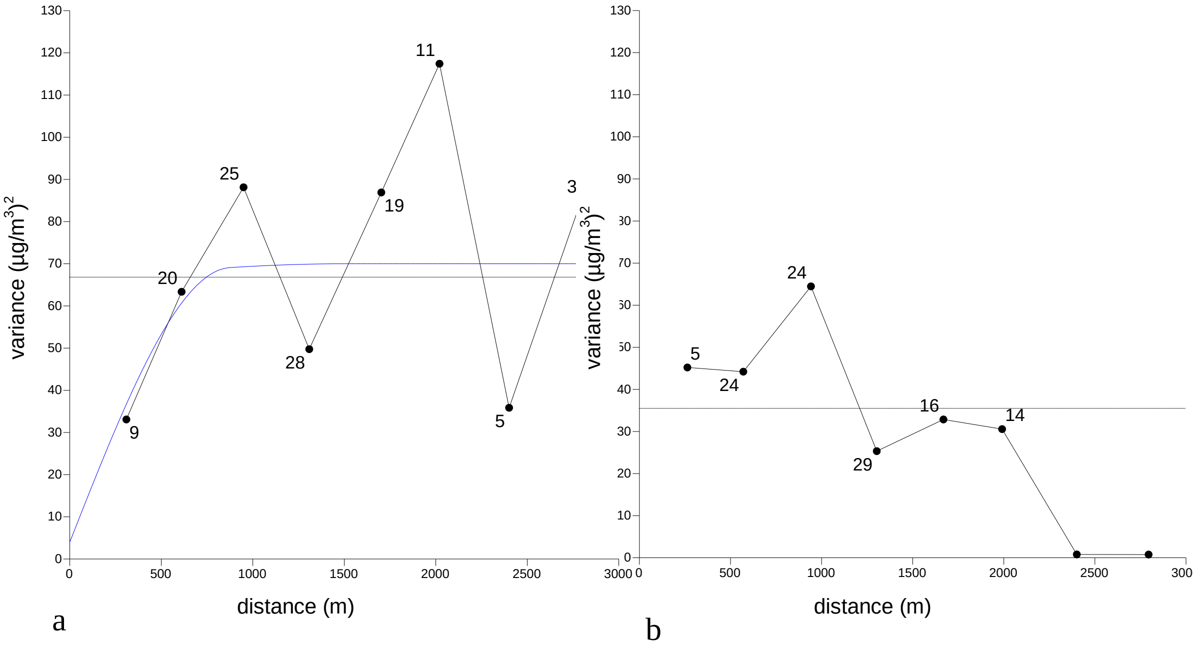
In the area represented in figure 11(a) it is possible to observe a clear decreasing trend of $PM_{2.5}$ of concentrations from SW to NE that is opposite to the altitude. In addition, the residuals in figure 11(b) show a hot spot (identified as outlier with the Grubbs test) with higher concentrations in the southern part of the domain surrounded by areas with lower levels.

According to the method of the geostatistical “universal kriging”, the trend and the residuals were combined to provide a weighted estimated value $T^*(X,Y)$ for the unsampled locations using the following expression [6]:

$$T^*(X,Y) = \sum_i \omega_i \varepsilon_i(X,Y) + \tilde{T}(X,Y) \qquad (5)$$

where ω_i are the ‘weights’ associated to each sample. The relationship between the semi-variance of the residuals *versus* the distance between their locations was plotted in variograms (Figure 12).

Figure 12. Variograms showing the relationship between the distances and the variance of $PM_{2.5}$ concentrations (a) and residuals (b). The blue line is the model that fits the observations.



Data were fitted using a spherical model with a linear trend. The curve has an intercept of 4 (µg/m^3)^2 and the range is approx. 875 m. In the variogram it could be observed that rather than stabilizing the variance strongly oscillates around 70 (µg/m^3)^2, suggesting that there is no significant relationship between variance and distance. The last would mean that the variance is relatively constant across the domain and the variogram is dominated by the nugget effect. This is hypothesis is not supported by figures 10 and 11 which display an evident trend of concentration from SW to NE (multiple R= 0.86; p=0.004). In addition, it has been observed an increase in the variance in variograms in which the directions of the distances are oriented SW-NE (not shown). When the trend is subtracted from the $PM_{2.5}$ concentrations the kriging variances (broken line) diminish significantly from circa 67 (µg/m^3)^2 to 36 (µg/m^3)^2 as shown in figure 12b. This means that the trend explains most of the variance. In addition, the highest values observed at the shortest distances in this variogram points out the presence of outliers.

The variogram was re-calculated using raw data (non detrended) without site 9 identified as outlier with the Grubbs test (Figure 13a). In this variogram is possible to observe a correlation between variance and distance that tends to stabilize at 2000 m and a variance of 43 $(\mu g/m^3)^2$.

The last point of the curve, the one with the highest values with respect to the "plateau", represents the distances between the points in the corners of the domain which concentrations are very variable. The point at the SW corner, (site 19) show high levels of $PM_{2.5}$ while those in the eastern part of the domain present much lower levels. This "edge effect" affecting sites at long distances (2700 m) is not representative of the whole domain and is not consistent with the geo-stationarity assumption in the theory of the regionalized variables. In order to avoid inconsistencies due to the edge effect, the additional variance represented by the highest point of the observed data curve should not to be taken into account when fitting the model to the experimental variogram.

Fitting the variogram with a spheric model and setting the maximum variance to the one in the "plateau" (circa 50 $\mu g/m^3)^2$ results in the following model:

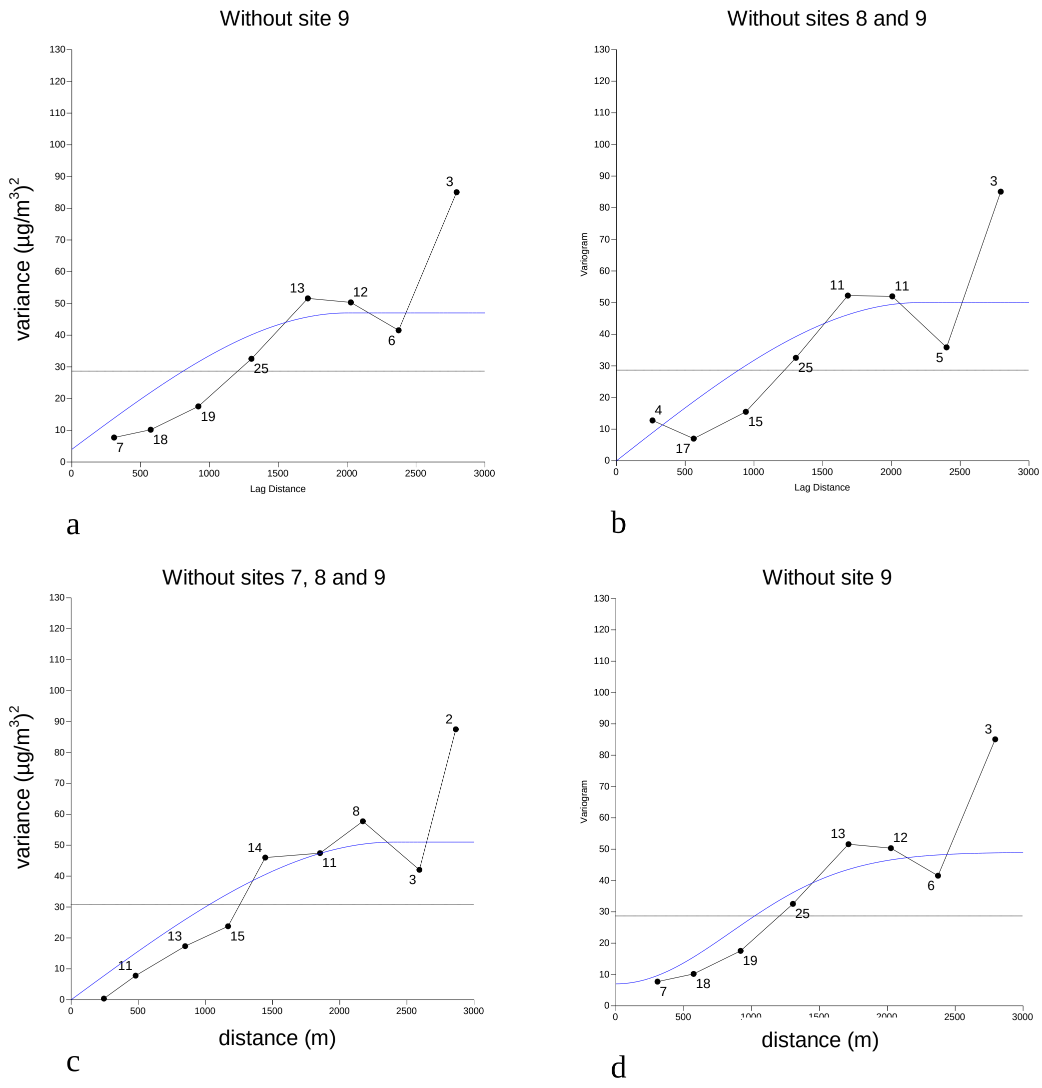
$$\begin{cases} if \quad l \le a \quad \gamma(l) = C_0 + C_1\left[1.5\,{}^{l}\!/_{a} - 0.5\left({}^{l}\!/_{a}\right)^3\right] \\ if \quad l > a \quad \gamma(l) = C_0 + C_1 \end{cases}$$

With a nugget effect C_0 of 4 $(\mu g/m^3)^2$, a sill C_1 of 43 $(\mu g/m^3)^2$ (*a priori* measurement's variance in a stochastic field) and a range *a* equal to 2000 m (the distance at which the variogram model reaches the *sill* or the one after which there is no correlation between measurements and their distances).

It was investigated the influence of the number and quality of data on the range and the maximum variance in the variogram. In addition to the outlier, were removed from the dataset stepwise site 8, the one with the second highest concentration level (not identified as outlier with the Grubbs test), and site 7, the one with the highest ratio: concentration difference/distance. The obtained variograms reported in figure 14b and 14c show no relevant changes. Only a slight increase in the maximum variance, becomes 50 $(\mu g/m^3)^2$, as well as a small rise in the range from 2000 m to 2200-2400 m could be observed.

Another source of uncertainty derives from the used variogram model. In this study was selected the spheric model since is the one presenting the best fit in PM_{10} and $PM_{2.5}$ variograms over national level domains in the U.S. [8].

Figure 13. Variograms of datasets in which has been removed one outlier (a), two outliers (b) three outliers (c). Variogram obtained with the Gaussian model (d) same dataset as (a). The blue line is the model that fits the observations.



a b c d

In order to check the differences that could derive from using different models, it was fitted to the same data a Gaussian model with the following equation:

$$\left\{\begin{array}{lll} if & l \le a & \gamma(l) = C_0 + C_1\left(1-\exp\left(l/a\right)^2\right) \\ if & l > a & \gamma(l) = C_0 + C_1 \end{array}\right\}$$

With a C_0 of 7 $(\mu g/m^3)^2$, a C_1 of 42 7 $(\mu g/m^3)^2$, and *a* equal to 1200 m. In the Gaussian model, is introduced a practical range *a’* in which the model reaches the

95% of the sill (*a'* = (sqrt(3). *a*), equal to 2078 m. The resulting variogram is shown in Figure 13d.

The estimated values $T^*(X,Y)$ of $PM_{2.5}$ mass concentration were interpolated over a fixed 25 x 25 m^2 grid of latitude and longitude and mapped in a contour plot (Figure 14). Subsequently the coloured contour map was superimposed to the raster map (CTR 10.000) of the area in order to better identify the levels of $PM_{2.5}$ in the different zones of the city (Figure 15a).

In the southern part of the city of Varese there is a steep slope (towards the lake) where no sampling sites were placed. In this area the modelled concentrations present a strong gradient. To avoid a misrepresentation of this area, where the uncertainty of $T^*(X,Y)$ is higher than in other parts of the domain, levels of $PM_{2.5}$ are not reported.

Figure 14. Contour plot of $T^*(X,Y)$ representing the $PM_{2.5}$ concentrations (units are in µg/m^3) in the city of Varese on February 10th 2010. Data were interpolated over a fixed 25 x 25 m^2 grid.

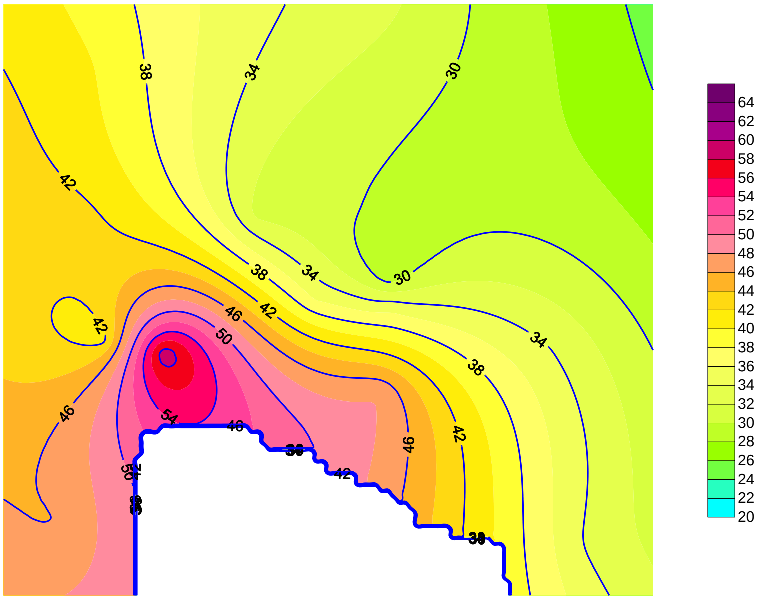
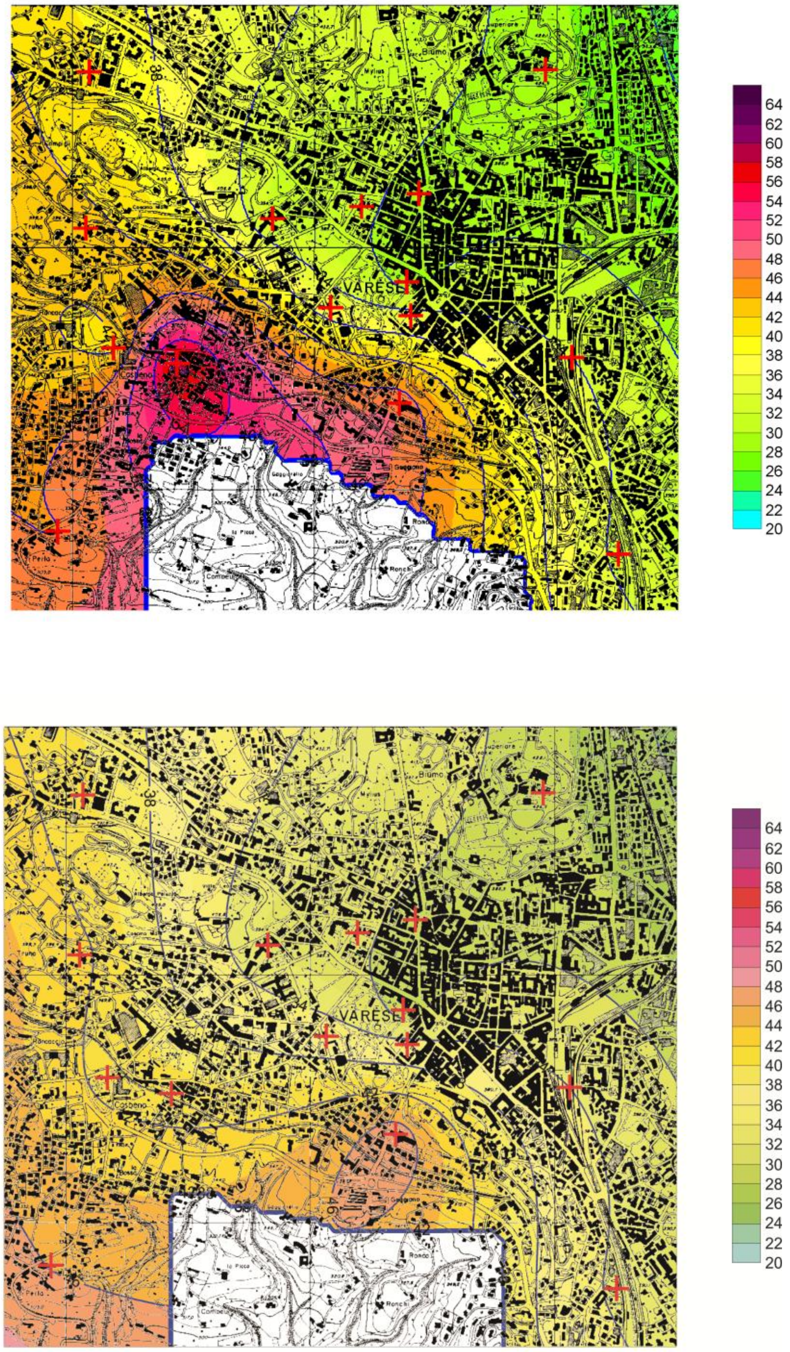


Figure 15. Overlap of the Contour plot $T^{*}(X,Y)$ with the map of Varese. $PM_{2.5}$ concentration (units: µg/m^3). a) all sites b) excluding the outlier site 9



a)

b)

In Figure 15a it can be observed a hotspot located in via Mulazzo which has been identified as an outlier. This site is probably influenced by a sum of local sources (pizzeria, unpaved parking). High $PM_{2.5}$ concentrations were found to the south of the fixed monitoring station what can be explained by the presence of a clearway with high vehicle traffic and by the orographic characteristic of this part of the domain which presents a steep slope that connects the city with the Varese lake shore. This area is likely more protected from winds causing the stagnation of air masses. Figure 15b shows the concentrations excluding the outlier site.

6. Conclusions

In this report are summarized the results of 9 monitoring campaigns with parallel measurements between PM_{10} reference samplers and automatic analyzers.

In order to compare different campaigns and check the consistency of the whole database for each measurement, the ratio automatic analyzer/reference sampler was calculated and plotted. The majority of the data fell in the range 0.9 – 1.0. The consistency check pointed out a significant data spread in the campaigns carried in Busto Arsizio and Milano Giuriati 2007. In addition, the data obtained in Busto Arsizio diverged significantly from the reference. As a whole, the performance of the analyzers assessed with this technique is comparable to the one observed in other European monitoring networks [9]. With the aim of supporting the development of the air quality network of Regione Lombardia according to the most up to date technical standards, the performance of some of the automatic analyzers used in everyday air quality monitoring was checked. Data have been elaborated according to a method conceived to compare reference and candidate methods.

In this analysis, the field uncertainty of two types of automatic analyzers present in the monitoring network of ARPA (OPSIS SM200and TEOM FDMS,) were evaluated by comparing them with the reference samplers (Leckel SEQ 47/50) operated by JRC. Both analyzers have an uncertainty at the limit value below 25%. In addition, the slope of the regression curve against the reference analyzers was significantly different from 1 only in OPSIS SM200.

A test revealed that the field blank mass change had no relevant influence on the comparison between automatic analyzers and reference samplers. There is no change in the regression slope and the variation in the intercept is lower than its uncertainty (<1 $\mu g/m^3$).

The adopted procedure may lead to a systematic underestimation of the uncertainty if the field tests diverge from the operating conditions in the networks [1]. The implementation of an appropriate regime of quality assurance/quality control (QA/QC) is essential. This regime shall be documented in the Standard Operating Procedure describing the operation of the method. Minimum requirements for ongoing QA/QC shall be as reliable as the requirements given in the EN standard methods for automated or manual methods.

A field campaign was carried out in the city of Varese in order to estimate the representativeness of the monitoring station in Via Copelli. During the campaign levels of $PM_{2.5}$ were measured simultaneously in 16 sites for a whole working day (8 hours). The representativeness of the monitoring station was estimated using a geostatistical approach relying on the relationship between the variance and the distance of the monitoring sites.

The variogram obtained using all sites, without considering the direction of the distances (isotropic), provided a picture of the study area in which there was no evident relationship between $PM_{2.5}$ concentration variance and the distance between sites.

A more detailed analysis revealed that most of the observed variance was explained by a general trend in the concentrations oriented in the direction NE-SW. In addition, the identification and exclusion of an outlier made it possible to obtain a variogram in which the distance of representativeness (range) stabilized at about 2 km. A number of sensitivity tests carried out showed that excluding other sites from the dataset and using different models do not have relevant influence on the model output, particularly in the distance of representativeness (range).

Despite it is a traffic station the $PM_{2.5}$ concentrations in via Copelli were comparable to the average of all the sites in the studied area during the working hours (outlier excluded). This may be explained by the central location of the station on the $PM_{2.5}$ concentration gradient (NE-SW) observed in this study.

This preliminary indication of the representativeness of the site in via Copelli was confirmed by the geostatistical analysis which indicated a representativeness of an area of 2 km radius, comparable to the size of the domain. In other words, one monitoring station located in the centre of the domain is enough to describe the level of $PM_{2.5}$ in whole area. The study provided evidence that representativeness is lower for locations close to the edges of the domain (edge effect).

Since the sampling design was oriented to evaluate the spatial variation of $PM_{2.5}$ concentrations during the working hours under unfavourable atmospheric conditions (i.e. which enhance $PM_{2.5}$ concentrations) the results of the survey are not necessarily valid for the whole day and for other atmospheric conditions.

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Annex 1

PM sampling artefacts

Sampling PM on filter entails interaction of the filter matrix with the gaseous and solid chemical species present in the sampling air. This may lead to positive artefacts due to the deposition of gaseous components (included water) onto the solid phase present on the filter or onto the filter matrix and to negative artefacts due to the removal of semivolatiles (included water) from the collected solid phase. Since many of these processes happen simultaneously the final artefact is the result of the sum of many effects. The magnitude of the artefact depends also on environmental factors like ambient air temperature, which modulates the solid/gas partition equilibrium, and ambient air humidity which control water condensation and evaporation processes. Also characteristics of the sampler like inlet heating, insulation, and air conditioning of the cabinet influence artefacts. Positive and negative artefacts can occur during or after sampling, depending on the storage and pre-weighing conditioning operations.

A study using a series of parallel measurements with denuders and backup filters for 24 h samples collected at 1 m^3/h air flow on quartz filter in Pittsburgh, reported positive and negative carbon artefacts (Subramanian, 2004). The negative artefact was 6.3% (±6.2%) of the **Particulate Organic Carbon** (POC). Winter average values of POC in Milan background station are about 15 $\mu g/m^3$ (5^{th} Intermediate Report R.L. Project), extrapolating the negative artefact should be 0.9±0.9 % of total PM_{10}. In the cited study the positive artefact was quantified as 0.5 $\mu g\text{-}C/m^3$ on annual basis, which represents 2.1% of the total PM mass (23.5 $\mu g/m^3$ PM_{10} annual average in Pittsburgh in 2005) what corresponds to 1 $\mu g/m^3$ at the European daily limit value for PM_{10} (50 $\mu g/m^3$). Both positive and negative artefacts were found to be higher in the warm season.

On the basis of the analysis of a 5-7 year time series, Ashbaugh and Eldred [11] reported negative artefacts in $PM_{2.5}$ using teflon sampling filters that reach 30-40% in summer in urban areas in the southwest of the US due to the loss of **nitrates**. Potential losses may reach 10-20% of the total PM mass in north-western and eastern US without any relevant seasonal pattern. Losses of **ammonium nitrate and chloride** from $PM_{2.5}$ samples have been observed at temperatures above 0°C with no significant differences between quartz filters and teflon filters [12].

Butterfield and Quincey [13] claim **humidity** affects both filter material and sampled particulate matter, following a hysteretic behaviour. That is, the hygroscopic growth of particles (< 60 nm) is different when they absorb water (deliquescence) than when they release water (efflorescence). These authors report that the influence of humidity on filter material is very variable even between filters of the same material. Water absorption in the filter matrix may lead to a potential error of up to 2 $\mu g/m^3$ in quartz and glass fibre filters (corresponding to 4% of the total mass at the PM_{10} limit value) and only 0.1 $\mu g/m^3$ for PTFE-coated glass fibre. Even more relevant appears the effect of humidity on hygroscopic components of PMx. It has been estimated to represent about 7% of PM_{10} in UK [14] and between 8% and 16% of $PM_{2.5}$ in Pittsburg [15] and it is independent of the filter material.

In a study in the city of **Milan** the organic positive artefact using quartz filters ranged between 2.4 $\mu g/m^3$ in summer and 3.8 $\mu g/m^3$ in winter [16]. Summer nitrate negative artefact was 24% and 51% of total nitrate using quartz and teflon filters respectively. Considering 3 $\mu g/m^3$ average nitrate values during the warm season in Milan urban background sites [17], the artefact would reach 1 $\mu g/m^3$ for quartz filters and 2 $\mu g/m^3$ for teflon filters. No relevant nitrate artefacts were observed in winter. However, the authors do not exclude an underestimation of the last artefact due to the nitric acid reaction with alkaline components of particulate matter.

In conclusion, an analysis of the scientific literature indicates that all filter based methods for estimating the mass are subject to positive and negative artefacts that cannot be avoided and can be partially identified only with the implementation of complex experimental designs which are beyond the scope of the work package. In the present report it has been chosen to stick as much as possible to the regulatory framework in force in the European Union. For that reason PM_{10} measurements have been carried out pursuant to the reference method EN 12341 as prescribed in Directive 1999/30/CE substituted by Directive 2008/50/CE which has been recently transposed in the Italian regulation with decree n. 155/2010 which substitutes decree n. 60/2002.

Annex 2

The reference method (JRC)

Leckel SEQ 47/50 sequential samplers have been chosen as reference for the intercomparison with instruments used by ARPA. For every campaign, JRC simultaneously used two Leckel SEQ 47/50 in order to assure the accuracy of the used method.

This instrument is a sequential sampler which collects PM_{10} particles on 47 mm quartz filters according to the technical standard EN 12341**Error! Reference source not found.**. This standard prescribes the determination of particulate matter mass using gravimetric method. The standard reports the design of the Low Volume Sampling reference system (LVS) that must be operated at 2.3 m^3/h flow rate.

Before sampling, filters were conditioned for 48 hours in a climatic room at 20ºC (±1ºC) and 50% (±5%) relative humidity. In the following, filters were weighted twice before sampling within a time range of 24 hours and weighted again after the campaign with the same procedure. A 1 µg resolution balance annually certified was used for weighing the filters. Before any measuring session, the balance was warmed up and checked with certified weights.

TEOM FDMS (ARPA)

This instrument is an on-line Tapered Element Oscillating Microbalance (Thermo, TEOM®, Series 1400) equipped with Filtered Dynamic Measurements System (Thermo, FDMS 8500). The FDMS system corrects the loss of semi-volatile particles during the measurement. In addition, the FDMS system operates at 30ºC rather than 50ºC in order to reduce particle losses. Data are collected on a half-hourly basis and then averaged on a 24h-hourly basis.

OPSIS SM 200 (ARPA)

This instrument is a combined dust monitor than can be used for both automatic measurements and filter sampling. Particles are collected on a filter substrate located between a beta-ray source and a beta-ray detector. The total mass of the collected particles is determined by the attenuation of the beta-ray radiation, as the attenuation is proportional to the amount of deposited particles. The SM200 instrument may provide an on-line value of the mass concentration as well as 24-hours average values collecting particles on 47 mm filters.

ENVIRONNEMENT MP 101 (ARPA)

As in the previous case the total mass of the collected particles is determined by the attenuation of beta-ray radiation using a Geiger Muller counter. The particulate matter is collected on a tape of glass fibre material. The instrument provides hourly means. Data are 24h averaged to be compared with the reference system.

FAI SWAM (ARPA)

This instrument is a dual sampler collecting samples on two independent lines. The exposed filters (quartz filters, 47 mm diameter) are stored in a tube after 24h sampling. This instrument is also equipped with a beta-ray source and therefore, the total mass of the collected particles can also be determined by the attenuation of beta-ray radiation. For the intercomparison campaign, the beta-ray technique of the FAI SWAM was used to record 24-hours average of PM_{10} mass concentrations.

Annex 3

PM_{10} concentrations measured in the parallel sampling campaigns used in this report

Milano (Parco Giuriati)

Three field campaigns were carried out in Parco Giuriati in Milano. ARPA used an **OPSIS SM200** automatic analyzer.

In this annex are reported the individual plots referred to each campaign:

Figure A1a. Time series of PM_{10} from 26 September to 9 October 2007 in Parco Giuriati (Milano).

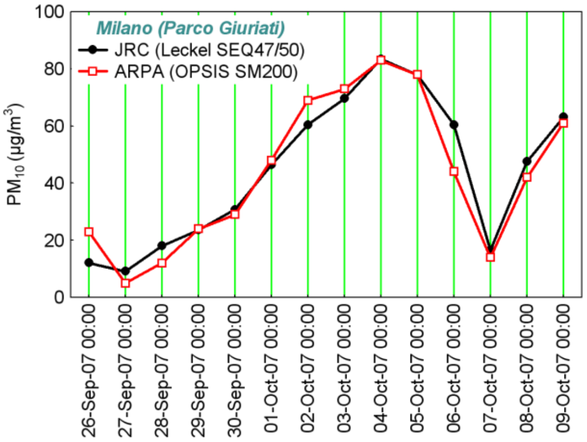


Figure A1b. Time series of PM_{10} from 12 to 25 January 2008 in Parco Giuriati (Milano).

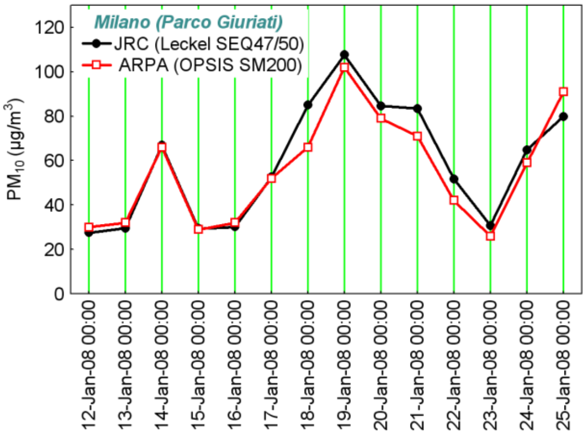
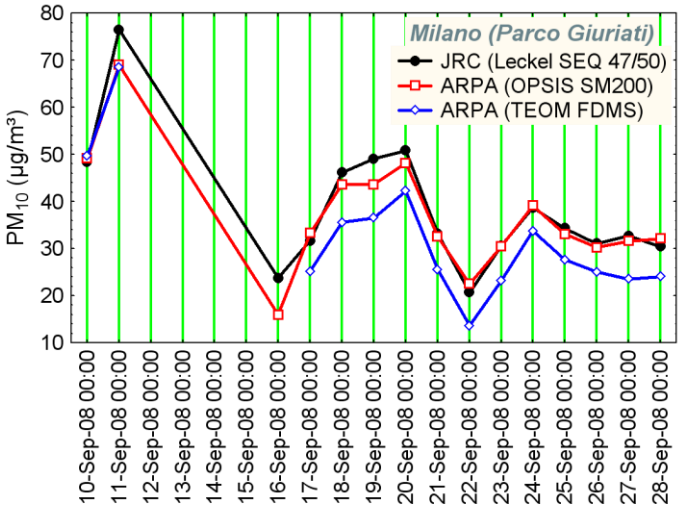


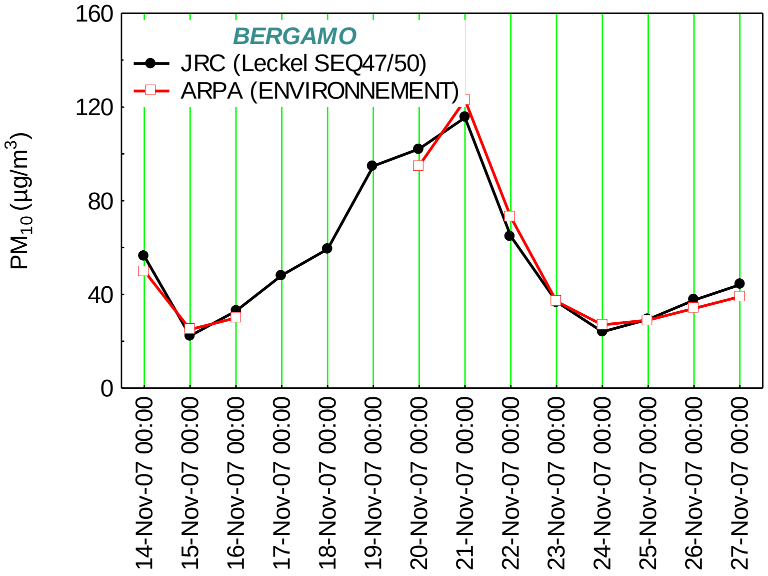
Figure A1c. Time series of PM_{10} from 10 to 28 September 2008 in Parco Giuriati (Milano). The TEOM FDMS sampler was used by ARPA only for an evaluation of relative variations of PM levels and not for the absolute evaluation of PM levels.



Bergamo (14 November – 27 November 2007)

For this campaign ARPA used a beta-ray attenuation on-line monitor **ENVIRONNEMENT**.

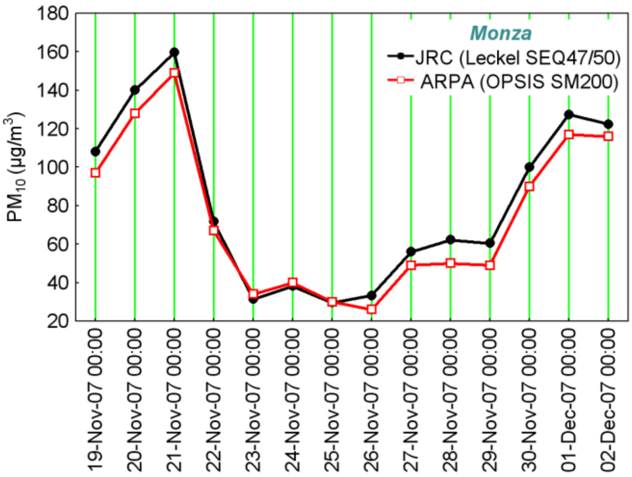
Figure A2. Time series of PM_{10} from 14 to 27 November 2007 in Bergamo.



Monza (19 November – 2 December 2007)

A full 2-weeks dataset of data for PM_{10} mass concentration was collected during the intercomparison campaign carried out in Monza. ARPA used an **OPSIS SM200** automatic analyzer.

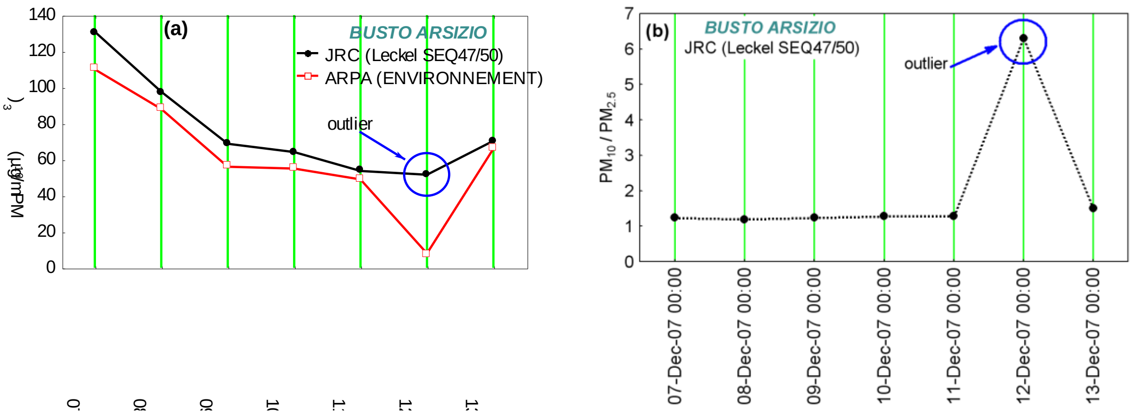
Figure A3. Time series of PM_{10} from 19 November to 2 December 2007 in Monza.



Busto Arsizio (Varese) (7 December – 13 December 2007)

For this campaign ARPA used a beta-ray attenuation on-line monitor **ENVIRONNEMENT**. For the intercomparison campaign in Busto Arsizio there are a limited number of samples. In particular, one sample of the reference sampler was identified as an outlier. Figure 3a report the $PM_{10}/PM_{2.5}$ ratio for the entire dataset obtained in Monza. On 12 December, the $PM_{10}/PM_{2.5}$ ratio indicates an anomaly in the sample.

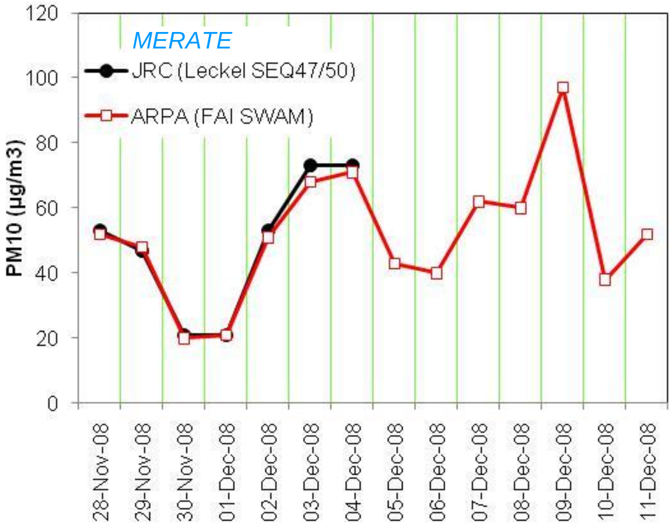
Figure A4. (a), time series of PM_{10} from December 7 to December 13, 2009 in Busto Arsizio (Varese). **(b)**, $PM_{10}/PM_{2.5}$ ratio referred to mass concentrations sampled by the reference low volume samples by JRC.



Merate (Como) (28 November – 11 December 2008)

A full two-weeks dataset of data for PM_{10} mass concentration was collected during the intercomparison campaign carried out in Merate. For this campaign ARPA used a **FAI SWAM** dual sampler. During the first half of the campaign both reference sampler inlets were at the same height than the one of the automatic analyzer. During the second half of the monitoring campaign one of the reference samplers was moved to a lower height. This sampler was excluded from the intercomparison for the second half of the campaign, therefore, during this part of the campaign only one reference sampler was available.

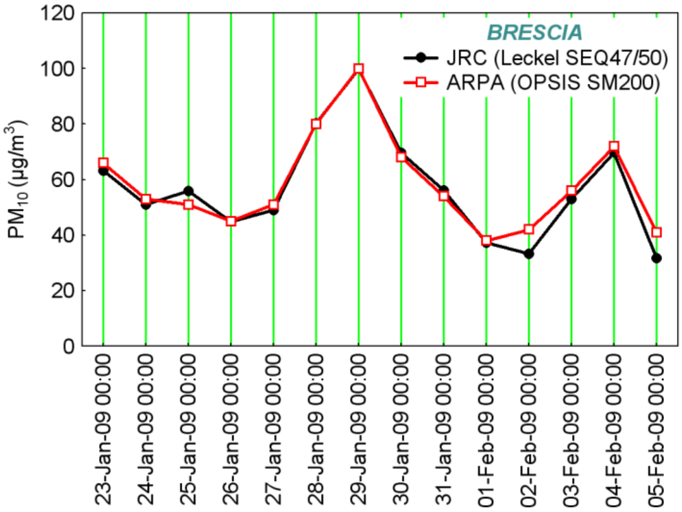
Figure A5. Time series of PM_{10} from November 28 to December 11, 2008 in Merate (Lecco).



Brescia (23 January – 5 February 2009)

For this two week campaign ARPA used an **OPSIS SM200**.

Figure A6. Time serie of PM_{10} from January 23 to February 5, 2009 in Brescia.

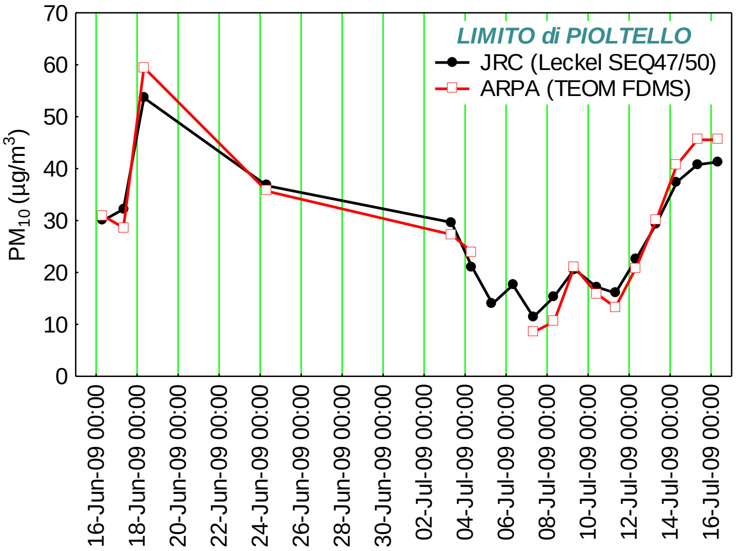


Limito di Pioltello (Milano) (16 June – 16 July 2009)

The intercomparison campaign in Limito di Pioltello was carried out in from 16 June and lasted until 16 July. For this campaign ARPA used a **TEOM FDMS** automatic analyzer.

Because of problems with power supply occurring during the first half of the campaign, most of data were present only for the period after July 7th.

Figure A7. Time serie of PM_{10} from June 16 to July 16, 2009 in Limito di Pioltello (Milano).



PM_{10} concentrations in chronological order

Milano Giuriati

start date	(JRC) Leckel n.64	Average Leckel	(ARPA) OPSIS SM200
26-Sep-07	12	12	23
27-Sep-07	9	9	5
28-Sep-07	18	18	12
29-Sep-07	24	24	24
30-Sep-07	31	31	29
01-Oct-07	46	46	48
02-Oct-07	60	60	69
03-Oct-07	70	70	73
04-Oct-07	83	83	83
05-Oct-07	80	80	78
06-Oct-07	60	60	44
07-Oct-07	17	17	14
08-Oct-07	48	48	42
09-Oct-07	63	63	61

Bergamo

start date	(JRC) Leckel n.64	(JRC) Leckel n.65	Average Leckel	(ARPA) ENVIRONNEMENT MP100
14-Nov-07	57	56	56	50
15-Nov-07	22	22	22	25
16-Nov-07	32	34	33	30
17-Nov-07	48	48	48	-
18-Nov-07	59	60	59	-
19-Nov-07	94	95	95	-
20-Nov-07	101	103	102	95
21-Nov-07	115	116	115	123
22-Nov-07	65	65	65	73
23-Nov-07	37	37	37	37
24-Nov-07	24	24	24	27
25-Nov-07	30	29	29	29
26-Nov-07	37	38	38	34
27-Nov-07	43	45	44	39

Monza

start date	(JRC) Leckel n.64	Average Leckel	(ARPA) OPSIS SM200
19-Nov-07	108	108	97
20-Nov-07	140	140	128
21-Nov-07	160	160	149
22-Nov-07	72	72	67
23-Nov-07	31	31	34
24-Nov-07	38	38	40
25-Nov-07	30	30	30
26-Nov-07	33	33	26
27-Nov-07	56	56	49
28-Nov-07	62	62	50
29-Nov-07	61	61	49
30-Nov-07	100	100	90
01-Dec-07	127	127	117
02-Dec-07	122	122	116

Busto Arsizio				
start date	**(JRC) Leckel n.64**	**(JRC) Leckel n.65**	**Average Leckel**	**(ARPA) ENVIRONNEMENT MP101**
07-Dec-07	131	130	131	110
08-Dec-07	98	97	98	88
09-Dec-07	69	69	69	56
10-Dec-07	65	64	64	55
11-Dec-07	54	53	54	49
12-Dec-07	-	52	51[*]	8*
13-Dec-07	70	70	70	66

[*] outliers

Milano Giuriati				
start date	**(JRC) Leckel n.64**	**(JRC) Leckel n.65**	**Average Leckel**	**(ARPA) OPSIS SM200**
12-Jan-08	28	27	27	30
13-Jan-08	30	29	30	32
14-Jan-08	67	66	67	66
15-Jan-08	30	29	29	29
16-Jan-08	30	30	30	32
17-Jan-08	53	52	53	52
18-Jan-08	85	85	85	66
19-Jan-08	108	108	108	102
20-Jan-08	85	85	85	79
21-Jan-08	84	83	83	71
22-Jan-08	52	52	52	42
23-Jan-08	30	31	31	26
24-Jan-08	65	65	65	59
25-Jan-08	80	80	80	91

Milano Giuriati					
start date	**(JRC) Leckel n.64**	**(JRC) Leckel n.65**	**Average Leckel**	**(ARPA) OPSIS SM200**	**(ARPA)TEOM FDMS(*)**
10-Sep-08	48	48	48	49	50
11-Sep-08	77	76	76	69	69
16-Sep-08	24	24	24	16	-
17-Sep-08	32	31	32	33	25
18-Sep-08	47	46	46	44	36
19-Sep-08	49	49	49	44	37
20-Sep-08	51	51	51	48	42
21-Sep-08	33	33	33	33	26
22-Sep-08	20	21	21	22	14
23-Sep-08	31	31	31	31	23
24-Sep-08	39	39	39	39	34
25-Sep-08	34	34	34	33	28
26-Sep-08	31	31	31	30	25
27-Sep-08	33	33	33	32	24
28-Sep-08	30	30	30	32	24

(*)The TEOM FDMS sampler was used by ARPA only for an evaluation of relative variations of PM levels and not for the absolute evaluation of PM levels.

Merate			
start date	(JRC) Leckel n.64	Average Leckel	(ARPA) FAI SWAM
28-Nov-08	53	53	52
29-Nov-08	47	47	48
30-Nov-08	21	21	20
01-Dec-08	21	21	21
02-Dec-08	53	53	51
03-Dec-08	73	73	68
04-Dec-08	73	73	71
05-Dec-08	-	-	43
06-Dec-08	-	-	40
07-Dec-08	-	-	62
08-Dec-08	-	-	60
09-Dec-08	-	-	97
10-Dec-08	-	-	38
11-Dec-08	-	-	52

Brescia				
start date	(JRC) Leckel n.64	(JRC) Leckel n.66	Average Leckel	(ARPA) OPSIS SM200
23-Jan-09	63	63	63	66
24-Jan-09	51	51	51	53
25-Jan-09	56	56	56	51
26-Jan-09	45	45	45	45
27-Jan-09	48	50	49	51
28-Jan-09	80	81	80	80
29-Jan-09	99	101	100	100
30-Jan-09	69	71	70	68
31-Jan-09	56	57	56	54
01-Feb-09	37	38	37	38
02-Feb-09	33	33	33	42
03-Feb-09	53	53	53	56
04-Feb-09	70	69	70	72
05-Feb-09	32	31	32	41

Limito di Pioltello				
start date	(JRC) Leckel n.64	(JRC) Leckel n.66	Average Leckel	(ARPA) TEOM FDMS
16-Jun-09	30	30	30	31
17-Jun-09	32	33	32	29
18-Jun-09	52	55	54	59
24-Jun-09	36	37	37	36
03-Jul-09	30	30	30	27
04-Jul-09	21	21	21	24
05-Jul-09	14	14	14	-
06-Jul-09	18	18	18	-
07-Jul-09	12	11	11	9
08-Jul-09	15	15	15	11
09-Jul-09	20	21	21	21
10-Jul-09	17	17	17	16
11-Jul-09	16	16	16	13
12-Jul-09	23	22	23	21
13-Jul-09	29	29	29	30
14-Jul-09	38	37	37	41
15-Jul-09	41	40	41	46
16-Jul-09	42	41	41	46

WP4

Integrated Assessment

(WP4 Leader: Panagiota Dilara)

RegioneLombardia

Collaborative Research Project for
Air Pollution Reduction in
Lombardia (2006- 2010)

JRC
EUROPEAN COMMISSION

Deliverable: IX.4.1. Report on the progress of the planned activities in the frame of Air Quality Modeling.

P. Thunis, E. Georgieva, D. Pernigotti

Outline

1 Introduction

The POMI Model inter-comparison exercise which started in 2008 has been finalized in December 2010. The final meeting which took place in Ispra on November 25th has been the occasion for the participating modeling groups to present their final results. This report summarizes the main conclusions of the meeting as well as the main findings and outcomes of the project in general.

We first review the emission scenarios which have been provided to the modeling groups as input for their air quality model simulations. For some scenarios, the hypotheses used to construct them are recalled. Each modeling group has been asked to deliver model outputs for a specific series of scenarios which is here summarized.

We then come back to the model performances obtained on the 2005 base case. Although this has already been discussed in previous interim reports (Deliverable VII.4.1 and VI.4.1.), we present here appropriate statistical indicators to assess the quality of model results against expected level of performances, based on literature.

As mentioned and illustrated in previous reports, one key factor affecting the performances of air-quality dispersion models is the quality of the meteorological input. Several sensitivity tests have been made with the MM5 meteorological driver using different degrees of observations nudging to investigate the impact on modeled PM10 concentrations. A synthesis of this work is presented here.

Finally an overview of the model responses to specific emission scenarios performed either for sensitivity analysis (e.g. impact of boundary conditions) or for policy-oriented purposes (e.g. the 2012 air quality plan) is presented.

2 Review of scenarios and model deliveries

Table 1 below provides an overview of the different scenarios which have been run in POMI. The right most columns indicate which of the six participating models took part in each listed scenario. For a better understanding of the model responses to these different scenarios, we here recall the main hypothesis used to create some of them. For more detailed information, the reader is referred to previous interim reports.

EMIL0: Base case 2005 simulation with Lombardy anthropogenic emissions switched off. As mentioned in the previous interim report this scenario which foresees the full suppression of all anthropogenic emissions within Lombardy is a virtual scenario which aims at quantifying the levels of PM and O3 which would result from a maximum (but impossible!) action restricted to Lombardy itself.

CLE12: Current Legislation 2012 simulation (over the entire Po-Valley). This scenario reflects the implementation of all presently decided emission related legislation. These projections are based on the RAINS Italy Integrated Assessment Model for all regions, excepted in Lombardy where estimate for some sectors follow a more detailed methodology: (1) non-industrial combustion plants emissions are estimated using correction factors for the change in fuel consumption and in emission factor for each fuel and activity based on the Lombardy energy plan (PAE 2007); (2) traffic emissions have been calculated by applying the European reference methodology (COPERT IV) adopted for the preparation of INEMAR 2005 and 2010 inventories, supplied by ARPA Lombardy; (3) Fuel consumption trends and vehicle technology trends are based on studies by ARPA Lombardy and by Pastorello (2007); (4) for point sources, focus is given to three main groups of equipment: power and thermal plants and cement factories where the major changes were related to the plant stock and to the introduction of more restrictive limits on emissions.

AQPL12: Simulation of the air quality plan 2012 applied in Lombardy (2012 CLE conditions are applied outside Lombardy). The “Air Quality Plan for 2012” emission scenario simulates the application of abatement measures designed in 2008 on the basis of the regional policy tools existing at that time. The abatement measures considered in this simulation mostly affect the transport and the energy sectors. For the transport sector a huge fleet renewal is foreseen, with the replacement of pre-Euro3 vehicles, and in some cases pre-Euro 4 vehicles (for diesel cars and gasoline) with newer generation cars. For the energy sector an important market penetration of renewable generation system and improved efficiency of buildings and electronic devices is assumed.

MFR12: This scenario is constructed by assuming that best available technologies are applied systematically regardless of their implementation costs. This scenario, unfeasible from a cost point of view, provides some insight on the expected levels of pollution that would result from a technological solution pushed at its maximum.

CLE15 and CLE20: These scenarios are constructed on the basis of the RAINS Italy Integrated Assessment Model for all regions.

AQP15 and AQP20: These scenarios are constructed on the basis of the RAINS Italy Integrated Assessment Model for all regions with information on AQP provided for some regions.

		Emission Scenario			Delivery					
		Po-Valley	Lombardy	Acronym	CH	EM	CA	RC	AU	TC
110	2005	Base case 1			▨	▨	▨	▨	▨	▨
210		Base case 2		BC	▨	▨	▨	▨	▨	▨
220		ISPRA emissions only				▨		▨	▨	
230		Base case 2	All emissions=0	EMIL0	▨	▨	▨	▨	▨	▨
240		Po-Valley biogenic emissions set to zero			▨	▨	▨	▨	▨	▨
250		Source apportionement (CAMx-PSAT)					▨			
260		First vertical model layer modified			▨					
270		Change in meteorological input						▨		
310	2012	CLE		CLE12	▨	▨	▨	▨	▨	▨
320		CLE	AQP	AQPL12	▨	▨	▨	▨	▨	
350		MFR		MFR12		▨	▨	▨	▨	
360		CLE but CHIMERE Boundary conditions			▨					
370		CLE with SOA parametrisation							▨	
380		AQP		AQP12		▨	▨	▨	▨	
510	2015	CLE		CLE15	▨	▨	▨	▨	▨	▨
520		CLE	AQP	AQPL15	▨	▨		▨		
530		AQP		AQP15	▨	▨	▨	▨	▨	
610	2020	CLE		CLE20	▨	▨	▨	▨	▨	▨
620		CLE	AQP	AQPL20		▨	▨		▨	
630		AQP		AQP20	▨	▨	▨	▨		

Table 1: Overview of the emission scenarios run in the frame of the POMI exercise. Emissions are split into two different geographic scales (Lombardy and entire Po-Valley basin). The acronyms used to identify the important scenarios in the remaining of the document are provided in column 5. Grey filled cells indicate a model delivery for one of the 6 participating models (CH: CHIMERE, EM: EMEP, CA: CAMx, RC: RCG, AU: AURORA, TC: TCAM)

Figure 1 illustrates the emission reduction resulting from the application of specific emission reduction scenarios when considering either Lombardy or the Po-Valley. As seen from this figure, application of CLE at the three time horizons (2012, 2015 and 2020) results in a significant emission reduction, which is more marked in terms of Lombardy than in Po-Valley emissions. The AQP 2012 leads to emission reductions in Lombardy that are in between the levels reached by CLE in 2015 and 2020 for three pollutants (NOx, PM10 and VOC) but not for SO2. As a result of the different assumption used to construct these scenarios, the AQP in 2012, 2015 and 2020 lead to similar level of emission reduction.

The most drastic emission reductions in terms of emission levels are obviously the ones imposed in the EMIL0 scenario at the scale of Lombardy but this scenario only reduces the total Po-Valley emissions by approximately 30%. At the scale of the Po-Valley, the most efficient emission scenario is MFR12.

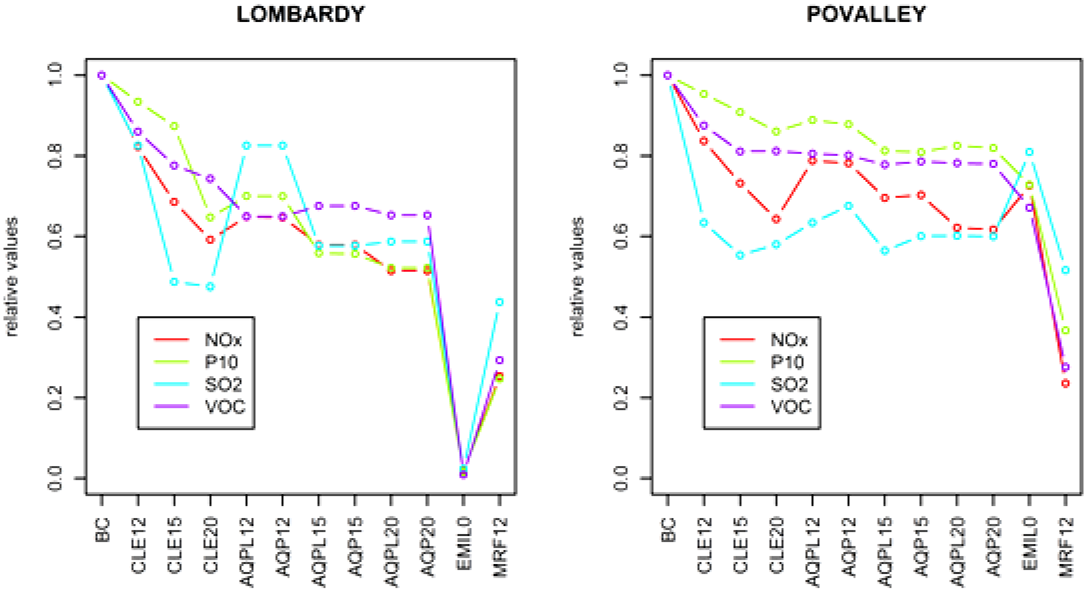


Figure 1: Normalized (with respect to the base case) emissions levels for different emission scenarios averaged over the Lombardy Region (left) and over the Po-Valley basin (right). Scenario acronyms are listed in Table 1.

3 Statistical evaluation of the base case model results

Although the 2005 base case results have been analyzed in some detail in Deliverable VII.4.1, we here present some additional information. This is motivated by the fact that some modeling groups have submitted updated results since the latest report but also by the wish to assess the quality of the current model performances in terms of quality criteria proposed in various publications (included the EU Air quality directive). The quality criteria refer to specific statistical indicators and pollutants.

The indicators used are the mean fractional bias (MFB), the mean fractional error (MFE), the relative directive error (RDE), the relative percentile error (RPE), the index of agreement (IOA), the correlation coefficient (R) and the percentage of values within a factor 2 (FAC2). These indicators are defined in Annex 1. The RDE and RPE are presented in details in the “Guidance on the use of models for the European Air Quality Directive” (Denby et al., 2010). Although their use is still subject to interpretation, we report the values for information.

The quality criteria for these indicators, related to PM10 and O3, are compiled based on a review of various air quality model applications (e.g. Boylan and Russel, 2006, Chemel et al., 2010 and Derwent et al, 2010):

	MFB	MFE	FAC2	RDE
PM10	± 60%	<75%	>50%	-
O3	± 30%	<45%	>50%	<50%

Table 2 Criteria for statistical indicators representing good model performance. RDE for PM10 has not been defined

Table 3 provides a statistical overview of the model performances obtained for mean daily PM10 and daily 8h maximum O3 concentrations averaged over all stations (urban for PM10 and rural for O3) within Lombardy and the Po-Valley.

Even if we exclude from the analysis MOD2 and MOD5, which exhibit strong difficulties and fail to achieve the quality criteria related to MFB, MFE and FAC2, annual PM10 levels are significantly underestimated (MFB lies in the range 30% - 60%) in the Po Valley. The only exception is MOD4 which has almost no bias. It must be noted that this significant underestimation is mostly a wintertime problem when all models (with no exception) then underestimate PM10 levels. There is no significant improvement when the focus is restricted to the Lombardy stations. The correlation coefficient levels are on the order of 0.5/0.6 with some models showing lower values (MOD2 and MOD4). For the latter model the relatively lower correlation coefficient is mostly due to the strong overestimation of PM10 during the summer time period.

As mentioned in previous reports and as discussed during the final POMI meeting, a significant part of the PM10 underestimation is caused by the overestimation of the wind fields in the whole Po-Valley. This point is discussed in more details in the next section.

Comparison for PM10 speciation was performed based on measurements collected at the EMEP-Ispra station; it appears that models correctly reproduce relatively well the levels of secondary inorganic aerosols but significantly underestimate the coarse and the organic fractions of the particulate matter. Unfortunately since only this station provides information on PM speciation on a regular basis it is difficult to generalize this conclusion.

Regarding ozone, model performances are better although some models do not fulfill all quality criteria. The MFB and MFE indicators reach similar values for all models and this is also the case for R and IOA which show relatively high values (around 0.7/0.9). The red values shown in the table for MOD3 arise from an overestimation of the summer O3 peaks while for MOD2 this is mostly due to an underestimation of the ozone levels at rural sites.

LOMBARDY	PM10		17 stations				
	OBS	MOD1	MOD2	MOD3	MOD4	MOD5	MOD6
Mean (ug/m3)	45	28	14	36	48	21	34
MFB (%)		-51	-106	-38	3	-73	-29
MFE (%)		60	109	60	53	77	49
RDE (%)		57	81	47	38	71	51
RPE (%)		53	75	50	28	71	49
IOA		0.69	0.50	0.70	0.62	0.57	0.71
R		0.63	0.38	0.55	0.43	0.58	0.63
FAC2 (%)		61	22	60	67	45	72

PO-Valley	PM10		48 stations				
	OBS	MOD1	MOD2	MOD3	MOD4	MOD5	MOD6
Mean (ug/m3)	42	23	12	30	41	19	30
MFB (%)		-59	-116	-48	-4	-76	-34
MFE (%)		67	118	66	51	82	53
RDE (%)		63	82	65	46	71	55
RPE (%)		62	77	50	43	66	49
IOA		0.64	0.49	0.68	0.63	0.55	0.68
R		0.59	0.40	0.56	0.43	0.53	0.58
FAC2 (%)		54	17	55	69	41	69

LOMBARDY	O3		20 stations				
	OBS	MOD1	MOD2	MOD3	MOD4	MOD5	MOD6
Mean (ug/m3)	68	67	61	75	74	66	69
MFB (%)		8	-6	7	4	0	8
MFE (%)		42	49	41	44	44	45
RDE (%)		30	36	76	63	24	39
RPE (%)		30	40	57	54	28	43
IOA		0.85	0.80	0.87	0.81	0.84	0.80
R		0.79	0.74	0.83	0.85	0.76	0.68
FAC2 (%)		80	77	81	77	78	75

PO-Valley	O3		46 stations				
	OBS	MOD1	MOD2	MOD3	MOD4	MOD5	MOD6
Mean (ug/m3)	71	67	62	76	54	71	72
MFB (%)		4	-4	6	14	5	9
MFE (%)		44	49	42	47	43	45
RDE (%)		30	36	51	52	21	32
RPE (%)		34	41	52	49	27	24
IOA		0.80	0.73	0.86	0.84	0.81	0.80
R		0.75	0.68	0.82	0.81	0.73	0.70
FAC2 (%)		79	77	79	76	78	76

Table 3: Overview of statistical indicators for PM10 and O3. The definition of these indicators is given in Annex 1. The two top tables provide statistics based on daily averaged concentrations of PM10 whereas the two lower tables provide statistics based on daily maximum 8h averaged O3. Green numbers are indicative of a criteria which is fulfilled (red if not fulfilled)

4 Impact of meteorological nudging on air quality modeling

As stated in previous reports it is believed that meteorology, and in particular wind speeds do have a great impact on the transport of chemical pollutants. Initially the meteorological driver (MM5) for the 2005 base case simulations was run without any additional input information from measurements. The analysis of these runs revealed a strong overestimation of the wind speed, by a factor of 2 or more at almost all stations in the Po Valley. Therefore a new base case was prepared based on a nudged MM5 version, where monitored meteorological parameters were taken into account through analysis profiles. The results (see Deliverable VII.4.1) supported the idea that the wind fields could yet be improved further by the inclusion of surface observations within the meteorological simulations.

In this section we discuss further possibilities to include meteorological observations in MM5 (nudging options) and their effects on the PM10 concentration levels obtained with CHIMERE based on an episodic simulation.

The results presented below refer to the period from 5th to 31st of January 2005, when very high PM concentrations at almost all stations in the Po Valley have been monitored. The peak PM10 values were observed during the period from 6th to 19th, characterized by low wind speeds, a stable atmosphere and the absence of precipitations.

4.1 MM5 configuration and nudging options

For the tests discussed here MM5 was run over two domains - a larger one with a resolution of 18km extending from central Italy up to southern Germany (Domain1) and a smaller one with a resolution of 6km over the Po-Valley (Domain2). These domains are different from the ones used for the base case in the following two points: a) the smaller domain over Lombardy (3km resolution) has been neglected, since no significant improvement in concentrations levels has been observed at this finer resolution; b) we now use an additional domain (at 18 km resolution) as a buffer between the large scale NCEP analysis at about 100km resolution and the 6km resolution domain

The nudging techniques allow taking into account various type of observations in MM5 runs. Nudging is a type of data assimilation where forcing functions are added to the governing model equations to gradually ‘nudge’ the model state towards the observations.

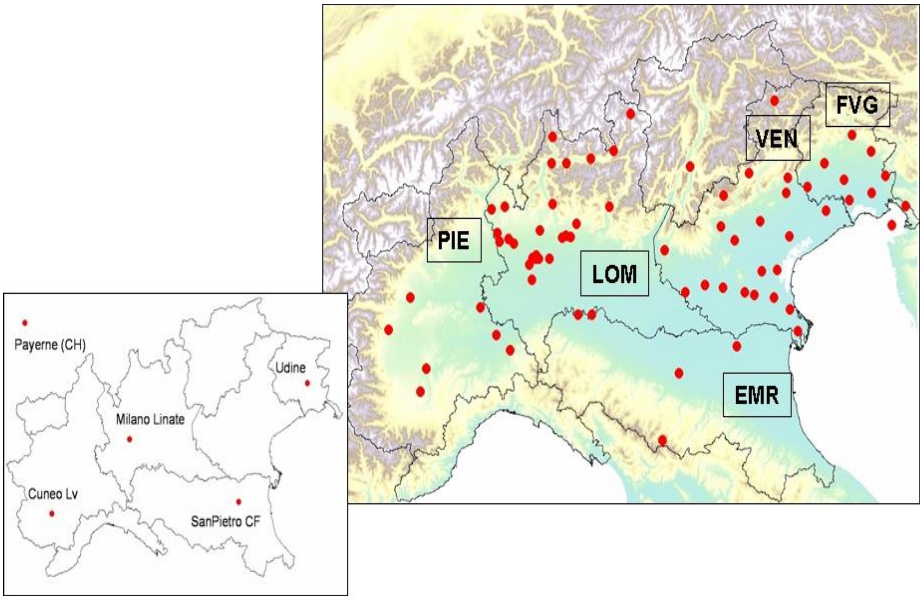


Figure 2: Overview of the meteorological data collected for the MM5 nudging sensitivity tests: 5 vertical soundings (left) and 70 surface meteorological stations (right).

The available meteorological observations (Figure 2) include two types of data, coming from:

- Radiosoundings - taken every 6/12h at 5 stations in Domain1 – Payerne (CH), Cuneo, Milano Linate, San Pietro Capofiume and Udine;
- Surface stations – From the available 70 stations in Domain2 56 stations have been selected as representative for the model resolution. Most of them are located in Lombardy and Veneto.

Seven nudging configurations have been defined with different combinations among the available data. The details are given in Table 4 where:

- NCEP stands for the nudging of the 3D analysis given by the model NCEP at 1 deg resolution every 6 hours;
- GD-3D stands for the nudging of the radio-soundings taken every 6/12h at the stations mentioned above;
- GD-SFC stands for the nudging of surface observations taken every 3h at the selected 56 stations. These observations are re-gridded within the NCEP analysis and then fed to MM5.
- OBS-SFC stands for the direct nudging into MM5 of the surface observations taken every 1h at the 56 stations.

Name of run	Domain1 & 2 NCEP (6h)	Domain1 &2 GD-3D (6h) (soundings)	Domain2 GD-SFC (3h) (surface Stations)	Domani2 OBS-SFC (1h) (surface Stations)
nofdda				
nfdda	X			
3fdda	X	X		
gdfdda	X	X	X	
obsfdda	X			X
3obsfdda	X	X		X
gdobsfdda	X	X	X	X

Table 4: Configuration of the 7 runs with different nudging options

The coefficients used here for the nudging are respectively 10^{-4} for wind and temperature and 10^{-5} for moisture.

4.2 Results on wind speed

Observed and simulated wind speeds averaged over the selected period and over the stations in a given administrative Region have been compared. The bias and the root mean square error for different nudging options are shown in Figure 3 and Figure 4.

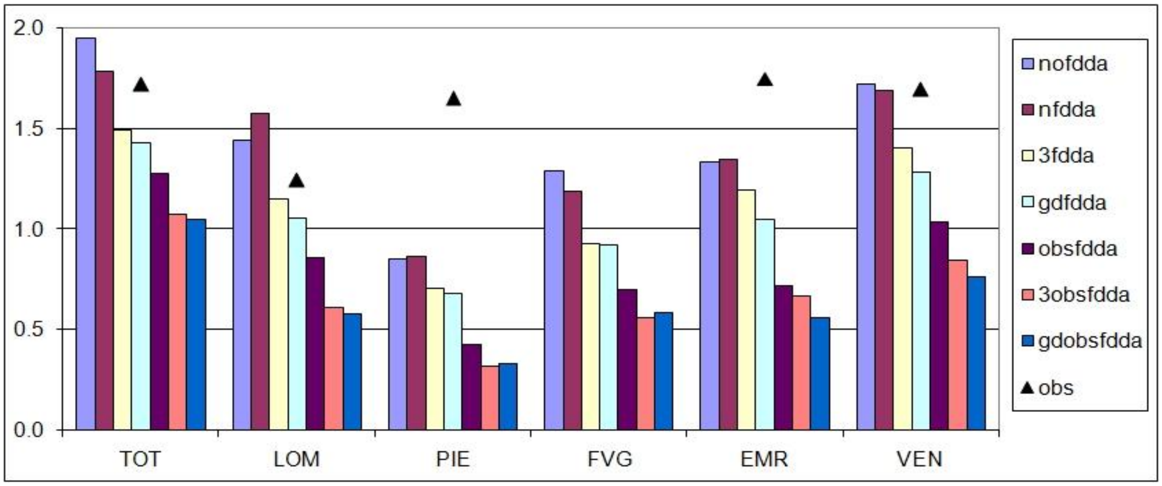


Figure 3: BIAS (m/s) of model results per region, black triangles represent mean observed wind speed (LOM- Lombardy, PIE- Piemonte, FVG – Friuli Venezia Giulia, EMr – Emilia Romagna, VEN – Veneto, TOT – all regions)

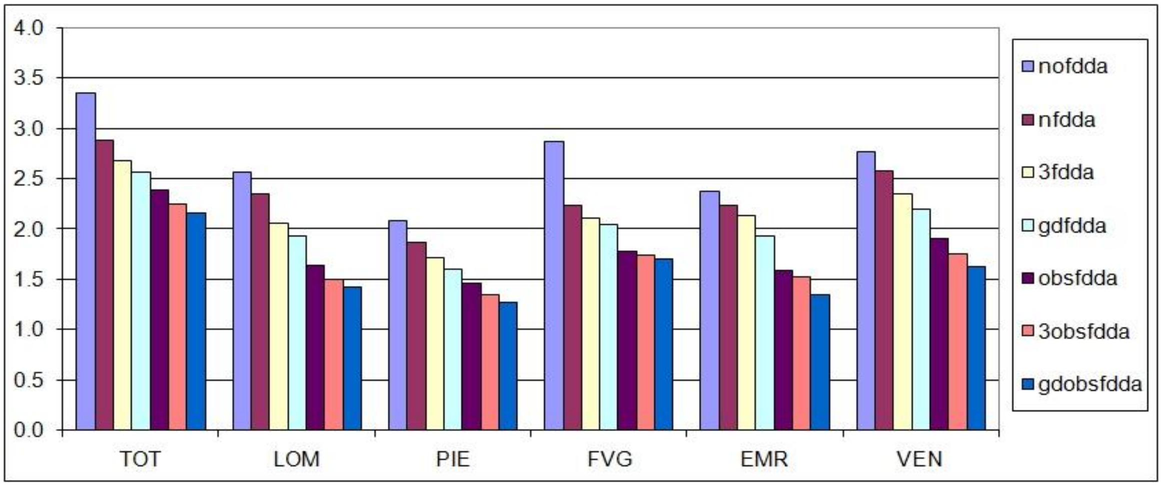


Figure 4: RMSE (m/s) of wind speeds with different nudging options, averaged per Region

Both BIAS and RMSE decrease within the PO-Valley domain with the different nudging options, especially in some regions (e.g Lombardy and the eastern part of the domain). Within Lombardy the bias decreases from 1.4 to 0.6m/s whereas over the whole Po valley it decreases from 2 to 1 m/s (from nofdda (no-nudging) to gdobsfdda (best run).

In the following we compare the results for three nudging options - ‘nofdda’ (no nudging at all), ‘nfdda’ (large scale NCEP analysis nudging, options used in preparing the 2005 base case) and ‘gdobsfdda’ (best run, surface observations, analysis results and radiosoundings included). BIAS and RMSE averaged for the different regions are shown in Table 5

		TOT	LOM	PIE	FVG	EMR	VEN
obs	**mean**	**1.7**	**1.2**	**1.7**	**2.1**	**1.7**	**1.7**
	mean	**3.7**	**2.6**	**2.5**	**3.4**	**3.0**	**3.4**
nofdda	bias	2.0	1.4	0.9	1.3	1.3	1.7
	rmse	3.3	2.6	2.1	2.9	2.4	2.8
	mean	**3.5**	**2.8**	**2.5**	**3.3**	**3.0**	**3.4**
nfdda	bias	1.8	1.6	0.9	1.2	1.3	1.7
	rmse	2.9	2.3	1.9	2.2	2.2	2.6
	mean	**2.8**	**1.8**	**2.0**	**2.7**	**2.3**	**2.5**
gdobsfdda	bias	1.0	0.6	0.3	0.6	0.6	0.8
	rmse	2.2	1.4	1.3	1.7	1.3	1.6

Table 5: Some statistical scores for three nudging options – nofdda, nfdda and gdobsffda

Figure 5 summarizes the spatial difference in the surface wind fields simulated by the “nfdda” (only large scale analysis) and “gdobsfdda” (all surface observations) runs. The impact of nudging local meteorological observations is clearly seen especially in the areas where the density of observations is the highest. Figure 6 shows the surface wind field simulated by the best run (‘gdobsfdda) and the corresponding observed values.

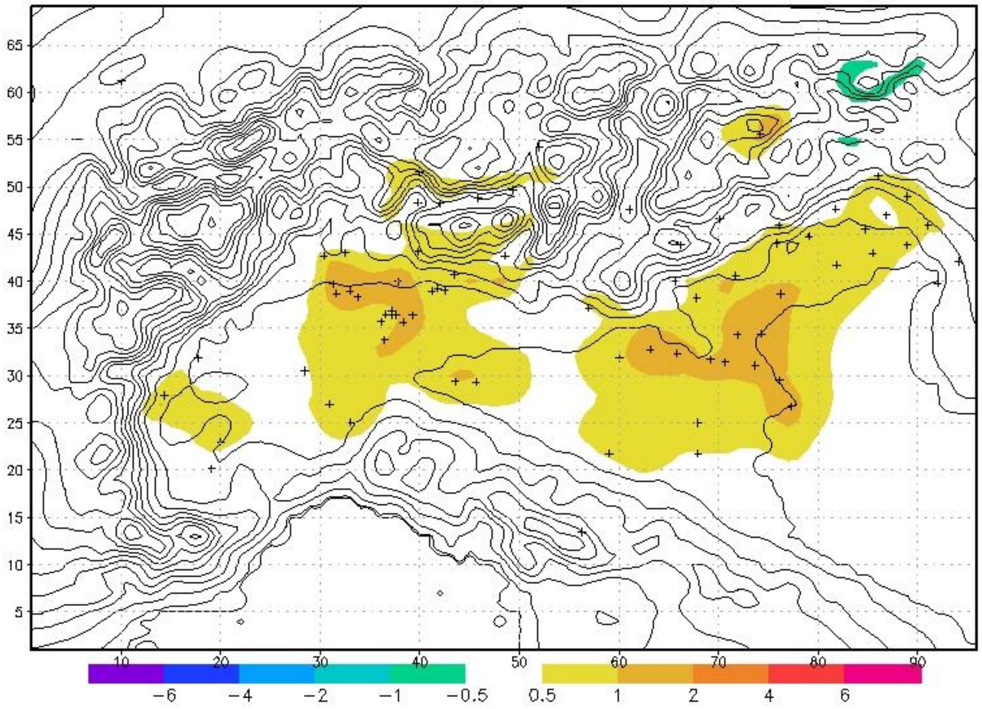


Figure 5: Differences in wind intensity between the run including only large scale NCEP analysis nudging (nfdda) and the run including nudging with all surface observations (gdobsfdda). The sign “+” marks the surface stations

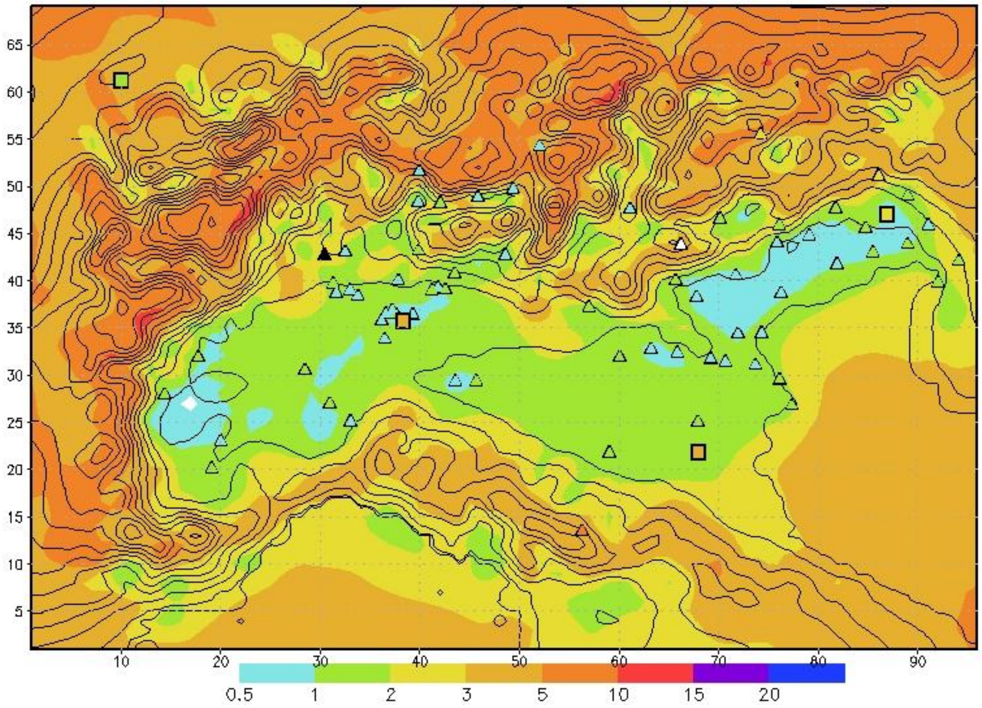


Figure 6: Wind field intensity map. Triangles indicate the measurement stations. Similar color for triangles and background indicate a good agreement of the model with measurements.

The improvement obtained through nudging on wind direction and temperature is not so obvious. The model cold bias remains around 0.5K and the RMSE around 3K over the whole domain.

4.3 Results on PM10

The CHIMERE model was used to test the sensitivity of simulated PM10 concentrations to the different nudging options in the meteorological driver MM5. The code was run with a 6 km spatial resolution over the Po-Valley domain.

Figure 7 summarizes the results for mean PM10, averaged by region. It indicates that the meteorological nudging has a non-homogeneous spatial effect on simulated PM10 concentration within the Po-Valley. As seen from this figure the nudging impact is stronger in Lombardy and in particular in the Milan area, where averaged PM10 concentrations increase by more than 60%

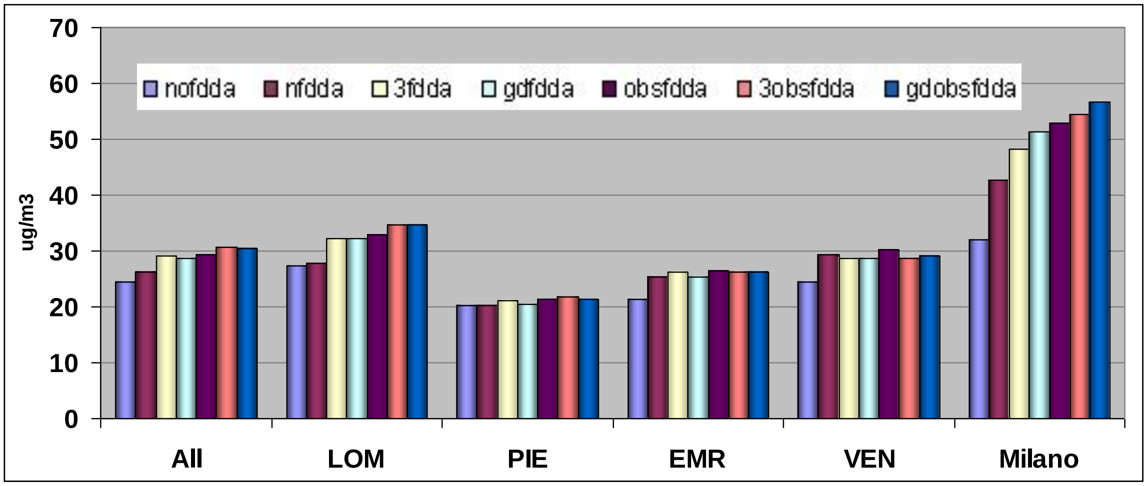


Figure 7: Average PM10 concentrations simulated by CHIMERE in the period 5-31 January 2005

Figure 8 shows the simulated PM10 concentrations, averaged for the selected period, at about 30 stations in the Po Valley, using different nudging options in MM5. At almost all stations nudging leads to an increase in mean PM10, excepted for some stations close to Brescia and to Biella.

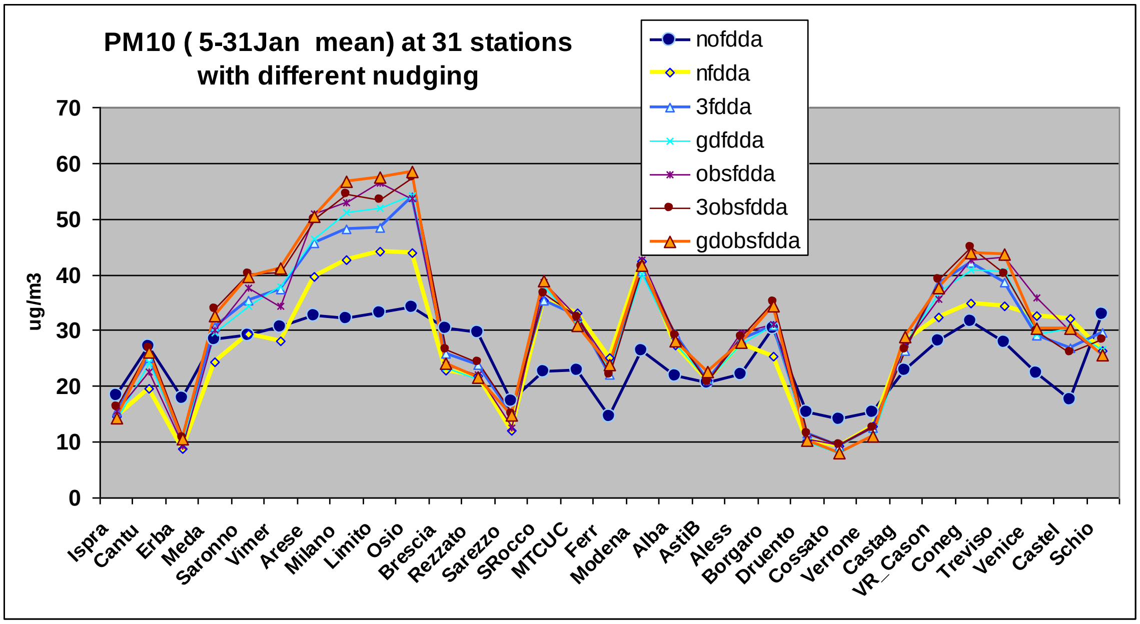


Figure 8: Average CHIMERE PM10 concentrations at various measuring stations obtained with different nudging options in MM5.

The spatial distribution of the percentage PM10 concentration differences (gdobsfdda and nfdda) is illustrated in Figure 9. As seen the Milan area exhibits the highest concentration increases (about 70-80%) while there is a decrease for some areas located in the pre-Alps.

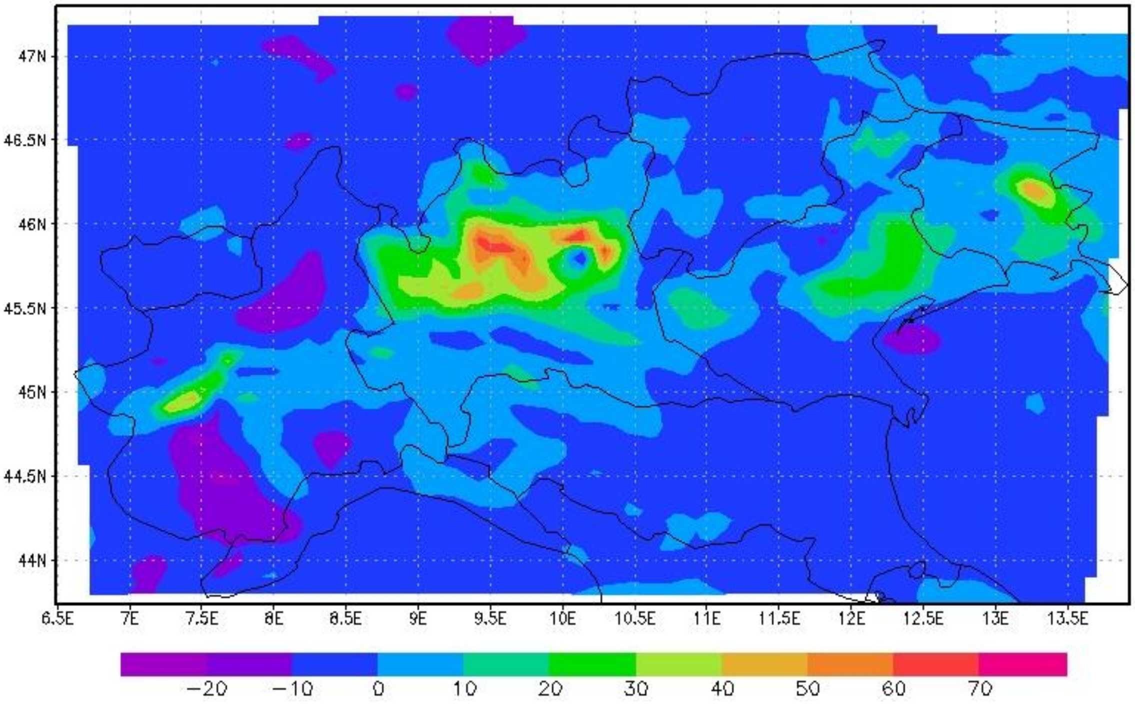


Figure 9: CHIMERE percentage differences in PM10 average concentration between two MM5 results obtained with different nudging options (gdobsfdda and nfdda)

In conclusion, MM5 model performance regarding wind speed clearly improves when nudging with surface observations is included as an option. The CHIMERE model performances in terms of PM10 concentrations are also improved, especially in the vicinity of the Milan metropolitan area. This work has been focusing on one specific time period in January. Further work is now required to extend this analysis to other periods of the year. It also clearly appears that no AQ model will be able to reproduce the observed PM10 levels within the Po-Valley without the use of an adequate set of meteorological data to drive the AQ model. From the experience gained within the POMI project, it appears that observation nudging represents a necessary step to achieve sufficient models performance.

5 Sensitivity analysis

In the interim report number VI; a few simulations have been made with the CHIMERE air quality model to test the sensitivity of the model results to different input data. For a specific period in January tests have been made to assess the impact of the following factors: emissions, meteorology and model process parameterization on PM10 mean concentrations. In parallel with these sensitivity tests, done by the JRC, modeling groups have also investigated the impact of other processes or factors on the AQ results. In particular the following simulations have been made. Only a brief summary of the main findings is here presented.

- Impact of boundary conditions (scenario 360) and model structure (scenario 260): These two tests have been made with the CHIMERE model. The impact of boundary conditions has been investigated by switching from EMEP to CHIMERE large scale concentration fields. Results show a large O3 increase in the whole Po-Valley while no change is seen for PM. The first vertical level may also impact the results. This has been tested by lowering the first level from 20 to 10m. Results show an O3 decrease due to higher NOx concentrations whereas for PM only a slight decrease is observed.

- Source apportionment study (scenario 250): The CAMx model includes a PSAT module which allows for estimating the contribution from different emission sectors or geographical areas of the domain to concentrations modeled at any location. The results point out to the fact that no particular emission sector or geographical area is guilty for the high PM concentrations. All sectors contribute but with traffic being the most important contribution. Wood burning is shown to provide high but localized contributions. Long range transport accounts for only 10 to 15%.

- Impact of meteorological input data (scenario 270). This factor has been analyzed and illustrated in section 4 on the base of a single model with different options. Here a complete change of the meteorological input has been done by switching from the MM5 to the TRAMPER meteorological input inside the RCG model. Significant changes are observed mostly related to the higher wind speeds recorded in the TRAMPER meteorological input.

- Impact of SOA parameterization (scenario 370): One particular key area where model improvement is required is the parameterization of secondary organic aerosols. This is particularly true within the Po-Valley where it has been identified that the underestimation of the PM concentration is in great part due to a strong underestimation of the organic particulate fraction. The AURORA model now includes a SOA formulation. This new SOA formulation has been shown to produce low increases in PM concentrations but much smaller than other changes made in the model.

6 Scenario analysis

In this section we focus on the analysis of model responses to policy oriented scenarios. Figure 10 illustrates the PM10 concentration averaged over all urban locations within Lombardy (left) and within the Po-valley (right) for a series of emission scenarios. The “asterisks” symbols in the “BC” column represent the mean base case concentration as modeled by the different modeling groups. As already mentioned previously, almost all models strongly underestimate the PM10 levels and model variability is extremely high. Two models underestimate by more than 50% (MOD 2 and MOD5) the observed concentrations.
Each “circle” in the figure represents the PM10 level reached by a model for a given scenario regardless of the model bias, i.e. each model results is corrected for its bias. As an example if the observed and modeled Base Case values are 50 and 25 µg/m3 respectively, then a reduction of 20% of the modeled concentration levels for a given scenario would be represented in the figure by a value of 40ug/m3. The first point to note is the great similarity of model responses for all scenarios with the slight exception of one model which tends to generate weaker responses to emission changes than other models. This similarity in terms of model responses has already been mentioned in the previous report but is now generalized to a much wider range of scenarios. CLE scenarios in 2012, 2015 and 2020 produce significant reductions of PM10 concentrations at urban location whereas the AQP for all time horizons tend to produce relatively similar results; consistently with the emission reductions imposed for these scenarios (see Figure 1). Similar conclusions can be drawn from the Po-valley picture. Consistently with the emission levels, the MFR12 scenario is here the most effective in reducing PM10 mean urban concentrations. These two pictures seem to indicate that the PM10 annual limit value (40 µg/m3) would be reached from emission reductions related to any AQP and to some of the CLE scenarios. **This is at least what different models do predict but we should keep in mind that most models experience difficulty in reproducing the observed base case levels.**

Regarding O3 (Figure 11) models show a larger variability in their responses, especially over the Lombardy domain. All scenarios tend to produce a slight increase in terms of average O3 levels. In terms of the number of exceedance days, all models predict a significant reduction for all scenarios but the model variability then becomes very large (not shown).

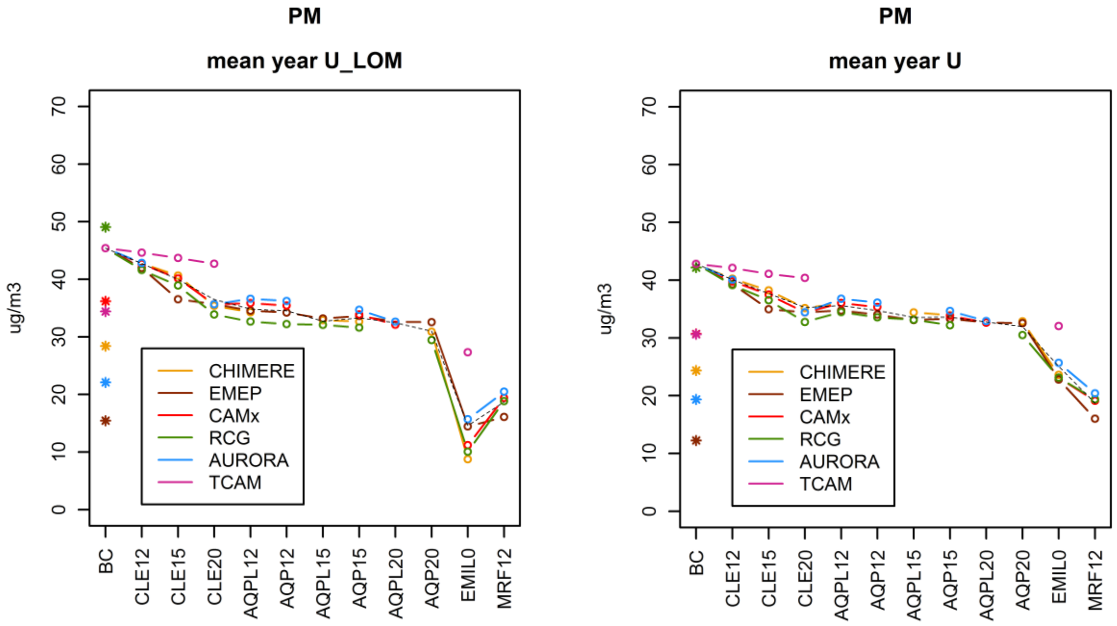


Figure 10: Modeled responses to different scenarios scaled on the base case observed annual PM10 concentrations. Results are averaged over all urban measurement stations in Lombardy (left) and Po-Valley (right). Acronyms for scenarios are provided in Table 1.

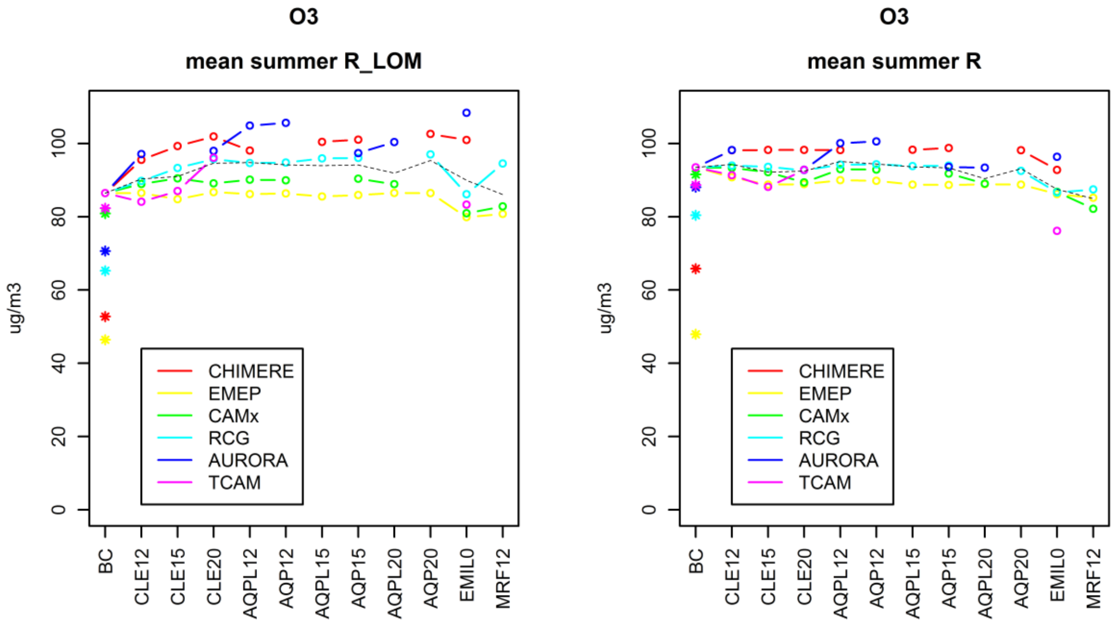


Figure 11: Modeled responses to different scenarios scaled on the base case observed summer O3 concentrations. Results are averaged over all rural measurement stations in Lombardy (left) and Po-Valley (right). Acronyms for scenarios are provided in Table 1.

7 Integrated Assessment (RIAT)

In recent years integrated assessment models to deal with complex non-linear atmospheric pollution problems have been developed at the continental scale (namely RAINS/GAINS) and then adapted to the national scale (RAINS-Italy by ENEA, RAINS-Netherlands, FRES (Finland), UK-IAM, Belgium-IAM), implementing a similar approach. Such methodology was developed mainly to support international negotiations and thus their spatial and temporal resolution is relatively coarse and their overall structure relatively rigid: the objective of the decision is fixed. In other words, they are not flexible and comprehensive enough to support the Air Quality Managers at the sub-national scale, which forces most air quality managers to use simpler approaches, typically scenarios analysis. Provided sufficient meteorological and emissive data are available, a complex multiphase air pollution model can be used to estimate the pollutant concentration in each point of the domain of interest at each time of their simulation horizon, assuming a certain reduction measure is in place, but they cannot solve more interesting problems such as defining where to invest more conveniently or how much money is necessary to achieve a given level of air quality.

To fill this gap a tool has been developed to identify efficient local policies complying, on one hand, with national and international air quality standards and, on the other hand, with local emission and meteorological characteristics, together with financial, technological and social constraints. The proposed Integrated Assessment Model (RIAT) is therefore focused on the local to meso-scale to interpret the specific features of the area, the domain meteorological and chemical conditions, the contribution of regional and local precursor emissions. Its peculiarity is to solve a multi-objective (air quality index and internal costs) optimization problem to select effective abatement strategies and present to the user the entire set of efficient solutions. The decision variables of such a problem are the emission abatement measures. Artificial neural networks (ANN) based on the output of long-term simulations of 3D deterministic multi-phase modelling system are constructed to describe the nonlinear relations between the control variables (precursor emissions reduction) and the air quality index. The use of such ANNs allows solving the problem in a reasonable computer time, which would be impossible if embedding directly the physically based 3D model into the optimization procedure.

Peculiar features of the system are the possibility for the user to define different air quality indexes, to constrain the overall expenditure to a specific value, to spatially visualize the improvement in air pollution concentration and air quality index to perceive their distribution on the territory. Clearly, a traditional scenario analysis is always possible. Another characteristic of the system is to automatically adjust to the foreseen development of legislation and technologies in time, adopting a specific classification of technologies to distinguish between those that can or cannot be replaced with time.

The RIAT is structured into different modules as illustrated in Figure 12. The system consists of:

- <u>Interface procedures</u> to retrieve information on: Air Quality Measures from GAINS and from regional Air Quality plans, emission inventory, air quality model simulations and internal costs for each technology abatement measure. These interfaces lead to the generation of related input databases for the RIAT.
- <u>Internal procedures</u> which takes care of the gridding, optimization and formatting of the results**.**
- <u>Delivery databases</u>: emissions, measures, Air Quality Indicators, internal costs and log files;

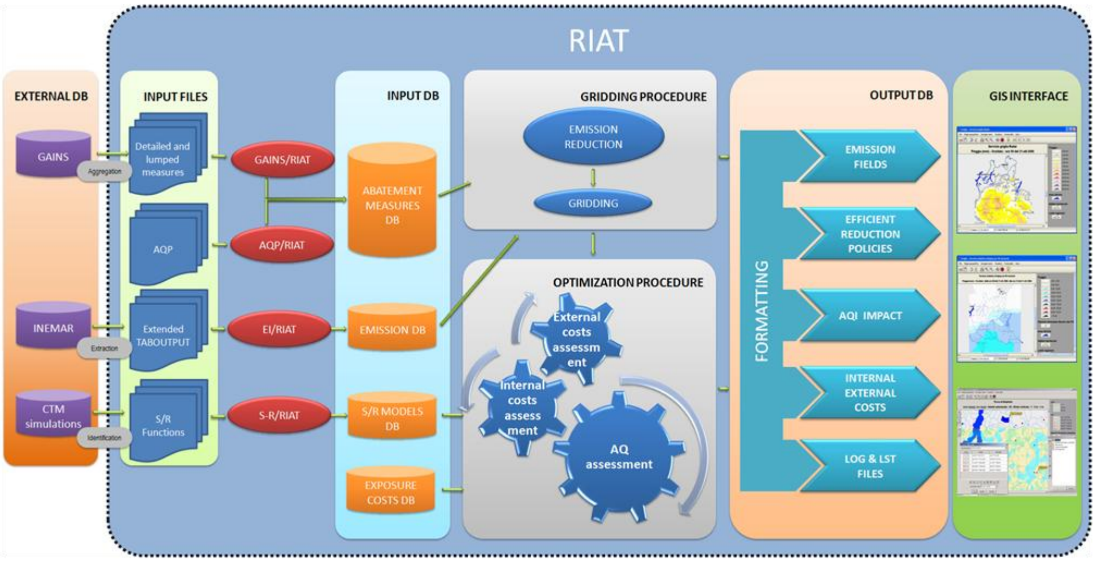


Figure 12: Architecture of the RIAT system.

S/R relationships are built from a series of air quality modelling (TCAM) simulations in order to relate emission reductions to concentration changes. These S/R relationships must provide a robust response over a wide range of possible emission changes. The GAINS (**G**reenhouse Gas and **A**ir Pollution **In**teractions and **S**ynergies) projections for Current legislation (CLE) and maximum technological feasible reductions (MTFR) are used as boundaries to define the range of possible emission reduction over which AQM simulations are performed. Base case emissions originate from an emission inventory based on INEMAR (INventario EMissioni ARia).

The abatement measure database is firstly populated (after pre-processing) with national abatement measures from the publicly available GAINS database. Additional emission abatement measures (e.g. originating from regional air quality plans) must be translated in terms of emission reduction and costs and included into the database. Currently mostly technical abatement measures are considered. Note that a series of filters may be applied to the abatement measures database to restrict the optimization application to specific groups of measures, geographical areas, sectors, etc.

Both the abatement measure database and the S/R relationships are used by the optimizer to produce a multi-objective optimization analysis (optimizing both air quality targets and internal costs) over a given area within the domain.

After optimization the RIAT delivers costs, emissions and impacts on the environment. The system allows the user to explore the space of optimized solutions and provides for each of those a complete list of the measures composing the optimized strategy (set of abatement measures). Figure 13 provides an example of the Pareto curve which allow for such an exploration. **It is important to note here that the results exposed hereafter in this section must be considered as preliminary. They are intended as examples to illustrate the potentialities of the RIAT and show what information policy maker may receive from this decision support system**. The Pareto curve provides the relation between optimized costs (beyond CLE) and given air quality indexes (here the average yearly PM2.5 concentrations averaged over Lombardy has been selected). An optimization is solved by computing first no-additional cost solution and then by obtaining 4 more points corresponding each to the resolution of the decision problem for an increasing cost target.

The same cost values are considered to compute the curve related to both the case with and without technological substitution. In the case without technological substitution it is possible to improve Air Quality Index reaching a value of 18 μg/m3, while, when substituting technologies, it is possible to reach the value of 14 μg/m3.

In this last case, reducing the air quality index to the minimum value is much more costly than in the no-substitution technology case. However, it must be noted that, for the same value of costs, say for instance, 300 M€/year above CLE, it is possible to reduce the AQI from 18,5 to 15,3 ug/m3 by allowing technology substitution.

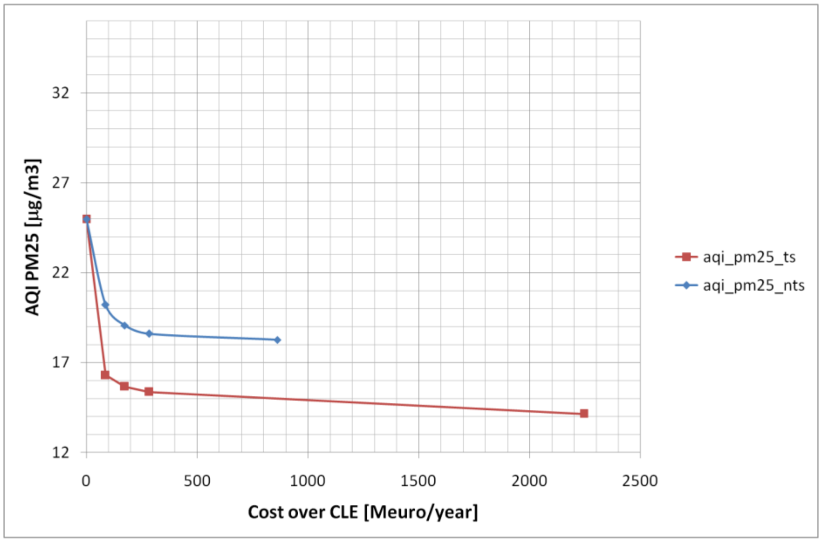


Figure 13: Pareto Curve for PM25, for the case with (red) and without (blue) technological substitution.

The Pareto curve gives an aggregated view of the optimal air quality indexes resulting from the multi-objective optimization approach but does not allow for assessing how the Air Quality Index changes spatially. The RIAT allows for visualizing emissions and AQI maps for the different points on the Pareto curve (see Figure 14)

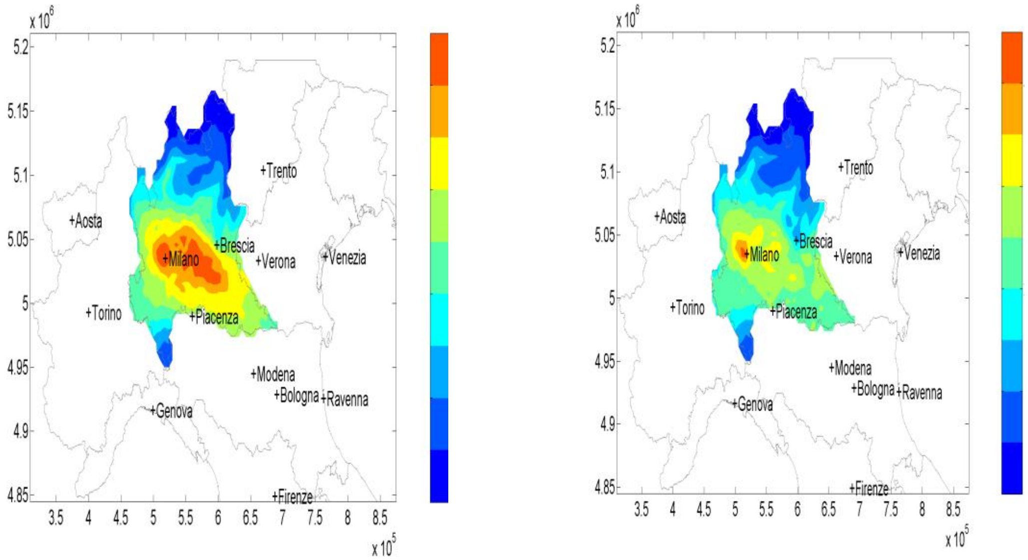


Figure 14: Air Quality Index (PM2.5 annual average concentration) map for the first (left) and second (right) points on the Pareto curve, The second point is representative of a 90 Meuro/year cost beyond 2020 CLE (no technological substitution allowed).

The reduced emissions related to a particular Pareto curve point can be split in terms of CORINAIR macrosectors. The following bar plots (Figure 15) are related to the second point of the Pareto curve (no substitution of technologies).

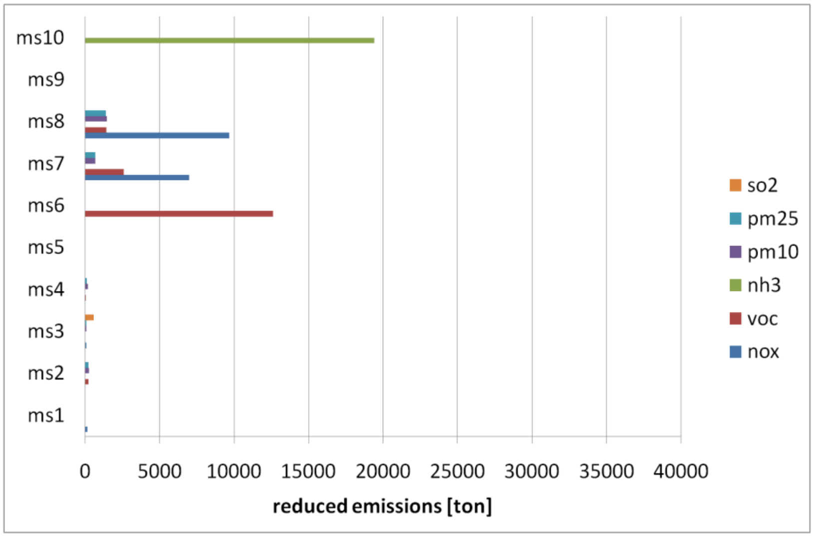


Figure 15: Reduced emissions per macrosector for point 2 on the Pareto curve, without technology substitution option.

Corresponding to the each optimal policy, internal costs can also be grouped in terms of macrosector (Figure 16).

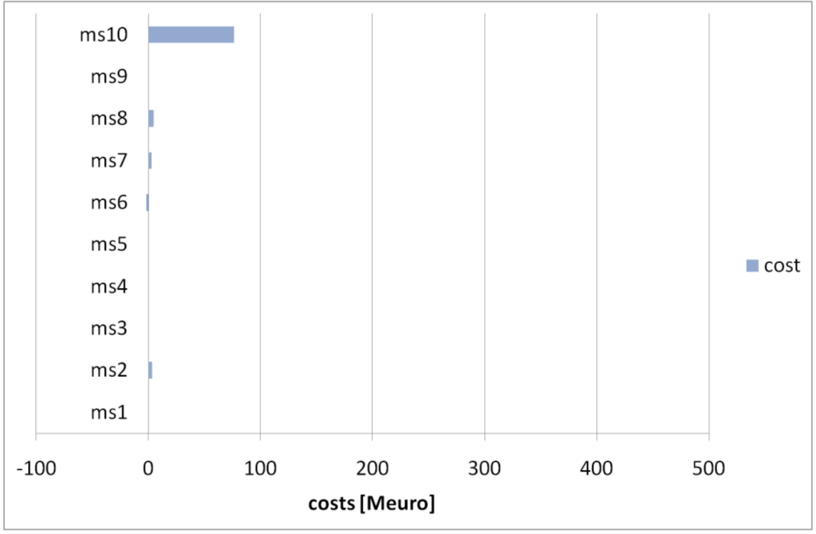


Figure 16: Costs per macrosector, point 2 of the Pareto curve, without technology substitution.

In addition details on the degree of implementation of the different technologies selected in each optimized solution can be provided (Figure 17).

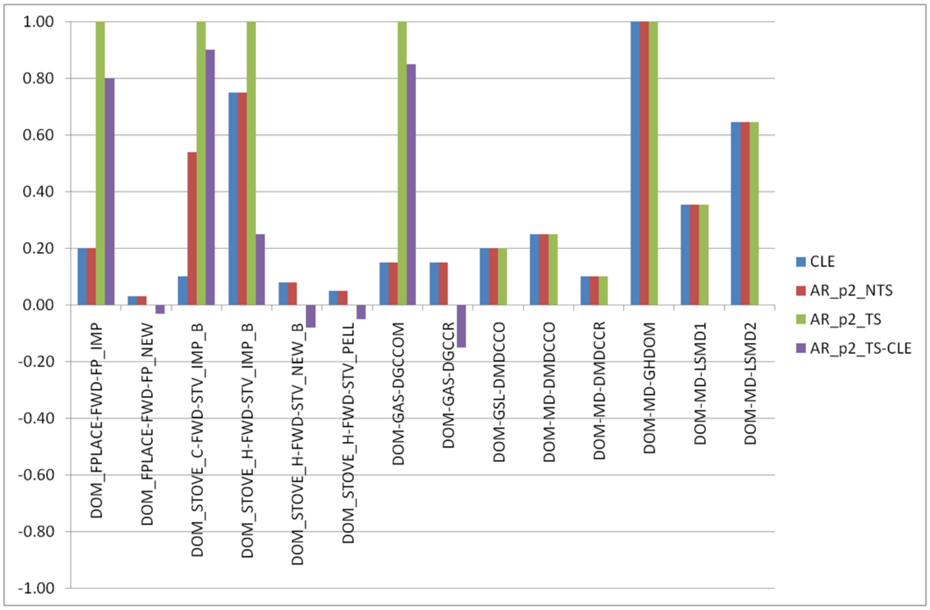


Figure 17: Decision variables related to macrosector 2, point 2 of the Pareto Curve. The blue column represent CLE, the red column the NTS (no technology substitution) application rate, the green one the TS (technology substitution) application rate, and the violet the technologies being substituted.

Finally a further output of the RIAT consists in delivering emission data in a format suitable for AQ Modeling, in order to assess alternative scenarios (sensitivity tests) or compliance related issues which are not directly included into the optimization process.

8 Conclusions

During the POMI project, a lot of attention has been paid to collect and deliver high quality input datasets (emissions, monitoring…) to the modeling groups. Despite these efforts and although models show relatively good performances regarding ozone, they continue to experience problems in reproducing the PM10 concentration levels observed in the Po-Valley. This underestimation is mostly visible during the winter season and mostly caused by an underestimation of the coarse and organic fractions of the PM (as seen from the observations collected at Ispra). One key factor which partly explains this PM underestimation is meteorology which despite the efforts put to improve it does not reach sufficient quality for air quality simulations. The main problem is in the overestimation of the wind speeds all over the Po-Valley but other factors such as the systematic cold bias in the temperature may also affect the results. As shown in this report, the work performed on the nudging with meteorological observation is promising and should greatly improve the results of the simulations.

Regarding the model responses to emission scenarios, the first conclusion is the great similarity in terms of relative response. All models tend to predict similar results to all prescribed scenarios. This is true for PM and O3 mean levels whereas for the number of exceedance days, the model results show a large variability.

In conclusion, more effort is still needed to improve meteorology modeling over the Po-Valley to obtain a sufficiently high quality input dataset for air quality modeling. The increased number of measurement stations for PM (and especially PM2.5) will help better identifying the problem in the future. More sites proposing a speciation analysis would also be extremely valuable.

Regarding integrated assessment the RIAT software has been developed in complement to the existing national and international instruments (RAINS, RAINS-Italy). It is specifically designed to cope with the regional specificities of the Lombardy area and provide the user with an alternative to the time-consuming scenario analysis. Optimized (in terms of cost) emission reductions to achieve given air quality targets are provided to the user together with various possibilities to explore the details of any given solution.

9 References

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ANNEX statistical indicators

- *The Pearson Correlation Coefficient (**R**)*:

$$R = \frac{\sum_{i=1}^{N}\left(M_i - \overline{M}\right)\bullet\left(O_i - \overline{O}\right)}{\left[\sqrt{\sum_{i=1}^{N}\left(M_i - \overline{M}\right)^2}\right]\left[\sqrt{\sum_{i=1}^{N}\left(O_i - \overline{O}\right)^2}\right]} \qquad (1)$$

M denotes modelled value, O denotes observed value, N is the number of paired values considered, $\overline{M}$ and $\overline{O}$ denote, respectively, the mean of modelled and observed values. ***R*** ranges from -1 to +1 and indicates the strength of a linear relationship between the two datasets. A value of +1, the so-called ”complete positive correlation” corresponds to all the pairs lying on a straight line with positive slope in the scatter diagram. A value of ***R*** near to zero indicates the absence of linear correlation between the variables.

- *The Index of Agreement (**IOA**)*

$$IOA = 1 - \frac{N \bullet RMSE^2}{\sum_{i=1}^{N}\left(\left|M_i - \overline{O}\right| + \left|O_i - \overline{O}\right|\right)^2} \qquad (5)$$

The perfect value of ***IOA*** is 1. ***IOA*** determines the extent to which magnitudes of $\overline{O}$ (mean) are related to the predicted deviations about $\overline{O}$, and allows for sensitivity toward differences in O and M.

- *The Mean Fractional Bias (**MFB**)*:

$$MFB = \frac{1}{N}\sum_{i=1}^{N}\frac{M_i - O_i}{\left[\left(M_i + O_i\right)/2\right]} \qquad (6)$$

The mean normalized bias ($MNB = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{M_i - O_i}{O_i}\right)$) can become very large when a minimum threshold is not used for the observed/measured data. The mean fractional bias is used as a substitute. The fractional bias for cases with factors of 2 under- and over-prediction are -67 and +67 percent, respectively (as opposed to -50 and +100 percent, when using normalized bias). ***MFB*** is a useful indicator because it has the advantage of equally weighting positive and negative bias estimates. It has also the advantage of not

considering observations as the true value. It can be especially useful for assessing performance in PM modelling where species might exhibit close to zero values.
MFB ranges from -200% to +200%.

- *The Mean Fractional Error (**MFE**)*:

$$MFE = \frac{1}{N}\sum_{i=1}^{N}\frac{|M_i - O_i|}{[(M_i + O)/2]} \qquad (7)$$

Similarly to the ***MFB***, the mean fractional error ***MFE*** gives equal weight to under- and over-prediction, is not sensitive to a threshold in measured values and does not assume that observations are the truth (i.e. the denominator is the sum of observed and predicted).
MFE ranges from 0% to +200%.

- *The Factor of predictions within a factor of two of observations (**FAC2**)*:

$$FAC2 = \frac{1}{N}\sum_{i=1}^{N} n_i \quad with \quad n_i = \begin{cases} 1 & for \quad 0.5 \le |M_i / O_i| \le 2 \\ 0 & else \end{cases} \qquad (8)$$

- *The Relative Directive Error (**RDE**)*:

The ***RDE*** has been defined in relation to the AQD, 2008 in order to give a mathematical expression of the “model uncertainty” term in the AQD. Following Denby, 2009 at a single station it is calculated as:

$$RDE = \frac{|O_{LV} - M_{LV}|}{LV} \qquad (9)$$

where O_{LV} is the closest observed concentration to the limit value concentration (LV) and M_{LV} is the correspondingly ranked modeled concentrations.

- *The Relative Percentile Error (**RPE**)*

RPE, proposed by Flemming and Stern, 2007 is an alternative model error measure for the purposes of the AQD. It is defined as the concentration difference at the percentile p corresponding to the allowed number of exceedances of the limit value normalized by the observation:

$$RPE = \frac{|O_p - M_p|}{O_p} \qquad (10)$$