Author’s response

Dear Editor,
Prof. Harald Saathoff,

Thank you and thank to the staff of ACP for the deadline extension given to our final revision paper. We are glad to notice that both referees appreciated the experimental efforts and the high relevance of the results presented in our paper, which was one of the most significant goal of our work, as clearly stated in the introduction. The present extensive field campaign allowed to collect data along 120 vertical profiles in less than 45 days, which already represents a novelty in literature for this type of measures. We are confident that the experimental study was conducted with care and technical quality and, in fact, the reviewers raised no criticisms on this part of the work.
Furthermore, both referees focused their attention on the calculation section of the paper, asking for elucidation of a number of technical points, which we are glad to focus on in the following responses to the referees. All the raised criticisms and relative answers have been addressed in the revised manuscript. Finally, we improved the quality of the figures, in order to help the reader to understand the vertical behavior of aerosol properties, and the whole text was proofread and edited to emendate the typos and to improve the language. We are pleased that this discussion based on the constructive criticisms of both referees has helped us to improve the scientific quality of the work done.

With our best regards,

Yours sincerely,

Dr. Luca Ferrero

Response to Reviewer#1

We thank the reviewer for his or her helpful comments and insight. We respond to the general and to the specific points below. All the comments are addressed in the revised manuscript. As requested, the whole text was proofread and edited, to emendate the typos and to improve the language.

General Comment 1: This manuscript reports comprehensive experimental findings of vertical profiles of black carbon aerosols and their impact on direct forcing over three Italian basin valleys. A lot of effort has been put in conducting this study by the authors. This is commendable.

Author Answer (AA)1: *Indeed, the main goal our study was to "present the first measured high resolution vertical profiles of black carbon and calculation of aerosol radiative forcing and atmospheric heating rates in the lower troposphere, over Italy and Europe". In this respect, we would like to underline that the present extensive field campaign allowed collecting data along 120 vertical profiles in less than 45 days, which already represents a novelty in literature for this type of measures.*

Nevertheless, the effort has been put not only in experimental vertical profiles measurements, but also on optical properties calculation and on radiative forcing (heating rate) determination. Specifically, a careful analysis, reported in sections 3.1.1 and 3.1.2, allowed an interpretation of the experimental results leading to the identification of a common behaviour of BC and aerosol dispersion over basin valleys, under atmospheric stagnant conditions. In this respect, the mixing layer dynamics were taken into account developing a standardized height.

Experimental measurements were then used for aerosol optical properties calculation. In order to perform an accurate and reliable calculation, a methodology based on Mie theory (section 2.3) was followed. In this respect, particular attention has been given to the choice of the method for calculating the refractive index (section 2.3.1) and to the introduction of appropriate corrections to aerosol number size distributions, measured by an OPC (section 2.3.2), as both these quantities can seriously affect the optical properties calculation. The attention paid in the methodological approach is also evidenced by the exhaustive literature documented in the paper. Moreover, we note that this methodology has been previously successfully applied in Ferrero et al. (2011) ("Vertical profiles of aerosol absorption coefficient from micro-Aethalometer data and Mie calculation over Milan"; The Science of the total environment).

The obtained aerosol optical properties underwent three validation procedures: 1) a columnar comparison of a set of parameters (i.e. refractive index, SSA, AOD…) independently obtained by the Aerosol Robotic Network (AERONET) at 441 nm, 657 nm and 880 nm (section 3.2.1; Table 2 and 3); 2) a detailed comparison along vertical profiles of the absorption coefficient measured by the micro-Aeth® AE51 at 880 nm with that calculated over TR, MI and ME at the same wavelength and 3) a comparison at ground-level of the absorption coefficient and the Ångström exponent independently obtained using the 7-λ Aethalometer AE31. This triple validation guarantees the quality of both the columnar-averaged optical parameters and their correct shaping along vertical profiles. This procedure was necessary to avoid the presence of compensatory effects along profiles and to perform a right estimation of the radiation absorbed in each atmospheric layer. Finally, the optical properties were discussed in section 3.2.3 in the light of changes in the aerosol chemical composition with height. Concerning the aerosol radiative forcing and heating rate we want to underline that this paper reports the first experimentally-derived vertical profiles of these quantities, at high resolution over Italy, and, as far as we know, over Europe. The highlighted common behaviour over basin valleys, with the higher atmospheric absorption and heating rate located within the mixing layer, will allow to study the potential feedbacks induced by this vertical shaping of the atmospheric forcing.

General comment 2. However, the paper is weak in technical quality. Contrary to the efforts put in conducting the field experiments, the authors have done a poor job in analysing and interpreting the data. Assumptions in the calculations are made without proper justification. No error or sensitivity analysis is done on the key parameters.

AA2: In light of what discussed above, it is difficult for us to accept this second part of the general comment (especially because of its lack of specificity) as we demonstrated (see AA1) that a big effort was also put in analysing and interpreting the data.

Moreover, we would like to point out that the methodology exploited in this paper was validated using three datasets of reference: 1) AERONET, 2) the absorption coefficient independently measured using the micro-Aeth® AE51 at 880 nm along the vertical profiles, 3) the absorption coefficient and the Ångström exponent independently obtained at ground-level using the 7-λ Aethalometer AE31. This triple validation guarantees the reliability of optical properties calculation considering different " validation levels" along vertical profiles: the columnar average, the single data points along vertical profiles and the ground level values. The validation was deepened in the revised version of the paper adding a new section: "3.2 Validation of aerosol optical properties".

Furthermore, the same methodology to calculate the aerosol optical properties was previously presented and validated in Ferrero et al. (2011) and Angelini et al. (2009).

Nevertheless, we address in the following discussion all the specific technical points raised in the reviewer's report. In particular, for what concern the methodology, and related assumptions, they are discussed as follows: the assumption of spherical particles and its applicability is discussed in the AA7, the internal mixing scenario in the AA6, the treatment of the aerosol size distribution in the AA3, the determination of the complex refractive index in the AA8. As previously done for the validation, a new section was added in the revised version of the paper also for the assumption: section "2.3.1 Assumptions".

For what concern the sensitivity analysis, some tests were conducted concerning the aerosol refractive index determination, varying the density and refractive index of pure BC in input to the Bruggeman mixing rule (see section 2.3.2). In particular, results obtained using the density (1.8 g cm^{-3}) and the refractive index (1.85+0.71i) suggested in Bond and Bengstrom (2006) were compared: 1) with those obtained with the density (1.0 g cm^{-3}) and the refractive index (1.75+0.44i) used in the OPAC software (Hess et al., 1998), 2) with those obtained with the density (2.0 g cm^{-3}) and the refractive index (2+1i) reported in Roessler et al. (1984). These two references are of high importance as they report the lowest density (never observed) value and one of the highest imaginary part in literature, respectively.

Calculations highlighted a substantial equivalence of the three sets of input parameters in determining the real part of the aerosol refractive index. On the contrary, the imaginary part experienced an average increase of 23.5±3.1% and 22.2±4.6% (all wavelengths), with respect of present results, when exploiting the OPAC and the Roessler et al. (1984) inputs, respectively. This effect was due to the exceedingly low density of OPAC data (never measured) and to the too high (one of the higher in literature) imaginary part of pure BC reported in Roessler et al. (1984).

These tests were not reported in the first version of the paper avoiding to increase its weight and length but, due to your question, we added them in section 3.2.1 (Pages 24-25, lines 696-703).

Sensitivity tests related to the size distribution correction and interpolation are reported and discussed in Ferrero et al. (2011) and were not repeated here. Thus, we added a sentence in section 2.3.3 (Page 16, lines 438-439) to address to this publication for tests on size distribution.

Finally, as required, we added the standard deviations (as reported in figure 4 for experimental measurements of the aerosol properties) for the optical properties and radiative forcing; thus, an updated version of figures (see Figures 7, 8, 9 and 10) is presented in the paper.

Here we also summarize some results reported in a new table added in Supplementary Material (Table S1): considering below mixing height data, the coefficients of variation for BC and aerosol *concentration were: 12.8% and 8.7% over TR, 21.1% and 15.0% over MI and 14.2% and 13.5% over ME; correspondingly the coefficients of variation for b_{abs}, b_{sca} and b_{ext} (at 675 nm) were 18.2%, 11.9% and 13.4% over TR, 22.4%, 26.1% and 25.4% over MI and 13.6%, 16.0% and 15.5% over ME in keeping with the aforementioned ones for aerosol properties.*

Considering above mixing height data, the coefficients of variation for BC and aerosol concentration were: 23.0% and 14.3% over TR, 25.4% and 14.9% over MI and 15.5% and 18.3% over ME; correspondingly the coefficients of variation for b_{abs}, b_{sca} and b_{ext} (at 675 nm) were 22.6%, 20.9% and 21.2% over TR, 27.8%, 23.1% and 23.6% over MI and 15.6%, 19.1% and 18.5% over ME in keeping with the aforementioned ones for aerosol properties.

Specific Comment 1 (SC1): The validity of the measured optical properties (scattering and absorption coefficients, SSA, and phase function) relies on the accuracy of the measured aerosol size distribution and refractive index. The size distribution was measured by a Grimm optical particle counter (OPC) in a wide size range. However, what the authors have failed to mention is that: (a) the Grimm OPC starts binning only from 250 nm and upwards in aerodynamic size. Below 250 nm, the instrument just gives an integrated number concentration without any information on the size distribution shape; and (b) typical black carbon (BC) aerosols have aerodynamic diameters less than 300 nm and mobility diameters less than 1000 nm. In this study, I would expect majority of BC to end up in the less than 250 nm stage of the Grimm OPC, since the instrument doesn't measure mobility diameters. Hence, shape of the size distribution of BC aerosols could not be inferred. Without the proper shape of the size distribution of BC aerosols, how can the authors predict their scattering and absorption coefficients? Aerosol properties are very sensitive to variation in shape of the size distribution. Carbonaceous aerosols follow a self-preservation size distribution, and the accumulation mode of their bimodal distribution peaks at around 200 nm. This information is needed to calculate faithfully the optical coefficients. The authors have attempted to calculate the aerosol coefficients without proper knowledge of this information.

AA3: We agree with the referee that both the size distribution and the refractive index can seriously affect the optical properties calculation. In fact, we clearly reported at page 557, line 10 (first submitted version) that using the OPC Grimm 1.107 the "lowest equivalent PLS size of OPC is 0.25 µm". In this section (2.3.2), we have deepened the OPC description and we have clearly reported at page 557, lines 8-15, that, using the OPC Grimm 1.107, a "Truncation Effect" is present and "the accumulation mode was only partially measured (lowest equivalent PLS size of OPC: 0.25 µm) and no measurements were available for Aitken mode particles (D_p<0.1 µm)". Conversely, "the coarse mode resulted completely defined". In this respect, as already reported in the paper, "a negligible error (~2-4%) comes from not considering the Aitken mode in the optical properties calculation (Bond and Bergstrom, 2006; Guyon et al., 2003; Liu and Daum, 2008; Randriamiarisoa et al., 2006); however, the "truncation effect" in the accumulation mode cannot be neglected".

That being clarified, in order to perform accurate optical properties calculations, the "truncation effect" was accounted for (page 557, lines 16-21) through "a log-normal interpolation of the aerosol number-size distribution" that "was conducted for each OPC data measured along vertical profiles to complete the aerosol size distribution function n(Dp). This method has already been successfully used by Ferrero et al. (2011), Deshler et al. (2003) and Angelini et al. (2009). This procedure makes the calculated optical properties closely dependent on the reliability of the number-size distribution interpolation, hence its accuracy is discussed in section 3.2.1" where the following comparison is reported (pages 565-566, lines 26-29 and 1-2): "the corrected and interpolated aerosol size distribution was compared to that retrieved by AERONET-Ispra: the calculated accumulation mode geometric mean diameter (D_g: 0.204±0.010 µm) and the geometric standard deviation (σ_g: 1.560 ± 0.060) agreed very well with AERONET-Ispra (D_g: 0.206 ± 0.016 µm, σ_g: 1.552 ± 0.045; Table 2) allowing, together with the aforementioned validation of m, to accurately estimate the profiles of optical properties using the Mie theory". Table 2 and 3 also *report results of the comparison between the obtained size distribution and that estimated from the AERONET network.*

Finally, we underline that the OPC Grimm 1.107 classifies the aerosol particles in terms of optical equivalent diameter and not of aerodynamic size. The optical equivalent diameter, as defined by Howell et al. (2006), "is the diameter of a sphere of known refractive index (that of polystyrene latex spheres of calibration) that scatters light as efficiently as the real particle in question". This effect originates the "undersizing" problem, which was solved correcting "the OPC size channels to account for the ambient aerosol refractive index m. The OPC response function (S: the partial light scattering cross section of the particle related to the specific optical design of the OPC) was computed at 655 nm (laser wavelength)" as reported in Baron and Willeke (2005) and Heyder and Gebhart (1979) (see section 2.3.2, page 556, lines 9-26).

Concerning the BC size distribution, at page 553, lines 17-23 it is reported: "The complex refractive index (m=n+ik) of aerosol was calculated considering a hybrid internal/external mixing scenario. The coarse ($D_p>1\mu m$) and fine ($D_p\leq 1\mu m$) particles were considered externally mixed, each one characterized by its proper value of m (Ferrero et al., 2011). Coarse particles ($D_p>1\mu m$) were assumed to be composed of dust, while m for fine particles was calculated from the measured $PM_{2.5}$ chemical composition (sections 2.2.2 and 3.1) using the Bruggeman mixing rule (Stier et al., 2007; Aspnes 1982; Heller, 1965; Bruggeman, 1935)".

Thus, the fine particles were treated under an internal mixing scenario in which, in each particle, BC is mixed with other chemical components. In this scenario, the optical properties are related to the size distribution of the whole internally mixed aerosol and not to the size distribution of the BC alone (in that case an externally mixing would be assumed).

In this respect, we have to underline that optical properties were calculated along vertical profiles (within and above the mixing layer) and not in proximity of a combustion source (i.e. close to a traffic line) thus giving the time for particles to age and promote an internal mixing. Aging along vertical profiles is described in section 3.1.2 and it is also reported in literature (McMeeking et al., 2011). A similar observation is reported in Cahill et al. (2012). Finally, this behaviour was also demonstrated by several observation conducted in the past along vertical profiles over the investigated sites (Ferrero et al., 2012; Moroni et al, 2013) (see also AA7).

Thus, in order to be clearer, the manuscript was modified including the above considerations in section 2.3.1 and 2.3.3.

<u>SC 2:</u> Without having confidence in the scattering and absorption coefficients of BC aerosols, further calculation of parameters such as SSA, phase function seem fraught with significant errors to me. Not to mention, both SSA and phase functions can blow up the direct forcing efficiencies. Therefore, one has to be very cautious when calculating these parameters. In this study, unfortunately, the authors have not taken the necessary care in calculating the fundamental aerosol optical properties needed for forcing estimations.

<u>AA4:</u> As discussed above (see AA1, AA2, AA3), in order to perform an accurate and reliable calculation of the aerosol optical properties, a rigorous methodology based on Mie theory (section 2.3) and a huge literature documentation were accounted for; they were followed by three validation procedures: 1) a columnar comparison of a set of parameters independently obtained by the Aerosol Robotic Network (AERONET); 2) a detailed comparison along vertical profiles of the absorption coefficient measured by the micro-Aeth® AE51 at 880 nm with that calculated over TR, MI and ME for the same wavelength and 3) a comparison at ground-level of the absorption coefficient and the Ångström exponent independently obtained using the 7-λ Aethalometer AE31. This triple validation guaranteed the quality both of the columnar-averaged optical parameters and also of a correct shaping of them along vertical profiles. The validation was deepened in the revised version of the paper adding a new section: "3.2 Validation of aerosol optical properties".

SC 3: The authors mention they compare the accuracy of the Grimm measured size distribution in Sec. 3.2.1. I couldn't find any comparison in that section.

AA5*: The comparison is reported in section 3.2.1, at page 565 (lines 26-29) and at page 566 (lines 1-2): "the corrected and interpolated aerosol size distribution was compared to that retrieved by AERONET-Ispra: the calculated accumulation mode geometric mean diameter (*D_g*: 0.204±0.010 μm) and the geometric standard deviation (*σ_g*: 1.560 ± 0.060) agreed very well with AERONET-Ispra (*D_g*: 0.206 ± 0.016 μm,* σ_g*: 1.552 ± 0.045; Table 2) allowing, together with the aforementioned validation of m, to accurately estimate the profiles of optical properties using the Mie theory". Finally, Table 2 and 3 also report a comparison of the main parameters of the size distribution measured using OPC Grimm 1.107 (after correction and log-normal interpolation; section 2.3.2) with that estimated from the AERONET network.*

SC 4: The authors also mention that they use a log-normal interpolation technique to compute the aerosol size distribution. How well does this method compare for BC aerosols? It could be that this method agrees better for coarse mode (like dust) aerosols, and Grimm is an appropriate instrument for measuring the number size distribution of such aerosols. However, for BC size distribution, Grimm is a poor choice.

AA6: *As stated also in AA3, fine particles were treated under an internal mixing scenario in which, in each particle, BC is mixed with other chemical components. In this scenario, the optical properties are related to the size distribution of the whole internally mixed aerosol and not to the size distribution of the BC alone. It has to be underlined that optical properties were calculated along vertical profiles (within and above the mixing layer) and not in proximity of a combustion source (i.e. close to a traffic line) thus giving the time for particles to age and promote an internal mixing. Aging along vertical profiles is decribed in section 3.1.2 (and references therein) and it is also reported in literature (McMeeking et al., 2011; Cahill et al., 2012; Ferrero et al., 2012; Moroni et al., 2013). In this respect, see also AA7. Moreover, the log-normal interpolation of OPC has already been successfully used in the past in Ferrero et al. (2011) and Angelini et al. (2009). It is also reported in Deshler et al. (2003) and it is currently applied in literature; see for example the log-normal interpolation in Saleh et al. (2013). We clarified this point on the revised manuscript in section 2.3.1.*

SC 5: The phase function is calculated using the Mie theory, which is appropriate for spherical particles. BC aerosols are not spherical. And phase function of non-spherical particles are markedly different than spherical aerosols. In the forcing efficiency calculations, this phase function propagates as the hemispherical back scatter parameter, which would change the forcing efficiency significantly if non-spherical particles are assumed.

AA7: We agree with the referee that a proper estimation of the phase function is fundamental for radiative forcing calculation. In this respect, at page 589, Figure 6a reports a validation of the calculated phase function, which shows its reliability and applicability to the radiative forcing calculations. Concerning the assumption of spherical particle, it is widely used in literature; however, it is also very well known that particles are not perfect spheres in the atmosphere and thus, we discuss here, and added in the manuscript, some further motivations for this choice. First of all, as stated in AA3, the fine particles were treated under an internal mixing scenario in which, in each particle, BC is mixed with other chemical components. In this scenario, the optical properties are related to the size distribution of the whole internally mixed aerosol and not to the size distribution of the BC alone (in that case an externally mixing would be assumed).

In this respect, we have to remind that the present study is focused on the aerosol behaviour along vertical profiles where aerosol can age (see Morgan et al., 2010 and 2006 and McMeeking et al. 2011; Cahill et al., 2012 and recent results from the PEGASOS campaign over Italy). This behaviour is also supported by several observations conducted in the past long vertical profiles: in particular, between 2005 and 2008 more than 300 profiles were measured over the investigated sites (especially over Milano and Terni). During these experiments it was evidenced (through size distribution analysis, chemical speciation and SEM-EDS analysis) that "fine particles experienced an increase of their mean volume with height; this fact along with the observed increase in secondary aerosol components (i.e. ammonium nitrate), sphericity, and correlation among fine aerosol particles" "suggested the influence of recurrent ageing dynamics (condensation/coagulation) in both contexts"; moreover, SEM data evidenced the internal mixing state of most of the collected particles. These results are reported in Ferrero et al. (2012) and in Moroni et al. (2013) and support the use of sphericity assumption in the present study as reasonable. The previous considerations were reported in section 2.3.1.

SC 6: The aerosol refractive index measured from the chemical composition uses the coated sphere assumption. It is okay to use such assumptions as long as the authors specify the uncertainties associated with using such assumptions.

AA8: *The aerosol refractive index was calculated using the Bruggeman mixing rule (or effective medium approximation), which is not a simple coated sphere assumption. The Bruggeman mixing rule is a part of more general mixing rule formulation resumed in Aspnes et al. (1982) that is as follows:*

$$\frac{\varepsilon_{eff}-\varepsilon_h}{\varepsilon_{eff}+2\varepsilon_h}=\sum_{i=1}^{n} f_i \frac{\varepsilon_i-\varepsilon_h}{\varepsilon_i+2\varepsilon_h}$$

where ε_{eff} *is the complex effective dielectric constant of the mixture (*$m_{eff}\approx\sqrt{\varepsilon_{eff}}$*),* ε_h *represents the dielectric function of the host medium,* ε_i *and* f_i *are the complex dielectric constant, and the volume fraction, of the i-th component respectively.*

Depending on the choice of host medium, we may obtain three different mixing rules: 1) Maxwell-Garnett (MG) if the host medium is one of the components ($\varepsilon_i=\varepsilon_h$*) (Stier et al., 2007; Schuster et al., 2005; Bohren and Huffman, 1983; Aspnes 1982; Heller, 1965) and in this case it is possible to refer to the Maxwell-Garnett as coated sphere assumption; 2) Lorentz-Lorenz (LL) if the host medium is the vacuum (*$\varepsilon_h=1$*) (Liu and Daum, 2008; Aspnes 1982; Heller, 1965); 3) Bruggeman (BR) if no choice of host medium is made, and inclusions are considered embedded in the effective medium itself (Stier et al., 2007; Aspnes 1982; Heller, 1965, Bruggeman, 1935). Stier et al. (2007) and Aspnes (1982) point out that the BR mixing rule overcomes the dilemma of the choice of host medium among the various aerosol components. From this point of view, the BR mixing rule considers all possible positions of each component (BC, dust, water soluble materials…) in an aerosol particle, respect to the other components. Thus, it allows simulating the real complexity of aerosols and making the BR mixing rule suitable for use in calculating the aerosol* m_{eff}*. For this reason, the BR mixing doesn't consider a simple coated sphere assumption and implies that the left part of the aforementioned equation vanishes giving the equation 8 reported in the paper at page 553, line 24, section 2.3.1.*

Finally, the Bruggeman mixing rule avoids the risk of overestimating the imaginary part (k) of m, thus reducing the uncertainties, as instead happens using both the linear volume-average and the linear mass-average mixing rules in the presence of highly absorbing inclusions (i.e. BC) in a non-absorbing medium (Stier et al., 2007; Lesins et al., 2002; Chýlek et al., 1995).

We would also underline that all the values (density, refractive indexes) used as input in the refractive index mixing rule were carefully chosen from the literature (especially for BC) considering only state-of-the-art values (i.e. see values in Bond and Bengstrom, 2006) as reported *in section 2.3.2 (see also AA2). Moreover, the E-AIM (used in the hygroscopic growth of the aerosol) was previously validated through measurements conducted in an Aerosol Chamber (results reported in Ferrero et al., 2014). Due to your question we reported the aforementioned considerations in the revised version of the paper (section 2.3.2).*

<u>SC 7:</u> The comparison with AERONET, although seems necessary, doesn't provide any in- sight to the authenticity of the findings and data interpretation. As I mentioned before, first the authors need to convince the readers that the fundamental optical parameters have been calculated with caution and with some degree of accuracy/confidence. I strongly suggest the authors to perform a sensitivity calculation and error analysis of their data analysis, before attempting to calculating the radiative forcing efficiencies and heating rates. In summary, I suggest the authors to redo their scattering and absorption coefficients calculation with a more robust and technically sound approach. Then present the uncertainties involved in these parameters in a tabular format in the revised manuscript. Only after this the authors should proceed to calculate SSA, phase functions, and forcing efficiencies. They also need to propagate the uncertainties in SSA, phase functions, and refractive index during their calculation of forcing efficiencies

<u>AA9:</u> *We take the opportunity here to better explain our validation procedure. First of all, the validation of the optical properties calculation was done using three datasets of reference (see sections 3.2.1 and 3.2.2): 1) AERONET, 2) the absorption coefficient independently measured using the micro-Aeth® AE51 at 880 nm along the vertical profiles, 3) the absorption coefficient and the Ångström exponent independently obtained at ground-level using the 7-λ Aethalometer AE31.*
This triple validation guarantees the reliability of optical properties calculation considering different " validation levels" along vertical profiles: the columnar average, the single data points along vertical profiles and the ground level values.
The comparison with AERONET allows assuring the reliability of the columnar data and has the advantage to be performed on several wavelengths. The comparison with the micro-Aeth® AE51 data allows to validate the correct shaping of the optical properties along vertical profiles but it is limited to one wavelength (880 nm). The comparison with the 7-λ Aethalometer AE31 allows validating one point of the profiles (ground-level) but on several wavelengths.
Thus, this triple validation was necessary considering the three target points of this study: 1) experimental vertical profiles measurements, 2) optical properties calculation and 3) radiative forcing (heating rate) determination.
In particular, the radiative forcing calculation requires that the aerosol optical properties were correctly determined. For this reason we have given particular emphasis and importance to the data quality, discussing data validation through two sections of the paper: 3.2.1 and 3.2.2.
The first section (section 3.2.1) has the aim to validate the columnar outputs of the optical properties calculation through a comparison with AERONET data. In this respect AERONET is a state of the art global network whose data are widely used in literature during several validation procedure (see an example, not exhaustive of the whole literature, in Levy et al., 2007). In section 3.2.1 not only the data averaged over the whole column were validated but also the free troposphere properties were validated comparing data above 1 km (derived as reported in section 2.2.2), with AERONET-Davos data.
The second section (section 3.2.2) allowed to perform a further step in the validation procedure; as a matter of fact, the comparison with the AERONET network guarantees the quality just of the columnar-averaged parameters (as stated at page 567, lines 4-9). However, also a correct shaping of the optical properties along vertical profiles is needed in order to understand the behavior of radiative forcing along vertical profiles. Thus, the validation reported in section 3.2.2 (absorption coefficient independently measured using the micro-Aeth® AE51 at 880 nm vs. calculated with Mie theory at the same wavelength) is necessary to avoid the presence of compensatory effects along

profiles and to subsequently perform a right estimation of the radiation absorbed in each atmospheric layer (sections 2.4 and 3.3). Another important aspect is that section 3.2.2 also reports a comparison of the absorption coefficient and the Ångström exponent independently obtained at ground-level using the 7-λ Aethalometer AE31.

Finally we would like to underline that the methodology followed in this paper to calculate the aerosol optical properties was previously validated and published in Ferrero et al. (2011) and Angelini et al. (2009). With the present work, instead, we are doing a step forward relying on previous works yet published.

We better clarified the validation methodology along the paper in section 3.2. Moreover, as reported in AA2, sensitivity tests on refractive index were added in section 3.2.1. Instead, sensitivity tests related to the size distribution correction and interpolation are reported and discussed in Ferrero et al. (2011) and were not repeated here. Finally, as required, we added the standard deviations (as reported in figure 4 for experimental measurements of the aerosol properties) to the optical properties and radiative forcing. An updated version of figures (see Figures 7, 8, 9 and 10) is presented in the paper.

<u>Response to Reviewer#2</u>

We thank the reviewer for his or her helpful comments and insight. We respond to the general and specific points below. All the comments are addressed in the revised manuscript. As requested, the whole text is going to be proofread and edited, to emendate the typos and to improve the language.

General Comment: The authors present measurements of BC and aerosol concentrations over three Italian sites, with particular emphasis on the vertical profiles of BC. As well pointed out in the paper, this is highly relevant data, both for understanding the local climate conditions, and for validating both regional and global climate models. The authors then proceed to calculate the atmospheric absorption at various heights due to BC, and the corresponding heating rates.

I enjoyed the first part of the paper, and believe the data are of high relevance. The second part, however, I feel is trying to go a bit too far, a bit too fast. I recommend that this paper advance to publication in ACP only if the authors either significantly extend, or greatly tone down, the discussion on what they label BC-DRE.

<u>Author Answer (AA)1:</u> *We thank you for your comment which remarks the big effort put in this work, and the quality of the experimental results obtained. Concerning the second part of the work, we would like to underline that linking the aerosol properties (size and chemistry) along vertical profiles to their radiative effect is a very important topic. As a matter of fact, similar examples of calculation of the radiative forcing starting from experimentally measured aerosol vertical profiles are reported in literature. For example, Ramana et al. (2010, Nature Geoscience) investigate the role of aerosol chemistry on the radiative forcing and heating rate over China, Chakrabarty et al. (2012) did a similar work over the Brahmaputra River Valley while Tripathi et al. (2007) investigated the heating rate behaviour over India after measuring BC concentrations along vertical profiles.*

Moreover, the present work is the natural consequence of past works (Ferrero et al., 2011; Angelini et al., 2009) in which the methodology (exploited in this paper) to calculate the aerosol optical properties was previously presented and validated. Along these lines, in the present work we are going one step further.

Thus, as we consider the atmospheric absorption induced by BC an important part of this paper, we followed your suggestion and expanded this part; we extended sections 2.4 and 3.4 by reporting the methodology and the results concerning the aerosol radiative effect, respectively. A detailed *description of the changes introduced in section 2.4 is reported in AA3 while changes introduced in section 3.4 are discussed in AA4.*

Specific Comment 1 (SC1): The authors place their measurements of BC vertical profiles in the context of recent publications – both model comparisons and experiments – that show that the uncertainty in the profiles is a major contributor to the current uncertainty in total BC forcing. This is true. However, most of that uncertainty comes from the region from 5km and upwards. It is also true that the community needs better measurements of near-ground profiles to validate regional modelling, but the vertical profile up to 600-800 meters above ground level, as measured here, is unlikely to greatly impact the total uncertainty. Hence, I believe that this part of the discussion is a bit misguided. A better comparison would be e.g. against AEROCOM model profiles for the region, to see if they reproduce the observed behavior w.r.t. the mixing height. (Which I doubt, as they will be much too coarse in both spatial and temporal resolution.)

AA2: *We suppose your comment refers to a sentence in the discussion of the experimental results (section 3.1.1, page 562, lines 4-8; first submitted version). In that sentence, our intention was just to underline the importance and the need for BC vertical profile measurements. In fact, they can contribute to improve the accuracy of modelled profiles around the globe thus contributing to reduce the current uncertainty in global BC forcing.*
However, we agree with your observation that this sentence should be better articulated, considering the context of measures reported in the paper. Thus, we rephrased it as follows: "As reported in literature (Samset et al., 2013; Zarzycki and Bond, 2010), a worldwide lack of knowledge about BC vertical distribution is generally present. Thus, the aforementioned results were used in section 3.3 and 3.4 to assess the related vertical behavior of both aerosol optical properties and aerosol DRE over basin valleys". We inserted this new sentence in the paper (section 3.1.1; Page 21, lines 588-591).
Finally, for what concerns a possible comparison with model outputs (i.e. AEROCOM), we have to underline that it is actually beyond the scope of this paper, which is instead focused on the results obtained through experimental field measurements in the atmosphere.

SC2: This leads me to the discussion of radiative transfer calculations in sections 2.4 and 3.3. It is unclear to me how the authors have defined and quantified their DRE. The definition is on page 557, line 25, and then further on page 570, line 3, but how was this used in practice? As I understand the description of the model, all measurements are within the first layer (1 km resolution from 0 to 25 km a.s.l.). The authors then say that dF is the difference of the aerosol DRE at the top and bottom of each atmospheric layer. How does this yield the profiles shown in Figure 8? Do they e.g. quantify the amount of radiation reaching the surface without any BC added, then add each individual measured point separately? Isn't the case then simply that they have a forcing per gram calculated from one model, and then scale the concentration in each measured layer by this factor?

AA3: *We agree with you that a deeper description of the radiative transfer calculation would help the reader, thus we first clarified better these aspects in the manuscript in order to avoid erroneous interpretations. In particular, in section 2.4 the main equations concerning the radiative transfer and heating rate calculation were reported. They are resumed here below.*
In this respect, the instantaneous aerosol DRE (W m^{-2}) was quantified as the change in the net radiative flux between the atmospheric conditions with and without the aerosols in the atmosphere as follows:
$DRE_z = F_{aer,z} - F_{w/o-aer,z}$
where F is the radiative flux, and the subscripts aer,z and w/o-aer,z refers to the atmospheric conditions with and without aerosol at the height z, respectively.

Because the atmospheric aerosol is characterized by a significant absorptive capacity, the difference between the DRE at the top and the bottom of each atmospheric layer represents the instantaneous radiative power density absorbed by the aerosol within that particular atmospheric layer ($\Delta\mathrm{DRE}_{ATM}$; W m^{-2}) as follows:

$$\Delta\mathrm{DRE}_{ATM} = DRE_{z+\Delta z} - DRE_z$$

where Δz is the differential thickness within each atmospheric layer.

$\Delta\mathrm{DRE}_{ATM}$ is expressed in W m^{-2} which is the common metric used in literature to quantify the integrated radiative power density absorbed by the aerosol in the atmospheric layer; the aerosol absorption in the atmosphere is evaluated over altitude thick layer of the atmosphere and/or over the whole atmospheric column (Heald et al., 2014; IPCC, 2013; Bond et al., 2013; Das et al., 2011; Kedia et al., 2010)

However, in order to study the Absorptive DRE (ADRE) of the aerosol in the atmosphere along continuous high resolution vertical profiles, the aforementioned metric could be misleading as absolute values of $\Delta\mathrm{DRE}_{ATM}$ depend on the thickness of the layer Δz across which the DRE difference is computed. To compare measurements taken at different sites with a different vertical resolution, the ADRE was computed simply normalizing $\Delta\mathrm{DRE}_{ATM}$ by the thickness Δz:

$$ADRE = \frac{\Delta DRE_{ATM}}{\Delta_z}$$

Thus, the ADRE represents the radiative power absorbed by the aerosol for unit volume of air (W m^{-3}) and allows describing continuous vertical profiles of atmospheric absorption induced by aerosol even comparing data taken at different sites. Moreover, the ADRE can be directly related to the atmospheric heating rate (HR; see below). In fact, on the basis of the energy conservation principle, the absorbed radiant power must heat the atmospheric layer. The instantaneous HR is conventionally given by (Chakrabarty et al., 2012; Kedia et al., 2010):

$$HR = \frac{\partial T}{\partial t} = -\frac{g}{C_p}\frac{\Delta DRE_{ATM}}{\Delta P}$$

where $\partial T/\partial t$ represents the instantaneous HR (K day^{-1}) of each atmospheric layer, g is the acceleration due to gravity, C_p (1005 J kg^{-1} K^{-1}) is the isobaric specific heat of dry air, Δp is the pressure difference between the top and the bottom of each atmospheric layer. From the previous equation, considering the relationship between atmospheric pressure and height trough the hydrostatic equation ($dp = -\rho g dz$) it is possible to relate the HR linearly to the ADRE in each atmospheric layer:

$$HR = \frac{\partial T}{\partial t} = \frac{1}{\rho C_p}\frac{\Delta DRE_{ATM}}{\Delta z} = \frac{1}{\rho C_p} \cdot ADRE$$

Consequently, both section 2.4 and section 3.4 were updated and improved and a new Figure (Figure 8) was added to compare graphically the difference between the aerosol DRE at the top and at the bottom of each atmospheric layer ($\Delta\mathrm{DRE}_{ATM}$), the ADRE and the resulting heating rate over the three investigated sites (Terni, Milano and Merano).

Concerning the vertical resolution reported in your comment ("all measurements are within the first layer (1 km resolution from 0 to 25 km a.s.l.)"), it is only referred to the "Atmospheric profiles of pressure, temperature, air density, ozone, oxygen, water vapour, CO_2 and NO_2 concentrations" "defined by using the standard atmospheric data as defined by Anderson et al. (1986) for Midlatitude Winter" (as stated at page 558, lines 10-14).

Regarding your last question, we did not use a simple forcing per gram calculated from one model. On the contrary, our approach accounts for the complex changes along height of all the characteristics of aerosol (chemical composition, size distribution). In fact, in the radiative transfer model simulations performed with libRadtran, we used as input the optical properties (i.e. Extinction, Single Scattering Albedo, Phase Function) calculated from aerosol vertical profiles.

In conclusion, as also reported in the AA1 and here above, we expanded the description of the radiative transfer methodology in section 2.4.

SC3: Comparing figure 8 with figure 4, this appears to be approximately the case for TR and MI, but not for HR where e.g. an extra feature appears just above the mixing height and the slope is changed. What is the difference between these cases? Also, how does the forcing strength of the model used compare to other mod- els in the literature (e.g. Myhre et al. 2013, ACP, which shows the AeroCom models, albeit on global mean?)

AA4: *We would like to thank you very much for this comment, which allowed us to discover a mix up of the data in input to the radiative transfer code. This occurred during the input of the optical properties data, due to an erroneous labelling; in fact, the radiative forcing calculations over the three sites were not conducted at the same time but were processed separately.*
Thus, in order to ensure the quality of the work done, first we checked all the calculations presented in the paper (confirming the results for all the optical properties) and then we recalculated the radiative forcing. Results are reported in section 3.4 in the revised version of the paper and in the new Figures 8, 9 and 10. The results presented are now consistent, for all the three sites, first with that reported in figure 7 (optical properties in input) and then with those reported in figure 4.
Concerning the comparison with literature data, our results were in keeping with values reported in other works (Perrone and Bergamo, 2011; Saha et al., 2008; Chakrabarty et al., 2012). The absorption in the atmosphere at TOA reported in Myhre et al. (2013) for the same latitude (~40-45°N) is not so far from that reported in the Free Troposphere in the present paper even if the values reported in Myhre et al. (2013) are globally averaged, referred to the radiative forcing, while in this study the instantaneous radiative effect is considered (see Heald et al., 2014).
Most important, however, is that few vertical profiles of radiative effect and HR are present in literature and usually only the average columnar HR is estimated. For example, "Chakrabarty et al. (2012) estimated a columnar average HR of ~2 K day^{-1} considering a Δp of 300 hPa; as a comparison, using the same approach over TR, MI and ME, the average columnar HR was ~1-2 K day^{-1} in agreement with the above mentioned study".
However, it has to be pointed out that the estimation of the average columnar HR could be misleading as it does not give any information regarding were the highest HR is located and which feedbacks can trigger.
In summary, as the vertical behavior of the HR can trigger different feedbacks, the common behaviour found along height over Italian basin valleys for radiative effect and HR values is a very valuable outcome.

SC4: In general, a more thorough presentation of the sensitivities of the RTM used to the various parameters given as input – either measured or assumed – is needed to add weight to this part of the paper. Given the issues above, I'm not sure how to interpret the resulting heating rate calculations. My advice to the authors would be to put emphasis on the measurements themselves, up to and including the extraction of optical properties (though I note that Reviewer 1 has made comments here, which should also be looked closely at), but not proceed to radiative forcing and/or heating rates for profiles. Conversely, if they still wish to do so, I recommend a much more detailed description and sensitivity check of the RTM calculations and subsequent results.

AA5: *We consider this question related to previous one and thus, after the recalculation of the radiative forcing profiles, we followed your suggestion and we expanded also this part of the paper (section 3.4), as we consider the radiative forcing an important part of this paper. In this respect, the standard deviations (reported in figure 4 for experimental measurements of the aerosol properties) were also reported for optical properties (Figure 7) and radiative forcing (new Figures 8, 9 and 10).*