PM2.5 source apportionment in Lombardy (Italy): Comparison of receptor and chemistry-transport modelling results

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1. Introduction

The assessment of the contribution of the different emission sources to the PM concentration (the so-called source apportionment, SA) is a crucial issue, needing robust and suitable approaches, for the development of proper strategies for air quality management. SA evaluations can be performed according to both a receptor-oriented and a source-oriented modelling approach: both the approaches are based on the same scientific principles, but the former is inferential whilst the latter is predictive of source contributions.

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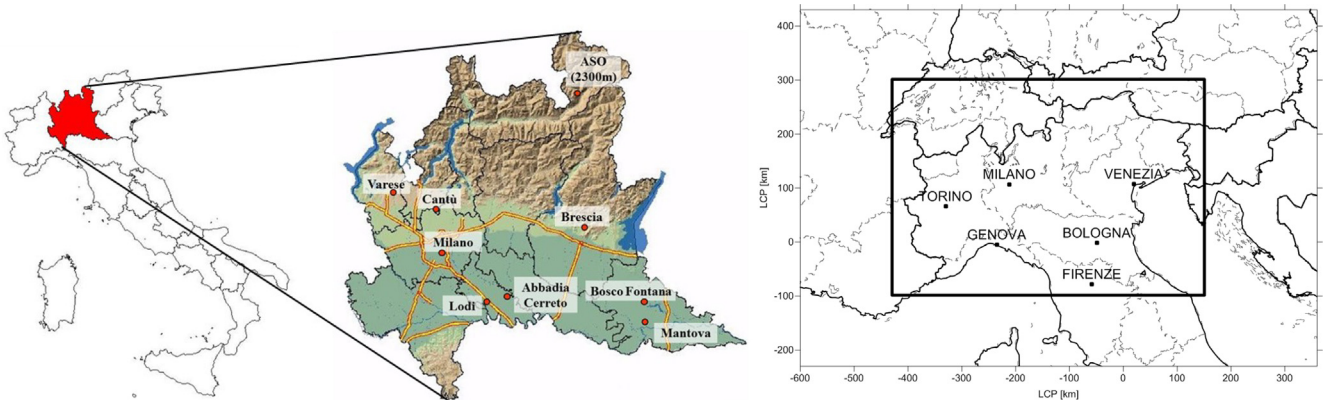


Fig. 1. Location of the PARFIL sites in the Lombardy region (left panel); CAMx computational domain (black rectangle in right panel).

Receptor models (RMs) are used to apportion sources of composite pollutants, typically VOCs and PM, to ambient air, starting from environmental concentration data at the receptor. Watson et al. (2002) provide an extensive list of references to studies using RMs in different applications and areas of the world; Belis et al. (2013) recently reviewed receptor models application for PM source apportionment in Europe.

Single sample models (e.g.: Chemical Balance Model, CMB), which require as input information also the emission profiles of the sources affecting air quality at the receptor sites, provide the source contribution estimates (SCEs) separately for each single PM sample; multivariate models (e.g.: Principal Component Analysis, PCA; Positive Matrix Factorization, PMF) identify both the number of sources, each associated to a composition profile of the emitted PM, and their SCEs processing the entire set of PM samples altogether; composition profiles are then interpreted, usually based on marker species, to recognize the different sources (e.g.: road traffic, combustion processes, soil resuspension).

Source-oriented modelling techniques are usually based on the application of Eulerian Chemistry and Transport Models (CTMs), relying on emission inventory and meteorological data and performing SA evaluations following two approaches: Zero-Out Modelling (Yarwood et al., 2004) and Reactive Tracers methods (Dunker et al., 2002; Zhang et al., 2005) that allow to overcome some limitations of the former approach.

The suitability of RMs and CTMs for PM source apportionment is stated by the rich literature on CMB and multivariate modelling, on tracer methods, and CTM techniques; a review on the recent use of SA approaches for atmospheric pollutant is given by Fragkou et al. (2012), where evaluation methods of SA studies are also reviewed. Validation of the SA results is a critical issue, due to the obvious lack in observed data suitable for this kind of analysis: the comparison of SA results obtained through different methods, such as source and receptor modelling, is a potential solution to overcome this relevant limitation (Lane et al., 2007; Park et al., 2013); however, this approach for SA evaluation is not usually applied as reported by Fragkou et al. (2012).

The comparison and the integration of the two approaches that are inherently different thus gives the chance to improve both the evaluation as well as the discussion of the SA results. For example, due to the fact that RMs outputs are usually 'tuned' to reconstruct the measured PM concentrations, they can represent a term of comparison for the CTMs. Furthermore, CTMs are designed to reconstruct a few main PM compounds, contributing to the most part of the bulk aerosol mass. Differently, RMs are designed to identify sources according to their fingerprint. As a consequence, CTMs are generally skilful in reproducing sources providing a strong signal in term of mass, even if they are collinear. Conversely, RMs can capture also the contribution of low emitting sources, if they show a distinct marker pattern, that generally are not captured by CTMs.

This work is focused on PM2.5 source apportionment over the Po valley area, providing a contribution to fill a gap of knowledge since the most part of SA studies in Europe considered PM10 as target metric, despite the recent evidence on adverse health effects due to ambient PM2.5.

Furthermore, the work provides a thorough investigation of PM2.5 source apportionment by receptor and chemistry-transport modelling through the comparison of CMB8.2 (Chemical Balance Model, version8.2) and CAMx/PSAT results, pointing out the main weaknesses and strengths of both approaches, as well as providing some additional insights about possible lack in the aerosol modelling approach. In particular, for a more powerful comparison the same source profiles have been used for emission speciation in CAMx/PSAT and source profiling in CMB8.2, thus reducing as much as possible the sources of difference between the two approaches.

2. Materials and methods

2.1. CMB receptor oriented model

In this work the standard EPA CMB8.2 (US EPA, 2004; Watson et al., 1984) was applied since the present ambient dataset was formed speciating each kind of compounds (carbon species, main ions, trace elements) every other week. The CMB model provides a weighted ordinary least squares solution to a set of linear equations which expresses the mass balance of n chemical species in PM samples collected at receptor site C (n $\times$ 1 vector) as a linear combination of products of source profile species F (n $\times$ p matrix) and source contributions S (p $\times$ 1 vector):

$$C = F \cdot S + \varepsilon \quad (1)$$

accounting for random measurement errors ε (n $\times$ 1 vector).

CMB8.2 model allows the solution of the least squares estimation problem accounting for the uncertainty in both the source profiles and speciated ambient PM (Watson et al., 1984); additionally, it provides measures of the collinearity of the given set of weighted source profiles and suggestions for combining highly collinear profiles (Henry, 1992).

2.1.1. PM2.5 ambient data

Ambient daily PM2.5 dataset is based on a multi-year campaign (PARFIL project 2004–2007) performed at 9 sites in Lombardy

Table 1
Location and classification (as 2008/50/EC Directive) of the PARFIL and EMEP sites.

Sampling site	Type	UTM-coordinates	
		UTM-East	UTM-North
Abbadia Cerreto	Urban background	637818	4983202
Alpe San Colombano (ASO)	Remote alpine site	601055	5145611
Bosco Fontana	Rural background	636933	5007756
Brescia	Urban background	594957	5045550
Cantù	Suburban traffic	509865	5064351
Lodi	Urban background	538975	5016901
Mantova	Urban background	641855	5000871
Milano	Urban background	518195	5036391
Varese	Urban traffic	485510	5074116
Ispra (EMEP site)	Background	469781	5073206

representative of different environmental conditions (Fig. 1, Table 1).

Daily PM2.5 samples were collected using low-volume US-EPA reference method samplers with a sampling rate of 1 m^3 h^{-1} at ambient conditions. Filters (47 mm diameter) were conditioned before and after use at 35% humidity and 20 ± 5 °C for 48 h and weighed with certified precision balances with 1 μg resolution. Filter media were selected based on the type of analysis required: PTFE with PMP support ring for ion chromatography (main ionic species), X-ray fluorescence analysis (elements with Z > 11), quartz for thermal-optical transmittance (NIOSH 5040 Protocol) analyses for elemental carbon (EC) and organic carbon (OC).

For each site the three-year average speciated concentrations of PM2.5 were used as *C* vector input in CMB model. Indeed the work was addressed to the assessment of the systematic source contributions and the comparison of the apportionment results from source- and receptor-oriented modelling in a long-term perspective (i.e.: seasonal basis) over the Lombardy region and not to the detailed investigation of source contributions at single sites over short time periods and under occasional local events. Furthermore, due to the schedule of the sampling campaigns, the spatial coverage of the PM2.5 speciated dataset for 2005, the year selected for the simulations with the source-oriented approach, is rather limited thus not enabling a region-wide source apportion-ment with high time resolution. Preliminary analyses on both speciated and total PM2.5 concentrations did not show statistically significant interannual variations, supporting the assumption that year 2005 could be considered suitable for the scope of the work since not characterized by peculiar meteorological conditions (Fig. 2).

2.1.2. Emission source profiles

For a successful application of CMB model all important sources affecting PM ambient concentration at the receptor site must be known and representative information on their emission profiles must be available. Speciation profiles of emission sources can be found in literature and extensive databases are available. However, whenever possible, it is preferable and recommended to use local speciation profiles, better representing the features of the sources actually present in the study area. In this work local source profiles, resulting from experimental determinations following the same analytical procedures as for environmental PM samples, were used for domestic biomass burning, agricultural open burning, and tyre and brake wear (Colombi et al., 2006). For the transport sources, literature profiles from US EPA SPECIATE 4.3 (Simon et al., 2010) were revised according to information on the local circulating fleet database, especially as EC and OC are concerned.

Mass closure analyses (Figure S.1 in Supplementary Materials) demonstrated the relevant contribution of secondary inorganic species, namely ammonium nitrate and ammonium sulphate, to ambient PM2.5. Therefore profiles consisting of "pure" ammonium

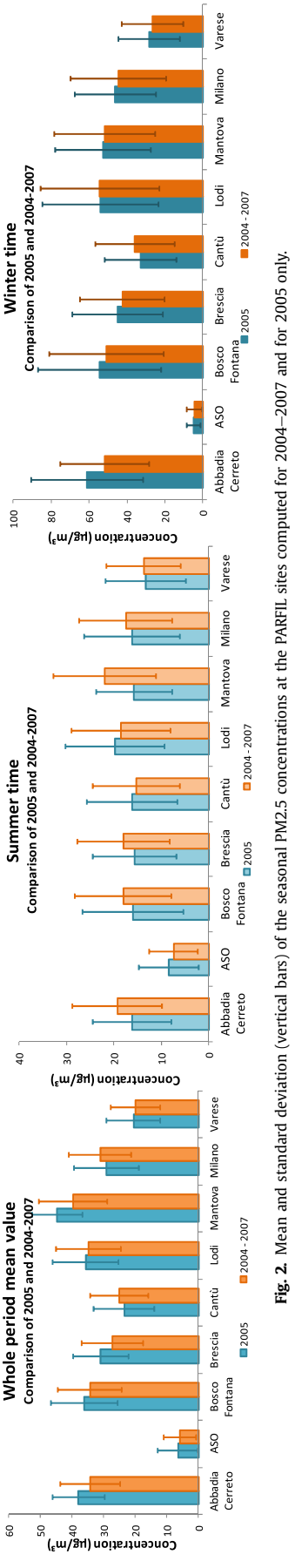


Fig. 2. Mean and standard deviation (vertical bars) of the seasonal PM2.5 concentrations at the PARFIL sites computed for 2004–2007 and for 2005 only.

Table 2
CMB source profiles used in this study, also adopted by CAMx as emission speciation profiles (CI: compression ignition engine; SI: spark ignition engine).

Source profiles	Markers
Agricultural open burning	OC, EC, K
Domestic heating – biomass burning	OC, EC, K
Road transport – Tire and break wear	Fe, Cu, Zn
Road transport – CI light duty vehicles	OC, EC
Road transport – CI heavy duty vehicles	OC, EC
Road transport – SI vehicles	OC, EC

sulphate and ammonium nitrate were used to apportion the remaining NH_4^+, SO_4^{2-}, NO_3^-, that otherwise would not be apportioned through the primary source profiles, according to CMB protocol (US EPA, 2004).

Table 2 lists the source profiles used for CMB source apportionment in this work; given the location of the sampling sites and based on knowledge on the study area and on Lombardy region emission inventory no specific industrial sources were considered.

2.2. CAMx source-oriented model

CAMx is a widely used three-dimensional chemistry transport model that simulates the atmospheric fate of ozone and PM (Environ, 2011). In this work CAMx version 5.41 with Carbon Bond 2005 (CB05) gas phase chemistry (Yarwood et al., 2005a) and the so called Coarse-Fine (CF) aerosol module was used. The CAMx modelling domain (580×400 km^2) includes the whole Po Valley and was defined in Lambert conformal coordinates with 116 by 80 grid cells of 5 km horizontal resolution and 13 vertical layers (Fig. 1).

2.2.1. CAMx input data

Input meteorological data for 2005 reference year were generated by WRF model (Skamarock et al., 2008) applied over three one-way nested domains covering the whole Europe, Italy and the Po valley, with resolution of 45, 15 and 5 km, respectively. The WRFCAMx preprocessor was used to create CAMx ready input files collapsing the 27 vertical layers used by WRF to 13 layers in CAMx but keeping identical the layers up to 1 km above ground level. In particular, the first layer height was around 25 m, thus being able to capture also very strong stable conditions that can produce very low PBL heights.

Anthropogenic gridded emissions were compiled with the Sparse Matrix Operator Kernel Emission processor (SMOKE version 2.6, http://www.smoke-model.org/). Three different kinds of inventories were used to set up both point and area sources. Regional official inventories were adopted where available (Lombardy, Veneto, Piemonte, and Emilia-Romagna region); for the remaining Italian regions emission data were derived from the Italian official inventory (ISPRA, 2009), while emissions from the neighbouring countries were taken from the EMEP database (http://www.emep.int/). The same source profiles used for CMB analysis (Table 2) were also adopted to speciate the bulk PM emissions for the corresponding categories, namely road transport, domestic heating and agricultural open burning. This choice represented a key aspect in order to reduce as much as possible the sources of difference between the two SA approaches. Literature profiles were used for the

Table 3
Emission categories tracked by CAMx, with corresponding SNAP categories and the fuels. The last two columns show the re-aggregation of the emission categories into the PSAT and CMB source classifications.

CAMx emission category	SNAP category	Fuel	PSAT classification	CMB classification
Power plants	01	Mix	Other sources	
Power plants	01	Biomass	Other sources	
Power plants	01	Other	Other sources	
Energy production in industrial activity (except power plants)	01	Mix	Other sources	
Energy production in industrial activity (except power plants)	01	Biomass	Other sources	
Energy production in industrial activity (except power plants)	01	Other	Other sources	
Domestic and commercial heating	02	Other	Domestic heating – Other fuels	
Domestic and commercial heating	02	Biomass	Domestic heating – Biomass burning	Domestic heating – Biomass burning
Industrial combustion	03	Other	Other sources	
Industrial combustion	03	Biomass	Other sources	
Road transport – cars	07-01	Mix	Road transport – SI vehicles	Road transport
Road transport – cars	07-01	Gasoline	Road transport – SI vehicles	Road transport
Road transport – cars	07-01	Diesel oil	Road transport – CI vehicles	Road transport
Road transport – cars	07-01	LPG-Natural gas	Road transport – SI vehicles	Road transport
Road transport – cars (tire and break wear)	07-01		Road transport – Wear emissions	Road transport – Wear emissions
Road transport (except 0701)	07	Mix	Road transport – SI vehicles	Road transport
Road transport (except 0701)	07	Gasoline	Road transport – SI vehicles	Road transport
Road transport (except 0701)	07	Diesel oil	Road transport – CI vehicles	Road transport
Road transport (except 0701) (tire and break wear)	07		Road transport – Wear emissions	Road transport – Wear emissions
Evaporation	07		Transport – SI vehicles	Road transport
Off road	08	Mix	Road transport – CI vehicles	Road transport
Off road	08	Gasoline	Transport – CI vehicles	Road transport
Off road	08	Diesel oil	Transport – CI vehicles	Road transport
Waste treatment	09		Other sources	
Agriculture	10		Agricultural open burning	Agricultural open burning
Natural emissions (without Sea Salt and Biogenic VOCs)	11		Background	
Sea Salt and Biogenic VOCs	11		Background	
Long range transport	–		Background	
Anthropogenic SOA	–		SOA – Anthropic	
Biogenic SOA	–		SOA – Biogenic	
Other	–		Other sources	

Table 4
Calculated values for the CMB diagnostic parameters: min–max range and average ± standard deviation (in brackets). Target values according to US EPA (2004).

Diagnostic parameter	Cold season	Warm season	Target values
R^2	0.21–0.82 (0.58 ± 0.22)	0.23–0.83 (0.58 ± 0.20)	>0.8
χ^2	15–73 (36 ± 20)	14–77 (38 ± 19)	<1 (good fit) 1–2 (acceptable fit)
Percent mass	70–128 (97 ± 19)	72–149 (125 ± 26)	80%–120%
SCEs t-statistics	always > 2	always > 2	>2

speciation of PM emissions from the leftover sources, such as industrial processes and waste treatment.

Biogenic VOC emissions were computed by applying the MEGAN emission model (Guenther et al., 2006). Sea salt emissions were computed using published algorithms (de Leeuw et al., 2000; Gong, 2003). Initial and boundary conditions were obtained by a CAMx model run at Italian scale with horizontal resolution of 15 km.

2.2.2. PSAT source apportionment model

The CAMx model implements the PM Source Apportionment Technology (PSAT), a SA algorithm embedded into the code providing an effective method for modelling source apportionment when a large number of sources is used for simulations.

PSAT uses reactive tracers to apportion both primary and secondary PM compounds among different source categories and source regions. More information on PSAT are available in Yarwood et al. (2004, 2005b), Wangstrom et al. (2008).

PSAT tool was configured to track several emission categories including transport sector, in turn split into cars and other vehicles, residential heating, energy production and agriculture. When relevant, emission categories were defined also based on the fuel used. The full list of the 31 source categories is presented in Table 3. Conversely, sources were not split into different emission areas, because CMB cannot detect them.

For comparison purpose of CMB and PSAT source apportionment results, CAMx/PSAT source categories were re-aggregated as domestic heating (split by fuel), transport (split by engine type and wear source), agriculture, background (including natural sources and long-range transport), and other sources (essentially including stationary industrial sources), as indicated in the last columns of Table 3.

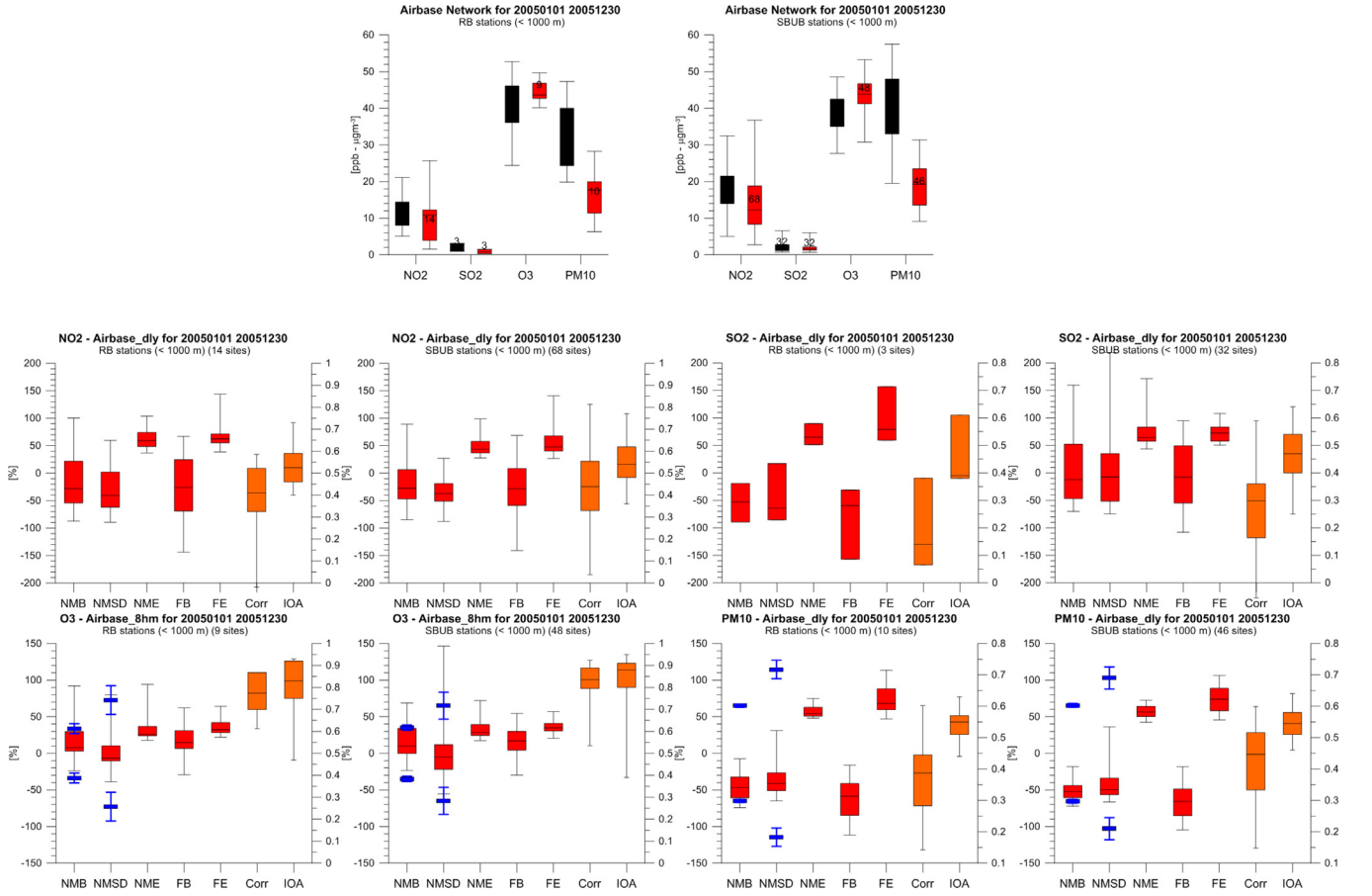


Fig. 3. Box and whisker plots of CAMx model performance at Airbase sites for year 2005. Top panels: distributions of the yearly mean concentrations observed (black) and computed (red) at Airbase background sites (RB = Rural Background; SBUB = Suburban and Urban Background). Middle and bottom panels: distributions of performance indicators computed at Airbase background sites (red boxes: left axes; orange boxes: right axes). Performance indicators: Normalized Mean Bias (NMB), Normalized Mean Standard Deviation (NMSD), Normalized Mean Error (NME), Mean Fractional Bias (FB), Mean Fractional Error (FE), correlation (r), Index of Agreement (IOA). For NMB and NMSD of O_3 and PM10 the panels show the distribution of the corresponding Model Performance Criteria (MPC). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

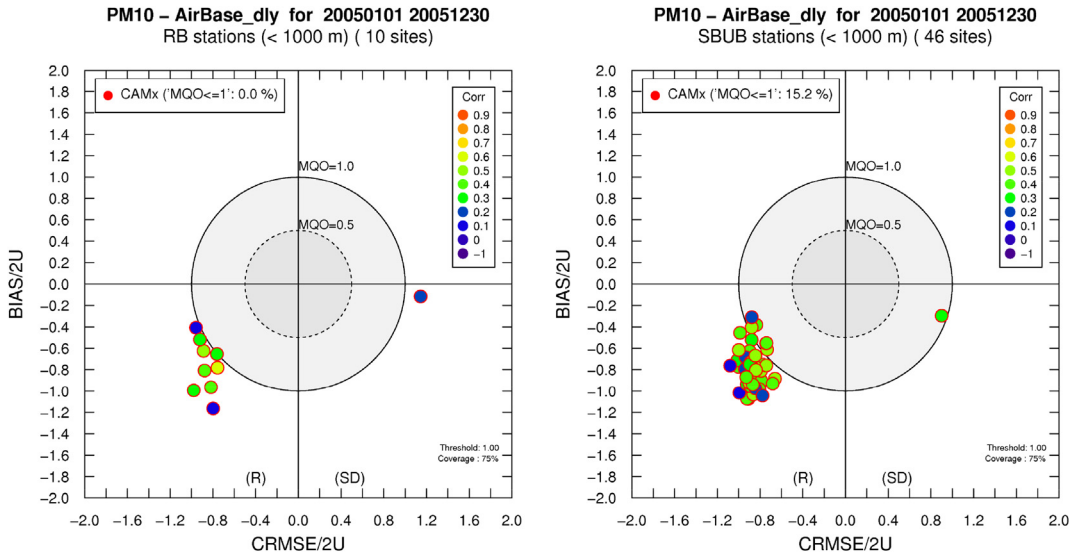


Fig. 4. Target diagrams of CAMx performance for PM10 at Airbase Rural (left) and Suburban/Urban (right) Background sites. Bullets show the values of the Model Quality Objectives computed at each site for year 2005 as distance from the axes centre; bullet colours show the correlation value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. CMB model performance

Source contribution estimates (SCEs) are the main output of CMB model and they represent the fractional contribution to ambient PM2.5 concentration by each source profile used in the model run. For each site CMB runs were reiteratively performed first including all the source profiles listed in Table 2 and then retaining only those that provided contributions to the measured mass, thus leading to the final solution with SCEs for the influential sources. Depending on the site from a 3-source to a 5-source solution was found, with the number of sources generally insensitive to seasonality, as discussed in the next paragraph 3.3.

Together with the SCEs output CMB model also provides a set of diagnostic parameters for the statistical assessment of the model performance. In particular, these diagnostic parameters provide performance measures of the least square calculations: R^2 is used to measure the variance in the ambient species concentrations explained by the calculated species concentrations, χ^2 to consider the uncertainty of the calculated species concentrations, percent mass to track the fraction of the measured PM2.5 concentration explained by model-calculated SCEs, standard errors of the calculated SCEs to enable t-statistic evaluations for SCEs. Suggested target values (US EPA, 2004) for the diagnostic parameters are reported in Table 4 together with the range of the values obtained through CMB runs for the PM2.5 seasonal datasets.

Percent mass and t-statistic values are generally in compliance with the suggested target values; conversely, R^2 values are greater than the target only in few cases and all χ^2 values largely exceed the target. These latter results suggest that the concentration of one or more species is not well explained by the calculated SCEs. Actually, the detailed analysis of the speciated reconstructed mass shows that CMB generally provides a poor reconstruction for most of the minor elemental species, essentially responsible for the large χ^2 values (Figure S.2); conversely, a closer match between observed

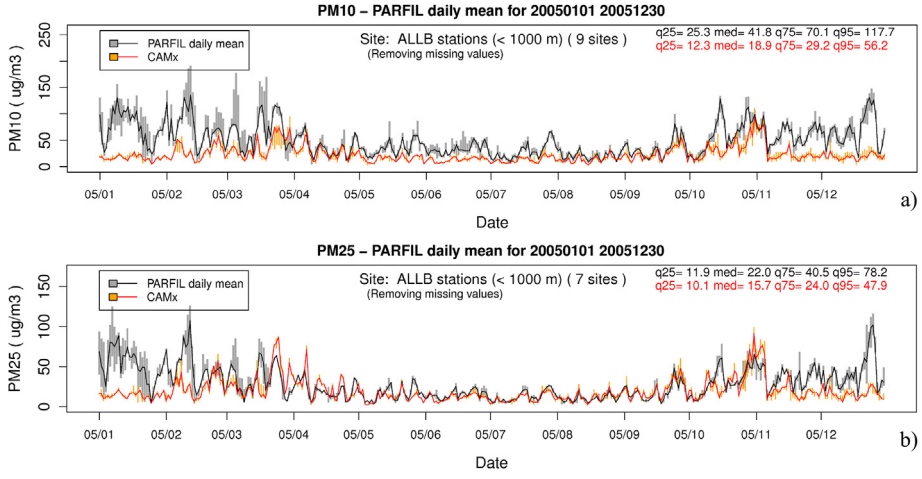
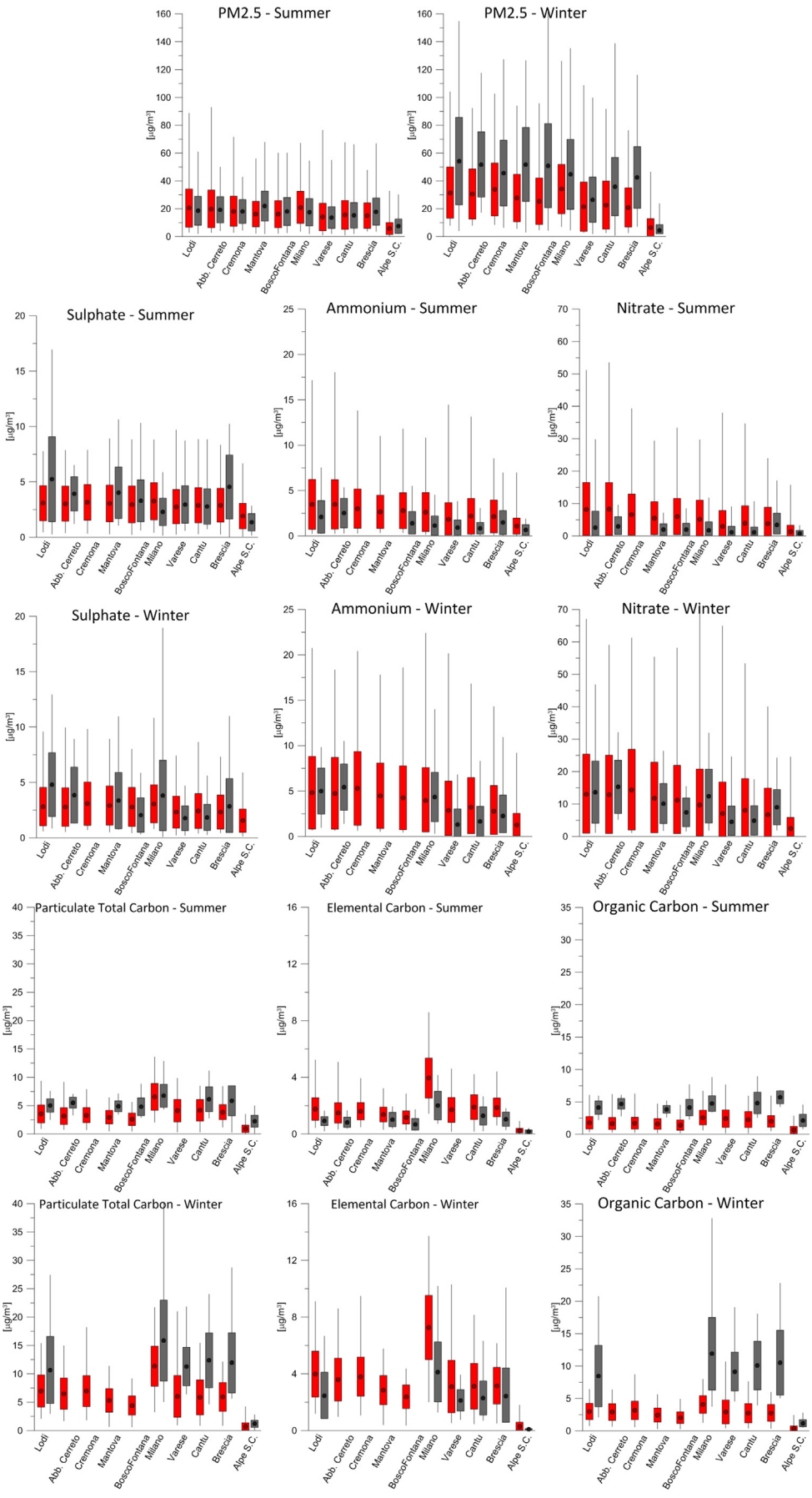


Fig. 5. Time series of the box and whisker plots for the distribution of the observed (black/grey) and computed (red/orange) daily concentrations of PM10 (a) and PM2.5 (b) at PARFIL sites. Bars show the interquartile range, lines the median values. Values for the 25th, 50th, 75th, and 95th quantiles of the whole yearly time series are reported too. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)


PM2.5 - Summer
PM2.5 - Winter
Sulphate - Summer
Ammonium - Summer
Nitrate - Summer
Sulphate - Winter
Ammonium - Winter
Nitrate - Winter
Particulate Total Carbon - Summer
Elemental Carbon - Summer
Organic Carbon - Summer
Particulate Total Carbon - Winter
Elemental Carbon - Winter
Organic Carbon - Winter
[µg/m³]
Lodi
Abb. Cerreto
Cremona
Mantova
BoscoFontana
Milano
Varese
Cantu
Brescia
Alpe S.C.

and calculated concentrations is obtained for the main PM2.5 components (EC, OC, sulphate, nitrate and ammonium), even though slightly overestimated, thus explaining the excess percent mass calculated at some sites.

The obtained performance pointed out the strong influence of the observed data set on the reliability of the RMs results. This finding did not hamper the further comparison with CAMx results, as it was focused on the main aerosol components and sources, but confirmed the need of implementing a multi-model approach in order to increase the overall robustness of SA results.

3.2. CAMx model performance

CAMx performance was firstly evaluated at a selection of sites belonging to the European database of national operational networks (AirBase, http://air-climate.eionet.europa.eu/databases/airbase/) in order to assess the reliability of the modelled ambient concentration. NO_2, SO_2, O_3 and PM10 data at background sites with data availability >75% were considered; sites were grouped in two subsets (rural background – RB, suburban and ur-ban background – SBUB) according to the official classification proposed by the European Environment Agency (European Community, 1997). Model performance evaluation (MPE) was based on daily mean concentrations for NO_2, SO_2 and PM10 and on the daily maximum 8-h running average concentration for O_3.

PM2.5 data from Airbase were not considered for MPE due to the very low data availability for 2005 over the Po valley. However, PM2.5 mass and composition data in 2005 from the EMEP (European Monitoring and Evaluation Programme, http://www.emep.int/) background site of Ispra in the Western part of Lombardy were used; furthermore PM2.5 data from the PARFIL dataset were used. For a comprehensive MPE seven performance indicator (PI) metrics were used, whose mathematical expressions are reported in the Supplementary Materials.

A concise description of CAMx performance at Airbase sites is reported in Fig. 3 by the box and whisker plots of the statistical distribution of the PI values computed at each site. Overall, CAMx slightly underestimates NO_2 and SO_2 concentrations, clearly underestimates PM10 concentrations, and conversely tends to overestimate O_3. Following Thunis et al. (2012), the distributions of the Model Performance Criteria (MPC) for NMB and NMSD are reported in Fig. 3 for O_3 and PM10. CAMx proved to be compliant with MPCs for both pollutants at both RB and SBUB sites. For NO_2 and SO_2, the median values of bias indices (NMB and FB) are close to zero, confirming the good skill of CAMx in reproducing the mean concentration of both pollutants that play a relevant role as PM precursors; for PM10 PI analysis confirms the CAMx low bias, with NMB and FB median values around −50%, as clearly shown by the target diagram in Fig. 4. These results are coherent with previous applications over the same area (Lonati et al., 2010; Pernigotti et al., 2013).

The CAMx underestimation takes place mainly in the cold season (Figure S.3), when the model is not able to capture the severe PM10 episodes in January, February and by the end of December. However, CAMx performance clearly improves when PM2.5 is considered, particularly during the warm season (March to October), although it still underestimates the severe episodes taking place during the coldest months.

Fig. 5 compares the daily time series of box and whisker plots of

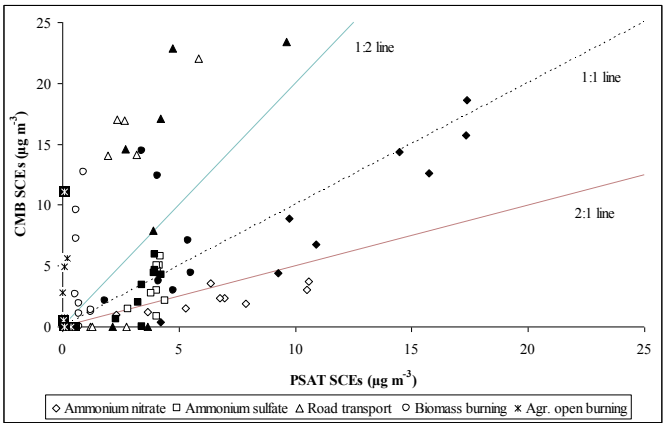


Fig. 7. Comparison of seasonal SCEs for PM2.5 at PARFIL sites for sources common to CMB and PSAT. Road transport source category includes both SI and CI vehicles as well as wear emissions contribution (black symbols: cold season; white symbols: warm season).

PM10 and PM2.5 concentrations at PARFIL sites. CAMx performance is very similar to Airbase sites, particularly for PM2.5. This latter allows extending the main findings stemming from the comparison against PARFIL sites also outside Lombardy region, at least in a qualitative manner.

CAMx performance is also confirmed, at least qualitatively, by the comparison of PM2.5 composition data, performed on a seasonal basis, due to the lack of extensive field data from PARFIL sites for 2005. CAMx is able to capture the summer distributions, conversely, showing a systematic underestimation of the winter concentrations at all sites (Fig. 6, top panels). CAMx is able to correctly reproduce the winter distributions of the main secondary inorganic aerosol species; differently, the model is less performing during summer, displaying a slight overestimation of ammonium and a more noticeable discrepancy for nitrate, whose overestimation could be caused by a negative artefact in the observed data, due to the volatilization of nitrate from the filter during the warm season. Furthermore, CAMx does not account for adsorption of nitrate and sulphate onto coarse particles, just limiting this process to the fine fraction, which might partly explain overestimations of PM2.5 secondary inorganic compounds. Additionally, it could be as well related to an overestimation of the photochemical activity, stated by the positive bias in ozone concentration giving rise to an enhanced production of nitric acid, that can be easily converted to nitrate, thanks to the great avail-ability of ammonia in the Po valley (Carnevale et al., 2012).

When total (TC) and speciated carbon are concerned, CAMx shows a clear worsening in model performance. TC is underestimated at all sites, mainly during winter, thus helping in partially explaining (about 25%) the corresponding underestimation of the PM2.5 total mass. As the stronger discrepancies take place during the winter season, they can probably be related to the primary fraction of carbonaceous aerosol, that in the cold season represents more than 75% of the total carbon fraction (Gilardoni et al., 2011). However, speciated carbon analyses show that CAMx underestimates the OC fraction, while overestimates the EC contribution. This suggests that the underestimation of the observed TC is actually mostly due to the organic fraction, but also that the

Fig. 6. Box and whisker plots of the seasonal distribution of the observed (grey) and computed (red) daily concentration of PM2.5 total and speciated mass. Boxes show the range $\mu \pm \sigma$, (mean and standard deviation of the seasonal distribution), bars the minimum and maximum seasonal values, bullets the observed (black) and computed (red) seasonal mean. The observed seasonal distributions refer to the whole PARFIL campaign (2004–2007), whereas computed values refer to 2005. Summer data refer to April–September, winter data to January–March and October–December. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

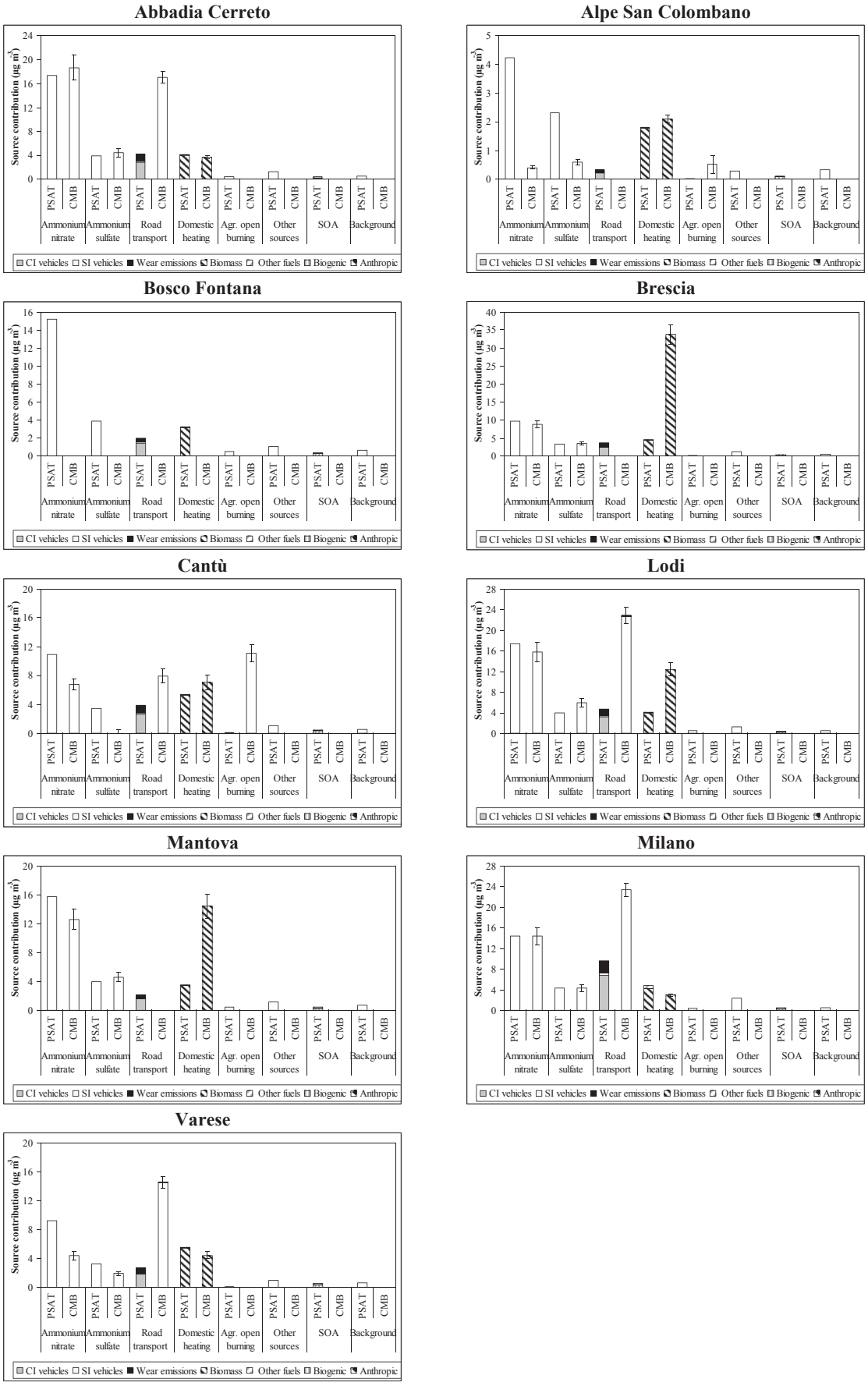


Fig. 8. Site by site comparison of PM2.5 SCEs at PARFIL sites in the cold season.

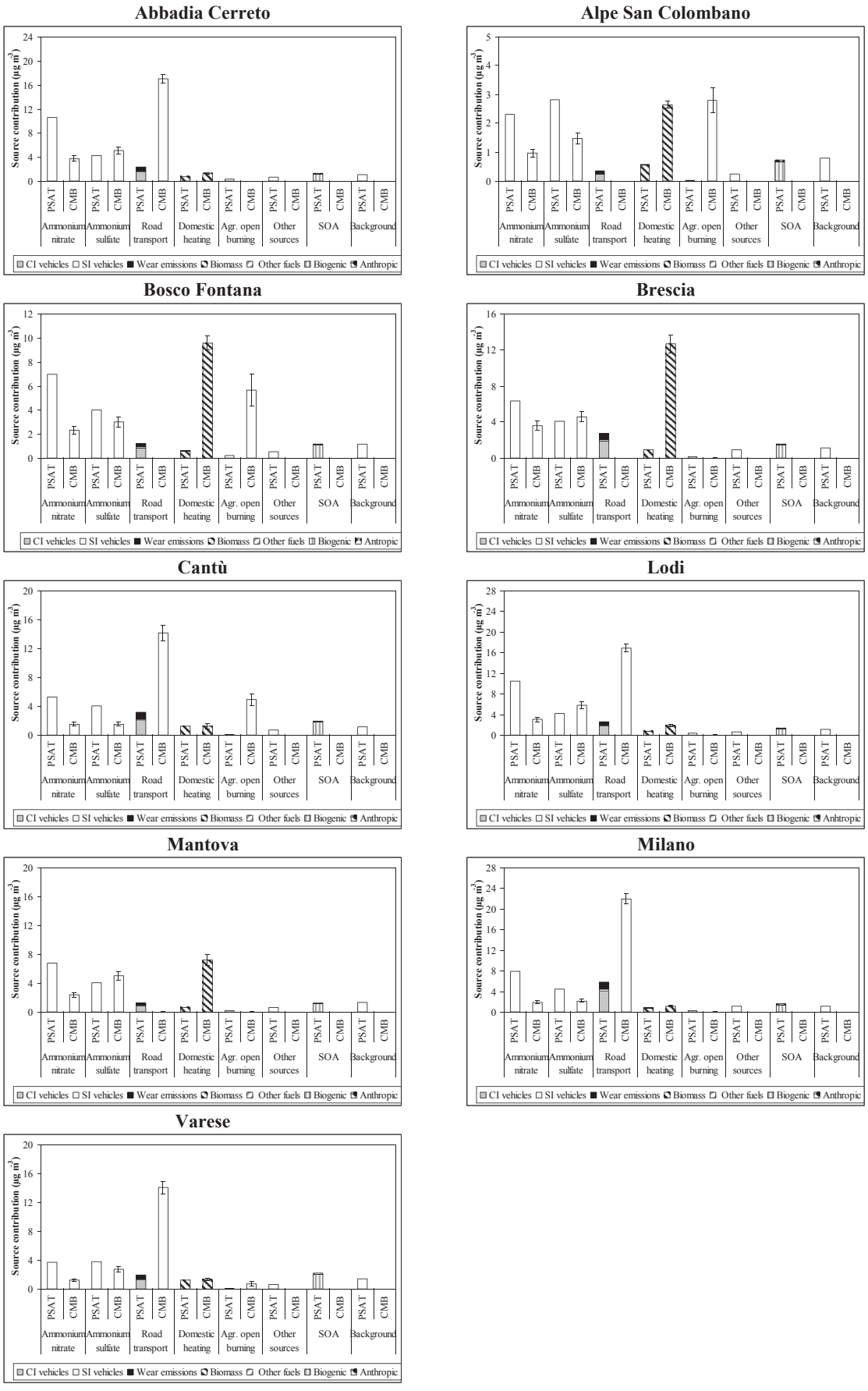


Fig. 9. Site by site comparison of PM2.5 SCEs at PARFIL sites in the warm season.

Table 5
Summary statistics (avg. ± st. dev.) of the seasonal SCEs to PM2.5 for sources commonly recognized by CMB and PSAT (warm season: normal typing; cold season: italic typing). Road transport source category includes both SI and CI vehicles as well as wear emissions contribution.

Source	Site-averaged SCEs ($\mu g\ m^{-3}$)		Site-by-site correlation
	CMB	PSAT	R
Ammonium sulphate	3.4 ± 1.8	4.0 ± 0.5	0.43
	3.2 ± 2.1	*3.6 ± 0.6*	*0.76*
Ammonium nitrate	2.3 ± 1.0	6.7 ± 2.8	0.80
	10.2 ± 6.2	*12.4 ± 4.6*	*0.96*
Road transport	9.4 ± 9.2	2.4 ± 1.6	0.73
	10.7 ± 10.1	*3.9 ± 2.7*	*0.73*
Domestic heating biomass burning	4.2 ± 4.5	0.8 ± 0.3	−0.22
	10.1 ± 10.6	*4.2 ± 1.2*	*0.10*
Agricultural open burning	1.6 ± 2.3	0.2 ± 0.1	−0.43
	1.4 ± 3.9	*0.3 ± 0.2*	*−0.44*

adopted EC/OC emission ratios need to be revised, particularly concerning diesel transport emissions that represent the most relevant contribution to EC emissions.

In the summer case it is less easy to establish whether CAMx underestimation is still mainly related to primary C or also involves secondary OC. Indeed, as shown by Gilardoni et al. (2011), during the warm season the primary fraction of C is around 33% of total carbon. However, a verification of this assumption would require very specialized observed data (e.g. AMS data) not available during the PARFIL campaign. Anyway, the subsequent analysis of source contribution, where CAMx SOA is evaluated, suggests that probably both fractions are partially underestimated. The qualitative results of the seasonal comparison of modelled and observed concentrations were further supported by additional analyses referring just to 2005 based on PM2.5 mass and composition data at Ispra site (Figure S.4) as well as at few PARFIL sites (Figure S.5 to S.9).

Even though the emission underestimation is likely the main reason for the discrepancies in modelled and observed PM2.5 levels during the cold season, the worsening in CAMx performance can be also related to the influence of meteorological fields. Actually, a slight positive bias in wind speed reconstruction was observed, mainly during the cold season (Figure S.10), thus explaining most of the CAMx low bias on PM concentration levels in winter (Figure S.11). Additionally, also the reconstruction of PBL height, particularly during the winter season, is a critical issue in the Po Valley (Pernigotti et al., 2012), as pointed out by some analysis on the daily cycle of the observed and modelled NO_2 concentration that suggests a too strong growth of PBL height during morning hours (Figure S.12).

3.3. CMB and PSAT source apportionment comparison

For comparison purpose the highly source-resolved results from PSAT were re-aggregated into the main source categories of residential heating (split by fuel), transport (split by engine type and wear source), agriculture, background (including natural sources and long-range transport), and other (essentially including stationary industrial sources), as indicated in the last column of Table 3. A comprehensive comparison of the SCEs for the sources commonly recognized by CMB and PSAT is provided by the scatterplot in Fig. 7; site by site comparisons of CMB and PSAT source apportionment results are provided by Figs. 8 and 9 for the cold and warm season, respectively; corresponding SCEs data are summarized in Table 5. For the cold season (October to March) the comparison of the source apportionment results was performed for eight sites only, since no PM2.5 monitored data for CMB analysis were available at the rural site of Bosco Fontana.

CMB source apportionment results solutions most frequently include four sources, but both 3-source and 5-source solutions were found. Contributions from the secondary inorganic sources (ammonium nitrate and ammonium sulphate) and from biomass burning for domestic heating are common to all the sites in both seasons (except ammonium sulphate in the cold season at Cantù site). The traffic source was recognized at all the urban sites except Mantova and Brescia, where CMB resulted in a 3-source solution.

Despite their statistically significant SCEs, these two latter 3-source solutions, totally missing the traffic contribution, look somewhat questionable, also in the light of the large under(over) estimation of the total PM2.5 mass. Likely, the source apportionment at these two sites missed the contribution of small, little PM-emitting industrial sources, furthermore without a peculiar source profile, as stated by the strong difference between observed and reconstructed elemental concentrations. As a consequence, for Mantova site CMB did not apportion about 30% of the total PM2.5 mass; conversely, for Brescia site CMB forced wood combustion for domestic heating up to its maximum seasonal contributions, thus over-reconstructing the PM2.5 mass.

CMB model proved unable to resolve the traffic source contributions by engine and fuel type, based on the three transport source profiles listed in Table 2, however recognizing the total traffic contribution based on a traffic composite profile obtained from the merge of those profiles. The background location of the sampling sites, the long-term average feature of the PM2.5 data, and the limited presence of light- and heavy-duty diesel vehicles in the urban fleet can justify such model outcome. SCEs from tyre and break wear, thus still associated with traffic, were only obtained for the urban traffic site (Varese) and for the most traffic exposed site (Lodi) among the urban background sites. The agricultural open burning source was recognized only at the rural and alpine sites, as well as at the suburban site in Cantù.

CMB and PSAT provided consistent SCEs for the secondary ionic sources: there is no statistically significant difference ($\alpha = 0.05$) between site-averaged SCEs for ammonium sulphate (both seasons) and for ammonium nitrate in the cold season; conversely, PSAT provided a significant overestimation for ammonium nitrate in the warm season. The models' agreement is also confirmed by the site-by-site comparison with generally small differences between SCEs and the coherent reproduction of their spatial distribution, as stated by R values (Table 5).

Interestingly, regardless for the high overestimation (PSAT estimates systematically about 3 times higher than CMB) the correlation between SCEs for ammonium nitrate is rather high in the warm season too ($R = 0.8$), further supporting the already recognized tendency of CAMx to overestimate the summer photochemical activity leading to nitrate formation. Conversely, as suggested by the low R value, PSAT estimates for ammonium sulphate contributions in summer are more uniform in space compared to CMB, whose estimates tend to be more site-specific, coherently with the features of the receptor-oriented approach

Table 6
Summary statistics (avg. ± st. dev.) of the seasonal SCEs to PM2.5 carbonaceous species for sources biomass burning in domestic heating and road transport sector. Road transport source category includes both SI and CI vehicles as well as wear emissions contribution.

Source	Species	Cold season		Warm season	
		CMB	PSAT	CMB	PSAT
Domestic heating biomass burning	EC ($\mu g\ m^{-3}$)	1.0 ± 1.1	1.2 ± 0.3	0.4 ± 0.4	0.2 ± 0.1
	OC ($\mu g\ m^{-3}$)	3.9 ± 4.1	1.4 ± 0.4	1.1 ± 1.1	0.3 ± 0.1
Road transport	EC ($\mu g\ m^{-3}$)	2.4 ± 1.4	2.7 ± 1.5	1.6 ± 0.8	1.7 ± 0.9
	OC ($\mu g\ m^{-3}$)	7.5 ± 3.8	0.8 ± 0.4	5.2 ± 1.8	0.5 ± 0.2

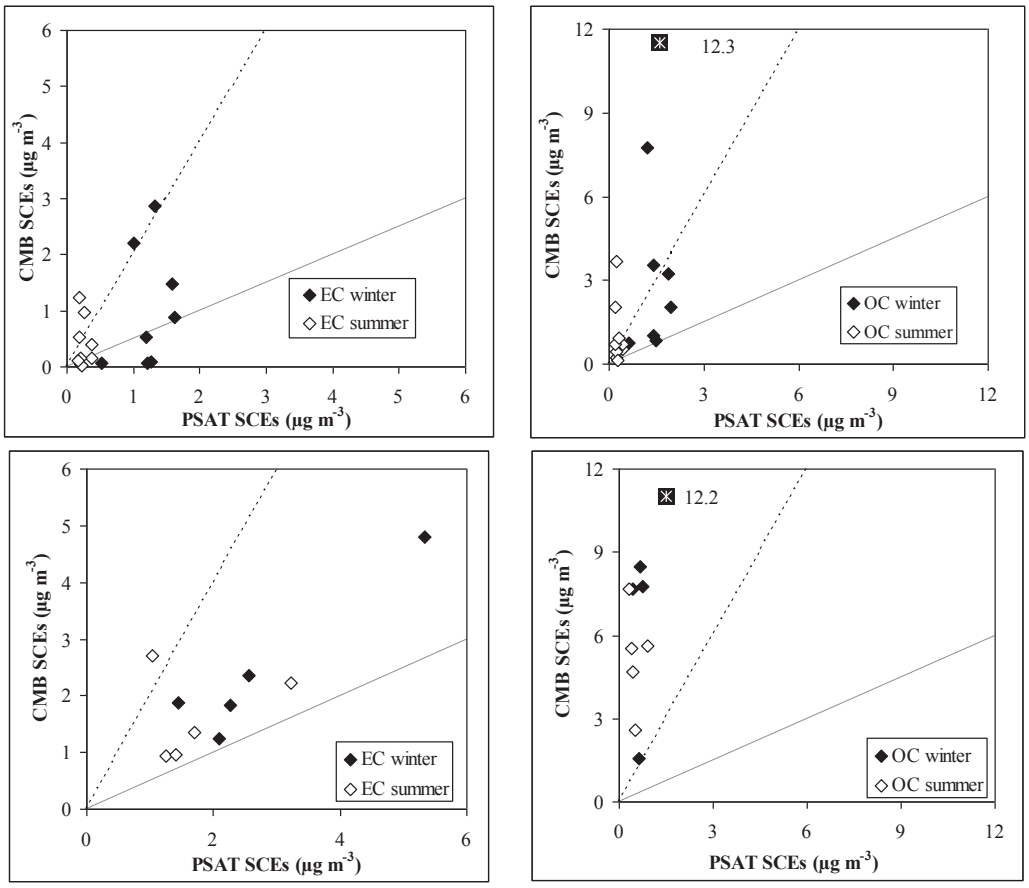


Fig. 10. Comparison of SCEs for PM2.5 carbonaceous species from the biomass burning in domestic heating (top panels) and road transport sector (bottom panels).

strongly linked to local environmental data.

Overall, CMB and PSAT results suggest that a robust assessment of the strength of the secondary sources is in the order of about 15 μg m^{-3} in wintertime and about 6 μg m^{-3} in summertime, without relevant variations between urban and rural sites, except for the Alpine site where the contributions of the secondary sources are at their minimum levels.

CMB and PSAT provided more contrasting results for road transport, domestic heating biomass burning and agricultural open burning sources, with discrepancies both related to SCEs values and to their spatial distribution.

For the road transport source CMB estimates a site-averaged contribution significantly higher than PSAT in both seasons (by a factor of 4 and 3 in the warm and cold season, respectively); however, such a larger average contribution is the result of both very large overestimations (up to a factor of about 8) and of underestimations at the three monitoring sites where CMB estimates a null contribution from road traffic (the previously mentioned Brescia and Mantova sites and the alpine remote site). The large standard deviations of CMB values clearly reflect the greater variability of the receptor model with respect to CAMx/PSAT modelling system; nevertheless, the R values suggest that CMB and PSAT reproduced the spatial variability of SCEs for road traffic according to a rather similar pattern.

For the domestic heating biomass burning source considerations similar to those concerning the road traffic source hold. CMB still estimated a site-averaged contribution significantly higher than PSAT in the warm season (by a factor of 4) and about 2.5 times higher in the cold season; neglecting SCEs for Brescia and Mantova site, where unlikely huge contributions are computed by CMB, the difference between the site-averaged contributions is consistently reduced and non-significant, but still with CMB values respectively about 3 and 1.25 times higher than PSAT estimated source contributions. Site-by-site analysis showed large differences also for the rural site in Bosco Fontana (9.6 μg m^{-3} vs. 0.6 μg m^{-3}) in the warm season and for the urban background site in Lodi (12.4 μg m^{-3} vs. 4.1) in the cold season; in all the other cases, the models provided much closer contributions, with SCE values of few μg m^{-3} in the warm season and in the 2–7 μg m^{-3} range in the cold season. However, even for these latter seasonal subsets, the models resulted in quite different spatial patterns for SCEs from domestic heating biomass burning, with CMB values displaying a stronger intersite variability compared to PSAT. Contributions from the consumption of fuels other than biomass resulted almost negligible according to PSAT values.

For agricultural open burning source the two models performed very differently, both in terms of the site-averaged SCE (still with CMB higher than PSAT) and especially in terms of site specific SCEs, with a strong difference in the SCEs spatial pattern, stated by the low (and even negative) R value and large discrepancies in the SCEs values.

Actually, while PSAT apportioned to this source only a small fraction of PM2.5 (few tenths of μg m^{-3} up to 0.5 μg m^{-3}) at all the sites, thus including urban sites too, CMB apportioned a more consistent fraction (few μg m^{-3}) essentially at the rural and at the remote alpine site, conversely estimating null contributions at the urban sites with the only relevant exception of Cantù, where contributions of 4.9 μg m^{-3} and 11.1 μg m^{-3} are estimated for the warm

and cold season respectively. Likely, this latter result finds explanation with the local presence of a large number of small-sized enterprises working in the field of wood furniture manufacturing: uncontrolled emissions from wood scrap burning and/or emissions from traditional stoves fed with wood manufacturing residuals for workplace heating, might have been misrecognized by CMB. The cold/warm season ratio in the same order of those found for domestic heating SCEs further supports this explanation.

Figs. 8 and 9 also report PSAT estimates for sources not recognized by CMB, namely stationary industrial combustion sources (labelled as "other sources"), background (natural sources and long-range transport), and SOA; overall, these sources account for a total contribution to PM2.5 mass in the order of 2–4 $\mu g\ m^{-3}$.

Combustion sources SCEs are in the 0.6–1.1 $\mu g\ m^{-3}$ range in the warm season and in the 1.0–2.3 $\mu g\ m^{-3}$ range in the cold season, respectively; however, much lower contributions (0.2 $\mu g\ m^{-3}$ and 0.3 $\mu g\ m^{-3}$) were computed for the remote alpine site. Background contributions are in the 0.3–0.7 $\mu g\ m^{-3}$ range in the warm season and about two times higher (0.8–1.4 $\mu g\ m^{-3}$ range) in the warm season, as from both enhanced biogenic emission rates and transboundary transport. The specific feature of the alpine remote site, namely its wintertime position over the mixing layer, is particularly highlighted by the lowest value for the background contribution (0.3 $\mu g\ \ m^{-3}$) compared to the rural and urban sites (0.5–0.7 $\mu g\ m^{-3}$) in the plain part of the region. Background SCEs do not account for the biogenic organic aerosols produced within the domain, since SOA contributions are separately estimated by CAMx. Overall SCEs for SOA are in the 0.7–2.2 $\mu g\ m^{-3}$ range in the warm season and in the 0.1–0.5 $\mu g\ m^{-3}$ range in the cold season, still with the minimum values for the alpine remote site; as for the background contributions, the seasonal difference is statistically significant. However, the model is able to split SOA SCEs between the share deriving from biogenic precursors (isoprene, terpenes, sesquiterpenes) and from anthropogenic precursors (benzene, toluene, semi-volatile VOCs), the former largely prevailing since accounting for 90% of total SOA in summertime and 70% in wintertime.

3.4. Carbonaceous species apportionment comparison

The discrepancies between SA results for the road transport and domestic heating source, in which carbonaceous species (namely, OC) are an important component of the PM2.5 emission, were further investigated focussing on the sector-resolved SCEs to EC and OC.

For a proper comparison with CMB data, primary organic matter (OM) contributions estimated by PSAT were converted to primary organic carbon (OC) using source-specific OM/OC ratios (Fujita et al., 2009). In this work a 1.6 ratio was used for the road trans-port source and a 1.8 was used for biomass burning for domestic heating. Both models provide higher contributions to EC and OC for the cold season; however, whilst for the road transport source the cold/warm season ratios are about 1.5, for the biomass burning source the ratios are much larger, with CMB resulting in a 2.5 (EC) and a 3.7 (OC) ratio and with PSAT up to 5 for both species (Table 6). On the average, road transport contribution to EC is twice as high as domestic heating contribution; the opposite occurs for OC. Site-by-site SCEs to EC and OC from transport source and biomass burning for domestic heating are compared in the scatter plots of Fig. 10.

For the road transport source CMB and PSAT provided comparable SCEs for EC in both seasons, with values mostly in the 1–3 $\mu g\ m^{-3}$ range and rather well correlated overall ($R = 0.8$). Conversely, for OC the SCEs from PSAT (0.4–1.5 $\mu g\ m^{-3}$ range) are always more than 50% lower than those from CMB (1.5–12.2 $\mu g\ m^{-3}$ range), but up to 90% for some of the cold season estimates.

For the biomass burning source SCEs for EC are rather scattered, in the 0.1–2.9 $\mu g\ m^{-3}$ range for CMB and 0.2–1.3 $\mu g\ m^{-3}$ range for PSAT, without a clear over/underestimating pattern but with a site-related bias insensitive to seasonality: PSAT largely overpredicts CMB at Milano Pascal and Abbadia Cerreto in both season whilst the opposite occurs for Mantova and Brescia. For OC the comparison highlights a substantial agreement in both seasons, though SCEs from CMB (0.2–12.3 $\mu g\ m^{-3}$ range) are generally about twice as high as PSAT results (0.2–1.9 $\mu g\ m^{-3}$ range). The largest discrepancies occur at Brescia (12.3 vs. 1.6 $\mu g\ m^{-3}$) and Mantova site (7.7 vs. 1.2 $\mu g\ m^{-3}$) in the cold season, where CMB apportionment is strongly offset towards domestic heating as a consequence of the missing road transport source.

These results provided a rather consistent SCEs for EC from the two approaches, especially for the road traffic source, stating the reliability of emission inventory data. Furthermore, the seasonal patterns of the SCEs properly reflect the lower atmospheric dispersion potential in the cold season affecting road traffic contribution to EC and the combined effect of the cold season meteorological conditions and of the source activity rate for biomass burning in domestic heating contribution.

Conversely, significant differences affected SCEs for OC; this is not surprising given the combined primary and secondary origin of OC, with chemical transformation processes making dispersion modelling calculations more complicated than for the primary species like EC. The EC/OC concentration ratio showed by CAMx reflects the corresponding EC/OC emission ratio adopted by CAMx for the two sources, This result is reasonable as CAMx/PSAT contribution to the carbonaceous fraction for these two sources accounts just for primary carbon, being SOA apportioned as a specific source. Differently, CMB was not able to split the OC concentration between primary and secondary contribution. This result thus states that most of the CAMx deficiency in reproducing winter OC relies on the description of the road transport emission processes. Discrepancies between CMB and CAMx/PSAT apportionment for carbon from the traffic source were reported for urban and rural sites in the United States (Lane et al., 2007; Morris et al., 2009), with the lower carbon contribution from traffic estimated by PSAT justified by deficiencies in both OC and semi-volatile OC emissions in the inventory data.

4. Conclusions

The comparison of CMB and CAMx/PSAT source apportionment approaches for PM2.5 at 9 sites in Lombardy provided useful insight into both methods and also helped in investigating the robustness of the resulting SCEs.

Accordingly with its conceptual bases, CMB showed a better reconstruction of the PM2.5 mass closure; conversely, CAMx suffered from inaccuracies in emission inventory data and meteorological fields reconstruction, systematically underestimating PM concentrations especially during the severe episodes in the cold season.

Nevertheless, both models provided the same ranking for SCEs at several receptors, with a general agreement in the reconstruction of secondary inorganic aerosol contributions and the most relevant discrepancies related to road transport and domestic heating.

CMB showed some troubles with the apportionment of emission from biomass combustion processes and provided rather questionable results at two urban receptors for the cold season, not identifying the road transport contribution, that, conversely, was clearly pointed out by CAMx/PSAT. These findings confirmed the usefulness of a combined RM and CTM approach, that proved to be helpful in both evaluating and explaining the obtained results.

Additionally, CMB proved unable to resolve the traffic source

contributions by engine and fuel type, simply recognizing the total traffic contribution. These weakness of the CMB approach may be ascribed either to the peculiar features of the environmental dataset, formed by aggregated seasonal data that impaired the use of other SA algorithms, like those based on multivariate analysis, or to the source profiles, despite the use of local profiles for some sources, or to the combination of both these reasons. For the traffic source, the urban background location of the sampling sites, the long-term average feature of PM2.5 data, the limited presence of light- and heavy-duty diesel vehicles in the urban fleet can justify such model outcome. However, road traffic profiles are a critical issue, also in the light of the rather fast evolution of the circulating fleet: effort in order to build local inventory of source profiles, frequently revised and updated, is one of the suggestions coming from this work.

An accurate definition of the source profiles represents a key point also for CTMs, particularly in the framework of source apportionment studies. However it is important to notice that CMB models make use of the source profile concept to describe the source fingerprint at the receptor, while CTMs adopt emission speciation profiles to split PM emissions into single chemical species. The two information overlap in case of non-reactive species, while they can differ a lot in case of secondary organic species. This incongruity must be taken into account when the contribution of a secondary source is not clearly identified by CMB approach, as highlighted by the case of OC in this study.

Separately simulating the dispersion from the various sources CAMx/PSAT could distinguish the contribution of sources sharing similar profiles and strongly correlated, such as spark and compression ignition vehicles. CAMx/PSAT could also identify the contribution of secondary PM deriving from complex chemical transformation, such as anthropogenic and biogenic SOA, and allowed identifying and quantifying the strength of sources not characterized by a clear emission pattern, such as mixed anthropogenic activities, or related to different emission areas, such as the long range transport burden.

However, in addition to PM2.5 mass underestimation, CAMx/PSAT experienced some troubles with the reconstruction of carbonaceous species, with OC rather systematically underestimated at all sites, especially during winter season. While the two approaches provided rather consistent SCEs for EC, significant differences affected SCEs for OC, with CAMx/PSAT missing the road transport contribution to OC, mostly as a consequence of deficiencies in the emission inventories concerning the primary OC from traffic in the cold season and of the concurrent underestimation of both primary emission, including the emission of semivolatile organic carbon, and secondary OC formation, due to the still high degree of uncertainty in the reconstruction of SOA processes, in the warm season.

These latter results also pointed that the availability of very specialized observed data able to provide additional information about the origin and the transformation pathway of the PM compounds, with particular reference to the carbonaceous fraction would allow a more accurate verification of SCEs from both CTMs and RMs.

Conflicts of interest

The authors disclose any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

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Appendix A. Supplementary data

Supplementary data related to this article can be found on line.

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