Atmospheric Environment: X 2 (2019) 100020

Contents lists available at ScienceDirect

Atmospheric Environment: X

journal homepage: www.journals.elsevier.com/atmospheric-environment-x

Enhanced CAMx source apportionment analysis at an urban receptor in Milan based on source categories and emission regions

N. Pepe[b,*], G. Pirovano[a], A. Balzarini[a], A. Toppetti[a], G.M. Riva[a], F. Amato[c], G. Lonati[b]

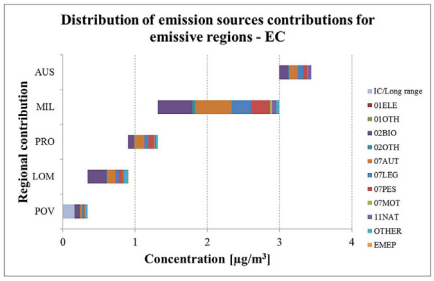
[a] RSE Spa, via Rubattino 54, 20134, Milano, Italy
[b] Department of Civil and Environmental Engineering, Politecnico di Milano, 20133, Milano, Italy
[c] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), 08034, Barcelona, Spain

HIGHLIGHTS

- Concurrent source apportionment by source regions and categories at an urban receptor.
- Source apportionment of total, primary and secondary PM, and gaseous NO_2.
- Agreement between CAMx/PSAT and PMF receptor model results for $PM_{2.5}$

GRAPHICAL ABSTRACT

Fig. 1. EC Regional absolute concentration distribution of each source activity contribution and emissive region defined within CAMx/PSAT approach. Long range transport term has been stacked with POV region contributions.



ARTICLE INFO

Keywords:
Source apportionment
CAMx
PSAT
Emission regions
Milan
Po valley

ABSTRACT

Source apportionment results from CAMx/PSAT v6.3 model simulation at an urban receptor placed in Milan city centre are presented. CAMx was run over a domain covering the Po valley for the calendar year of 2010. Model simulations considered nitrogen dioxide (NO_2), fine particulate matter ($PM_{2.5}$), and its primary and secondary components, i.e.: elemental carbon (EC) and nitrate (NO_3^-). Source apportionment results are separately reported with respect to emission regions (e.g.: local, urban, metropolitan areas, counties) and emission categories (e.g.: transport, space heating, industrial activities) and to the combination of emission regions and categories. Five emission regions were considered, starting from a narrow region covering Milan city centre, up to Milan municipality, Milan metropolitan area, Lombardy region, and to the entire Po valley. In terms of emission region contributions, Milan municipality, its metropolitan area, and Lombardy region account for about 60% of $PM_{2.5}$ total mass at the selected receptor. However, local scale emissions contribute for more than 50% to EC ambient levels at this receptor. Conversely, the sources located in the farthest emission regions (Lombardy and Po valley) and long range transport determine the largest contribution (80%) to NO_3^- concentration. For NO_2, local scale emissions are responsible for more than 60% of the ambient concentration levels in Milan city centre. In terms of source categories, traffic is the main contributor to NO_2 and NO_3^-, biomass burning and traffic to EC and $PM_{2.5}$ mass. The emission categories contributions to $PM_{2.5}$ estimated by CAMx/PSAT for the selected receptor show a rather good agreement with Positive Matrix Factorization (PMF) source apportionment results available for Milan area. However, the two approaches provide similar estimations only for biomass burning and traffic contributions (24% and 20%, respectively) whereas CAMx gives remarkably lower estimates for the share of secondary organic aerosol (SOA), likely because of missing formation processes in CAMx chemical module.

* Corresponding author. Via Gian Giacomo Gilino 9, 20128, Milano, Italy.
E-mail address: nicola.pepe@polimi.it (N. Pepe).

https://doi.org/10.1016/j.aeaoa.2019.100020
Received 24 April 2018; Received in revised form 28 December 2018; Accepted 30 January 2019
Available online 19 February 2019

1. Introduction

Air quality represents a significant public health problem because of the negative impacts on respiratory and cardiovascular health and of premature deaths as a result of exposure to ambient air pollutants (Kelly and Fussel, 2015; WHO, 2013). Globally, air pollution is estimated to cause 4.2 million deaths every year and 91% of the world's population lives in places where air quality exceeds WHO guideline limits (WHO, 2016). Low- and middle-income countries experience the highest burden, but air quality is still an issue in the big cities and rural areas of the developed countries. Policies and investments supporting emission control strategies, combined with technological progress, can effectively reduce air pollution levels.

Specifically, quantifying the contribution of different emission categories (e.g.: transport, space heating, industrial activities) and emission regions (e.g.: local, urban, metropolitan areas, counties) to air pollution is critical for the further implementation of effective environmental policies. This type of analysis, known as source apportionment (SA), is indicated in the 2008/50/EC European air quality directive as a tool to investigate and support emission control strategies.

SA can be performed either through Receptor Models (RM), that is analyzing direct observations from an air quality station, or through Chemical Transport Models (CTM), using pollution concentrations simulated by model runs. RM techniques are widely used to estimate the contributions of the emission sources to the concentration levels of particulate matter (PM) and its components (Belis et al., 2013). RMs mainly rely on the following three statistical techniques: principal component analysis (PCA), chemical mass balance (CMB), and positive matrix factorization (PMF) (Hopke, 2016; Belis et al., 2014). Although these techniques produce relevant insights for the implementation of environmental strategies, they present some weaknesses:

- RMs are mostly suitable for particulate matter (e.g PM_{10} and $PM_{2.5}$), while the detection of source contributions for other pollutants (e.g. NO_2, SO_2) would be less straightforward (Belis et al., 2013).
- even though relying on detailed data for PM chemical composition, RMs present limited capacities to track the origin of secondary PM, whose precursors are often emitted by a wide range of sources (Belis et al., 2013, 2015).
- the location of the emission sources can be only partially detected and the apportionment to specific sources is generally more effective when their emissions present a peculiar chemical profile. Contrary, RMs results need to be supported by further piece of information on meteorological conditions (e.g.: wind roses or back trajectories analysis, Belis et al., 2014).
- SA analysis conducted by RMs is site-dependent and SA outcomes are valid only near the receptor point. Necessarily, further measurement campaigns need to be performed in order to track emission contributions over larger areas.

Alternatively to RMs, CTMs are widely used to conduct SA analyses. In particular, CTMs like CAMx (Ciarelli et al., 2017; Karamchandani et al., 2017; Wang et al., 2017b), CMAQ (Buonocore et al., 2014; Zhang et al., 2014; Appel et al., 2013) and LOTOS-EUROS (Hamm et al., 2015; Curier et al., 2014; Mues et al., 2014) include specific tools enabling source apportionment analysis. However, similarly to RMs, CTMs present some limitations:

- model reliability strongly depends on emission inventories' accuracy, in turn depending on both emission factors, activity data, and spatial resolution (López-Aparicio et al., 2017; Denier Van Der Gon et al., 2015; Guevara et al., 2014).
- extensive datasets of meteorological data, either from diagnostic or prognostic meteorological models, are required for a proper reconstruction of air masses motion and pollutant transport and diffusion (Bessagnet et al., 2016; Pernigotti et al., 2012).
- secondary organic aerosols (SOA) are generally hardly simulated and often strongly underestimated (Meroni et al., 2017; Bergstrom et al., 2012).

In this work, SA analysis have been performed through the CAMx model (Comprehensive Air Quality Model with Extensions, ENVIRON, 2016), which comprises an embedded SA algorithm, PSAT (Yarwood et al., 2004), able to track the contribution of different user defined emission categories and regions (Pirovano et al., 2015; Bedogni and Pirovano, 2011). CAMx is applied over nested domains covering Northern Italy and Milan urban area, while SA through CAMx/PSAT is focused on an urban receptor point located in Milan city centre. Model simulations were performed for the entire 2010 calendar year. SA analysis focuses on fine particulate mass ($PM_{2.5}$) and on nitrogen dioxide (NO_2), whose compliance with the current air quality limits is a critical issue in Northern Italy and Milan area. Additionally, SA was also performed for one of both primary and secondary PM2.5 components, namely elemental carbon (EC) and particulate nitrate (NO_3^-).

The multi-pollutant feature of this work, together with the combination of emission categories and regions in SA analyses, thus splitting the estimated contributions of emission sources based on their geographical location, make it quite a novelty in the context of CTM-based SA studies in literature. For example, Bove et al. (2014) performed CAMx simulations with the aim of quantifying source contributions for $PM_{2.5}$ for the city of Genova (Italy) and Ciarelli et al. (2017) focused on the SA of SOA over Europe through CAMx, but they both did not account for the location of the sources. Conversely, Kim et al. (2017) and Wang Y. et al. (2017) applied CAMx-PSAT to quantify the impacts of emissions from different regions on PM concentrations during a high PM event in Seoul and for haze episodes in Beijing, but without investigating source contributions. Combined source region and source category apportionment of $PM_{2.5}$ have been performed by Timmermans et al. (2017) for the cities of Beijing and Shanghai and by Li et al. (2015) for the Beijing-Tianjin-Hebei region; however, both these works were focused on fine PM only.

The paper firstly describes the setup of the modelling chain, the computational domains, and input data. CAMx skills in capturing $PM_{2.5}$ and NO_2 concentrations over Northern Italy are shown relative to direct observations from an air quality monitoring network including urban, suburban and rural stations. SA results for $PM_{2.5}$, EC, NO_3^-, and NO_2 annual mean concentrations are then presented and discussed. Finally, CAMx/PSAT results for PM2.5 at the Milan receptor are compared with SA outcomes from PMF receptor modelling based on $PM_{2.5}$ speciated data collected during an air quality monitoring campaign performed in Milan. Strengths and weaknesses of both SA approaches for Milan receptor are illustrated.

2. Methods

2.1. Modelling chain setup

The modelling chain used for the source apportionment analysis is composed by two main components: the Weather Research and Forecasting (WRF; Skamarock et al., 2008) model version 3.4.1 and the Comprehensive Air Quality Model (CAMx) model version 6.30 (ENVIRON, 2016). The modelling system setup, which includes the Sparse Matrix Operator for Kernel Emissions model version 3.5 (SMOKE; UNC, 2013), is detailed in Supplementary Material (SM)

Figure S1. Meteorological fields were reconstructed by WRF which was setup with 30 vertical layers, spanning from 25 m above the ground up to 15 km. Horizontally, four nested grids adopting a Lambert Conformal Projection and covering Europe, Italy, Po valley, and the metropolitan area of Milan have been used; grid resolutions are 45 km, 15 km, 5 km and 1.7 km, respectively (SM Figure S 2). WRF was driven by ECMWF analysis fields every 6 h. Air quality simulations and source apportionment analysis were based on CAMx simulations covering the two innermost domains (Po valley and Milan metropolitan area, Fig. 1). CAMx was run at the same spatial resolution of WRF, but with a slight reduction of the domain size in order to remove boundary effects. Details on WRF and CAMx domains are showed in SM Table S.1. The vertical structure of CAMx domain was divided into vertical layers, keeping the same vertical resolution of WRF up to 1 km above ground level.

Emissions were input from inventory data at three different spatial resolution levels: European Monitoring and Evaluation Programme data (EMEP, http://www.ceip.at/emission-data-webdab/emissions-used-in-emep-models/) available over a regular grid of 50 × 50 km^2; ISPRA Italian national inventory data (http://www.sinanet.isprambiente.it/it/sia-ispra/inventaria/disaggregazione-dellinventario-nazionale-2010) which provides a disaggregation for province; regional inventories data based on INEMAR methodology (INEMAR – ARPA Lombardia, 2015) for the administrative regions of Lombardy, Veneto and Piedmont, which provide detailed emissions data at single municipality level. Each emission inventory was processed using the SMOKE model in order to

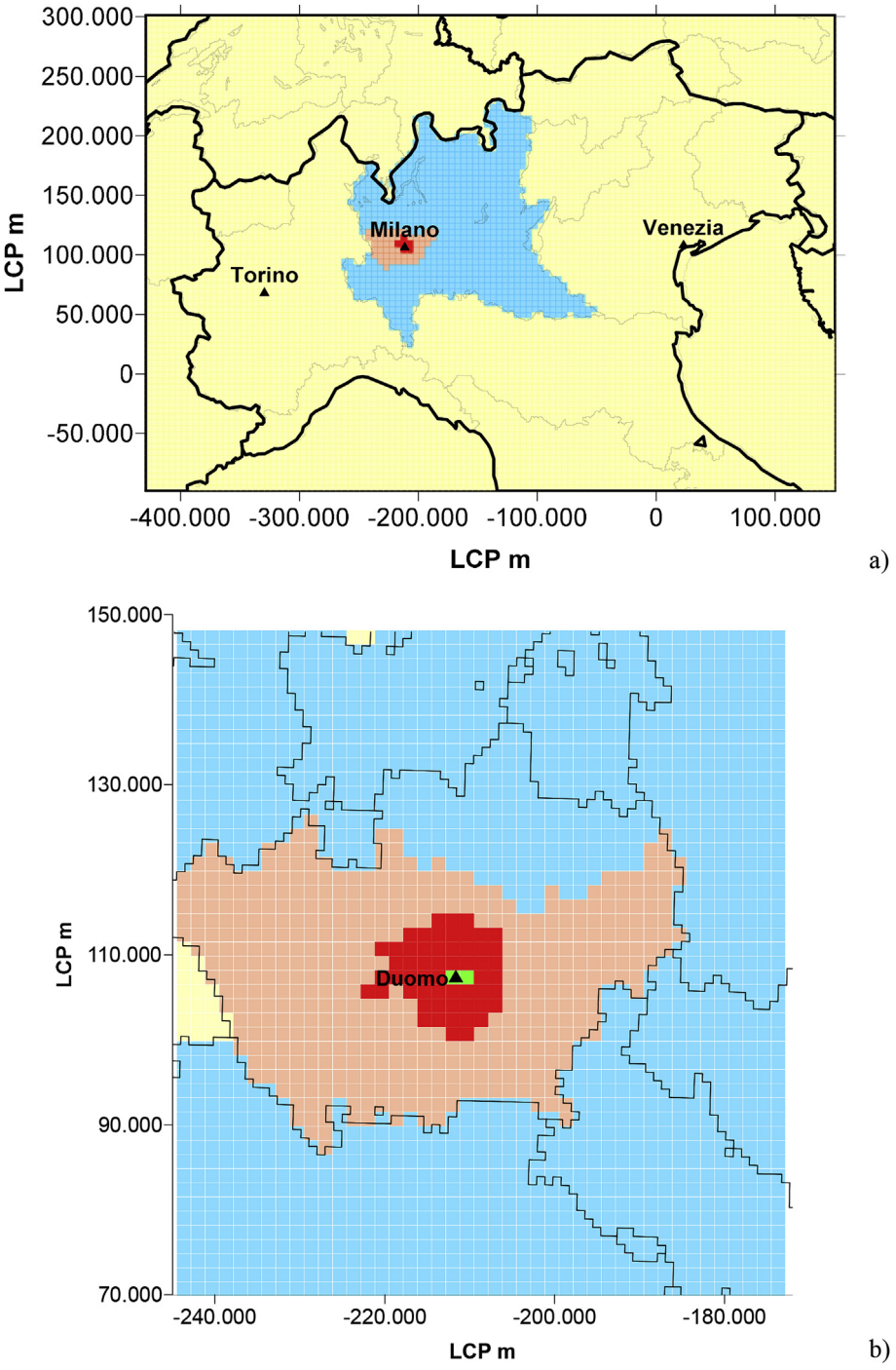


Fig. 1. Emission regions within Po valley (POV, 5 km grid step, a)) and Milan metropolitan area (MIL, 1.7 km grid step, b)) computational domains.

obtain the hourly time pattern of the emissions. Most relevant sources (e.g.: power plant stacks) were considered as elevated point sources with a specific quantification of the emission plume rise. Differently, all other sources were placed in the first vertical layer of CAMx domain. Temporal disaggregation was based on monthly, daily and hourly profiles deducted by CHIMERE model (INERIS, 2006) and EMEP model from Institute of Energy Economics and the Rational Use of Energy (IER) project named GENEMIS (Pernigotti et al., 2013). Details on meteorological and emissions input data and chemical schemes adopted for this work are reported in Pepe et al. (2016), together with the model validation phase for calendar year 2010 comparing model results with measurements at meteorological and air quality stations.

2.2. Emission regions and emission categories

In order to track the impact on air quality at Milan receptor of the emissions from different areas of Northern Italy we defined five emission regions over the Po valley computational domain, reflecting the concept of local, urban background and regional emission regions (see for example: Lenschow et al., 2001; Annex I(I) of European Commission decision 2011/850/EU). The definition of such emission regions was constrained to administrative boundaries in order to clearly link the pollution contribution to the corresponding administrative level (i.e.: municipality, metropolitan area, region, country). The emission regions are shown with different colors in Fig. 1.

The wider area in yellow, named Po valley (POV), includes all sources outside the Lombardy region; in blue, the Lombardy area (LOM), extending from the boundaries of Lombardy to those of the metropolitan area of Milan (formerly Province of Milan); in orange, the metropolitan area of Milan (PRO), except the municipality of Milan (MIL) which is indicated by the red area in Fig. 1a. The fifth area, the green one in Fig. 1b, represents a very local emission region within the Milan city centre (AUS) where the receptor considered for the SA analysis is located.

Accordingly to Lenschow's definition (Lenschow et al., 2001), emissions from POV and LOM regions are responsible for the regional background concentration level, those from PRO and MIL regions are responsible for the urban background, those from the smallest region determine the very local contribution to the ambient concentration levels in the centre of Milan. Such a local contribution does not represent a street level contribution, because it cannot be handled by a gridded model, but it takes into account the smallest and closest emission region that can be defined with respect to the selected receptor.

Finally, it is worth noticing that emission data for the emission regions closer to the Milan receptor (LOM, PRO, MIL, AUS) come from the same emission inventory, (i.e. the INEMAR inventory of Lombardy region), which provides data at municipality level resolution. Thus, any relevant inconsistency on SA results, potentially caused by the different spatial resolution of the emission inventories available for this study, is avoided.

Together with the five emission regions we defined the 11 emission categories listed in Table 1.

These categories comprise the main sources which generally affect the air quality in the Po valley. In particular, we defined two emission groups for industrial plants, divided into electricity production (01 ELE) and no electricity production (01 OTH), and two emission groups for residential heating based on the kind of fuel (02 BIO, 02 OTH) in order to separate the biomass burning impact on air quality, which is typically interesting for the Alpine regions. However, according to national emission inventories, biomass burning is a relevant source also within the urban context of Milan. The road transport source was split into four categories: cars, light and heavy duty vehicles, mopeds and motorcycles. The natural sources such as fires and sea salt are indicated as 11 NAT; the latter is considered only for the Po valley area. The OTHER SECTORS category includes all other anthropogenic sources within the Italian boundaries but not explicitly tracked in the previous categories, such as agriculture, waste treatment, landfill management and other transport modes, as shipping or aviation. The EMEP category accounts for the contribution of the transboundary sources located outside Italian boundaries but included in the Po valley computational domain of Fig. 1a. An additional emission category, not listed in Table 1, is the "Long range transport", representing all contributions due to the emissions of sources located outside the computational domain that get in from the lateral boundaries and from the top of the domain (Boundary Conditions – BC and Initial Conditions IC).

3. CAMx performance evaluation

CAMx performance was separately evaluated over both POV and MIL domains, based on NO_2 and $PM_{2.5}$ data for 2010 provided by the stations of regional air quality networks. In particular, NO_2 and $PM_{2.5}$ data sets were composed by 144 and 40 urban and suburban stations, respectively. Fig. 2 illustrates the comparison between CAMx output (orange line) and monitored data (black line) for the daily average concentrations of NO_2 and $PM_{2.5}$ over the Po valley domain. CAMx shows a systematic underestimation of NO_2 concentration during the whole year, that becomes more pronounced in the winter months (January–February and December). Similarly, the model underestimates $PM_{2.5}$ in the winter months, but shows a better performance in the other months. Table 2 and Table 3 summarize the values of the model performance indicators (see their list and definitions in SM), separately computed for NO_2 and $PM_{2.5}$ over the two domains. Mean relative bias for NO_2 and for $PM_{2.5}$ is about -40% and -34% over the POV domain and about -22% and -30% over the MIL domain. Correlation and index of agreement for hourly NO_2 concentrations are rather weak over both the domains, pointing out the troubles of CAMx also in reproducing the seasonal and weekly time patterns of the observed concentrations. Simulation results for daily $PM_{2.5}$ concentrations show better correlation and agreement, with no relevant differences between the two computational domains. Actually, CAMx was able to correctly capture the temporal evolution of $PM_{2.5}$ from early spring to late fall but missed several severe episodes that took place in the winter months. CAMx performance improved at rural stations (Tables S2-S3, Figure S3), suggesting that some of the discrepancies observed at urban and suburban sites can be ascribed to local scale sources, whose influence cannot be reproduced at the adopted spatial resolution, particularly with the larger grid step used over the POV domain.

The difficulty of the model in reproducing NO_2 and $PM_{2.5}$ peak concentrations is clearly highlighted by the increasing gap between the percentiles of the modelled and observed time series that become larger and larger in the upper tail of the distribution, as reported in Fig. 2. The origin of CAMx underestimation was extensively discussed in Pepe et al.

Table 1
Emission categories defined for CAMx/PSAT application.

Label	*Description*
01 ELE	Electrical energy production by industrial plants
01 OTH	Industrial plants (no electrical energy production)
02 BIO	Residential and commercial heating with biomass
02 OTH	Residential and commercial heating with fossil fuels (no biomass)
07 AUT	Passenger cars
07 LEG	Light duty vehicles (weight < 3.5 tons)
07 PES	Heavy duty vehicles (weight > 3.5 tons)
07 MOT	Mopeds and motorcycles
11 NAT	Natural sources: fires, volcanic eruptions, marine salt (only for Po valley area)
EMEP	All sources located outside Italy (no disaggregation on emission sources is provided)
OTHER SECTORS	Other anthropogenic sources: agriculture, waste treatment, landfill, off-road transports

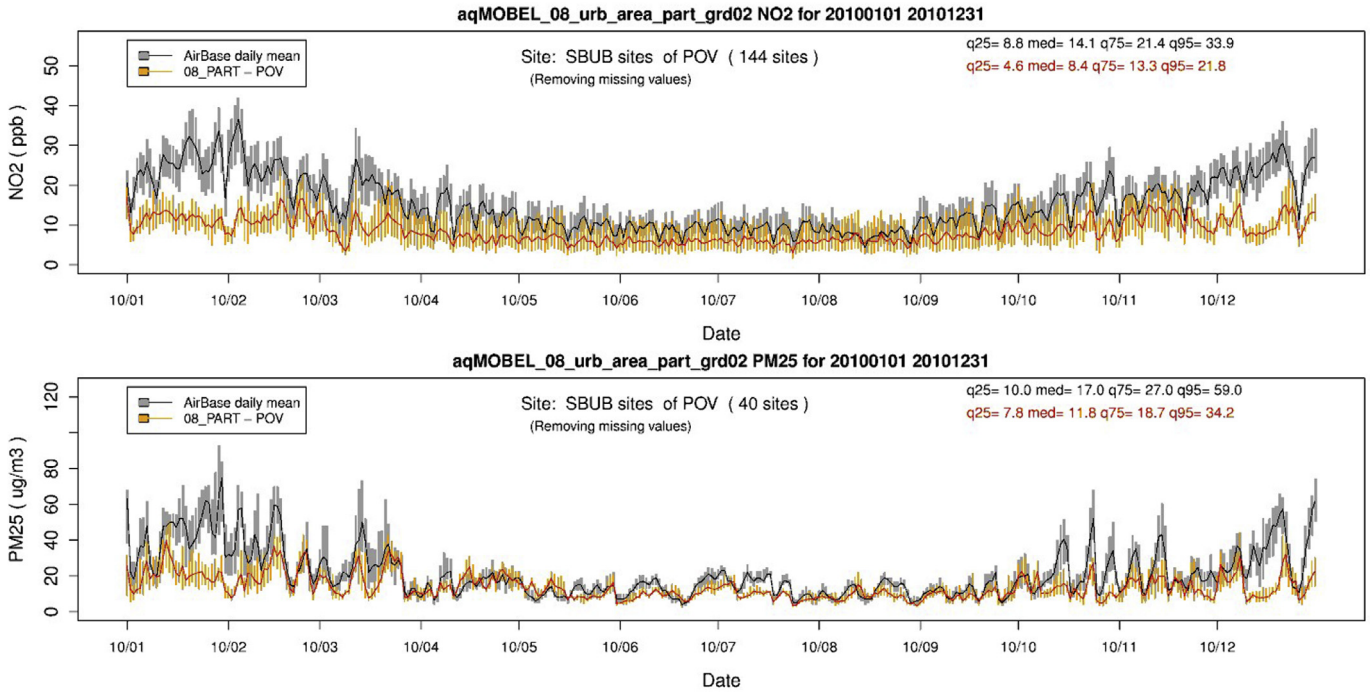


Fig. 2. Time series of the box plots for the distribution of the observed (black/grey) and computed (red/orange) values of NO_2 and $PM_{2.5}$ daily concentrations at respectively 144 and 40 air quality network sites, computed over the POV and MIL domains for 2010. Bars show the interquartile range (25^{th}-75th) and lines the median values. Values for the 25th, 50^{th}, 75th, and 95th quantiles of the whole yearly time series are reported too. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2
CAMx model performance for NO_2 hourly concentrations computed for 2010 at Urban and Suburban air quality stations of POV and MIL domain.

	POV domain		*MIL domain*	
	Observations	Model	Observations	Model
Mean [ppbV]	16.2	9.7	19.8	15.5
Standard Deviation [ppbV]	11.8	8.3	14.0	9.8
Number Observations [-]	11659117		238321	
Correlation [-]	0.39		0.33	
Mean Bias [ppbV]	- 6.4		- 4.4	
Mean Error [ppbV]	9.5		10.7	
Index of Agreement [-]	0.59		0.57	
RMSE [ppbV]	13.14		14.8	

Table 3
CAMx model performance for $PM_{2.5}$ daily concentrations computed for 2010 at Urban and Suburban air quality stations of POV and MIL domain.

	POV domain		*MIL domain*	
	Observations	Model	Observations	Model
Mean [μg/m^3]	22.0	14.6	27.3	19.1
Standard Deviation [μg/m^3]	16.9	9.7	19.9	11.2
Number Observations [-]	12890		2369	
Correlation [-]	0.54		0.52	
Mean Bias [μg/m^3]	- 7.4		- 8.2	
Mean Error [μg/m^3]	10.5		12.6	
Index of Agreement [-]	0.64		0.63	
RMSE [μg/m^3]	16.1		18.8	

(2016) with particular reference to the influence of meteorological parameters on NO_X, but similar conclusions can be drawn for NO_2 and $PM_{2.5}$. The large discrepancies between model results and observations in the winter months are most likely due to the overestimation of the vertical mixing in the lower atmosphere under actual meteorological conditions that, conversely, do not favor atmospheric dispersion. Low wind speed, dry air and cold temperature are very frequent in the winter period in the Po valley: often concurring with strong lapse rate inversion and with very low mixing layer depths, these conditions favor pollutant accumulation, as confirmed in other recent works (Squizzato et al., 2017; Arvani et al., 2016; Pernigotti et al., 2013). Underestimation of $PM_{2.5}$ emissions from biomass burning in emission inventory data (Denier Van Der Gon et al., 2015) can be also responsible for its improper reconstruction in winter time. Likewise, the systematic underestimation of NO_2 could be also due to the underestimation of the real NO_X emissions in the emission inventory data (Oikonomakis et al., 2018).

CAMx performance evaluation for EC and NO_3^- relied only on data from the EMEP monitoring site of Ispra (45°28′43″N, 9°13′56″E, about 50 km North West of Milan), because the regional air quality networks did not monitor PM components in 2010. The monitoring site is located at a rural background site, but is still affected by anthropogenic emissions as reported by Gilardoni et al. (2011). The visual inspection of CAMx and monitored data time series (Figure S4) shows that the model is able to reproduced quite well EC and NO_3^- behavior, especially for NO_3^- in the warm part of the year. On yearly basis fractional bias for EC ranges between 30% and 35% over POV and MIL domain, whereas it is lower than 30% for NO_3^-. Nevertheless, as for the whole $PM_{2.5}$ mass, CAMx finds some troubles with peak NO_3^- events and sudden EC fluctuations in the winter period, as pointed out by the correlation value that for both pollutants ranges between 0.4 and 0.5.

4. Source apportionment results: Milan case study

In this work we focused on a receptor (Duomo receptor) located within the urban city centre, near the main cathedral square. Duomo receptor is located in a residential area where local traffic is at 90% composed of taxies, and residential/commercial heating are the main emission sources. Given the downtown location, biomass is not used for space heating in this area.

The source apportionment analysis was focused on the whole $PM_{2.5}$ mass and on two of its main components, EC and NO_3^-, whose reproduction proved to be satisfactorily reliable and correct. Currently, $PM_{2.5}$ is one of the regulated pollutants of major concern, due to its health relevance and to its rather high average and episodic concentration levels, especially during the winter months. EC and NO_3^- present a different nature: EC is a primary component of $PM_{2.5}$ whilst NO_3^- has a secondary origin. Thus, through the approach presented in this paper, it has been possible, firstly, to investigate weaknesses and strengths of the source apportionment tool, which was developed not only with respect to the primary particles, directly emitted into the atmosphere and tracked by EC, but also for secondary particles such as NO_3^-. This latter analysis is intended to overcome a RMs weakness, as it develops a source apportionment that tracks the contribution of the different sources to a secondary pollutant.

Additional source apportionment analysis considered a gaseous pollutant as NO_2 because, as well as $PM_{2.5}$, in Milan area NO_2 frequently reaches high concentration levels during winter time. As for the secondary component of $PM_{2.5}$, CAMx/PSAT represents a step-forward in the understanding of NO_2 source apportionment, because RMs are mainly applied for PM. Even though CAMx/PSAT reconstructs the contribution of the different sources on hourly basis, results are presented as annual mean values, suitable for comparison with RMs results, as discussed in the Discussion section 5.

4.1. Particulate matter (PM2.5)

Through CAMx source apportionment the $PM_{2.5}$ mean annual concentration at Duomo receptor (about 18 $\mu g/m^3$) has been split by emission source categories, by emission regions, and by the combination of emission categories and regions.

In terms of region contributions (Fig. 3a), both the regional (POV + LOM) and the urban background contribution (PRO + MIL) largely prevail on the local contribution (AUS). Actually, POV and LOM regions, together with the long range transport (i.e.: contribution from sources located outside of POV computational domain) provide the largest contribution, overall accounting for about 53% of the modelled $PM_{2.5}$, the metropolitan area of Milan and its municipality (PRO + MIL), excluding the local sources, account for 38%, and the local contribution (AUS) is responsible for less than 8%. Both primary and secondary nature of fine particles that compose $PM_{2.5}$ are reflected by the similar contributions coming from urban background and local sources near to the receptor point and from the other sources located farther.

In terms of source categories, road traffic, residential heating by biomass, and long range transport represent the most important sources for $PM_{2.5}$ with a total contribution of 73% (Fig. 3b). The transport sector yields the principal contribution (28%), with half contribution due to cars, 8% and 5% respectively due to heavy and light duty commercial vehicles, and 1% due to mopeds and motorcycles. Residential and commercial heating by biomass burning, accounts for 24%, resulting the second most important source for fine particles even though wood or pellet burning for residential heating is not so common in Milan metropolitan area. This quite surprising results is addressed below when the contribution breakdown by both source categories and emission regions is discussed. Long range transport is the third most

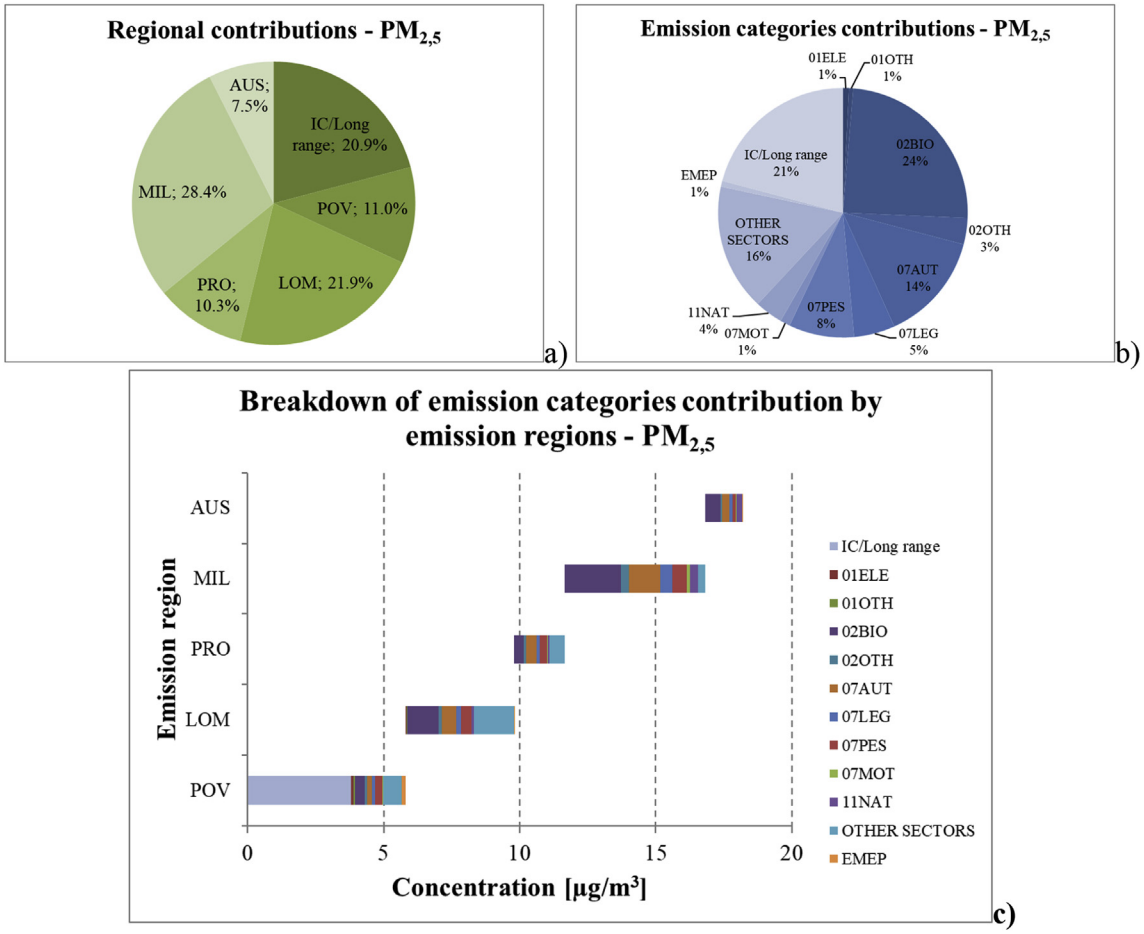


Fig. 3. $PM_{2.5}$ percentage distribution of emission regions (3a, top-left) and emission categories (3b, top-right) contributions. (3c, bottom) is the regional absolute concentration distribution of each source activity contribution defined within CAMx/PSAT approach for $PM_{2.5}$. In the bottom graph the Long range transport term has been stacked with POV region contributions.

impacting source (21%), followed by the OTHER SECTORS category (i.e.: other anthropogenic sources like agriculture) that contributes up to 16%. Emissions from the non-biomass residential heating (3%), natural sources (4%) and industrial sources (2%) show a minor impact, as the emission sources outside of Italy, but still included in the POV domain (EMEP emission category) that contribute for only 1%.

Contribution breakdown by region and emission category is synthesized in Fig. 3c, showing that the highest contribution (4 μg/m^3) comes from long range transport from sources located outside the domain; the second highest contribution (2 μg/m^3) comes from biomass burning in MIL region and the third is given by the OTHER SECTORS anthropogenic sources in the LOM region.

4.2. Elemental carbon (EC) and nitrate (NO_3^-)

Elemental carbon (EC) is a primary component of $PM_{2.5}$ directly emitted in atmosphere by combustion processes. As such, EC ambient concentration at receptor points is mainly driven by the contribution of local or short-range sources. For the Duomo receptor CAMx simulation estimated a mean annual EC concentration of 3.4 μg/m^3 in 2010. The geographic contribution analysis (Fig. 4a) shows that more than 60% is due to urban background sources (MIL + PRO) and that the local sources (AUS) contribute for almost 13%. Nevertheless, the regional background contribution (POV + LOM) has a notable impact, reaching a total of 26% of the EC concentration when including also the long range transport. Regarding the contribution from the source categories (Fig. 4b), the transport sector represents the most impactful source for EC with a 55% share; in details, 26% comes from cars, 15% and 13% are associated to heavy and light duty vehicles, respectively, while the contribution from mopeds and motorcycles is practically negligible (1%). Overall, the road source almost doubles the biomass burning, the second source for EC with 30%. The contribution from the other sources is rather limited: long range transport accounts for 5%, natural sources and the OTHER SECTORS sources for 4%, whilst EMEP sources and industrial processes do not impact significantly on EC concentration level.

Fig. 4c points out that the three most impacting sources are the transport sector in the and biomass burning in residential and commercial sources municipality of Milan (MIL), which respectively contribute to EC concentration with 1.1 μg/m^3 (31%) and 0.49 μg/m^3 (15%), and transport in the metropolitan area of Milan (PRO), which gives a 0.28 μg/m^3 (8%) contribution. Overall, these three most impacting sources are responsible for almost 55% of the EC yearly mean concentration at Duomo receptor. In particular, two of these sources are located within Milan municipality area highlighting the importance of urban sources, accordingly with the primary nature of this pollutant.

Particulate nitrate is one of the secondary inorganic components of $PM_{2.5}$. For the Duomo receptor CAMx simulation estimated a mean annual NO_3^- concentration of 3.2 μg/m^3 in 2010.

NO_3^- shows a different spatial distribution over the domain with respect to EC as well as a different source contribution pattern. As shown in Fig. 5a, the regional background contribution, given by long range transport, POV and LOM contributions, largely prevails on all the other emission regions. These sources, together with long range transport contribution, determine 86% of the NO_3^- mean annual concentration, with the remainder 14% totally due to urban background sources located in the Milan area (MIL + PRO). The emissions of the local area (AUS) give a negligible contribution (less than 1%). Overall, the local and short-range contribution, the most important for EC, has a limited role on the total concentration of this secondary component of $PM_{2.5}$. In terms of source categories, the transport sector provides the largest contribution (43%), with heavy duty vehicles (20%) and cars

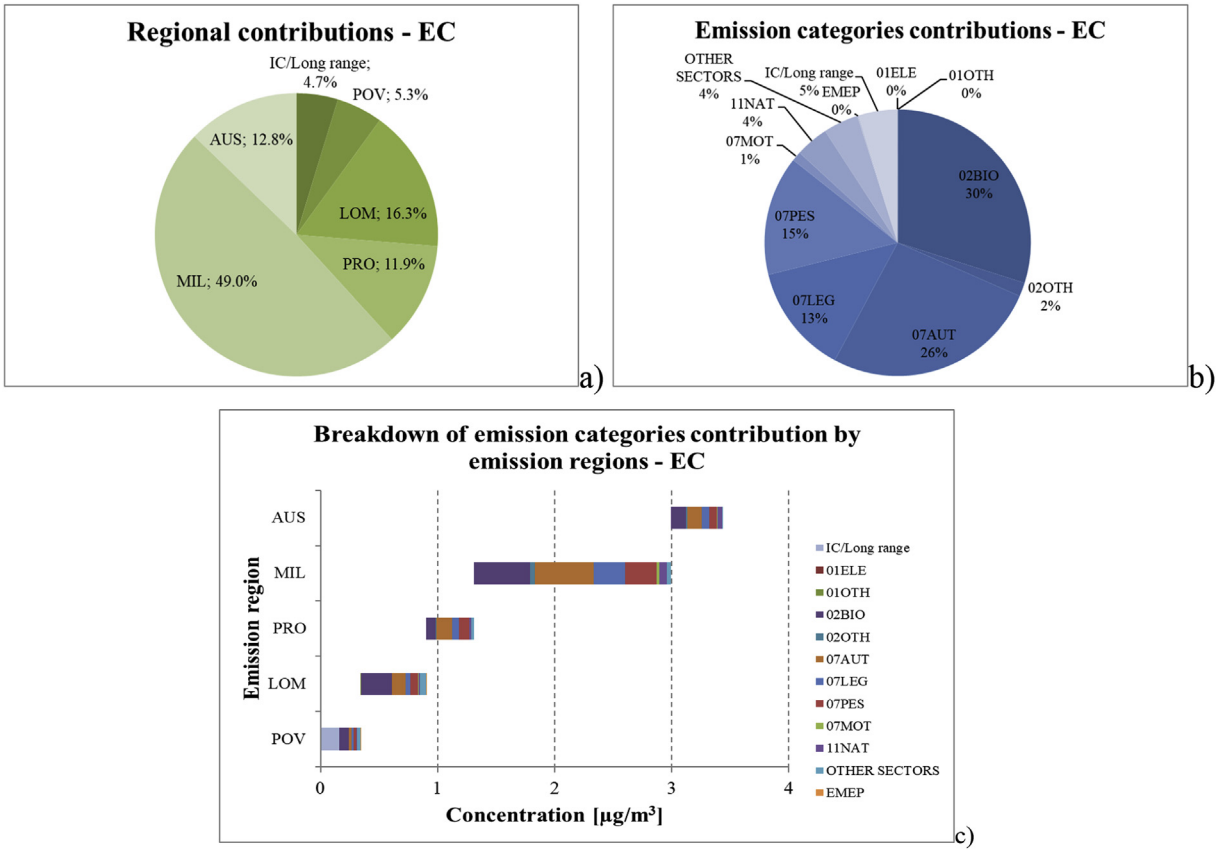


Fig. 4. EC percentage distribution of emission regions (4a, top-left) and emission categories (4b, top-right) contributions. (4c, bottom) is the regional absolute concentration distribution of each source activity contribution defined within CAMx/PSAT approach for EC. In the bottom graph the Long range transport term has been stacked with POV region contributions.

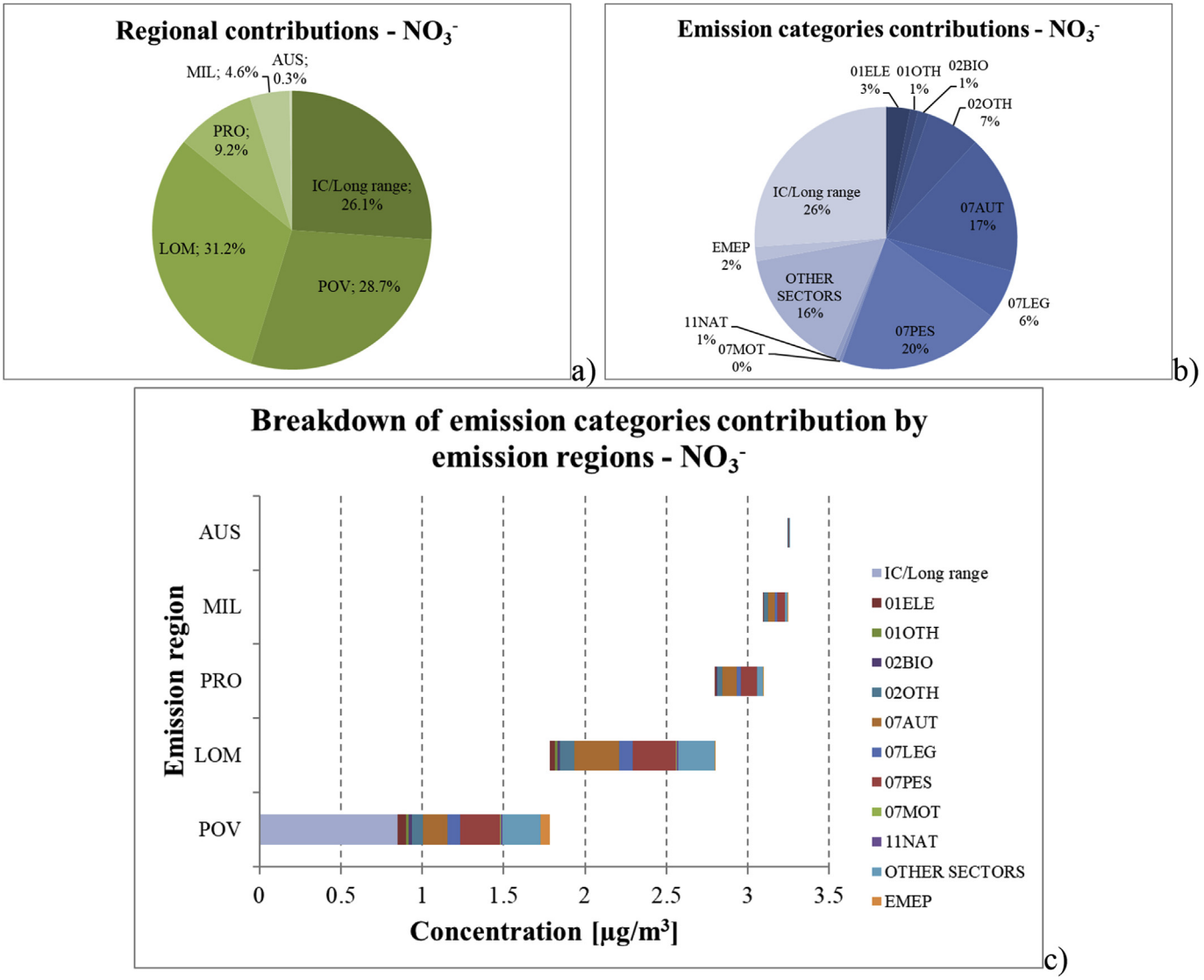


Fig. 5. NO_3^- percentage distribution of emission regions (5a, top-left) and emission categories (5c, top-right) contributions. (5c, bottom) is the regional absolute concentration distribution of each source activity contribution defined within CAMx/PSAT approach for NO_3^-. In the bottom graph the Long range transport term has been stacked with POV region contributions.

(17%) yielding the highest share, the OTHER SECTORS sources for 16% and non-biomass residential and commercial combustion for 7%. Contributions from the other sources are in the order of 1–3% (Fig. 5b).

Fig. 5c points out the contributions of each source category by emission regions. Regardless for the long range contribution from all the emission outside the POV domain (0.8 µg/m^3), the two most impacting sources are transport in LOM and POV regions, with respectively 0.6 µg/m^3 and 0.5 µg/m^3. All the sources related to urban background (MIL and PRO) and local region (AUS), generate a moderate contribution. In particular, the overall contribution from the sources within the urban area of Milan is less than 0.3 µg/m^3 and from the local area less than 0.15 µg/m^3.

The different contribution patterns obtained for EC and NO_3^- are in agreement with the origin of these PM components. The secondary nature of NO_3^- is underlined by the higher contributions due to sources far away from the metropolitan area of Milan, as can be seen in Fig. 6. Chemical reactions that produce secondary PM from gaseous precursors require adequate time scales, that favor their production far beyond the city boundaries. This fundamental aspect is demonstrated by contributions due to vehicular traffic. The local sources (AUS) of the transport sector provide a negligible contribution to NO_3^- at Duomo receptor. Moving far from the city area, the contribution due to the transport sector to NO_3^- of the different emission regions, gradually increases up to farthest regions like LOM and POV. where the 80% of the contribution to $PM_{2.5}$ at Duomo is related to NO_3^-. In particular, cars and heavy duty vehicles circulating in LOM area (0.5 µg/m^3) and in POV area (0.4 µg/m^3) are more impacting than those circulating in Milan municipality (0.08 µg/m^3) and in the metropolitan area (0.18 µg/m^3). This result directly descends from nitrate chemical pathway. The first step in nitrate formation is the oxidation of NO_X emissions to NO_2 and HNO_3. Once formed, HNO_3 combines with ammonia forming ammonium-nitrate. The oxidation time scale of NO_X, combined with the need of ammonia emissions, almost totally related to agricultural activities, to develop chemical equilibrium, favor nitrate produced over wider emission regions more than from local scale sources, even in a high NO_X emitting area like Milan city centre. Indeed, NO_X emissions at local scale move away from the receptor before being oxidized and therefore they can contribute in a very limited way to nitrate concentration where the emission itself is released. Conversely, nitrate formed over wide regions like LOM and POV has surely more chance s to be transported to Milan receptor. As illustrated in Fig. 6 the other two emission categories (residential heating and OTHER SECTORS

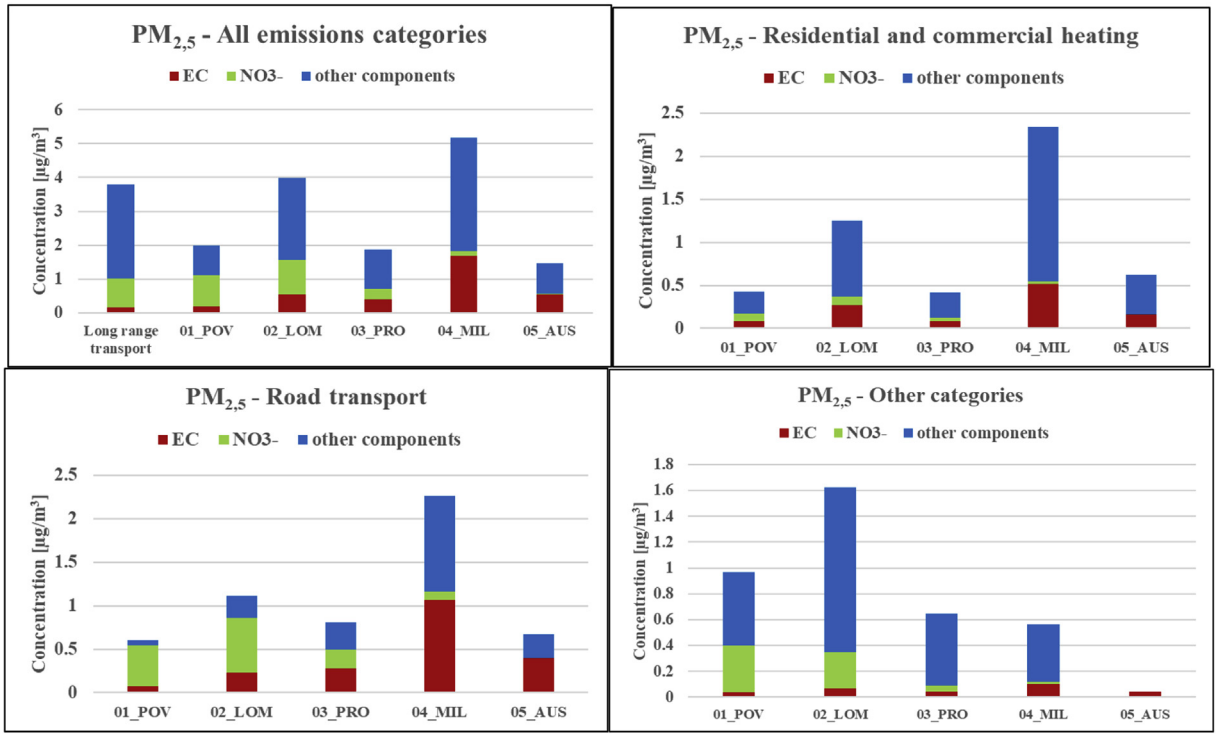


Fig. 6. $PM_{2.5}$ chemical profile of the contributions from each emission region: all emission categories (top-left), residential and commercial heating (top-right), road transport (bottom-left), and all the other categories (bottom-right). The chemical species considered are elemental carbon (EC), particulate nitrate (NO_3^-), and the other $PM_{2.5}$ components altoghether.

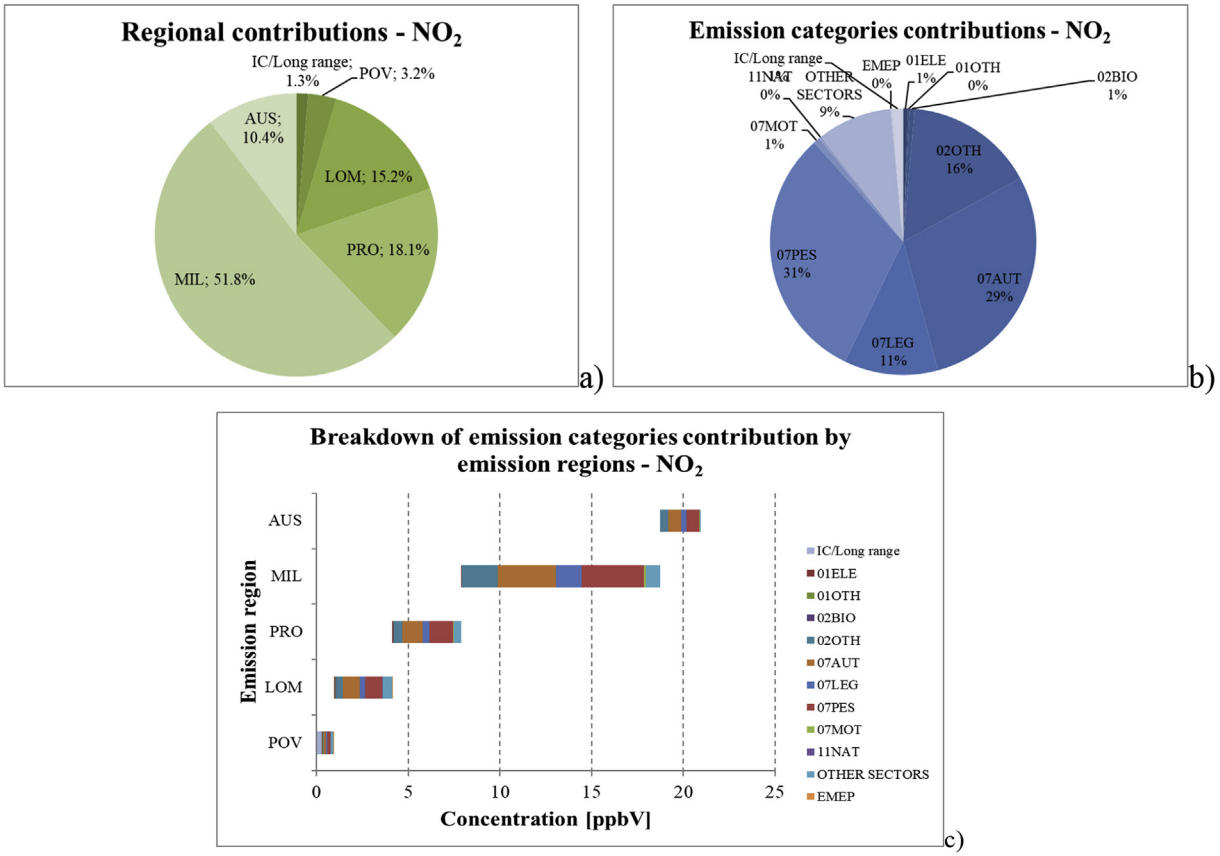


Fig. 7. NO_2 percentage distribution of emission regions (7a, top-left) and emission categories (7b, top-right) contributions. (7c, bottom) is the regional absolute concentration distribution of each source activity contribution defined within CAMx/PSAT approach for NO_2. In the bottom graph the Long range transport term has been stacked with POV region contributions.

sources) detect the same behavior for the secondary component, higher in POV and LOM regions and lower or zero in AUS and MIL regions. This result confirms that: i) SA techniques like PSAT are powerful tools to efficiently diagnose the main processes and interactions among sources giving rise to the development of pollution levels; ii) the definition of remediation policies involving pollutants showing a strongly non-linear behavior such as nitrate need to be carefully designed and tested with proper modelling techniques (e.g. sensitivity analysis tests).

Conversely, the pollution emitted directly in the atmosphere (elemental carbon) affects principally the contribution of sources located near the receptor point. Regarding road transport, almost 50% of road transport contribution of MIL area is due to EC as well as for AUS area. Either for residential and commercial heating, EC contribution shows an important role in MIL and AUS areas (20%). Regardless the total contribution related to each region, the "all emission categories" graph shown in figure below presents the general distribution of primary and secondary components over a wide area. Including the long range transport, EC growth is evident approaching regions near Duomo receptor point, while nitrate distribution is opposite. Farther regions present an important contribution of particulate nitrate rather than elemental carbon.

4.3. Nitrogen dioxide (NO_2)

Nitrogen dioxide is a criteria pollutant and one of the gaseous precursors of particulate nitrate. At the Duomo receptor, the NO_2 yearly mean concentration estimated by CAMx for 2010 is 21 ppb, in agreement with the observations at other urban background stations in Milan (29 ppb). As discussed in the first part of this work, one of the RMs weaknesses is the difficulty to apportionment analysis either to gaseous pollutant like NO_2. Conversely this issue can be addressed by CAMx.

The panels of Fig. 7 show the relative contributions of regions, source categories, and geographically apportioned sources.

Overall, the urban background sources are responsible for about 70% of NO_2 concentration and considerably prevail over the regional background sources (20%) and over the very local sources in proximity of the receptor point (10%). The urban background contribution is principally given by the emissions from the MIL region (51.8%), with only 18.1% from the metropolitan area of Milan (PRO). The regional background contribution is mainly determined by the LOM region (15.2%), with only minor contributions from POV region (3.2%) and long range transport (1.3%). The AUS region provides a rather small contribution. However, considering the limited number of sources in this area with respect to the surrounding emission regions, the estimated 10% contribution states that the local sources actually play a relevant role on NO_2 concentration at the receptor point and in urban areas in general.

Focusing on source categories, road transport, residential and commercial combustion, and the OTHER SECTORS sources determine 98% of NO_2 concentration, whilst natural sources, EMEP sources and long range transport are practically negligible. The most impacting source is, by far, the road transport with a 72% share: 60% of NO_2 concentration derives from heavy duty (31%) and passengers cars (29%) emissions, 11% from light duty vehicles reach only the 11%, about 1% from mopeds and motorcycles. The incomplete combustion of diesel oil or gasoline produces a large amount of NO that reacts immediately with the atmospheric oxidants like O_3, generating NO_2. Residential and commercial combustion yields an overall contribution of 17%, but almost totally due to fossil fuels (16%). The OTHER SECTORS anthropogenic sources category, namely industrial sources, gives a 9% contribution.

Fig. 7c clearly shows that vehicular traffic in the municipality of Milan is the main source of NO_2 at Duomo receptor point. Actually, road transport from the MIL region is responsible for 8 ppb, that is almost 40% of total NO_2 concentration. In details, cars and heavy duty vehicles contribute at the same extent for 15%, that roughly corresponds 3 ppb. The impact of transport emissions from the surrounding regions is also significant, as traffic emissions from PRO and LOM regions provide the second and third most relevant contributions, the former with a 13% share (2.8 ppb), the latter with a 10% (2.1 ppb).

The wide spatial distribution of source yielding a relevant contribution to NO_2 concentration at Duomo receptor, particularly for road transport, points out that coordination of local and regional policy is desirable in order to see visible reduction of NO_2 concentration levels.

5. Discussion

CAMx results for $PM_{2.5}$ chemical speciation and CAMx/PSAT results for $PM_{2.5}$ source apportionment are discussed in comparison with experimental data and Positive Matrix Factorization (PMF) source apportionment from AIRUSE project (Amato et al., 2016).

$PM_{2.5}$ data for 2013 from a one-year measurement campaign at Milano-Torre Sarca, an urban background site near Milan city centre (about 5 km as crow fly distance from Duomo receptor) have been used for comparison purpose. Notwithstanding AIRUSE data and CAMx simulation output do not refer to the same period and receptor, the following analysis can be regarded as a qualitative validation of CAMx/PSAT results.

Reported $PM_{2.5}$ yearly mean concentration from gravimetric measurements at Milano-Torre Sarca (29.9 $\mu g/m^3$) is in agreement with automatic monitoring network data for another urban background site in Milan (30.7 $\mu g/m^3$). Table 4 summarizes yearly mean concentrations of speciated $PM_{2.5}$ for AIRUSE and for CAMx simulation in this work. Other than the reference year and site, the two datasets also differ for the chemical species considered for mass closure. Actually, in AIRUSE data mass closure was not complete, with 4.8 $\mu g/m^3$ not determined, likely due to water molecules of residual moisture, crystallization and formation water, and metal oxides. These latter, conversely are considered in CAMx speciation as the primary elements generated by anthropogenic sources, labeled "other fine particles".

Table 4 highlights the strong difference in $PM_{2.5}$ concentration (29.6 $\mu g/m^3$ vs. 18.8 $\mu g/m^3$) that also holds in a dry-basis comparison (25.2 $\mu g/m^3$ vs. 18.8 $\mu g/m^3$), with CAMx estimated concentration 6.5 $\mu g/m^3$ lower than measured one. Although the reference years and the sites are different, such missed concentration of 6.4 $\mu g/m^3$ cannot be justified by a different yearly emission regime or meteorological conditions, thus confirming that CAMx tends to underestimate the $PM_{2.5}$ mass.

According to AIRUSE data, organic matter (OM = POA + SOA) is

Table 4
$PM_{2.5}$ chemical composition by AIRUSE measurement campaign (Amato et al., 2016) and CAMx/PSAT output.

Species	AIRUSE (2013)		This work (2010)	
	Concentration ($\mu g/m^3$)	%	Concentration ($\mu g/m^3$)	%
Primary organic aerosol (POA)	4.0	16%	4.6	24%
Secondary organic aerosol (SOA)	8.0	32%	0.5	2%
Elemental carbon (EC)	1.8	7%	3.4	18%
Sulfate	1.8	7%	3.0	16%
Nitrate	5.7	23%	3.2	17%
Ammonium	2.1	8%	2.0	11%
Sea salt	0.6	2%	0.2	1%
Mineral dust	1.2	5%	0.1	1%
Other fine particles (CAMx only)	–		1.8	9%
Total	25.2	100%	18.8	100%
Undetermined mass	4.4		–	
Total	29.6			

the main component of $PM_{2.5}$, followed by secondary inorganic aerosol (SIA = nitrate + sulfate + ammonium), elemental carbon, soil fine dust and sea salt. Comparison with CAMx data points out relevant discrepancies for OM and EC, as well as a reasonably good agreement for SIA. CAMx gives a remarkably lower value for OM (5.1 μg/m^3 vs. 12 μg/m^3) due to an incorrect reconstruction of secondary organic aerosol (SOA), almost totally missed by the model (0.5 μg/m^3 vs. 8 μg/m^3). Troubles in properly estimating SOA through the SOA formation algorithm implemented in CAMx version used in this work have been reported in literature (Meroni et al., 2017; Pirovano et al., 2015). The relevant contribution of SOA to PM concentrations in Milan and over the Po valley region was reported in previous works (Pietrogrande et al., 2016; Sandrini et al., 2014; Perrone et al., 2012; Gilardoni et al., 2011; Lonati et al., 2007).

Conversely, CAMx gives higher values for the primary fractions of $PM_{2.5}$: slightly for POA concentration (4.6 μg/m^3 vs. 4 μg/m^3) whereas at a larger extent for EC, as CAMx result (3.4 μg/m^3) is almost twice as high as the measured concentration (1.8 μg/m^3). A better performance is observed for SIA, whose total concentrations are in good agreement, both in absolute (8.2 μg/m^3 vs. 9.6 μg/m^3) and relative terms (44% vs. 38% of $PM_{2.5}$ dry mass). More in details, ammonium is correctly reproduced (2.0 μg/m^3 vs. 2.1 μg/m^3) whereas there are some discrepancies for sulfate and nitrate. Namely, CAMx overestimates sulfate (3.0 μg/m^3 vs. 1.8 μg/m^3), thus giving rise to a corresponding underestimation of nitrate (3.2 μg/m^3 vs. 5.7 μg/m^3). The minor components (sea salt and soil dust) do not reach remarkable concentration values in both datasets; however, CAMx to predict lower value for sea salt (0.2 μg/m^3 vs. 0.6 μg/m^3) and especially for soil dust (0.1 μg/m^3 vs. 1.2 μg/m^3).

The comparison between source apportionment results is not as straightforward as for speciated $PM_{2.5}$ because of the different output of the two approaches. PMF finds a number of factors together with the related contribution and chemical profile. For AIRUSE dataset PMF found a 7-factor solution: based on their profiles, these factors have been identified as vehicle exhaust (VEX) and non-exhaust (NEX), biomass burning (BB), secondary nitrate (SNI), secondary sulfate and organics (SSO), marine aerosols (SEA), industrial emission (IND), and mineral emissions (MIN) with about 12% of the $PM_{2.5}$ mass still not apportioned.

Conversely, CAMx/PSAT output consists of concentration values for each species and each source category considered. Thus, in Table 5 overall source contributions have to be reconstructed by adding the single $PM_{2.5}$ components generated by the different sources.

CAMx/PSAT traffic factor was computed taking into account the related estimated concentrations for EC, POA and “Other fine particles” and compared with VEX + NEX source form PMF. Similarly, biomass burning factor was defined as the sum of EC, POA and “Other fine particles” produced by residential heating through biomass combustion. Sodium and chlorine concentrations estimated by CAMx/PSAT from the “Natural sources” emission category have been added in order to assess sea salt contribution, for comparison with SEA source from PMF. Because CAMx did not simulate soil dust emissions and industrial sources were not specifically tracked but simply included in the generic OTHER SECTORS source category, the comparison with the PMF factors MIN and IND was not possible.

For the secondary source the comparison is not straightforward because the profiles of the SNI and SSO sources (the former mainly identified by nitrate and ammonium, the latter by sulfate and ammonium) are also characterized by the presence of organic carbon. Thus, altogether these sources account for SIA but also for a relevant amount of SOA. Actually, the sum of SNI and SSO factor concentrations is higher than the sum of the concentrations of the corresponding SIA species (Table 5), thus confirming the presence of other species in SNU and SSO factors. Additionally, even though they account for the most part of SIA, small sources of SIA are also associated by PMF to the other sources, but both also containing organic matter; thus, the sum of these factors also account for a fraction of the SOA. In practice, these two factors are also responsible for almost all of the SOA.

In spite of the difference in the modelling approaches, of year and receptor, and of the processes missed by CAMx, the results of source apportionment comparison are quite encouraging, especially for the primary sources. The traffic source is responsible for about 4 μg/m^3 (PMF: 4.3 μg/m^3; CAMx/PSAT: 3.6 μg/m^3), accounting for about 20% of $PM_{2.5}$. A good agreement is also observed for the biomass burning source too, with a mean concentration of 4.6 μg/m^3 (PMF: 5.1 μg/m^3; CAMx/PSAT: 4.3 μg/m^3) and a 24% relative contribution. The lower contributions estimated by CAMx/PSAT may derive from the inclusion of fractions of SIA and SOA in the VEX + NEX and BB profiles by PMF. However, part of such may also derive from the low bias of CAMx for the total $PM_{2.5}$ mass that could be ascribed to meteorology, namely to the reduced dispersion of pollutants under strong inversion conditions in winter time, not correctly detected by the meteorological model WRF. The mismatch on the contribution from secondary sources is essentially due to CAMx underestimation of SOA. However, if a SOA-free secondary source is computed out of PMF source profiles and contributions, the two values get much closer and confirm the substantial agreement for the secondary inorganic source.

Therefore, excluding missed processes, principally SOA formation, CAMx/PSAT model detects correctly the principal source contributions to $PM_{2.5}$. Nevertheless, this methodology needs further improvement in order to track SIA and SOA formation for their proper apportionment and to consider also the contribution of soil dust and resuspension. On the other hand, the main asset of CAMx/PSAT methodology is the possibility to localize both source regions and categories also for the secondary aerosols and for the gaseous pollutants, providing additional and complementary information to PMF results.

Once the results of the two modelling approaches are better reconciliated, the combination of the piece of information coming from their concurrent implementation can improve the overall quality of source apportionment analysis. Such improved source apportionment analysis could help to assess the real health impacts of biogenic and anthropogenic sources over the domain and also better support the further development of intervention strategies for air quality.

6. Conclusions

The modelling chain based on the combination of the meteorological model (WRF), the chemical and transport model (CAMx), and the PSAT source apportionment algorithm was developed for source apportionment of both primary and secondary pollutants ($PM_{2.5}$, elemental carbon (EC), nitrate particulate (NO_3^-) and nitrogen dioxide

Table 5
Comparison of $PM_{2.5}$ source apportionment analysis conducted by two approaches: PMF (Amato et al., 2016) and CAMx/PSAT. Percentage distribution and absolute concentration values are expressed for each emission factor.

Sources	AIRUSE (2013)		This work (2010)	
	Concentration (μg/m3)	%	Concentration (μg/m3)	%
Vehicle Exahust (VEX)	1.8	6%	3.6	19%
Vehicle non-exhaust (NEX)	2.5	8%		
Biomass burning (BB)	5.1	17%	4.3	23%
Salt (SEA)	0.4	1%	0.2	1%
Industrial (IND)	1.3	5%	not tracked	–
Mineral (MIN)	1.4	5%	not tracked	–
Secondary nitrate (SNI)	8.9	30%	8.7	46%
Secondary sulfate (SSO)	5.6	19%		
Not apportioned or not comparable	2.6	9%	2.0	11%
Total	29.6	100%	18.8	100%

(NO_2) at an urban receptor point located in Milan city centre. The CAMx v6.30 version of the chemical and transport model enabled to track the emission categories effects combined with the source regions contributions.

Source apportionment for $PM_{2.5}$ depicted fine PM urban pollution in Milan as a regional problem, pointing out that local actions alone could not reduce significantly the ambient level of $PM_{2.5}$ because regional background emissions contribute for more than half (53%) of total $PM_{2.5}$ level in the city centre, while urban background and local sources contribute for the 39% and 8%, respectively. In terms of emission categories, long range transport prevails among regional emission sources (21%) while the transport sector (17%) among urban background sources. Biomass burning and transports were the most important emission categories for the local sources (3% each). EC source apportionment analysis showed its pronounced primary behavior: more than 70% of total contribution originated from urban background areas, including a 13% contribution from local sources, whereas regional background emissions generated a 26% contribution. The transport sector was responsible for the highest contribution (55%) among the emission sources, but with a 40% share from vehicular traffic enclosed within the urban background area. In contrary to EC, NO_3^- mostly presented a regional origin (86%), with a small contribution from urban background (14%), and a negligible contribution (< 1%) from local sources. The largest contribution derived from transports (44%) through their emission of gaseous precursors, originated principally from regional background regions. The relevant contribution of secondary species to PM concentrations points out the need of carefully designing and testing emission reduction policies in order to correctly take into account the possible non-linearity between source contributions and effective emission reduction impacts. Finally, source apportionment analysis for NO_2 produced results similar to EC both in terms of source regions and source categories: 80% of the total concentration was originated by urban background (70%) and local (10%) sources, and vehicular traffic contribution largely predominated (72%) over all the other emission categories. More than half of total NO_2 in Milan city centre derived from traffic located in the urban background region.

CAMx/PSAT results have been validated through a two-tier approach: first, CAMx outputs were compared with $PM_{2.5}$ chemical speciation data, and then CAMx/PSAT outputs with PMF source apportionment results from the AIRUSE project (Amato et al., 2016) at Milan urban background site.

As a good agreement between CAMx reconstruction and speciation data was observed for primary organic aerosols (POA) (4.6 μg/m^3 vs. 4 μg/m^3) and for total secondary inorganic aerosols (SIA) (8.2 μg/m^3 vs. 9.6 μg/m^3), the model reconstruction lacked the most part of secondary organic aerosols (SOA) processes (0.5 μg/m^3 vs. 8 μg/m^3). Thus, the clear underestimation of $PM_{2.5}$ annual mean concentration (18.8 μg/m^3 vs. 29.6 μg/m^3) could be almost entirely ascribed to SOA concentrations and partially to WRF underestimation of low dispersion conditions during the winter period which influenced performance of regional scale model.

The validation of source apportionment results showed that CAMx/PSAT and PMF factors for traffic and biomass burning were in good agreement, both in terms of absolute concentrations and percentage distributions. Such a good result states that, first of all, also CTMs can represent an affordable tool to estimate source contribution of the different emission categories to PM concentration at a specific receptor. A second important outcome is that CTMs can represent a powerful tool to provide additional information on source apportionment, particularly concerning the geographical origin of source contribution, the role of sources contributing to secondary PM and the contribution estimates for other pollutants, such as NO_2. However, this work pointed out some relevant limitations of CAMx/PSAT, principally concerning SOA formation and other processes, that reduced the feasibility of comparison with PMF results.

In conclusion, this work points out that improvements are needed in order to increase performance of CAMx, namely with future work focusing on the improvement of SOA modelling, on the characterization of dust resuspension processes, together with further analysis of WRF underestimation of stagnation events during winter periods. Additionally, ad-hoc field campaigns are required to draw more robust conclusions on CTMs reliability for source assessment, based on a comparison with RMs results less qualitative than in this work, for better support the development of an integrated source apportionment methodology through both CTMs and RMs results.

Declaration of interest statement

All the authors state that there's no financial/personal interest or belief that could affect their objectivity and don't exist potential conflicts.

Acknowledgements

This work has been financed by the Research Fund for the Italian Electrical System under the Contract Agreement between RSE S.p.A. and the Ministry of Economic Development - General Directorate for Nuclear Energy, Renewable Energy and Energy Efficiency in compliance with the Decree of March 8, 2006. Authors are grateful to EU project AIRUSE-LIFE + for all PM concentrations data at Milan air quality station. Authors wish also to thank the EU Joint Research Centre that through EBAS platform shares observed data collected at Ispra (Italy) EMEP site.

The authors are grateful to the anonymous reviewers for their useful comments and suggestion as well as to Prof. Paola Crippa from the University of Notre Dame for her valuable comments and help in the final revision of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2019.100020.

References

Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Gianelle, V., Colombi, C., Alves, C., Custodio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillon, M.C., Manousakas, M., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X., 2016. AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities. Atmos. Chem. Phys. 16, 3289–3309.

Appel, K.W., Pouliot, G.A., Simon, H., Sarwar, G., Pye, H.O.T., Napelenok, S.L., Akhtar, F., Roselle, S.J., 2013. Evaluation of dust and trace metal estimates from the Community Multiscale Air Quality (CMAQ) model version 5.0. Geosci. Model Dev. (GMD) 6, 883–899.

Arvani, B., Bradley Pierce, R., Lyapustin, A.I., Wang, Y., Ghermandi, G., Teggi, S., 2016. Seasonal monitoring and estimation of regional aerosol distribution over Po valley, Northern Italy, using a high-resolution MAIAC product. Atmos. Environ. 141, 106–121.

Bedogni, M., Pirovano, G., 2011. Source apportionment technique: inorganic aerosol transformation processes in the Milan area. Int. J. Environ. Pollut. 47, 167–183.

Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos. Environ. 69, 94–108.

Belis, C.A., Larsen, B.R., Amato, F., El Haddad, I., Favez, O., Harrison, R.M., Hopke, P.K., Nava, S., Paatero, P., Prevot, A., Quass, U., Vecchi, R., Viana, M., 2014. European Guide on Air Pollution Source Apportionment with Receptor Models. JRC Reference Report EUR 26080. Luxemburg Publication Office of the European Union978-92-79-32514-4. https://doi.org/10.2788/9332.

Belis, C.A., Karagulian, F., Amato, F., Almeida, M., Artaxo, P., Beddows, D.C.S., Bernardoni, V., Bove, M.C., Carbone, S., Cesari, D., Contini, D., Cuccia, E., Diapouli, E., Eleftheriadis, K., Favez, O., El Haddad, I., Harrison, R.M., Hellebust, S., Hovorka, J., Jang, E., Jorquera, H., Kammermeier, T., Karl, M., Lucarelli, F., Mooibroek, D., Nava, S., Nøjgaard, J.K., Paatero, P., Pandolfi, M., Perrone, M.G., Petit, J.E., Pietrodangelo, A., Pokorná, P., Prati, O., Prevot, A.S.H., Quass, U., Querol, X., Saraga, D., Sciare, J., Sfetsos, A., Valli, G., Vecchi, R., Vestenius, M., Yubero, E., Hopke, P.K., 2015. A new methodology to assess the performance and uncertainty of source apportionment models II: the results of two European intercomparison exercises. Atmos. Environ. 123, 240–250. https://doi.org/10.1016/j.atmosenv.2015.10.068.

Bergstrom, R., Denier van der Gon, H.A.C., Prevôt, A.S.H., Yttri, K.E., Simpson, D., 2012.

Modelling of organic aerosols over Europe (2002-2007) using a volatility basis set (VBS) framework: application of different assumptions regarding the formation of secondary organic aerosol. Atmos. Chem. Phys. 12, 8499–8527.

Bessagnet, B., Pirovano, G., Mircea, M., Cuvelier, C., Aulinger, A., Calori, G., Ciarelli, G., Manders, A., Stern, R., Tsyro, S., García Vivanco, M., Thunis, P., Pay, M.-T., Colette, A., Couvidat, F., Meleux, F., Rouïl, L., Ung, A., Aksoyoglu, S., Baldasano, J.M., Bieser, J., Briganti, G., Cappelletti, A., D'Isidoro, M., Finardi, S., Kranenburg, R., Silibello, C., Carnevale, C., Aas, W., Dupont, J.-C., Fagerli, H., Gonzalez, L., Menut, L., Prévôt, A.S.H., Roberts, P., White, L., 2016. Presentation of the EURODELTA III intercomparison exercise – evaluation of the chemistry transport models' performance on criteria pollutants and joint analysis with meteorology. Atmos. Chem. Phys. 16, 12667–12701. 2016. https://doi.org/10.5194/acp-16-12667-2016.

Bove, M.C., Brotto, P., Cassola, F., Cuccia, E., Massabò, D., Mazzino, A., Piazzalunga, A., 2014. An integrated PM2.5 source apportionment study: positive Matrix Factorization vs. the chemical transport model CAMx. Atmos. Environ. 94, 274–286.

Buonocore, J.J., Dong, X., Spengler, J.D., Fu, J.S., Levy, J.I., 2014. Using the Community Multiscale Air Quality (CMAQ) model to estimate public health impacts of $PM_{2.5}$ from individual power plants. Environ. Int. 68, 200–208.

Ciarelli, G., Aksoyoglu, S., El Haddad, I., Bruns, E.A., Crippa, M., Poulain, L., Äijäkä, M., Carbone, S., Freney, E., O'Dowd, C., Baltensperger, U., Prévôt, A.S.H., 2017. Modelling winter organic aerosol at the European scale with CAMx: evaluation and source apportionment with a VBS parameterization based on novel wood burning smog chamber experiments. Atmos. Chem. Phys. 17, 7653–7669.

Curier, R.L., Kranenburg, R., Sergers, A.J.S., Timmermans, R.M.A., Schaap, M., 2014. Synergistic use of OMI NO_2 tropospheric columns and LOTOS-EUROS to evaluate the NO_x emission trends across Europe. Rem. Sens. Environ. 149, 58–69.

Denier Van Der Gon, H.A.C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S.N., Simpson, D., Visschedijk, A.J.H., 2015. Particulate emissions from residential wood combustion in Europe - revised estimates and an evaluation. Atmos. Chem. Phys. 15, 6503–6519.

ENVIRON, 2016. CAMx (Comprehensive Air Quality Model with Extensions) User's Guide Version 6.3. ENVIRON International Corporation, Novato, CA.

European Commission, 2011. Commission Implementing Decision of 12 December 2011 laying down rules for Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council as regards the reciprocal exchange of information and reporting on ambient air quality. Official Journal of the European Union L 335, 86–106 17.12.2011.

European Union, 2008. Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union, L 152 (11), 1–44 6.2008.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J.P., Larsen, B.R., Karl, M., Stenström, K., Genberg, J., Henne, S., Dentener, F., 2011. Better constraints on sources of carbonaceous aerosols using a combined 14C e macro tracer analysis in a European rural background site. Atmos. Chem. Phys. 11, 5685–5700. https://doi.org/10.5194/acp-11-5685-2011.

Guevara, M., Pay, M.T., Martínez, F., Soret, A., Denier van der Gon, H.A.C., Baldasano, J.M., 2014. Inter-comparison between HERMESv2.0 and TNO-MACC-II emission data using the CALIOPE air quality system (Spain). Atmos. Environ. 98, 134–145. https://doi.org/10.1016/j.atmosenv.2014.08.067.

Hamm, N.A.S., Finley, A.O., Schaap, M., Stein, A., 2015. A spatially varying coefficient model for mapping PM_{10} air quality at European scale. Atmos. Environ. 102, 393–405.

Hopke, P.K., 2016. Review of receptor modeling methods for source apportionment. J. Air Waste Manag. Assoc. 66, 237–259.

INEMAR, Inventario Emissioni in Atmosfera: Emissioni in Regione Lombardia Nell'anno 2012 - Revisione Pubblica. ARPA Lombardia Settore Monitoraggi Ambientali.

INERIS, 2006. Documentation of the chemistry-transport model CHIMERE [version V200606A]. Available at: http://euler.lmd.polytechnique.fr/chimere/.

Karamchandani, P., Long, Y., Pirovano, G., Balzarini, A., Yarwood, G., 2017. Source-sector contributions to European ozone and fine PM in 2010 using AQMEII modeling data. Atmos. Chem. Phys. 17, 5643–5664.

Kelly, F.J., Fussel, J.C., 2015. Air pollution and public health: emerging hazards and improved understanding of risk. Environ. Geochem. Health 37, 631–649.

Kim, B.-U., Bae, C., Kim, H.C., Kim, E., Kim, S., 2017. Spatially and chemically resolved source apportionment analysis: case study of high particulate matter event. Atmos. Environ. 162, 55–70.

Lenschow, P., Abraham, H.-J., Kutzner, K., Lutz, M., Preuß, J.-D., Reichenbächer, W., 2001. Some ideas about the sources of PM_{10}. Atmos. Environ. 35, S23–S33.

Li, X., Zhang, Q., Zhang, Y., Zheng, B., Wang, K., Chen, Y., Wallington, T.J., Han, W., Shen, W., Zhang, X., He, K., 2015. Source contributions of urban PM2.5 in the Beijing-Tianjin-Hebei regions: changes between 2006 and 2013 and relative impacts of emissions and meteorology. Atmos. Environ. 123, 229–239.

Lonati, G., Ozgen, S., Giugliano, M., 2007. Primary and secondary carbonaceous species in PM2.5 samples in Milan (Italy). Atmos. Environ. 41, 4599–4610.

López-Aparicio, S., Guevara, M., Thunis, P., Cuvelier, K., Tarrasón, L., 2017. Assessment of discrepancies between bottom-up and regional emission inventories in Norwegian urban areas. Atmos. Environ. 154, 285–296.

Meroni, A., Pirovano, G., Gilardoni, S., Lonati, G., Colombi, C., Gianelle, V., Paglione, M., Poluzzi, V., Riva, G.M., Toppetti, A., 2017. Investigating the role of the chemical and physical processes on organic aerosol modeling with CAMx in the Po valley during a winter episode. Atmos. Environ. 171, 126–142.

Mues, A., Kuenen, J., Hendriks, C., Manders, A., Segers, A., Scholz, Y., Hueglin, C., Builtjes, P., Schaap, M., 2014. Sensitivity of air pollution simulations with LOTOS-EUROS to the temporal distribution of anthropogenic emissions. Atmos. Chem. Phys. 14, 939–955.

Oikonomakis, E., Aksoyoglu, S., Ciarelli, G., Baltensperger, U., Prévôt, A.S.H., 2018. Low modeled ozone production suggests underestimation of precursor emissions (especially NOx) in Europe. Atmos. Chem. Phys. 18, 2175–2198.

Pepe, N., Pirovano, G., Lonati, G., Balzarini, A., Toppetti, A., Riva, G.M., Bedogni, M., 2016. Development and application of a high resolution hybrid modelling system for the evaluation of urban air quality. Atmos. Environ. 141, 297–311.

Pernigotti, D., Georgieva, E., Thunis, P., Bessagnet, B., 2012. Impact of meteorology on air quality modeling over the Po valley in Northern Italy. Atmos. Environ. 51, 303–310. https://doi.org/10.1016/j.atmosenv.2011.12.059.

Pernigotti, D., Thunis, P., Cuvelier, C., Georgieva, E., Gsella, A., De Meij, A., Pirovano, G., Balzarini, A., Riva, G.M., Carnevale, C., Pisoni, E., Volta, M., Bessagnet, B., Kerschbaumer, A., Viaene, P., De Ridder, K., Nyiri, A., Wind, P., 2013. POMI: a model inter-comparison exercise over the Po valley. Air Quality Atmosphere Health 6, 701–715.

Perrone, M.G., Larsen, B.R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R., Zangrando, R., Gambaro, A., Bolzacchini, E., 2012. Sources of high $PM_{2.5}$ concentrations in Milan, Northern Italy: molecular marker data and CMB modelling. Sci. Total Environ. 414, 345–355.

Pietrogrande, M.C., Bacco, D., Ferrari, S., Ricciardelli, I., Scotto, F., Trentini, A., Visentin, M., 2016. Characteristics and major sources of carbonaceous aerosols in $PM_{2.5}$ in Emilia Romagna Region (Northern Italy) from four-year observations. Sci. Total Environ. 553, 172–183.

Pirovano, G., Colombi, C., Balzarini, A., Riva, G.M., Gianelle, V., Lonati, G., 2015. $PM_{2.5}$ source apportionment in Lombardy (Italy): comparison of receptor and chemistry-transport modelling results. Atmos. Environ. 106, 56–70.

Sandrini, S., Fuzzi, S., Piazzalunga, A., Prati, P., Bonasoni, P., Cavalli, F., Bove, M.C., Calvello, M., Cappelletti, D., Colombi, C., Contini, D., de Gennaro, G., Di Gilio, A., Fermo, P., Ferrero, L., Gianelle, V., Giugliano, M., Ielpo, P., Lonati, G., Marinoni, A., Massabò, D., Molteni, U., Moroni, B., Pavese, G., Perrino, C., Perrone, M.G., Perrone, M.R., Putaud, J., Sargolini, T., Vecchi, R., Gilardoni, S., 2014. Spatial and seasonal variability of carbonaceous aerosol across Italy. Atmos. Environ. 99 587-298.

Skamarock, W.C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Duda, M.G., Huang, X.-Y., Wang, W., Powers, J.G., 2008. A Description of the Advanced Research WRF Version 3. NCAR Technical Note NCAR/TN-475 + STR, Boulder, Colorado.

Squizzato, S., Cazzaro, M., Innocente, E., Visin, F., Hopke, P., Rampazzo, G., 2017. Urban air quality in a mid-size city – $PM_{2.5}$ composition, sources and identification of impact areas: from local to long range contributions. Atmos. Res. 186, 51–62.

Timmermans, R., Kranenburg, R., Manders, A., Hendriks, C., Segers, A., Dammers, E., Zhang, Q., Wang, L., Liu, Z., Zeng, L., Denier van der Gon, H., Schaap, M., 2017. Source apportionment of PM2.5 across China using LOTOS-EUROS. Atmos. Environ. 164, 370–386.

UNC, 2013. SMOKE v3.5 User's manual. Available at: http://www.smoke-model.org/index.cfm.

Wang, Y., Bao, S., Wang, S., Hu, Y., Shi, X., Wang, J., Zhao, B., Jiang, J., Zheng, M., Wu, M., Russell, A.G., Wang, Y., Hao, J., 2017a. Local and regional contributions to fine particulate matter in Beijing during heavy haze episodes. Sci. Total Environ. 580, 283–296.

Wang, L., Wei, Z., Fu, J.S., Meng, C., Ma, S., 2017b. Source apportionment of PM2.5 in top polluted cities in Hebei, China using the CMAQ model. Atmos. Environ. 122, 723–736.

World Health Organization (WHO) Regional Office for Europe, 2013. Review of Evidence on Health Aspects of Air Pollution - REVIHAAP Project, Technical Report.

World Health Organization (WHO), 2016. Ambient Air Pollution: A Global Assessment of Exposure and Burden of Disease, Geneva, Switzerland. 9789241511353. http://wwwwho.int.

Yarwood, G., Morris, R.E., Wilson, G.M., 2004. Particulate matter source apportionment technology (PSAT) in the CAMx photochemical grid model. In: Proceedings of the 27th NATO/CCMS International Technical Meeting on Air Pollution Modeling and Application. Springer Verlag.

Zhang, H., Chen, G., Hu, J., Chen, S., Wiedinmyer, C., Kleeman, M., Ying, Q., 2014. Evaluation of seven-year air quality simulation using the Weather Research and Forecasting (WRF)/Community Multiscale Air Quality (CMAQ) models in the eastern United States. Sci. Total Environ. 473–474, 275–285.