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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long term trends in aerosol optical characteristics in the Po Valley (IT)" *by* J. P. Putaud et al.

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Reply to Referee #2's comments

We would like to thank Referee #2 for useful suggestions for improving our manuscript, and important comments regarding the length of time series needed to derive significant trends.

About Referee#2's general comment: The major question I have is whether a record of 7 years can be considered appropriate for determining aerosol trends. Suppose the duration of this study had been 3 years? You can obtain statistically significant slopes in the time series data but what does it mean? Could this have been a 7-year period of decreasing aerosol loadings bounded on either side by increasing or flat aerosol

levels? If so, the longer term trend might not be decreasing. It is too bad that the data for this study ended at the end of 2010.

Our reply follows:

The length required for a data set to reveal a real long term trend is indeed an important question. According to Tiao et al. (J. Geophys. Res., 95, 20,507-20,517, 1990), it depends on the short term (e.g. month-to-month) variability, the autocorrelation in the data series, the magnitude of the trend to be detected, and the probability of detecting the real trend. Following the rules described by Tiao et al., 1990, we would need data series of approx. 7.5 years (case of PM2.5) at least (e.g. 9.5 years for the aerosol SSA) to have 90% of chance to detect a non zero trend. This is more than the length of the data series we studied, which means that the probability that we detected real trends is less than 90%.

The reason why we limited our study to the 2004 – 2010 period was initially because the data retrieved from the sun photometer almucantar measurements were not available after April 2010 at the time we wrote the manuscript. Including 2011-2013, we still observe negative trends in the variables discussed in the manuscript, but slopes apparently changed after 2010. We therefore believe that our ground-level observations, which are consistent with independent column integrated measurements and retrievals, reflect the impact of policies implemented during that period. We will attentively follow these trends in the future to detect whether they were perennial or transitional.

Our replies to Specific Comments:

- Abstract: The units for the decreasing trend are % yr-1. Corrected, sorry for this.

- pg. 9043, Line 20: Define 'intensive', and also 'extensive' when first used. Please provide a reference.

R: The terms "intensive" and "extensive variables" are defined in text books, and have been commonly used for 2 decades in the field of atmospheric science (see e.g. Ogren,

"A systematic approach to in situ observations of aerosol properties," in Aerosol Forcing of Climate, R. J. Charlson and J. Heintzenberg, Eds. New York: Wiley, 1995, pp. 215–226). The revised version of our manuscript will (if possible) include a footnote stating "intensive variables are independent from the aerosol concentration, while extensive variables are proportional to amount of particles".

- pg. 9044, Lines 25-27: The Weingartner et al. (2003) correction scheme is used for calculating absorption coefficients from the aethalometer. The atmospheric aerosol data from which this correction was developed were from the JFJ site, where aerosol loadings are light and the aerosols are highly aged. This is a simple scheme to apply and does not rely on concurrent light scattering measurements. It does give good agreement with some other methods for certain types of aerosols. The authors, however, have concurrent light scattering measurements available so why not use them to correct the aethalometer data? The prevailing scientific opinion is that scattering particles deposited on the filter surface of a filter-based light absorption instrument along with light absorbing particles will affect the measurement and should be taken into account. See the paper by Collaud-Coen et al., Atmos. Meas. Tech., 3, 457-474, 2010. There are several other methods evaluated in the AMT review, as well as 2 new methods. There is no real problem with using the Weingartner correction but the authors should say why this one was chosen over the other more recent ones given that they have nephelometer data that can be useful in correcting the aethalometer data for different aerosol types.

R: The correction proposed by Weingartner et al. (2003) does rely on concurrent light scattering measurements to determine the aerosol single scattering albedo, on which depends the correction of the shadowing effect. We compared years ago the absorption coefficients obtained using 2 other correction schemes (Arnott et al., 2005; Schmid et al., 2006) for the whole year of 2006. No significant difference appeared, due to the fact that the aerosol single scattering albedo is pretty low at our site. Since there is currently no standard method for correcting Aethalometer data, we stuck to the Wein-

gartner formula we used from 2004. According to us, the good agreement between the aerosol absorption coefficient values derived from the Aethalometer and the Multi Angle Absorption Photometer measurements (which are "automatically" corrected for scattering) suffices to prove the robustness of the correction scheme we used.

- pg. 9045, Lines 11-14: The authors need to be careful in relating growth in mobility diameter to growth in physical diameter or scattering coefficient. What assumptions go into this?

R: We have inserted in the revised manuscript a brief description of the method we used to correct in-situ aerosol data for hygroscopic growth, which indicates also the assumptions on which our calculations are based. This description is copied here below:

In brief, the particle hygroscopic growth factor GF(RH) at any relative humidity RH is estimated from the GF(90) assuming that GF(RH) = (1 – RH)ˆ(-y). This "y law" allows us to calculate the particle diameter in e.g. dry conditions. Assuming that particles are spherical, the volume of water in particles at instrumental RH is obtained as the difference between the particle volume at instrumental RH and at 0% RH. The aerosol refractive index at instrumental RH is retrieved by minimizing the difference between the aerosol scattering and absorption coefficients derived from measurements and computed from the Mie theory, and expressed as the refractive index of a mixture of dry aerosol and water. The refractive index and the number size distribution of the dry aerosol are then used to compute the optical properties of the dry aerosol.

- pg. 9045, Lines 24-25: AERONET Level 2.0 data are those data that are both cloud screened and quality assured, but they are also available for only the higher AOT episodes (e.g., AOT > 0.4 @ 500 nm). How much of the IPR surface aerosol data could not be compared with AERONET Level 2.0 data because there were no Level 2.0 data? Monthly mean values are presented for the aerosol data but some months undoubtedly have more data than others.

R: AERONET AOT Level 2.0 data are quality assured only (Pre- and post-field calibration applied, automatically cloud cleared and manually inspected) without further filtering. In contrast, AERONET-retrieved Level 2.0 SSA values are further filtered according to a series of criteria like AOT > 0.4 at 440 nm and solar zenith angle > 50°. As a consequence, the monthly averages for variables derived from AERONET measurements are indeed calculated from various amounts of data. However, IPR surface data and AERONET data are not compared to each other in our manuscript. Monthly mean AOT data are just combined with monthly mean aerosol optical properties at the ground to estimate the impact of our observations on the direct radiative forcing by aerosols. For this, we assume that the intensive properties of aerosols are uniform within the aerosol layer. This assumption is somewhat supported by the decrease in the Level 2.0 aerosol SSA data retrieved from sun photometer measurements, which is consistent with the decrease we observed at the ground.

However, to make clear that Level 2.0 aerosol SSA data are available for periods where AOT > 0.4 at 440 nm only, we inserted in the revised manuscript the statements “Level 2.0 SSA data are available for episodes where AOT440 > 0.4 only”, and “over periods where AOT440 > 0.4, i.e. about 25% of the time at IPR”.

- pg. 9047, first paragraph: Please add a sentence on how the residuals in Fig. 1 and other figures were calculated. There are different ways to calculate residuals.

R: Residuals E(t) are calculated according to Eq. 1 in the manuscript as the difference between the observation and the fit for each month. To clarify this, we have inserted “which is plotted in Figures 1 to 6.” in the explanation of Eq. 1.

- pg. 9047, Lines 12-13: ’A significant decreasing trend... is observed... at 0% RH too.’ Again, care must be taken in making this adjustment using the results from an HTDMA. Perhaps a paragraph explaining the method and assumptions belongs in this paper in addition to the reference to Adam et al. (2012).

R: Please see our reply to the question on p. 9045, line 11-14.

- pg. 9048, Lines 13-14: Change to ’...(defined as the ratio between the truncation corrected aerosol backscattering coefficient and the truncation-corrected aerosol total scattering coefficient)...’. Corrected.

- pg. 9049, Lines 3-6: Please explain how measurement uncertainties for nephelometer and aethalometer of 10% and 30% (should have references), respectively, result in a ’median uncertainty’ of 8% for the aerosol SSA. What kind of uncertainty is being discussed? Quadrature sum of errors, or RSS error?

R: As stated in the manuscript, our estimates of the random uncertainty of the scattering and absorption coefficients are based on results of recent inter-laboratory comparisons at the World Calibration Centre for Aerosol Physics. Our estimates are in line with the figures found in Heintzenberg et al., J. Atmos. Oceanic Technol., 23, 902–914, 2006 and Mueller et al, Atmos. Meas. Tech., 4, 245–268, 2011. Combining the random uncertainties of the scattering and absorption coefficients according to the law of propagation of error (quadratic sum) for independent variables, and applying the result to the median SSA value, we obtained a random uncertainty of 8% for the aerosol SSA. It is lower than this for high SSA, and higher for low SSA values. To clarify the way this uncertainty estimate was obtained, we specified “the uncertainty of the aerosol SSA estimated from the law of propagation of errors is 8% only for the median SSA value”.

- pg. 9050, Lines 3-6: This is a bit troubling. The argument is made in this work that EC is well related to absorption and PM2.5 is well related to scattering. I believe that is the point behind Figs. 7a and 7b. A decreasing SSA means that the ratio of scattering to extinction, or scattering to (scattering plus absorption) decreased. Put another way, absorption increased relative to scattering. In Line 5 the authors suggest, however, that changes in the ratio of EC to PM2.5 could not be responsible for the observed decreasing trend in the SSA. Do the authors believe that other absorbing substances could be responsible for this trend? If so, this should be stated clearly with whatever proof is available. Was enough brown carbon or organic carbon measured to account for this discrepancy? Was the wavelength dependence of light absorption as measured

with the aethalometer consistent with increased levels of OC (e.g., larger AAE's, more absorption at shorter wavelengths)?

R: Fig. 7a and 7b indeed show that scattering and absorption are correlated with PM2.5 and EC, respectively. Therefore, a straightforward explanation for the increase in the absorption/scattering ratio would be an increase in the EC/PM2.5 ratio. This increase was observed till 2006 but no more later on. However, Fig 7b also shows that the ratio absorption/EC tends to increase with time (reddish points mostly above the line, bluish points mostly below the line for the largest values, which are observed during wintertime). We do not have a definitive explanation for that. An increase in the brown carbon content of PM2.5 during wintertime in the last years would lead to such an increase in the absorption/EC ratio. This hypothesis is in line with the observed increase in the absorption Ångström exponent (+0.5% yr-1) calculated from the slope of the log(absorption) vs. log(wavelength) from UV to IR, but we cannot prove it since we do not have direct measurements of brown carbon. Actually, other phenomena like changes in mixing state of EC with the other PM2.5 constituents (towards more and more internal mixing) might also lead to the observed trends. To clarify, we have revised the following sentences as follows:

"Changes in the EC content of PM2.5 alone cannot therefore explain the trend observed in the aerosol SSA from 2004 to 2010"

"This might be due to increasing concentrations of other light absorbing substances like brown carbon (detected as OC) during cold months over this period".

Technical corrections:

- Abstract, Line 2: Change 'Aerosols' to 'Aerosol'. Corrected.

- Introduction, Line 1: Change 'Air suspended' to 'Air-suspended'. Corrected.

- pg. 9044, Lines 21-22: TSI nephelometer should be model 3563. Nephelometer should not be capitalized. Corrected.

- pg. 9048, Lines 22-23: Change 'A significant decreasing trends is...' to 'Significant decreasing trends are...'. Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 9041, 2014.

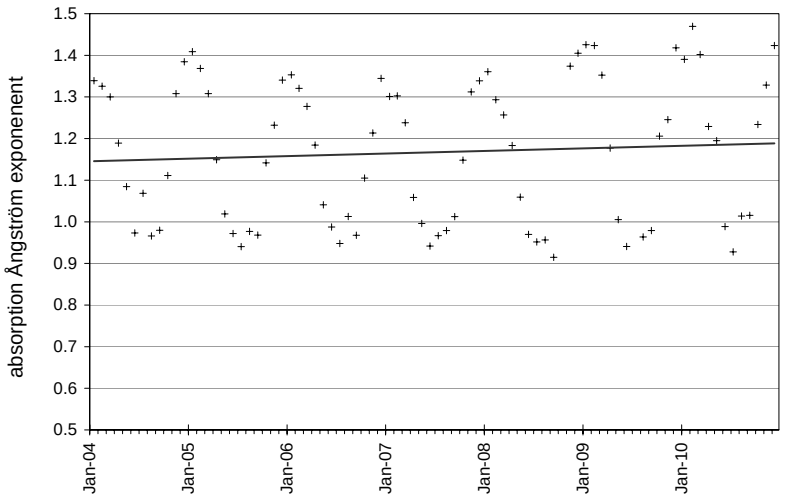

Fig. 1. variations in the absorption Ångström exponent at IPR, calculated from the Aethalometer absorption raw data at 7 wavelengths from 370 to 950 nm.