MS No.: acp-2019-123

Title: *Exploiting multi-wavelength aerosol absorption coefficients in a multi-time resolution source apportionment study to retrieve source-dependent absorption parameters*

Authors: Alice C. Forello et al.

Response to Reviewers

In addition to reviewers, the authors acknowledge very much the co-Editor for his suggestions. Comments from Referee #1 were also taken into account in the final version of the paper. The text was carefully checked and revised.

Co-Editor Decision: Publish subject to minor revisions (review by editor) (03 Aug 2019)
Comments to the Author:

Dear authors, Thank you very much for your revised manuscript.

The reviewer and I are generally satisfied with your changes. However, there are still many language and grammar issues in the current version. Therefore, the manuscript needs another thorough editorial read (preferable by a native speaker). Although it is not the work of the editor, I marked a few issues below (but not all of them due to limitations in time).

In addition, there are some other minor content issues which need clarification or improvement.

• Line 22: It should be “resolutions”.

• Line 28: Please remove the ‘…’ (you already say ‘e.g.’ at the beginning of the parenthesis).

• Line 32: Add ‘the’ before ‘atmosphere’.

• Line 34 and 36: Alpha and MAC are already defined in Line 19 and 20.

• Line 38: Suggest to move ‘approach' behind ‘here presented’.

• Line 46: Suggest to replace ‘At the state of the art’ with ‘Currently' or ‘As the state of the art’.

• Line 49: ‘proved’ -> ‘proven’. There should probably be a comma after ‘In the late 1990s’.

• Line 64: The variable of the absorption coefficient was already defined in line 58. Please add ‘to be’ before ‘proportional’.

• Line 76, line 81 and later: The word ‘source apportionment optical models’ sounds like a weird construct that is probably not correct. Strictly speaking, it is a model dealing with source apportionment and not with optics. Could you maybe rephrase it as e.g. “Source apportionment models based on optical measurements” or “Source apportionment models using optical measurements as input”?

• Line 82: ‘fuels’ -> ‘fuel’

• Line 84: Add ‘the’ before ‘atmosphere’.

• Line 85: ‘need a priori assumption about alpha values’ -> ‘need a priori assumptions on the alpha values’

• Line 94: This sentence is very long a hard to read. In addition, I would replace ‘In the frame’ by ‘In the framework’.

• Line 95: Also this sentence is difficult to understand. I guess you want to say “Instead of using alpha as an a priori input, this approach even allows to retrieve alpha as a source-dependent value.’?

• Line 102 (and throughout the manuscript): The word ‘that’ should not be preceded by a comma.

• Line 103: Please remove the ‘…’.

• Line 104: Alpha has already been introduced many times before.

• Paragraph starting in line 106: This paragraph is a bit confusing and I suggest to rephrase it.

• Line 121: ‘in activity’ -> ‘active’

• Line 178: ‘Jülich Forschungszentrum’ -> ‘Forschungszentrum Jülich’

• The citation of ‘Valentini et al.’ is not an accepted or peer-reviewed publication and as such should be avoided as reference. I suggest to remove these sentences. It is sufficient that the comparison of the instrument is mentioned in the reply to the reviewers.

• Line 248 and 263: Add ‘such’ before ‘as’.

• Line 265: What do you mean with under-weighed? Less weighed? How?

• Line 297: Suggest to replace ‘Opposite’ with ‘In contrary’.

• Line 304: Add ‘the’ before ‘factor’.

• Line 310: Alpha has been defined already many times before.

• Figure 1: Please add proper y-axis labels (e.g. ‘Concentration’ or ‘Concentration Fe’).

• Figure 2: Please add y-axis labels to the unit.

• Line 346: I suggest to add ‘the’ or ‘a’ before ‘multi-time resolution model’

• Figure 3: It would be helpful to the reader if you describe ‘F’ and ‘EVF’ once more in the caption.

• Line 446: The reference to figure S3 is missing in this paragraph.

• Figure 4: As in the right axis, please also add the word ‘concentration’ or ‘conc.’ to the y-axis label in the left axis.

• Figure 5: The number on the y-axis for the biomass burning component are somehow wrong. Please check. The font size of the axis numbers is very small (it should be similar to the caption font size).

• Line 511: Alpha was already defined several times before.

• Line 539: Suggest to put a hyphen between alpha and value.

• Line 560: ‘At’ -> ‘For’ and add a comma after ‘nm’.

• Line 561: Suggest to change it to ‘report a MAC value of …’.

• Line 581: Suggest to add a ‘the’ or ‘a’ before ‘Multiliniear’.

• Line 604: Remove the word ‘works’.

• Figure S2: What does ”scaled residuals” mean? Normalized by the mean/median? Please clarify in the caption. The y- and x-axis are also missing their proper labels and units.

• Figure S2: Suggest to also mention the year.

Please also consider and reply to the comments by reviewer #1.

Answer: all comments and changes were implemented in the final version of the paper

REFEREE #1

The authors have responded well to the many points raised in the initial reviews. In particular, the inclusion of far more detail on the methods, and justifications for some of the procedures and assumptions are very welcome. There remain just a few minor points which could be improved.

(a) Lines 512-516 – the wording here is a little confusing. It seems to imply that the Delta-C method is not based on a 2-source hypothesis, whereas clearly it is. It may not have been the intention of the authors to imply this, but to refer to the Delta-C parameter as an input variable in receptor models. Some clarification would be beneficial.

Answer: the sentence has been changed as follows "Another literature approach used Delta-C as an input variable together with chemical aerosol components in source apportionment models and was very effective in separating traffic (especially diesel) emissions from biomass combustion emissions (Wang et al., 2011, 2012)."

(b) When discussing the factor associated with sulphate, the authors seek to explain the presence of EC within this factor in relation to the optical absorption, lines 497-501. It is worth bearing in mind that many receptor modelling studies have shown some presence of EC and trace elements in a secondary sulphate factor. This is most probably explicable by the fact that both EC and trace metals are emitted by many sources which also emit sulphur dioxide, for example, fuel oil combustion. Subsequent conversion of sulphur dioxide to sulphate will tend to lead to sulphate condensation on the primary emitted particles, hence leading to a more complex composition for this factor.

Answer: the sentence has been changed as follows "Opposite to sulphates, EC has a primary origin; however, its presence with a very similar percentage (4-5 %) in a sulphate chemical profile was previously pointed out in Milan, indicating a more complex mixing between primary and secondary sources (Amato et al., 2016) e.g. with sulphate condensation on primary emitted particles. The sulphate factor accounted for 21 % of the PM10 mass."

(c) It is stated that during the monitoring campaign no significant contribution from mineral dust was observed (lines 549-550). This is expressed in the context of aerosol absorption. However, lines 505 to 508 attribute absorption by resuspended dust to the likely presence of iron minerals. If the term mineral dust is taken to refer to crustal materials and other largely inorganic particles such as those from construction works, then there is ample evidence of the presence of mineral dusts. The statement that there was no significant contribution from mineral dust may have been meant to refer to sources of pure crustal dust such as Saharan dust emissions, but greater clarity is needed here as the text currently appears contradictory.

Answer: the sentence has been changed as follows "During our monitoring campaign, no contribution from Saharan dust was observed; opposite, biomass burning was proven to be an

important source so that BrC was certainly a significant contributor (Fuzzi et al., 2015) as also suggested by αBB = 1.83 in the biomass burning factor."

REFEREE #2

Paper accepted as is.

Exploiting multi-wavelength aerosol absorption coefficients in a multi-time resolution source apportionment study to retrieve source-dependent absorption parameters

Alice C. Forello[1], Vera Bernardoni[1], Giulia Calzolai[2], Franco Lucarelli[2], Dario Massabò[3], Silvia Nava[2], Rosaria E. Pileci[1,a], Paolo Prati[3], Sara Valentini[1], Gianluigi Valli[1], Roberta Vecchi[1,*]

[1]Department of Physics, Università degli Studi di Milano and National Institute of Nuclear Physics INFN-Milan, via Celoria 16, Milan, 20133, Italy

[2]Department of Physics and Astronomy, Università di Firenze and National Institute of Nuclear Physics INFN-Florence, via G. Sansone 1, Sesto Fiorentino, 50019, Italy

[3]Department of Physics, Università degli Studi di Genova and National Institute of Nuclear Physics INFN- Genoa, via Dodecaneso 33, Genoa, 16146, Italy

[a]now at: Laboratory of Atmospheric Chemistry (LAC), Paul Scherrer Institut (PSI), Forschungsstrasse 111, Villigen, 5232, Switzerland

[*]*Correspondence to*: Roberta Vecchi (roberta.vecchi@unimi.it)

Abstract. In this paper, a new methodology coupling aerosol optical and chemical parameters in the same source apportionment study is reported. In addition to results on sources ~~assessment~~contribution, this approach ~~gives relevant~~provides information such as estimates for the atmospheric Absorption Ångström Exponent (α) of the sources and Mass Absorption Cross section (MAC) for fossil fuel emissions at different wavelengths.

A multi-time resolution source apportionment study using Multilinear Engine ME-2 was performed on a PM10 dataset with different time resolutions (24 hours, 12 hours, and 1 hour) collected during two different seasons in Milan (Italy) in 2016. Samples were optically analysed by a home-made polar photometer to retrieve the aerosol absorption coefficient b_{ap} (in Mm^{-1}) at four wavelengths (λ=405 nm, 532 nm, 635 nm and 780 nm) and were chemically characterised for elements, ions, levoglucosan, and carbonaceous components. The dataset joining chemically speciated and optical data was the input for ~~Time-resolved chemically speciated data were joined to b_{ap} multi-wavelength measurements and used as input data in~~ the multi-time resolution receptor model; this approach was proven to strengthen the identification of sources thus being particularly useful when important chemical markers (e.g. levoglucosan, elemental carbon~~, ...~~) are not

available. The final solution consisted in 8 factors (nitrate, sulphate, resuspended dust, biomass burning, construction works, traffic, industry, aged sea salt); the implemented constraints led to a better physical description of factors and the bootstrap analysis supported the goodness of the solution. As for b_{ap} apportionment, consistently to what expected, ~~the two factors assigned to~~ biomass burning and traffic were the main contributors to aerosol absorption in the atmosphere. A relevant feature of the approach proposed in this work is the possibility of retrieving many other information about optical parameters; for example, opposite to the more traditional approach used by optical source apportionment models, here we obtained the source-dependent ~~atmospheric~~ α value ~~Absorption Ångström Exponent (α)~~ ~~of the sources (α biomass burning = 1.83 and α fossil fuels = 0.80),~~ without any a priori assumption (α biomass burning = 1.83 and α fossil fuels = 0.80). In addition, ~~an estimate for the~~ MAC estimated ~~Mass Absorption Cross section (MAC)~~ for fossil fuel emissions ~~at four wavelengths~~ was ~~obtained and found to be~~ consistent with literature ~~ranges~~values.

It is worth noting that the ~~approach~~ here presented approach can be also applied using ~~widespread~~ more common receptor models (e.g. EPA PMF instead of multi-time resolution ME-2) if the dataset comprises variables with the same time resolution as well as optical data retrieved by ~~commercial~~ widespread instrumentation (e.g. an Aethalometer instead of home-made instrumentation).

1. Introduction

Atmospheric aerosol impacts both on local and global scale causing adverse health effects (Pope and Dockery, 2006), decreasing visibility (Watson, 2002), and influencing the climate (IPCC, 2013). To face these issues an accurate knowledge of aerosol emission sources is mandatory.

~~At the state of the art~~Currently, multivariate receptor models are considered a robust approach (Belis et al., 2015) to perform source apportionment studies and the Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) has become one of the most widely used receptor models (Hopke, 2016) in the aerosol community. In the late 1990s, the Multilinear Engine (ME-2) was developed and proven~~d~~ to be a very flexible algorithm to solve multilinear and quasi-multilinear problems (Paatero, 1999). The scripting feature of this algorithm allows the implementation of advanced receptor modelling approaches; one example is the multi-time resolution model (~~, developed for the first time by~~ Zhou et al., ~~(~~2004), which uses each experimental data in its original time schedule as model input. Source apportionment studies carried out by multi-time resolution model are still scarce in the literature (Zhou et al., 2004; Ogulei et al., 2005; Kuo et al., 2014; Liao et al., 2015; Crespi et al., 2016; Sofowote et al., 2018) although this methodology is very useful in measurement campaigns when ~~instrumentation~~ instruments with different time resolutions (minutes, hours or days) ~~is~~ are available as high time resolution data can be exploited without averaging them over the longest sampling interval.

It is noteworthy that the combination of time-resolved chemically speciated data with the information obtained from instrumentation measuring aerosol optical properties at different wavelengths (e.g. the absorption coefficient b_{ap}) is suggested as one of the future investigations of receptor modelling (Hopke, 2016); however, to the best of our knowledge, very few attempts in this direction have been done (e.g. Peré-Trepat et al., 2007; Xie et al., 2019). Wang et al. (2011, 2012) ~~introduced~~ in a source apportionment study used the Delta-C (Delta-C = BC@370 nm – BC@880 nm from Aethalometer measurements) as an additional input variable and found that Delta-C was very useful in separating traffic from biomass burning source contributions.

The wavelength dependence of b_{ap} ~~the aerosol absorption coefficient (b_{ap})~~ can be empirically considered to be proportional to $\lambda^{-\alpha}$, where α is the Absorption Ångström Exponent; α depends on particles composition and size, and it is a useful parameter to gain information about particles type in atmosphere (see e.g. Yang et al., 2009). Among ~~PM~~ aerosol components, black carbon (BC) is the main responsible for light absorption in atmosphere; in fact, it is considered the main ~~PM~~ aerosol contributor to global warming and the second most important anthropogenic contributor after CO_2 (Bond et al., 2013). Black carbon refers to a fraction of the carbonaceous aerosol ~~that shares~~ characterised by peculiar features ~~about~~ as for microstructure, morphology, thermal stability, solubility, and light absorption (Petzold et al., 2013); in particular, it is characterised by a wavelength-independent imaginary part of the refractive index over visible and near-visible regions. ~~In the last decade, experimental studies evidenced also the role of a~~Another aerosol absorbing component ~~i.e.~~is brown carbon (BrC), referred to as light-absorbing organic matter ~~of various origins~~ with increasing absorption towards lower wavelengths, especially in the UV region (Andreae and Gelencsér, 2006). BrC is an aerosol component that also affects the elemental vs. organic carbon correct separation when using thermal-optical methods as ~~recently~~ outlined by Massabò et al. (2016).

Source apportionment ~~optical~~ models based only on multi-wavelength ~~measurements of~~ b_{ap} data are available in the literature, i.e. the widespread Aethalometer model (Sandradewi et al., 2008a) and the more recent Multi-Wavelength Absorption Analyzer (MWAA) model (Massabò et al., 2015; Bernardoni et al., 2017b). Briefly, these models ~~allow to~~ estimate the source contribution ~~of sources~~ to aerosol absorption ~~in atmosphere~~ exploiting their different dependence on λ (i.e. different α). As a step forward, MWAA provides the b_{ap} apportionment in relation to both the sources (i.e. fossil fuel combustion and biomass burning) and the components (i.e. BC and BrC) and ~~gives~~ also provides an estimate for α of BrC. Indeed, ~~S~~source apportionment ~~optical~~ models based on optical ~~measurements~~data usually assume two contributors to b_{ap}, namely fossil fuel~~s~~ combustion and biomass burning (only few exceptions are present in the literature, e.g. Fialho et al., 2005). In most cases this assumption is well founded, except ~~in presence of~~when episodic events ~~that give~~giving a not negligible contribution to aerosol absorption in the atmosphere occur, such as in presence of ~~the transport of~~ mineral dust from the Saharan desert (Fuzzi et al., 2015). Moreover, the above-mentioned models need a priori

assumptions ~~about~~on the α values of the sources and wide ranges for α are reported in the literature (e.g. Sandradewi et al., 2008a); this is the most critical step, since α depends on the kind of fuel, burning conditions and aging processes in the atmosphere~~ and wide ranges for α are reported in the literature (e.g. Sandradewi et al., 2008a)~~. Without accurate determination of source-specific atmospheric α (for example exploiting the information derived from source apportionment using ^{14}C measurements), the applicability of models based on optical ~~measurements~~ data is questionable (Bernardoni et al., 2017b; Massabò et al., 2015; Zotter et al., 2017). Moreover, the generally accepted assumption of α=1 for fossil fuels and BC, ~~that is derived~~arising from the theory of absorption ~~of~~by spherical particles in the Rayleigh regime (Seinfeld and Pandis, 2006), might not always be valid ~~in the atmosphere due to aerosol aging processes~~for aged atmospheric aerosol (Liu et al., 2018).

In the framework of a source apportionment study based on multi-time resolution receptor modelling, ~~in this work~~ optical and chemical datasets were joined to ~~explore the possibility of retrieving~~ retrieve a multi-λ apportionment of b_{ap} with no need of a-priori assumptions on the contributing sources. ~~Opposite, with this approach source-dependent α values were provided as output~~Instead of using α as an a priori input, this approach ~~even allows to retrieve it as~~directly provided ~~a~~ source-dependent α values. Moreover, the multi-λ apportionment of b_{ap} in each source allowed to estimate MAC values at different wavelengths, exploiting the well-known relation EBC=$b_{ap}(\lambda)$/MAC(λ) (Bond and Bergstrom, 2006) ~~and considering the apportioned concentrations of~~where elemental carbon (EC) apportioned by the model was considered as a proxy for BC. The evaluation of atmospheric MAC values is also not trivial due to the possible presence of absorbing components different from BC (e.g. contribution from BrC, especially at lower wavelengths).

The original approach proposed in this work shows that coupling the chemical and optical information in a receptor modelling process is particularly advantageous because: (1) strengthens the source identification~~,~~ that is particularly useful when relevant chemical tracers (e.g. levoglucosan, EC~~, …~~) are not available; (2) gives estimates for source-specific atmospheric α ~~Absorption Ångström Exponent (α)~~ which are typically assumed a-priori in ~~optical~~ source apportionment models based on optical ~~measurements~~data; (3) ~~assesses~~ provides MAC values at different wavelengths for specific sources.

In this work, optical data were r~~etrieved~~measured by a home-made multi-wavelength polar photometer and input data (chemical+optical) in the receptor model comprised variables acquired with different time resolutions. Anyway, it is worth noting that the here presented approach is of general interest as the same methodology could be applied to (1) datasets combining aerosol chemical and optical ~~measurements~~data obtained by widespread instrumentation (e.g. Aethalometers for optical data); (2) variables with the same time resolution.

~~It is also worth noting that the approach here presented is of general interest as (1) in this work optical data were retrieved by a home-made multi-wavelength polar photometer but the same methodology could be applied to datasets combining aerosol chemical and optical data obtained by widespread instrumentation (e.g. Aethalometers for optical data); (2) input data to the receptor model not necessarily should comprise variables acquired with different time resolution as we did here.~~

2. Material and methods

2.1 Site description and aerosol sampling

Two measurement campaigns were performed during summertime (June-July) and wintertime (November-December) 2016 in Milan (Italy). Milan is the largest city (more than 1 million inhabitants, doubled by commuters everyday) of the Po Valley, a very well-known hot-spot pollution area in Europe due to both large emissions from a variety of sources (i.e. traffic, industry, domestic heating, energy production plants, and agriculture) and low atmospheric dispersion conditions (e.g. Vecchi et al., 2007 and 2019; Perrone et al., 2012; Bigi and Ghermandi, 2014; Perrino et al., 2014).

The sampling site is representative of the urban background and it is situated at about 10 meters above the ground, on the roof of the Physics Department of the University of Milan, less than 4 km far from the city centre (Vecchi et al., 2009). It is important to note that during the sampling campaigns, a large building site was ~~in activity~~ active next to the monitoring station.

Aerosol sampling was carried out using instrumentation with different time ~~-~~resolutions. Low time resolution PM10 data, with a sampling duration of 24 and 12 hours during summertime (20 June-22 July 2016) and wintertime (21 November-22 December 2016), respectively, were collected in parallel on PTFE (Whatman, 47 mm diameter) and pre-fired (700 °C, 1 hour) quartz-fibre (Pall, 2500QAO-UP, 47 mm diameter) filters. Low volume samplers with EPA PM10 inlet operating at 1 m^3 h^{-1} were used. High time resolution data were collected during shorter periods (11 July-18 July and 21 November-28 November 2016) by a streaker sampler (D'Alessandro et al., 2003). Shortly, the streaker sampler collects the fine and coarse PM fractions (particles with aerodynamic diameter $d_{ae} < 2.5$ µm, and $2.5 < d_{ae} < 10$ µm, respectively) with hourly resolution. Particles with $d_{ae} > 10$ µm impact on the first stage and are discarded; the coarse fraction deposits on the second stage, consisting of a Kapton foil; finally, the fine fraction is collected on a polycarbonate filter. The two collecting supports are kept in rotation with an angular speed of about 1.8° h^{-1} to produce a circular continuous deposit on both stages.

Meteorological data were available at a monitoring station belonging to the regional environmental agency (ARPA Lombardia) which is less than 1 km far away.

2.2 PM mass concentration and chemical characterisation

In this Section, chemical analyses performed on samples are summarised. As ~~measured~~ concentration detected in each sample was characterised by its own uncertainty, only ranges for experimental uncertainties and minimum detection limits (MDLs) for every set of variables are reported.

PM10 mass concentration was determined on PTFE filters by gravimetric technique. Weighing was performed by an analytical balance (Mettler, model UMT5, 1 µg sensitivity) after a 24 hours conditioning period in an air-controlled room as for temperature (20 ± 1 °C) and relative humidity (50 ± 3 %) (Vecchi et al., 2004).

These filters were then analysed by Energy Dispersive X-Ray Fluorescence (ED-XRF) analysis to obtain the elemental composition (details on the procedure can be found in Vecchi et al., 2004). For most elements and samples, concentrations were characterised by relative uncertainties in the range 7-20 % (higher uncertainties for elements with concentrations next to MDLs) and minimum detection limits of 0.9-30 ng m^{-3} with the above mentioned sampling conditions.

For each quartz-fibre filter, one punch (1.5 cm^2) was extracted by sonication (1 h) using 5 ml ultrapure Milli-Q water and ~~; this extract was analysed to measure both~~ levoglucosan and inorganic anions concentrations were quantified. Levoglucosan concentration was determined by High-Performance Anion Exchange Chromatography coupled with Pulsed Amperometric Detection (HPAEC-PAD) (Piazzalunga et al., 2010) only in winter samples. Indeed, as already pointed out by other studies at the same sampling site (Bernardoni et al., 2011) and ~~as~~ routinely ~~measured~~ assessed at monitoring stations in Milan by the Regional Environmental Agency (private communication), levoglucosan concentrations during summertime are lower than the MDLs ~~of the technique~~ (i.e. about 6 ng m^{-3}), due to both lower emissions (no influence of residential heating and negligible impact from other sources) and higher OH levels in the atmosphere depleting molecular markers concentrations (Robinson et al., 2006; Hennigan et al., 2010). Uncertainties on levoglucosan concentration were about 11 %. The ~~measurement~~ quantification of main water-soluble inorganic anions (SO_4^{2-} and NO_3^-) was performed by Ion Chromatography (IC); ~~these data had~~ MDLs were ~~of~~ 25 and 50 ng m^{-3} with summertime and wintertime sampling conditions, respectively, and uncertainties ~~of~~ were about 10 %. Unfortunately, due to technical problems no data on ammonium were available. Details on the analytical procedure for IC analysis are reported in Piazzalunga et al. (2013).

Another punch (1.0 cm^2) of each quartz-fibre filter was analysed by Thermal Optical Trasmittance analysis (TOT, Sunset Inc., NIOSH-870 protocol) (Piazzalunga et al., 2011) in order to assess organic and elemental carbon (OC and EC) concentrations. MDLs were ~~was~~ 75 and 150 ng m^{-3} with summertime and wintertime sampling conditions, respectively, and uncertainties were in the range 10-15 %.

Hourly elemental composition was assessed by Particle Induced X-ray Emission (PIXE) technique, using a properly collimated proton beam and scanning the deposits in steps corresponding to 1-hour aerosol deposit (details in Calzolai et

al., 2015). As low time resolution PM10 samples were also available~~In this work~~, fine and coarse elemental concentrations determined by PIXE analysis were added up to obtain PM10 concentrations with hourly resolution~~ as low time resolution PM10 samples were also available~~. PM10 hourly concentrations ~~of~~ for most elements and samples were characterised by relative uncertainties in the range 10-30 % (higher uncertainties for elements near MDLs) and MDLs ranged from a minimum of 0.1 to a maximum of 15 ng m^{-3} (higher MDLs typically detected for Z<20 elements).

2.3 Aerosol light-absorption coefficient measurements

The aerosol absorption coefficient (b_{ap}) at the 4 wavelengths λ = 405, 532, 635 and 780 nm was measured on both low and high time resolution samples with the home-made polar photometer PP_UniMI (Vecchi et al., 2014; Bernardoni et al., 2017c).~~ Results on b_{ap} obtained by this custom photometer resulted in very good agreement against multi-angle absorption photometer (MAAP) data at 635 nm (Vecchi et al., 2014; Bernardoni et al., 2017c). More recently, in the frame of a collaboration with the Jülich Forschungszentrum (Germany), the Absorption Ångström Exponents retrieved by extinction minus scattering measurements were compared at two wavelengths (630 nm and 450 nm) with the one obtained by PP_UniMI data for laboratory generated aerosols. The agreement with Cabot soot was in general very good as for both b_{ap} at two wavelengths and Absorption Ångström Exponent estimates, i.e. comparability within one standard deviation (data not yet published, preliminary results reported in Valentini et al., 2019).~~

Low time resolution optical measurements taken into account were those performed on PTFE filters since their physical characteristics can be considered more similar to polycarbonate filters used by the streaker sampler. Moreover, previous works reported a bias on b_{ap} measured by instrumentation using fibre filters (e.g. Cappa et al., 2008: Lack et al., 2008; Davies et al., 2019; and references therein~~); ~~). Vecchi et al. (2014) found that b_{ap} at 635 nm was 40% higher when measured on quartz-fibre filter compared to parallel samples collected on PTFE. ~~quantified in about 40 % the effect caused in b_{ap} values (assessed at 635 nm) by sampling~~ This effect was ascribed to sampling artefacts due to organics in aerosol samples collected in Milan~~ when comparing aerosol samples collected in parallel quartz fibre and PTFE filters~~. As f~~F~~or high time resolution samples, b_{ap} was measured only in the fine fraction collected on polycarbonate filters~~,~~ since absorption ~~from~~ of the Kapton foil on which the coarse fraction was collected did not allow b_{ap} assessment. Anyway, b_{ap} values in PM2.5 and PM10 were expected to be fairly comparable, as ~~most of the contribution to~~ aerosol absorption in atmosphere is ~~typically given by~~mostly due to particles in the fine fraction at heavily polluted urban sites like Milan. To verify this assumption, high time resolution b_{ap} data in PM2.5 were averaged ~~on~~ over the time scale of low time resolution b_{ap} in PM10 and compared; the agreement was good, ~~for comparison. They turned out to be in good agreement,~~ between 11 % and 13 % depending on the λ, except for b_{ap} at λ=405 nm that showed a higher difference (27 %) but with most data (83 %) within experimental uncertainties. To take into account ~~for~~ this difference, b_{ap} data at λ=405 nm were homogenised

before ~~their insertion into~~using them in the model, following the criterion used for chemical species (for further detail about homogenisation procedure, see Sect. 2.4 and Sect. 2.5).

Uncertainties on b_{ap} were ~~estimated as~~quantified in 15 % and MDL was in the range 1-10 Mm^{-1} depending on sampling duration and wavelength as already reported in ~~our previous works (~~Vecchi et al. (~~,~~2014) and ~~;~~Bernardoni et al~~.,~~. (2017c). ~~Experimental uncertainties and MDL of optical absorption data were used as a starting point to estimate the uncertainties introduced in the model.~~ Pre-treatment procedure for experimental uncertainties and MDLs~~these data~~ was the same used for chemical variables in order to create suitable input matrices required by the multi-time resolution model (see also Sect. 2.5). Optical system stability was checked during the measurement session, evaluating the reproducibility of the measurement on a blank test filter. Laser stability was also checked at least twice a day and the recorded intensities were used to normalise blank and sampled filters analysis.

2.4 Model description

Multivariate receptor models (Henry, 1997) are among the most widespread and robust approaches used to carry out source apportionment studies for atmospheric aerosol (Belis et al., 2014 and 2015). In particular, the Positive Matrix Factorization PMF2 (Paatero and Tapper, 1994; Paatero, 1997) had been extensively used in the literature and, afterwards, the Multilinear Engine ME-2 (Paatero, 1999 and 2000) introduced the possibility of solving all kinds of multilinear and quasi-multilinear problems. The fundamental principle of these modelling approaches is the mass conservation between the emission source and the receptor site; using the information carried by aerosol chemical composition assessed ~~on a number of~~ in samples collected at the receptor site, a mass balance analysis can be performed to identify the factors influencing aerosol mass concentrations (Hopke, 2016). Factors can be subsequently interpreted as the main sources impacting the site, ~~exploiting~~ through the knowledge about ~~the most relevant~~major sources in the investigated area and the ~~adoption~~ exploitation of chemical fingerprints available from previous literature works (Belis et al., 2014). Referring to the input data as matrix X (matrix elements x_{ij}), the chemical profile of the factors as matrix F (matrix elements f_{kj}), and the time contribution of the factors as matrix G (matrix elements g_{ik}), the main equation of a bilinear problem can be written as follows:

$$x_{ij} = \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where the indices i, j, and k indicate the sample, the species, and the factor, respectively; P is the number of factors and the matrix E (matrix elements e_{ij}) is composed by the residuals, i.e. the difference between measured and modelled values. In this way, a system of NxM equations is established, where N is the number of samples and M is the number of species. The solution of the problem is computed minimising the object function Q defined as:

$$Q = \sum_{i=1}^{N}\sum_{j=1}^{M}\left(\frac{e_{ij}}{\sigma_{ij}}\right)^2 \qquad (2)$$

where σ_{ij} are the uncertainties related to the input data.

The multi-time resolution receptor model was developed in order to use each data value in its original time schedule, without averaging the high time resolution data or interpolating the low time resolution data (Zhou et al., 2004; Ogulei et al., 2005). The main Eq. (1) is consequently modified as below:

$$x_{sj} = \frac{1}{t_{s2}-t_{s1}+1}\sum_{k=1}^{P} f_{kj} \sum_{i=t_{s1}}^{t_{s2}} g_{ik}\eta_{jm} + e_{sj} \qquad (3)$$

where the indices s, j, and k indicate the sample, the species and the factor respectively; P is the number of factors; t_{s1} and t_{s2} are the starting and ending time for the s-th sample in time units (i.e. the shortest sampling interval~~,~~ that is 1 hour for the dataset used here) and i represents one of the time units of the s-th sample. η_{jm} are adjustment factors for chemical species replicated with different time resolution and measured with different analytical methods (represented by the subscript m).

If η is close to unity, species concentration measured by different analytical approaches can be considered in good agreement; non-replicated species have adjustment factors set to unity by default. In this work, the adjustment factors were always set to unity in the model; to take into account the use ~~of different~~two types of aerosol samplers (i.e. low volume sampler with EPA inlet and streaker sampler) and different analytical techniques to obtain the elemental composition (i.e. ED-XRF and PIXE), concentrations of replicated species with ~~different~~multiple~~-time resolution~~time resolutions were homogenised before inserting them into the input matrix X, as will be explained in Sect. 2.5. ~~Applying~~ ~~t~~This data treatment ~~procedure, it is possible to avoid to~~avoids the consistency check between~~if the~~ η values calculated by the model ~~are consistent with~~and differences in experimental data characterised by high and low time resolution. Otherwise, this step should always be performed after running the model.

In the multi-time resolution model ~~a~~ the following regularisation equation is introduced to take into account that~~, since~~ some sources could contain few or no species measured with high time resolution:

$$g_{(i+1)\,k} - g_{ik} = 0 + \varepsilon_i \qquad (4)$$

where ε_i represent the residuals.

As already pointed out by Ogulei et al. (2005), a weighing parameter for low resolution species might be necessary; in this study, it was implemented in the equations and set at 0.5 for strong species (not applied to weaker species such as Na, Mg, and Cr, see Sect. 2.5) in 24-h or 12-h samples.

Equations (3) and (4) are solved using the Multilinear Engine (ME) program (Paatero, 1999). In Eq. (2), the object function Q takes into account residuals from the main Eq. (3) and from the auxiliary equations (regularisation Eq. (4), normalisation equation, pulling equations, and constraints).

In this work, the multi-time resolution model implemented by Crespi et al. (2016) was used; therefore, constraints were inserted in the model and the bootstrap analysis was also performed to evaluate the robustness of the final solution.

2.5 Input data

As already mentioned in Sect. 2.4, instead of using adjustment factors in the model (all set equal to one), concentrations of replicated species with different~~ time resolution~~time resolutions were pre-homogenised and then inserted into the input matrix X. Concentration data with longer sampling interval (24 and 12 hours in this work) were considered as benchmark, since analytical techniques usually show a better accuracy on concentration values far from MDLs (i.e. samples collected on longer time intervals) (Zhou et al., 2004; Ogulei et al., 2005).

Variables were then classified as weak and strong according to the signal-to-noise ratio (S/N) criterion (Paatero, 2015). For hourly data only strong variables (S/N ≥ 1.2) were considered; for low time resolution data also weak~~er~~ variables such as Na, Mg and Cr (with S/N equal to about 0.8)~~,~~ that resulted strong variables in hourly samples, were also included although~~ under-weighed (i.e.~~ with associated uncertainties comparable to concentration values~~)~~ in order to avoid the exclusion of too many data. Indeed, excluding these low time resolution variables from the analysis gave rise to artificial high values in the time contribution matrix for sources traced by these species (in this case it was ~~particularly important~~an issue for aged sea salt traced by Na and Mg, see Sect. 3.2); this oddity was already reported by Zhou et al. (2004).

Every measured variable in each sample is characterised by its own uncertainty; ranges of experimental uncertainties and MDLs are reported in Sect. 2.2 and 2.3 for chemical and optical analyses, respectively. Variables with more than 20 % of the concentration data below MDL values were omitted from the analysis (Ogulei et al., 2005). Uncertainties, missing values and data below minimum detection limits were pre-treated according to~~The procedure described in~~ Polissar et al. (1998)~~ was followed to treat uncertainties and below MDL data, starting from experimental uncertainties and MDLs~~. In general, missing concentration values were estimated by linear interpolation of the measured data and their uncertainties were assumed as three times this estimated value (Zhou et al., 2004; Ogulei et al., 2005). As for summertime levoglucosan data (~~not available~~always below MDLs), the approach was to include them as below MDL data and not as missing data following Zhou et al. (2004)~~,~~ who underlined that the multi-time resolution model is more sensitive to missing values than the original PMF model. In order to avoid double counting, in this study S was chosen as input variable instead of SO_4^{2-} as it was determined on both low time and high time resolution samples (by XRF and PIXE analysis, respectively, see Calzolai et al., 2008). However, elemental SO_4^{2-} and S concentrations showed a high correlation (correlation

coefficient R=0.98) and the Deming regression gave a slope of 2.69 ± 0.13 (sulphate vs. sulphur) with an intercept of -198 ± 82 ng m^{-3}, i.e. compatible with zero within 3 standard deviations. The slight difference (of the order of 10%) between the estimated slope and the SO_4^{2-}-to-S stoichiometric coefficient (i.e. 3) can be ascribed to either a small fraction of insoluble sulphate or to the use of different analytical techniques.

PM10 mass concentrations were included in the model with uncertainties set at four times their values (Kim et al., 2003). In the end, 22 low time resolution variables (PM10 mass, Na, Mg, Al, Si, S, K, Ca, Cr, Mn, Fe, Cu, Zn, Pb, EC, OC, levoglucosan, NO_3^-, b_{ap} 405nm, b_{ap} 532nm, b_{ap} 635nm, b_{ap} 780nm) and 17 hourly variables (Na, Mg, Al, Si, S, K, Ca, Cr, Mn, Fe, Cu, Zn, Pb, b_{ap} 405nm, b_{ap} 532nm, b_{ap} 635nm, b_{ap} 780nm) were considered.

The input matrix X consisted in 386 samples and the total number of time units was 1117. The analysis was performed in the robust mode; lower limit for G contribution was set to -0.2 (Brown et al., 2015) and the error model em=-14 was used for the main equation with C_1= input error, C_2= 0.0, and C_3=0.1 (Paatero, 2012) for both chemical and optical absorption data.

Sensitivity tests on the uncertainty of absorption data were performed starting from a minimum uncertainty of 10 %. Lower uncertainties were considered not physically meaningful from an experimental point of view. ME-2 analyses performed with 10 % uncertainty on absorption data gave very similar results to the base case solution presented in the Supplement (Figure S1 and Table S3), with no differences in mass apportionment and a maximum variation in the concentrations of chemical and optical profiles (matrix F) of 7 % when considering significant variables in each profile (i.e. EVF higher or near 0.30). ~~Opposite~~In contrary, considering an uncertainty of 20 % on absorption data, the solution significantly differed from ~~the base case one presented~~the one reported in the Supplement and showed less physical meaning (e.g. a couple of factors got mixed, an additional unique factor appeared giving a null mass contribution)~~. Indeed, the factors assigned to resuspended dust and construction works got mixed, and a new unique factor (traced almost exclusively by Pb) appeared, with mass contribution equal to zero.~~ Thus, the estimated relative uncertainty of 15 % was here considered appropriate for optical variables.

It is also noteworthy that ME-2/PMF analysis is not a-priori harmed by the use of joint matrices containing different units (see e.g. Paatero, 2018). Indeed, if different units are present in different columns of matrix X, the output data in the factor matrix G are pure numbers and elements in a column of the factor matrix F carry the same dimension and unit as the original data in matrix X. In addition, ~~as we did in this work,~~ the average total contribution to the mass of a specific source due to species in a certain factor in matrix F must be retrieved a-posteriori summing up only mass contributions by chemical components (i.e. excluding optical components in matrix F).

To the authors' knowledge, this ~~is~~ was the first time that the absorption coefficient~~s~~ at different wavelengths ~~wasere~~ was introduced in the multi-time resolution model jointly with chemical variables and used to more robustly identify the

sources; moreover, this approach led to the assessment of source-dependent ~~the optical information was also exploited to retrieve additional information such as the~~ α ~~values~~ ~~Absorption Ångström Exponent (α)~~ ~~of the sources~~ and MAC values in an original way.

3. Results and discussion

3.1 Concentration values

In Table S1 (Supplement) basic statistics on mass and chemical species concentrations at different time resolutions are given.

Most variables showed higher mean and median concentrations during the winter campaign, when atmospheric stability conditions influenced the monitoring site; exceptions were Al, Si and Ca which had lower median concentrations (as detected in low time resolution samples). This was not unexpected as they are typical tracers of soil dust resuspension (Viana et al., 2008) that can be more relevant during summertime due to drier soil conditions and ~~higher~~ stronger atmospheric turbulence. Moreover, the good correlation between these elements (Al vs Si: R^2=0.94 and Ca vs Si: R^2=0.78) suggested their common origin.

Potassium showed the clearest seasonal behaviour in concentration values ~~was the element showing the most different median concentrations in the two seasons; its median concentration in low time resolution samples was~~going from 284 ng m^{-3} (10th-90th percentile: 151-344 ng m^{-3}) ~~and~~ to 660 ng m^{-3} (10th-90th percentile: 349-982 ng m^{-3}) in summer and winter, respectively, in low time resolution samples. K is an ambiguous tracer, since it is emitted by a variety of sources ~~such as~~among which there are crustal resuspension and biomass burning. In our dataset, wintertime K values showed a good correlation with levoglucosan concentrations (R^2=0.71) suggesting ~~an~~ the impact of biomass burning as levoglucosan is a well-known tracer for biomass burning emissions in winter samples (Simoneit al., 1999). Also looking at K-to-Si ratio (~~the latter~~where Si was taken as soil dust marker) significant seasonal differences came out; it was 0.35 ± 0.15 in high time resolution summer samples and 2.0 ± 2.2 in winter ones, to be compared with the much more stable Al-to-Si ratio ~~for Al/Si~~ (i.e. 0.26 ± 0.04 and 0.28 ± 0.09 in summer and winter, respectively) indicating a soil-related origin. Among the elements typically associated to anthropogenic sources, Fe and Cu showed a good correlation (e.g. R^2=0.72 on hourly resolution samples) as well as Cu and EC (Cu vs EC: R^2=0.84, on low time resolution data~~).~~); i~~I~~n addition, the diurnal pattern of Fe and Cu showed traffic rush-hours peaks (7-9 a.m. and around 19 p.m. as shown in Fig.1). These results were suggestive of a common source~~.~~ ;~~Indeed,~~ in the literature these aerosol chemical components are reported ~~in the literature~~ as tracers for vehicular emissions (e.g. Viana et al., 2008; Thorpe and Harrison, 2008).

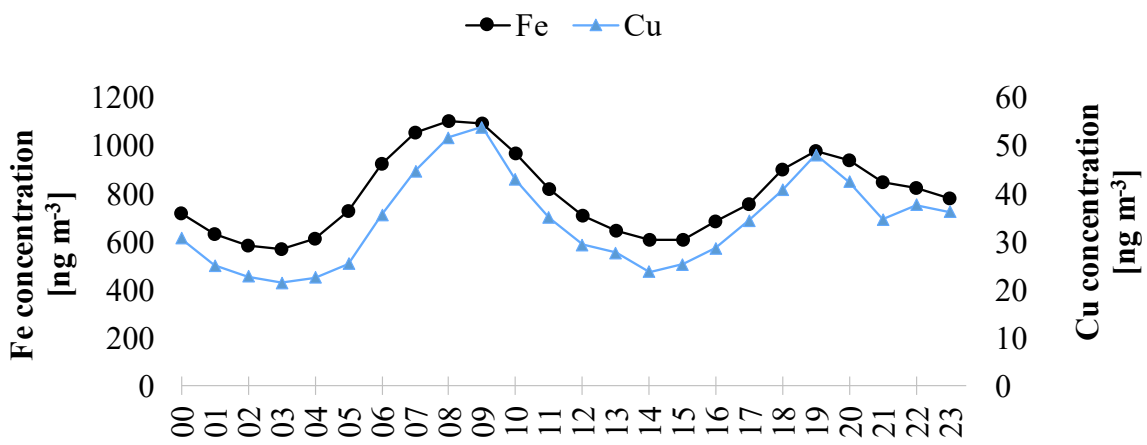

Figure 1: Diurnal profile of Fe and Cu concentrations (in ng m^{-3}).

In Table S2 (Supplement) also basic statistics on b_{ap} values referred to low resolution samples collected on PTFE are reported. Diurnal mean temporal patterns for b_{ap} at different wavelengths (retrieved from hourly resolved data) are displayed in Fig. 2.

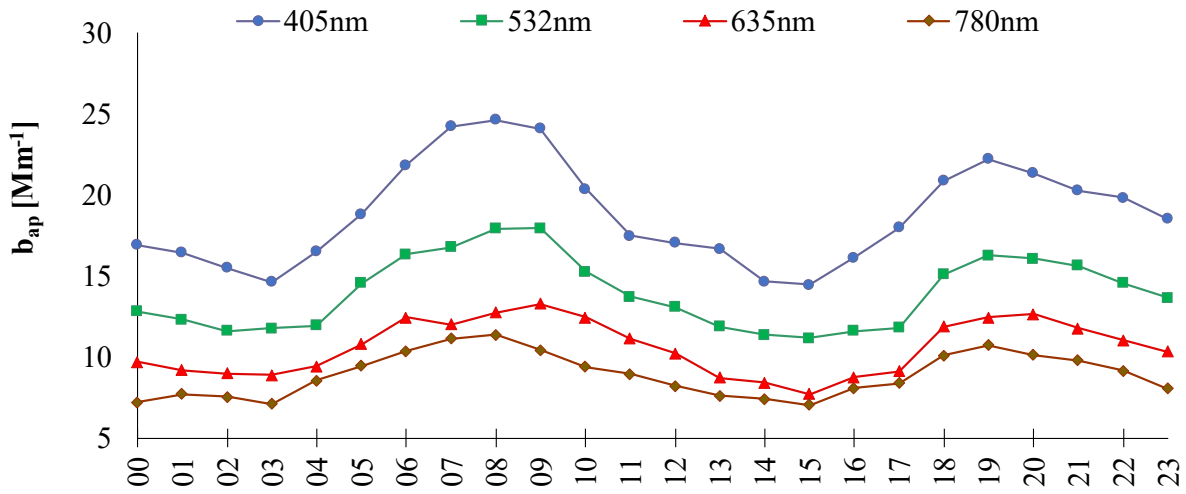

Figure 2: Diurnal profile of aerosol absorption coefficient (Mm^{-1}) measured at different wavelengths.

3.2 Source apportionment with the multi-time resolution model

Different solutions (from 5 to 10 factors) ~~number of factors (5-10)~~ were explored; after 30 convergent runs, the 8-factor base-case solution corresponding to the lowest Q value (2086.88) was firstly selected (see Fig. S1 in the Supplement). It is important to ~~notice~~note that the model was run using all variables (chemical + optical) as explained in Sect. 2.5. A lower or higher number of factors caused ambiguous chemical profiles and the physical interpretation ~~singled out~~suggested clearly mixed sources for a lower number of factors or unique factors in case of more factors (i.e. Pb for 9 factors); moreover, inconsistent mass closure was detected increasing the number of factors (e.g. the sum of species contribution was up to 25 % higher than the mass for the 10-factor solution). In the 8-factor base case solution, the mass was well reconstructed by the model (R^2=0.98), with a slope of 0.98 ± 0.02 and negligible intercept (~~=~~0.51 ± 0.89 μg m^{-3}~~,~~).

The factor-to-source assignment ~~process~~ was based on both the Explained Variation for F matrix (EVF) values - which are typically higher for chemical tracers (Lee et al., 1999; Paatero, 2010) - and the physical consistence of factor chemical profiles. In the chosen solution, the not explained variation was lower than 0.25 for all variables. The uncertainty-scaled residuals (Norris et al., 2014) showed a random distribution of negative and positive values in the ± 3 range, with a Gaussian shape for most of the variables (Fig. S2 in the Supplement).

Using EVF and chemical profiles reported in Fig. S1(a), the 8 factors were tentatively assigned to ~~specific atmospheric aerosol sources:~~ nitrate, sulphate, resuspended dust, biomass burning, construction works, traffic, industry, and aged sea salt. In Table S3 (in the Supplement) absolute and relative average source contributions to PM10 mass are reported.

Although the above mentioned base-case solution was a satisfactory representation of the main sources active in the area (as reported in previous works, see e.g. Marcazzan et al., 2003; Vecchi et al., 2009 and 2018; Bernardoni et al., 2011 and 2017a; Amato et al., 2016), the chemical profiles of some factors were improved exploring rotated solutions. The most relevant case was represented by aged sea-salt where typical diagnostic ratios such as Mg/Na and Ca/Na (in bulk sea water equal to 0.12 and 0.04, respectively, as reported e.g. in Seinfeld and Pandis, 2006) were not well reproduced in the base-case solution ~~(in bulk sea water equal to 0.12 and 0.04, respectively, as reported e.g. in Seinfeld and Pandis, 2006)~~ and the chemical profile ~~itself~~ was too much impacted by the presence of Fe compared to bulk sea water composition. Therefore, the above-mentioned diagnostic ratios were here used as constraints and Fe was maximally pulled down in the chemical profile. The effective increase in Q was of about 61 units (Q=2147), with a percentage increase of about 3 %; as a rule of thumb, an increase in the Q value of a few tens is generally considered acceptable (Paatero and Hopke, 2009). It is noteworthy that the constrained solution led to an improvement in the chemical profile of the aged sea salt ~~profiles was achieved~~ and~~with~~ negligible differences in all other relevant features of the solution (i.e. EVF, residuals, mass reconstruction, source apportionment) were found compared to the base-case solution ~~as for all other relevant features of~~

~~the solution (i.e. EVF, residuals, mass reconstruction, source apportionment)~~. Therefore, the 8-factor constrained solution was considered the most physically reliable; results are presented in Table 1 and Fig. 3 and discussed in detail in the following.

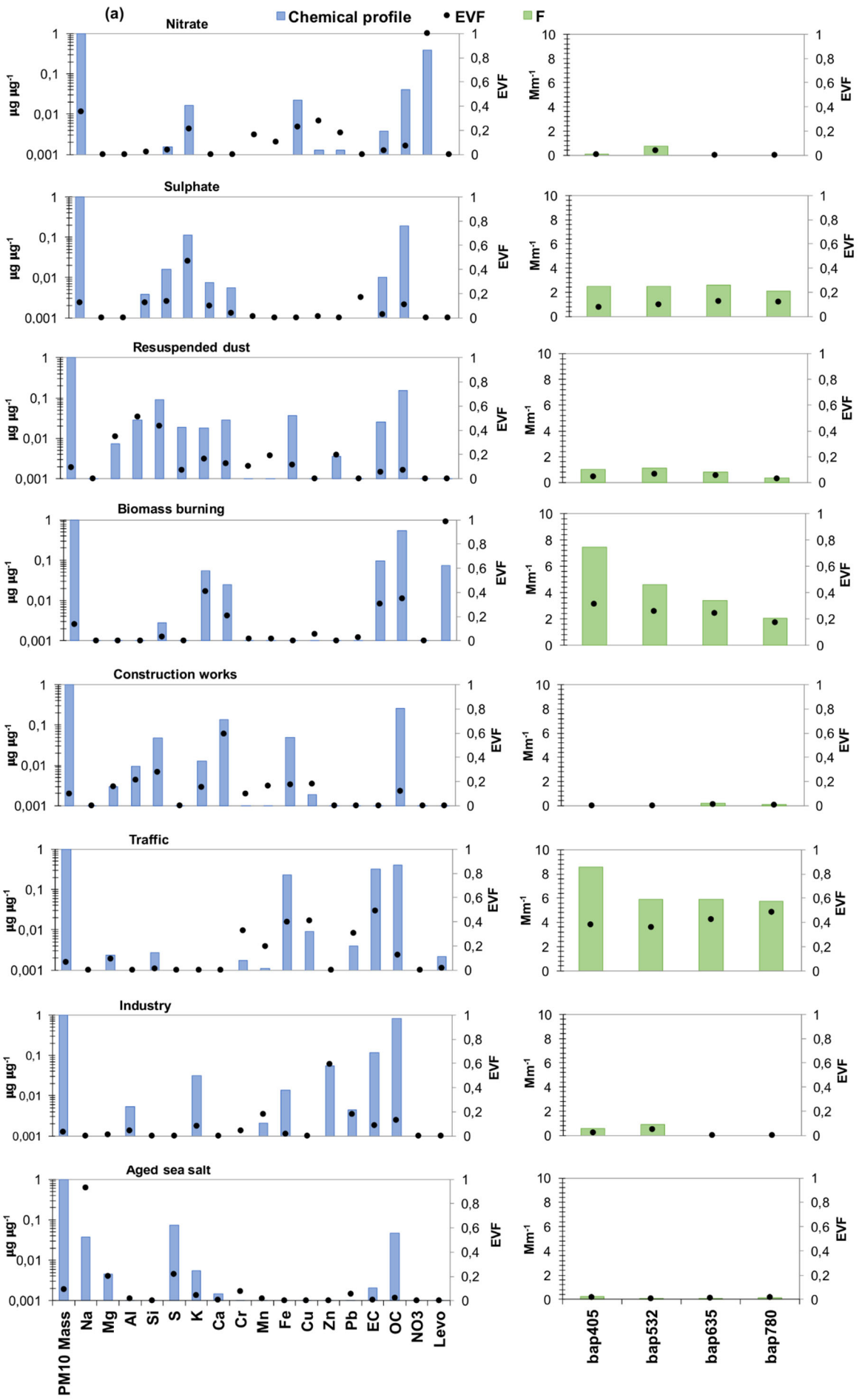
(a)
Chemical profile
EVF
F
Nitrate
Sulphate
Resuspended dust
Biomass burning
Construction works
Traffic
Industry
Aged sea salt
µg µg-1
Mm-1
EVF
PM10 Mass
Na
Mg
Al
Si
S
K
Ca
Cr
Mn
Fe
Cu
Zn
Pb
EC
OC
NO3
Levo
bap405
bap532
bap635
bap780

Figure 3: (a) Chemical profiles of the 8-factor constrained solution ; (b) b_{ap} apportionment of the 8-factor constrained solution. The blue bars represent the chemical profile (output of the matrix F normalised on mass), the green bars the output values of the matrix F for the optical variables, and the black dots the EVF.

Factors	Summer [μg m^{-3}]	Winter [μg m^{-3}]	Total [μg m^{-3}]
Nitrate	3.6 (15 %)	21.1 (44 %)	10.2 (31 %)
Sulphate	6.3 (26 %)	8.1 (17 %)	7.0 (21 %)
Resuspended dust	4.6 (19 %)	1.7 (4 %)	3.5 (11 %)
Biomass burning	0.32 (1 %)	8.3 (17 %)	3.3 (10 %)
Construction works	5.9 (24 %)	3.4 (7 %)	4.9 (15 %)
Traffic	1.4 (6 %)	2.2 (5 %)	1.7 (5 %)
Industry	0.86 (4 %)	1.2 (3 %)	1.0 (3 %)
Aged sea salt	1.4 (6 %)	1.8 (4 %)	1.6 (5 %)

Table 1: Absolute and relative average source contributions to PM10 mass in the 8-factor constrained solution.

The factor interpreted as nitrate fully accounted for the explained variation of NO_3^-. This factor contained a significant fraction of nitrate in the chemical profile (39 %) and all nitrate was present only in this factor. This source was by large the most significant one at the investigated site, explaining about 31 % of the PM10 mass over the whole campaign (a similar estimate – 26 % - was reported by Amato et al. (2016) during the AIRUSE campaign in Milan in 2013) raising up to 44 % during wintertime (comparable to 37 % reported by Vecchi et al. (2018)). Indeed, the Po valley is well-known for experiencing very high nitrate concentrations during wintertime (Vecchi et al., 2018; and references therein) because of large emissions of gaseous precursors related to urban and industrial activities, biomass burning used for residential heating, high ammonia levels due to agricultural fields manure and ~~– last but not the least –~~ poor atmospheric dispersion conditions.

The factor associated to sulphate ~~shows~~ showed EVF=0.47 for S and much lower EVF for all the other variables in the factor. Considering the sulphur contribution ~~of S~~ in the chemical profile in terms of sulphate and ammonium sulphate, the relative contribution of sulphur components in the profile ~~increases~~ increased from 11 % (S) up to 45 % (ammonium sulphate). The latter is the main sulphur compound detected in the Po valley as reported in previous papers such as e.g. Marcazzan et al. (2001) and was by far the highest contributor in the chemical profile. The other important contributor was OC (19 %), whose impact on PM mass increased up to 30 % when reported as organic matter using 1.6 as the organic carbon-to-organic matter conversion factor for this site (Vecchi et al., 2004). Due to the secondary origin of the aerosol associated to this factor, it was not surprising to find also a significant OC contribution; indeed, aerosol chemical composition in Milan is impacted by highly oxygenated components due to aging processes favoured by strong atmospheric stability (Vecchi et al., 2018 and 2019). In this factor, EC contributed for about 1 %. Considering the total EC concentration reconstructed by the model, the EC fraction related to the sulphate factor was about 6 %. Opposite to

sulphates, EC has a primary origin; however, its presence with a very similar percentage (4-5 %) in a sulphate chemical profile was previously pointed out in Milan, indicating a more complex mixing between primary and secondary sources (Amato et al., 2016) e~~.~~.g. with sulphate condensation on primary emitted particles. ~~-~~The sulphate factor accounted for 21 % of the PM10 mass.

The factor identified as resuspended dust is mainly characterised by high ~~EVFs~~EVF and contributions coming from Al, Si and Mg, i.e. crustal elements. The Al/Si ratio is 0.31, very similar to the literature value for average crustal composition (Mason, 1966); the relatively high OC contribution ~~of OC~~ in the chemical profile (15 %) ~~and~~ together with the presence of EC (about 2.6 %) is suggestive of~~, indicate that there is very likely~~ a mixing with road dust (Thorpe and Harrison, 2008). This source accounts for about 11 % of the PM10 mass.

The factor identified as biomass burning was characterised by high EVF for levoglucosan (0.98), a known tracer for this source as it is generated by cellulose pyrolysis; EVF higher than 0.3 were also found for K, OC, and EC. In the source chemical profile, OC contributed for 54 %, EC for 10 %, levoglucosan for 7 %, and K for 5 %. The average biomass burning contribution during this campaign was 10 % (up to 17 % in wintertime). Anticipating the discussion presented in detail in Sect. 3.3, it is worth ~~noticing~~noting that the second largest contribution to the aerosol absorption coefficient after traffic was detected in this factor.

The factor with high EVF (0.60) for Ca was associated to construction works, following literature works (e.g. Vecchi et al., 2009; Bernardoni et al., 2011; Dall'Osto, 2013; Crilley et al., 2017; Bernardoni et al., 2017a; and references therein). Major contributors to the chemical profile were Ca (13 %), OC (26 %), Fe, and Si (5 % each). This factor accounted on average for 15 % to PM10 mass. As already mentioned, during the campaign a not negligible contribution from this source was expected, due to the presence of a ~~construction~~ building site nearby the monitoring location.

In the factor ~~here~~ assigned to traffic (primary contribution), EVF larger than 0.3 characterised EC, Cu, Fe, Cr, and Pb. The highest relative mass contributions ~~in terms of mass~~ in the chemical profile were given by OC (41 %), EC (32 %), Fe (23 %), and Cu (1 %). The lack of relevant crustal elements such as Ca and Al in the chemical profile, suggested a negligible impact of road dust in this factor. As reported above, at our sampling site the road dust contribution was very likely mixed to resuspended dust and further separation of these contributions was not possible. This traffic (primary) contribution over the whole dataset accounted for 5 % of the PM10 mass with a slightly lower absolute contribution in summer (see Table 1). This contribution is comparable to the percentage (7 %) reported by Amato et al. (2016) for exhaust traffic emissions but it is lower than our previous estimates (Bernardoni et al., 2011; Vecchi et al., 2018), i.e. 15 % in 2006 in PM10 and 12 % in PM1 recorded in winter 2012. However, the current estimate seems to be still reasonable when considering the efforts done in latest years to reduce vehicles exhaust particle emissions and the fraction of secondary nitrate due to high nitrogen oxides and ammonia emissions in the region (INEMAR ARPA-Lombardia, 2018) which has

to be added to account for the overall traffic impact~~; indeed, a significant traffic contribution due to nitrate should be accounted for the relevant nitrogen oxides and ammonia emissions from agriculture in the region (INEMAR-ARPA-Lombardia, 2018~~). Unfortunately, the non-linearity of the emission-to-ambient concentration levels relationship and the high uncertainties in emission inventories still prevent a robust estimate of this secondary contribution to total traffic exhaust emissions. As shown i~~I~~n Sect. 3.3, ~~it will be shown that~~ traffic is the largest contributor to aerosol absorption coefficient thus strengthening~~, a result that reinforces~~ the interpretation of this factor as a traffic emission source.

The industry factor showed high EVF for Zn (0.59) and the second highest EVF was related to Mn (0.13). Previous studies at the same sampling site identified these elements as tracers for industrial emissions (e.g. Vecchi et al., 2018; and references therein). The chemical profile resulted enriched by heavy metals and, after traffic, it was the profile with the highest share of Cr, Mn, Fe, Cu, Zn, and Pb (explaining about 8 % of the total PM10 mass in the profile). The industry contribution was not very high in the urban area of Milan, accounting for 3 % on average.

The factor interpreted as aged sea salt was characterised by high EVF of Na (0.93) and this element was - as a matter of fact - present only in this factor chemical profile. To check the physical consistency of this assignment and considering that Milan is about 120 km away from the nearest sea coast, back-trajectories coloured by the aged sea salt concentration (in ng m^{-3}) were calculated through the NOAA HYSPLIT trajectory model (Draxler and Hess, 1998; Stein et al., 2015; Rolph et al., 2017) and represented using the R package~~Openair software~~ (Carslaw and Ropkins, 2012; R Core Team, 2019). As an example, results from a very short event (13/07 h.16-18) singled out by the model and representing the highest sea salt contribution during summer are reported in Fig. S3 (Supplement). Before and during the event, south-western air masses ~~originated from south-west compatible with~~coming from the Ligurian sea where observed while soon after the event, there was a rapid change of wind direction. ~~These hours were characterised by an average h~~High wind speeds were recorded during the episode (~~of~~ 4.8 ± 1.7 m s^{-1} ~~(~~with a maximum peak of 9.5 m s^{-1}) compared to 1.9 ± 1.0 m s^{-1} average wind speed ~~recorded during~~characterising the summer campaign.~~.~~

When marine air masses are transported to polluted sites, sea salt particles ~~are characterised by~~show a Cl deficit due to reactions with sulphuric and nitric acid (Seinfeld and Pandis, 2006~~).~~) and~~In this case,~~ the factor chemical profile ~~was~~ is expected to be enriched in sulphate and nitrate. In this work, nitrate was not present in the aged sea salt chemical profile; a very rough estimate (Lee et al., 1999) gave a maximum expected contribution of 2 % (about 82 ng m^{-3}) of the total nitrate mass in atmosphere~~,~~ that can be considered negligible in terms of mass contribution of the sources.

Temporal patterns of Cl concentrations (not inserted in the multi-time resolution analysis as being a weak variable) during marine aerosol episodes were exploited to further confirm the factor-to-source association. ~~As an example, a very short event (13/07 h.16-18) singled out by the model and representing the highest sea salt contribution during summer was analysed in further detail. Before and during the sea salt event, air masses originated from south-west compatible with~~

~~Ligurian sea while soon after the event, there was a rapid change of wind direction (Fig. S3, in the Supplement). These hours were characterised by an average high wind speed of 4.8 ± 1.7 m s^{-1} (with a maximum peak of 9.5 m s^{-1}) compared to 1.9 ± 1.0 m s^{-1} average wind speed recorded during the summer campaign. In addition,~~ Cl concentration and aged sea salt pattern showed an evident temporal coincidence in peak occurrence during the short summer event (Fig. 4), thus supporting the source identification. Moreover, during this episode only the Cl coarse fraction increased (Fig. S4, in the Supplement) and reached about 90 % of total PM10 Cl concentration; Cl/Na ratio was 0.38 ± 0.05, consistent with an aging of marine air masses during advection showing the typical Cl depletion. ~~due to the interaction between sea salt particles and polluted air masses (Seinfeld and Pandis, 2006).~~

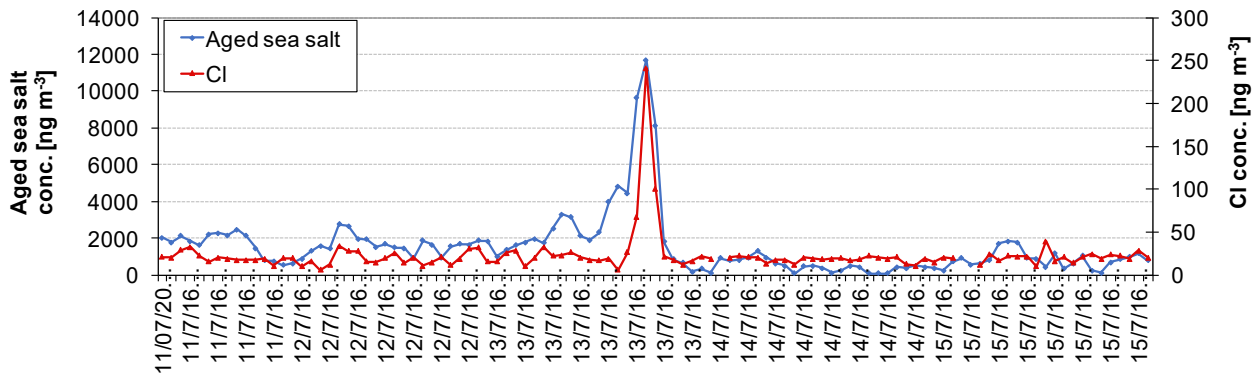

Figure 4: Temporal patterns of aged sea salt source retrieved from the multi-time resolution model and Cl concentrations measured in atmospheric aerosol.

Bootstrap analysis was performed to evaluate the uncertainties associated to source profiles (Crespi et al., 2016). 100 runs were carried out (see Fig. 5, values expressed in ng m^{-3} or Mm^{-1} on a logarithmic scale); factors were well mapped, with Pearson coefficients always higher than 0.97, and tracers for each source showed small interquartile range, supporting the goodness of the solution presented in this work.

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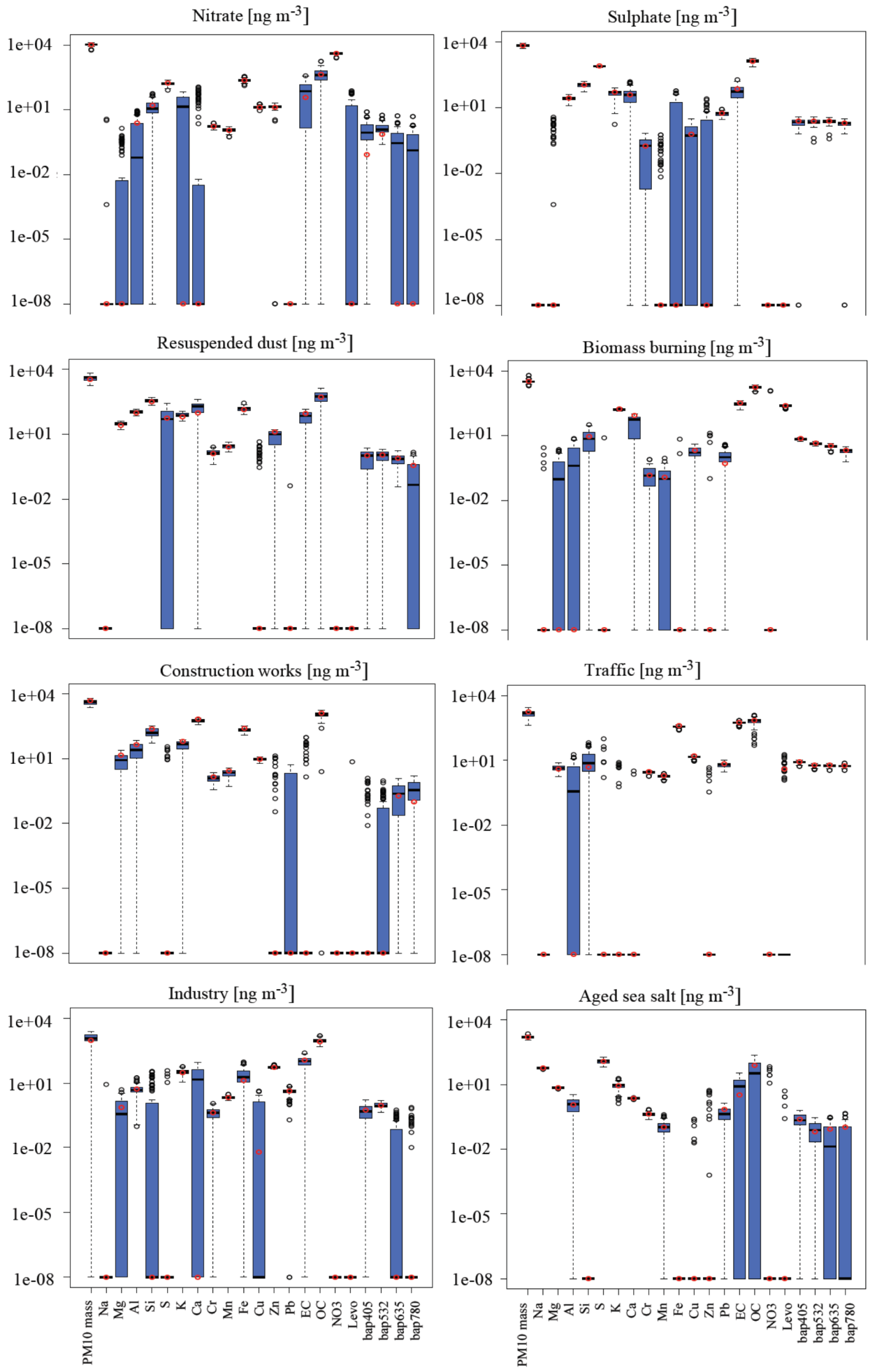
Nitrate [ng m-3]
Sulphate [ng m-3]
Resuspended dust [ng m-3]
Biomass burning [ng m-3]
Construction works [ng m-3]
Traffic [ng m-3]
Industry [ng m-3]
Aged sea salt [ng m-3]
1e+04
1e+01
1e-02
1e-05
1e-08
PM10 mass
Na
Mg
Al
Si
S
K
Ca
Cr
Mn
Fe
Cu
Zn
Pb
EC
OC
NO3
Levo
bap405
bap532
bap635
bap780

Figure 5: Box plot of the bootstrap analysis on the 8-factor constrained solution. The red dots represent the output values of the solution of the model; the black lines the medians from the bootstrap analysis; the blue bars the 25th and 75th percentile; the dotted lines the interval equal to 1.5 the interquartile range and the black dots the outliers from this interval.

3.3 Improving source apportionment with optical tracers

First of all, the use of the absorption coefficient determined at different wavelengths as input variable in the multi-time resolution model, strengthened the identification of the sources~~,~~ suggesting that it can be exploited when specific chemical tracers are not available (e.g. levoglucosan for biomass burning). To prove that, a separate source apportionment study was performed with EPA PMF 5.0 (Norris et al., 2014)~~, introducing~~ using only hourly elemental concentrations from samples collected by the streaker sampler and hourly b_{ap} at different λ measured by PP_UniMI on the same filters as input variables. Streaker samples typically lack of a complete chemical characterisation; in particular, important chemical tracers such as levoglucosan and EC are not available. In this analysis, b_{ap} assessed at different wavelengths resulted ~~particularly useful for the identification~~effective in identifying ~~of~~ the biomass burning factor that explained a significant percentage of the b_{ap} itself (from 25 % to 35 % depending on λ) (Fig. S5, in the Supplement); without ~~this additional information~~the optical variables, the factor-to-source assignment would be otherwise based only on the presence of elemental potassium although it is well-known that K cannot be considered an unambiguous tracer as it is emitted by a variety of sources (see for example Pachon et al., 2013; and references therein). Furthermore, results showed that the absorption coefficient contribution was higher than 45 % in the factor labelled as traffic, highlighting the importance of exhaust emissions in a factor that would be ~~otherwise~~ differently characterised ~~mainly on~~by elements related to non-exhaust emissions (Cu, Fe, Cr).

From the multi-time resolution model, the two factors identified as biomass burning and traffic were the main contributors to aerosol absorption in atmosphere and showed significant EVF values. At 780 and 405 nm, traffic contributions ~~Contributions~~ to b_{ap} were 55 % and 42 ~~%~~%; biomass burning accounted for~~for traffic and~~ 20 % and 36 % ~~for biomass burning at 780 and 405 nm, respectively~~. The Explained Variation (EVF) of b_{ap} has the maximum value at 405 nm for biomass burning (0.32) and at 780 nm for traffic (0.49), showing the tendency to decrease and increase with the wavelength, respectively.

The third contributor to aerosol absorption in atmosphere was the sulphate factor, with a contribution comparable to the biomass burning one at 780 nm (about 20 % of the total reconstructed b_{ap} at this wavelength). The sulphate factor contained a small fraction of EC, as previously discussed (see Sect. 3.2). This might be explained considering that non/weakly light-absorbing material can form a coating able to enhance particle absorption (Bond and Bergstrom, 2006;

Fuller et al., 1999) within a few days after emission~~ (Bond et al., 2006)~~. Laboratory experiments and simulations from in-situ measurements highlighted absorption amplification for absorbing particles coated with secondary organic aerosol (Schnaiter et al., 2003; Moffet and Prather, 2009). ~~These processes related to~~ P~~p~~article~~s~~ aging ~~can become important in~~ is a significant process in the Po valley due to low atmospheric dispersion conditions and ~~they~~ it might explain the relatively high contribution of the sulphate factor to the absorption coefficient in respect to the other sources (~~excluding~~ apart from traffic and biomass burning). ~~Among the other sources,~~ R~~r~~esuspended dust was the main contributor at all wavelengths (between 3 % and 7 % of the total reconstructed b_{ap}, depending on the wavelength), likely due to the role of iron minerals. The other ~~four~~ sources were less relevant in terms of EVF values and overall contributed for less than 11 %.

~~It is noteworthy that opposite~~In contrast to the approach used in source apportionment ~~optical~~ models based on optical ~~measurements~~data~~,~~ like the widespread Aethalometer model (Sandradewi et al., 2008a) and MWAA model (Massabò et al., 2015; Bernardoni et al., 2017b), it is noteworthy that no a-priori information about α values ~~the Absorption Ångström Exponent (α)~~ of the fossil fuel and biomass burning sources was introduced in the multi-time resolution model~~; instead~~ and~~,~~ an estimate for the~~its~~ values was directly retrieved from the model. ~~A further~~Another literature approach used Delta-C as an input variable together with chemical aerosol components in source apportionment models and was very effective in separating traffic (especially diesel) emissions from biomass combustion emissions (Wang et al., 2011, 2012).~~It has to be mentioned that optical models are typically based on a two-source hypothesis (i.e. biomass burning and fossil fuel emissions); an exception reported in previous works (Wang et al., 2011) concerned the use of Delta-C used as an input variable together with chemical aerosol components in source apportionment models and proved to be very effective in separating traffic (especially diesel) emissions from biomass combustion emissions.~~

~~Hereafter, i~~In order to compare the multi-time resolution model and ~~optical~~ models based on optical ~~measurements~~data ~~results~~, contributions due to traffic and industry (i.e. emissions most likely connected to fossil fuel usage) were added up and labelled as "fossil fuel emissions". In accordance with the two-source approach used in the Aethalometer model, the discussion about optical properties will be hereafter focused on the biomass burning and fossil fuel sources considering that sulphate and resuspended dust factors were less significant also in terms of EVF for optical variables, ranging from 0.08 to 0.12 and from 0.03 and 0.06, respectively, depending on the wavelength.

In Fig. 6 the wavelength dependence of b_{ap} for the biomass burning and the fossil fuel profiles obtained with the multi-time resolution model is shown; as α values can show significant differences when calculated using different pairs of λ (Sandradewi et al., 2008b), here we performed a fitting procedure considering $b_{ap} \propto \lambda^{-\alpha}$. Results were α_{BB} (α biomass burning) = 1.83 and α_{FF} (α fossil fuels) = 0.80; the range of variability of α values was estimated with the bootstrap analysis obtaining 0.78-0.88 for α_{FF} and 1.65-1.88 for α_{BB} (as 25th and 75th percentile, respectively).

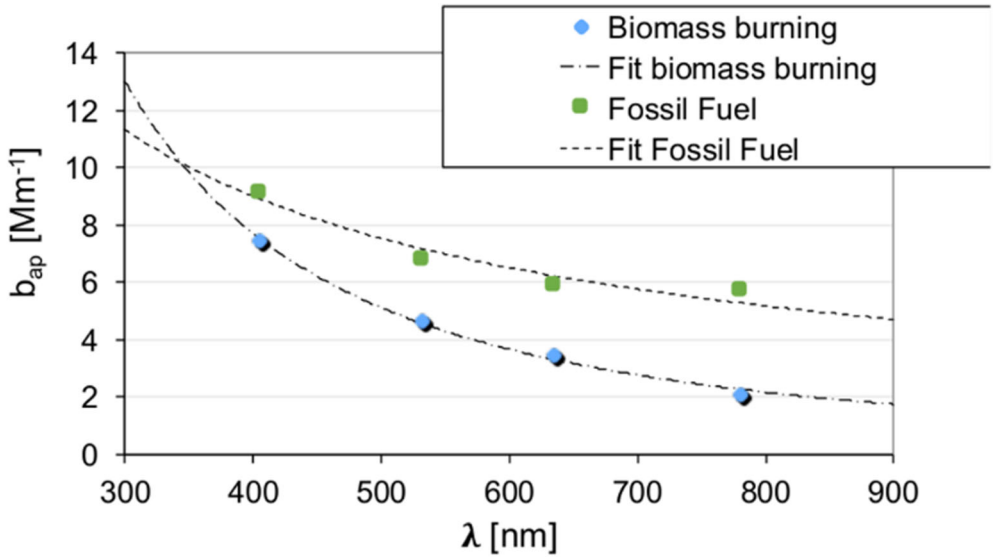

Figure 6: b_{ap} dependence on λ for biomass burning and fossil fuel emissions.

Zotter et al. (2017) reported a possible combination of α_{FF}=0.8 and α_{BB}=1.8 when EC concentration from fossil fuel combustion (estimated with radiocarbon measurements) is between 40 % and 85 % of the total EC concentration; in this work, the fraction of EC ascribed by the multi-time model to fossil fuel sources was 56 %. The combination 0.9 and 1.68 for α_{FF} and α_{BB}, respectively, was also suggested when in the study there are no or only limited additional information (e.g. from ^{14}C measurements). ~~Therefore, f~~From the wide range of possible combinations reported in the literature it is clear that t~~t~~he assessment of α_{BC} (assumed to be equal to α_{FF} in source apportionment ~~optical~~ models based on optical ~~measurements~~data) is still an issue and both experimental and simulation studies are in progress to reduce uncertainties and give a better evaluation of this ~~relevant~~ key~~optical~~ parameter.

The α_{BB} value retrieved by the model was very similar to values reported by Zotter et al. (2017) and also comparable to 1.86 found for biomass burning by Sandradewi et al. (2008a) and 1.8 obtained by Massabò et al. (2015) who used also independent ^{14}C measurements for checking. The α_{FF} value resulted in the range 0.8-1.1 typically reported in ~~optical~~ source apportionment studies based on optical ~~measurements~~data (e.g. Bernardoni et al., 2017b; Zotter et al., 2017; and references therein). Indeed, the sampling site was an urban background station in Milan ~~where aerosol aging is a relevant process~~ and our samples were hardly ~~had been~~ impacted by fresh traffic emissions. Considering ~~this feature~~the aged nature of Milan aerosol, the average α_{FF} was ~~included in the wide range of~~comparable to estimates for BC coated particles reported in the literature ~~works~~ (approx. 0.6-1.3, see e.g. Liu et al., 2018) and obtained by both ambient measurement (e.g. Fischer and Smith, 2018; and references therein) and numerical simulations (e.g. Gyawali et al., 2009; Liu et al. 2018; and references therein).

Results here reported allow also to study the relationship between the absorption coefficient and the mass of black carbon (BC), i.e. the so called Mass Absorption Cross section ~~(MAC)~~ at different wavelengths. The MAC(λ) =b_{ap}(λ)/BC relationship assumes that ~~black carbon (~~BC~~)~~ is the only light-absorbing species present; however, this assumption is not always valid~~,~~ since the transport of mineral dust from desert areas and brown carbon ~~(BrC)~~ can significantly contribute to aerosol absorption. During our monitoring campaign, no ~~significant~~ contribution from Saharan ~~mineral~~ dust was observed; opposite, biomass burning was ~~proved~~ proven to be ~~a relevant~~an important source so that BrC was certainly a significant contributor (Fuzzi et al., 2015) as also suggested by α_{BB} = 1.83 in the biomass burning factor. The possible overestimation of BC when total b_{ap} is ascribed to BC only is usually minimised choosing a wavelength higher than 600 nm, exploiting the spectral dependence of absorption from different aerosol compounds (Petzold et al., 2013).

EC concentration retrieved from the chemical profiles (see Fig. 3) was used as a proxy for BC to estimate source-dependent b_{ap}(λ)-to-BC ratio. Results are represented in Fig. 7. It is noteworthy that here this ratio is intentionally not indicated as MAC, since overestimation of the BC absorption especially at lower λ might occur (see previous discussion). BrC is expected to give a small contribution in the fossil fuel source; therefore, the best approximation for MAC(λ) values are likely the b_{ap}(λ)-to-BC ratios observed in the fossil fuel source at our monitoring site. They resulted ~~to be~~ 13.7 m^2 g^{-1} ~~at~~for λ = 405 nm~~;~~, 10.2 m^2 g^{-1} for~~at~~ λ = 532 nm,~~;~~ 8.8 m^2 g^{-1} ~~at~~ for λ = 635 nm,~~;~~ 8.6 m^2 g^{-1} ~~at~~ for λ = 780 nm. For~~At~~ λ = 550 nm Bond and Bergstrom (2006) reported a MAC value of~~=~~ 7.5 ± 1.2 m^2 g^{-1} for uncoated fresh emitted particles and MAC values in polluted regions ranging from 9 to 12 m^2 g^{-1}, attributable to absorption enhancement due to particles coating. The MAC estimate obtained in this work from multi-time resolution model for~~at~~ 532 nm is comparable to literature values above reported thus confirming~~and it confirms~~ the importance of aging processes in atmosphere on the optical properties of particles.

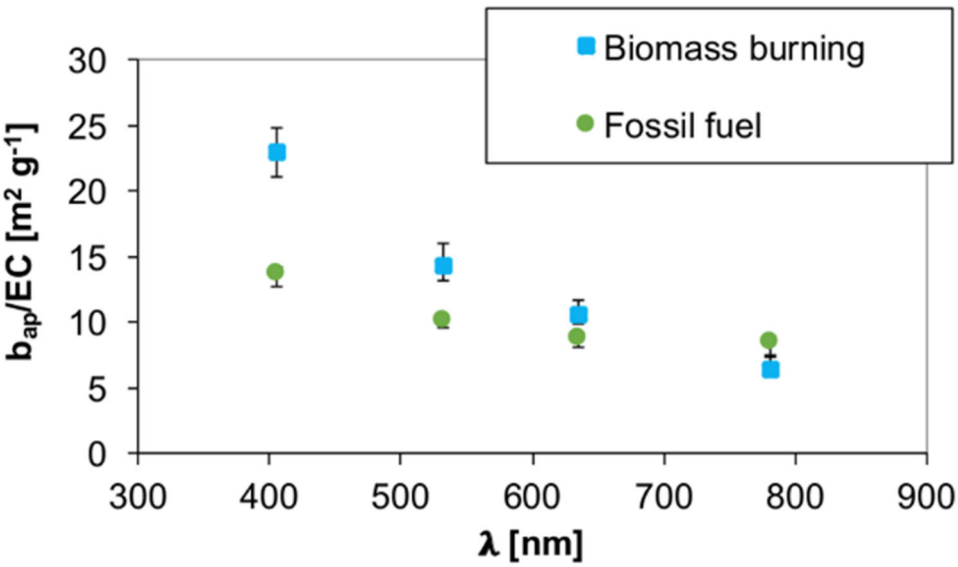

Figure 7: b_{ap}-to-EC ratio dependence on λ for biomass burning and fossil fuel emissions. Error bars represent the 25th and 75th percentile retrieved from the bootstrap analysis.

Ratios represented in Fig. 7 are less comparable at λ=405 nm (see also Table S4, in the Supplement) due to the significant contribution of BrC to b_{ap} at this wavelength in the biomass burning factor.

No seasonal differences in the atmospheric ratios were observed but at λ = 405 nm (see Table S4, in the Supplement), for which winter values ~~are~~ were higher than summer ones (17.8 ± 0.4 and 14.2 ± 0.5, respectively); ~~this result can be explained considering~~due to the influence of biomass burning emissions on BrC concentration in atmosphere during the ~~winter~~ cold season.

From the outputs of the modelling approach here proposed, the apportionment of the biomass burning and fossil fuel contributions to b_{ap} at different wavelengths was also obtained. As expected, the relative contribution to the total reconstructed b_{ap} ascribed to the biomass burning factor ~~decreases~~ decreased with increasing λ, opposite to the contribution from fossil fuel combustion which ~~gives~~ gave the highest contribution at 780 nm (Table 2); in addition, the latter contribution ~~prevails~~ prevailed at all wavelengths at the investigated site.

	λ = 405 nm	**λ = 532 nm**	**λ = 635 nm**	**λ = 780 nm**
Biomass burning	36 % (31 %-36 %)	29 % (25 %-30 %)	26 % (23 %-27 %)	20 % (16 %-22 %)
Fossil fuels	45 % (41 %-46 %)	43 % (39 %-44 %)	45 % (41 %-47 %)	55 % (48 %-55 %)

Table 2: Average contribution to total reconstructed b_{ap} for the biomass burning and fossil fuel factors; in parenthesis 25th and 75th percentile are reported.

4. Conclusions

The multi-time resolution model implemented through the Multilinear Engine (ME-2) script allowed the analysis of experimental data collected at different time scales, coupling the detailed chemical speciation at low time resolution and the temporal information given by high time resolution samples. The effect of the introduction of the aerosol absorption coefficient (b_{ap}) measured at different wavelengths in the modelling process was investigated and gave promising results. First of all, a more robust identification of sources was provided; secondly, it paved the way to the retrieval of optical apportionment and optical characterisation of the sources (e.g. estimate of source-specific Absorption Ångström Exponent - α - and Mass Absorption Cross section – MAC - at different wavelengths). It is worthy to note that ~~– at the state of the art –~~ currently in source apportionment ~~optical~~ models based on optical ~~measurements~~data (e.g. Aethalometer model)

values for α related to fossil fuel emissions and biomass burning are fixed by the modeller thus carrying a large part of the uncertainties in the model results. Considering that the estimates for the Absorption Ångström Exponent were here obtained as a result of a quite complex modelling approach (i.e. using multi-time resolution datasets ~~collected on limited periods~~joining chemical and optical variables) and without any a-priori assumption, the results obtained ~~– although obviously affected by a certain degree of uncertainty due to both experimental data and modelling process (here estimated while typically not taken into consideration for fixed α values used in the literature) –~~were fairly comparable to literature results and gave a further tool ~~aimed at assessing~~to assess more robust source-related α values. Obviously these estimates are affected by a certain degree of uncertainty due to both experimental data and modelling process (while uncertainties are typically not taken into consideration for fixed α values used in the literature). In perspective, joining together different approaches such as the receptor modelling here proposed and e.g. ^{14}C ~~measurements~~data and artefact-free b_{ap} measurements will lead to better estimates of the Absorption Ångström Exponent~~; work is in progress at our laboratories to achieve this goal.~~.

The original approach described in this work can be applied to ~~any~~ source apportionment ~~study~~ studies using any suitable dataset (not necessarily with multi-time resolution). Besides the traditional source apportionment, the impact of different sources on the aerosol absorption coefficient was estimated; this piece of information can be very useful to formulate strategies of pollutants abatement, in order to improve air quality and to face climate challenges. In particular, at the investigated site secondary compounds constituted the highest contribution in terms of PM10 mass (52 % on average), while the two factors identified as biomass burning and traffic were found to be the most significant contributors to aerosol light absorption in atmosphere, in agreement with available literature~~works~~.

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Data availability.

The data in the study are available from the authors upon request (roberta.vecchi@unimi.it).

Supplement.

The supplement related to this article is available online.

Author contributions.

ACF performed streaker sampling and related optical analysis, implemented the advanced model, analysed the results, and drafted the paper. GV contributed to model implementation, data reduction and Hysplit back-trajectories retrieval. VB, SV, and REP carried out the sampling campaign on filters, performed the optical measurements and data analysis. GC, SN, and FL performed PIXE analysis and data reduction. DM and PP carried out ionic characterisation on filters and data analysis. RV was responsible for the design and coordination of the study, the synthesis of the results and the final version of the paper. All authors contributed to the interpretation of the results obtained with the new approach here described and revised the manuscript content giving a final approval of the version to be submitted. RV and ACF reviewed the paper addressing reviewers' comments.

Competing interests.

The authors declare that they have no conflict of interest.

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Figure 1: Diurnal profile of Fe and Cu concentrations (in ng m^{-3}).

Figure 2: Diurnal profile of aerosol absorption coefficient (in Mm^{-1}) measured at different wavelengths.

~~Diurnal profile of the aerosol absorption coefficient measured at different wavelengths in Mm^{-1}).~~

Figure 3: (a) Chemical profiles of the 8-factor constrained solution ; (b) b_{ap} apportionment of the 8-factor constrained solution. The blue bars represent the chemical profile (output of the matrix F normalised on mass), the green bars the output values of the matrix F for the optical variables, and the black dots the EVF.

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Figure 4: Temporal patterns of aged sea salt source retrieved from the multi-time resolution model and Cl concentrations measured in atmospheric aerosol.

Figure 5: Box plot of the bootstrap analysis on the 8-factor constrained solution. The red dots represent the output values of the solution of the model; the black lines the medians from the bootstrap analysis; the blue bars the 25th and 75th percentile; the dotted lines the interval equal to 1.5 the interquartile range and the black dots the outliers from this interval.

Figure 6: b_{ap} dependence on λ for biomass burning and fossil fuel emissions.

Figure 7: b_{ap}-to-EC ratio dependence on λ for biomass burning and fossil fuel emissions. Error bars represent the 25th and 75th percentile retrieved from the bootstrap analysis.

Table 1: Absolute and relative average source contributions to PM10 mass in the 8-factor constrained solution.

Table 2: Average contribution to total reconstructed b_{ap} for the biomass burning and fossil fuel factors; in parenthesis 25th and 75th percentile are reported.