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Atmospheric
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Discussions

Interactive comment on "The time evolution of aerosol size distribution over the Mexico City plateau" *by* L. I. Kleinman et al.

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Interactive comment on The time evolution of aerosol size distribution over the Mexico City plateau by L. I. Kleinman et al.

We would like to thank the reviewers for their encouraging comments and useful suggestions. For the readers convenience, the 3 reviews are repeated here along with a point by point response.

Anonymous Referee #1

This paper presents results from airborne measurements on PM size distributions and time evolutions over the Mexico City plateau. The size spectra of aerosol number and volume were analyzed as a function of photochemical age estimated by NOx/NOy. CO was used as a conservative trace to account for the dilution of urban plume. The

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age-dependent changes in the number and volume distributions of accumulation mode particles were examined. The observed aerosol size evolution is in better agreement with condensation growth mechanism. This work represents a further analysis of the aerosol data from the MILAGRO Campaign, for which a high quality article was published by the same authors last year on the evolution of aerosol composition over the Mexico City plateau. This work is of good quality too. The analysis was clearly well performed and the paper was well written. This topic clearly suits the scope of ACP. I highly recommend its publication after the following comments have been addressed.

I find the meaning of this sentence in the Abstract - "There is growth in aerosol volume because there are more accumulation mode particles, not because particles are larger "- is somewhat vague. The additional accumulation mode particles seem to have grown from the Aitken mode. So, even though the mode size did not seem to increase, "particles are larger "was indeed the reason for the observed growth in aerosol volume.

Response: Sentence changed to indicate that the average size of the accumulation mode particles has not increased. The growth of Aitken mode particles into the accumulation mode size range is already mention two sentences down.

For the differences in the morning and afternoon size distributions observed in this study it will be interesting to hear the authors elaborate a bit more on the causes.

Response: I agree that this is an interesting question. It is possible that these differences are linked to the photochemistry responsible for nucleation/growth events observed at the surface. Lacking a way to model the time evolution of small particles, I hesitate to speculate.

P 1624, line 2, please cite the values for the "typical densities"used in the calculations. Response: 1.2 g m-3 for organics and 1.77 g m-3 for inorganics added to text

P 1626, 2nd paragraph, will be useful to discuss how good the homogenous assumption is. What’s the typical spatial coverage of a flight during a min?

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Response: Text added specifying that the aircraft covers 10 km in 1 minute. A DMA uncertainty was estimated from the PCASP standard deviation divided by the mean. Text added: Based on the standard deviation of 6 consecutive 10 s average PCASP number concentrations, we estimate that the average effects of air mass inhomogeniety contribute a 1 σ uncertainty of 14% to a 1 minute DMA measurement.

P 1627, line 6-8, please clarify the meaning of "It is required that the CO/NOy ratio be near that observed in plumes which unmistakingly have an urban origin. "It will be useful to give the range of ratios used as criterion. Same for the CH3CN/CO ratio used for eliminating biomass burning influences. Response: Text added giving both conditions for the urban data set.

P 1627, line 7, replace -unmistakingly- with -unmistakably-? Response: Spelling corrected.

P 1630, line 23, it seems that a ". "is missing after "AM ". Response: corrected

P 1633, line 20, "organic spectra "is often used to refer "organic mass spectra ". Although it is quite clear from the context what it is referring to at here, I would like to suggest using "organic size spectra "to avoid confusion. Response: Size distribution substituted for spectra through out text

Regarding the discussions on the observed rapid "growth "of AM1 to AM5 (p 1635), it was suggested that the precursor to AM5 being particles emitted the previous day or overnight. It could be useful to mention the possible sources of these "older "particles. Is the morning boundary layer development mainly responsible for it? Response: I have suggested entrained from the residual layer into the growing AM boundary layer as a mechanism

Table 1, it could help the readers if the "definition "of aging is repeated in the table caption. Response: Text added giving the definition of aging.

Fig. 1, in the figure caption, please spell out the particle size range selected for integration for each method. The figure will also be easier to see if different colors, in addition to different symbols, are used for the AM and PM data points. The linear regression coefficients and Pearson R for the two sets of correlations could be useful to see.

Response: Particle size is explicit in Fig. 1, so I assume that you are referring to Figs 2, 3, and/or 4. Text has been rearranged and modified so that a complete definition of accumulation mode volume and number appears in one place at the end of Sec 4.1. Regarding colors: In Fig. 2 data is presented from the AMS and either the PCASP or DMA. I wanted to distinguish between instruments by using colors from the same (blue) family for the PCASP (2a) or DMA (2b). In response to your suggestion, I tried adding a dark blue but was not satisfied because the AM and PM points (now dark blue and cyan) had very different visual weights. I have made the AM and PM points slightly larger. Linear regressions slopes have been added to the captions of Figs. 2 – 4. Correlation coefficients are high, averaging about 0.95, so there is not much to be gained by including them.

For the discussions on p1630, 2nd last paragraph, a question I have is how variable the AM and PM ratios are within each photochemical age bin? How about adding error bars to the AM and PM data points in Fig. 3?

Response: Error bars are generally smaller for the AM and PM data points than for the combined AM+PM data. In most cases, the 2 sigma error bars from the AM and PM overlap. Adding AM and PM error bars to Fig. 3 makes the graph very crowded.

Fig. 4, missing x-axis label for the bottom plot Response: Incorrect cropping on my part. x-axis scale and label restored.

Regarding the analysis on dependence of aerosol number and mass on photochemical age (4.2), it could be interesting (and useful) to summarize either in a table or a figure the linear regression statistics (slope and intercept and the corresponding uncertainties) and the correlation coefficients for the 10 plots show in Fig. 5.

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Response: I hesitate to add an additional Table. The intercept is the aerosol number concentration at CO = 0 ppb. As this is not a physically relevant quantity, I have elected to show the aerosol concentration at CO = 130 ppb, along with the 1 sigma uncertainty. These should be more legible when the Figure is in ACP format. I have added text to the Figure caption indicating that the slopes are data points in Fig. 4a. The correlations are excellent for this type of relation (average r2 = 0.72, minimum = 0.55).

It could be interesting to see the size spectra of the background aerosol (number and volume) in AM and PM separately, assuming there is enough signal to noise in such data. They may be presented in Fig. 6.

Response: The background spectra depends on how background is defined. The spectra for CO=120 – 140 looks different than the spectra for CO $<$ 130 ppb. I experimented some with background subtraction and could not find anything that I could justify.

I believe the absolute values of the size spectra are informative. I therefore suggest Fig. 6 to be modified. Instead of showing normalized spectra, it is better to plot the spectra on separate y axes and scale the y axes to the corresponding maxima. In this way, one can see clearly the differences in shapes of the size spectra. One can also see well the absolute differences between spectra. A same comment applies to Fig. 7.

Response: This requires 6 y-axies yielding a very crowded plot. While there is value in showing absolute values, I felt that there was only room for one set of plots and the normalized spectra were more important.

Fig. 8, how do the nitrate and sulfate size distributions from AMS vary as a function of photochemical age? Also, I am curious, why is only the organic mass, not the total (= organics + inorganics) from the AMS shown? Fig. 10, please add the letters on the corresponding plots.

Response: Size distribution graphs as a function of age for inorganic constituents and total AMS volume were not included for the sake of brevity and focus. It was important to show organic spectra to indicate a general similarity with the DMA observations that are the basis for growth calculations. I have modified the discussion of Fig. 8 to indicate that AM and PM organic size spectra have a similar mode diameter and that: Spectra of sulfate and nitrate (not shown) have an AM to PM decrease in mode diameter comparable to that seen in the DMA measurements. As with the DMA and PCASP age differences within the AM or PM subset are minor. Letters added to Fig. 10.

In my opinion, a more straightforward display of the Fig. 11 data is to show the same set of plots as those in Fig. 10. Better, to merge these two sets of plots and place the volume growth plots next to the condensational growth plots. Response: I preferred to create a separate graph for Fig. 11 as it is a change in topic from condensation to volume growth and gives a less crowded appearance in the figure and figure caption. I will ask the editor if these figures could be displayed on the same page to make comparison easier. Anonymous Referee #2

This manuscript is generally well-written, presenting results clearly (with a few exceptions that are pointed out below) and with a suitable amount of discussion and analysis. The topic is appropriate for ACP, and I recommend its publication once the following issues are addressed.

1. The authors should be aware of the following manuscripts: Smith, J.N., M.J. Dunn, T.M. VanReken, K. Iida, M.R. Stolzenburg, P.H. Mc- Murry, and L.G. Huey, Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, Geophysical Research Letters, 35 (L04808), L04808, doi:10.1029/2007GL032523, 2008. Iida, K., M.R. Stolzenburg, P.H. McMurry, and J.N. Smith, Estimating nanoparticle growth rates from size-dependent charged fractions - Analysis of new particle formation events in Mexico City, Journal of Geophysical Research, 113 (D05207), doi:10.1029/2007JD009260, 2008. These papers are probably better than the Wang

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2006 reference from the MILAGRO science meeting. The observations from these papers support many of the conclusions of the current paper, e.g., organics play a key role in growth and this growth of the nucleation mode into the accumulation mode occurs frequently and often in the afternoon.

Response: Both papers are relevant. References have been added. Wang (2006) is not in the referred literature but is the only study that I am aware of that supports the statement that there is an AM (10:00 – 12:00) to PM (12:00 – 15:00) increase in number concentration (dominated by the Aitken mode) even though aerosol volume is decreasing.

2. I am a little unclear about the size ranges selected for the analyses of volume and number growth. In Sec. 4.2 it is stated that the accumulation mode is used for the analyses, however this is defined earlier as extending to 1 micron, which is outside the range of SMPS measurements made with the DMA. In some cases, as in the PCASP measurements, the authors add in DMA-obtained volumes, but it is not clear whether the same is done for the DMA data at the high diameter end (in fact, it seems from the sentence that begins on line 1, page 1630, that the upper size limits for each instrument were used to define the accumulation mode, but surely this cannot be the case for the DMA, which cuts off at 400 nm and thus cannot fully capture the accumulation mode). It seems what is missing is a clearer description of the size ranges covered with each instrument for each analysis. It seems most appropriate in the first paragraph of Sec. 4.2, where the authors already state the ranges and modifications for some of the measurements.

Response: Text has been rearranged and modified so that a complete definition of accumulation mode volume and number appears in one place at the end of Sec 4.1. The DMA measures particle out to 440 nm. This is not evident in the graphs as the geometric mean of the size bins are used for the diameter axis. Some of the accumulation mode is cut off by the DMA, especially in the AM. The error is tolerable as judged from a comparison of regression slopes added to the captions of Figs. 2-4. There is very

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little PCASP volume above 440 nm so adding that to the DMA will have little effect.

3. Why is the AMS-derived data included in Figure 2a and 3a. By including them separately it implies that they are different data, but I believe that Figure 3a "all" is the same as that shown in Figure 2a "AMS." If this is true, and brief mention of this would confirm the reader’s understanding of the data.

Response: Correct. The AMS all data is included in Fig. 2a to show it’s agreement with the PCASP data. It also agrees very well with DMA volume as indicated in Fig. 2b which only shows the regression fit. I have added text to Figure 3’s caption indicating that the AMS all data is the same as shown in Fig. 2.

4. Some discussion of the expected lifetimes of the accumulation mode would add value to this paper. For example, the Jaenicke parameterizations of the atmospheric lifetimes of accumulation mode aerosol are approx. 10 days (ref: Jaenicke, R., Physical Aspects of the Atmospheric Aerosol, in Chemistry of the Polluted and Unpolluted Troposphere, edited by H.W. Georgii, and W. Jaeschke, pp. 341-373, D. Reidel Publishing Co., Dordrecht, 1982. - other similar manuscripts by Jaenicke abound). By contrast, the chemical clock used in the current paper estimates a maximum processing time of about a day (pg 1627, line 20). Also, growth rates of at most 20 nm/hour have been observed in Mexico City (ref: Iida 2008, above), thus it seems unlikely that the observations reported here will see appreciable differences in the volume distribution (in particular) over just a one-day time span. That is, most of the particles measured in the accumulation mode have probably advected into site, thus differences in chemical processing times would seem to make little difference in the mass or volume distribution. The authors state this as a conclusion of the current work (and point out that the Brock et al. paper also did not observe differences in the volume distribution), however it stands to reason that one would mostly expect this to be the case wherever such measurements are performed.

Response: Text added to page 1627 stating that lifetime of boundary layer, accumu-

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lation mode aerosol is of order 1 week (Jaenicke, 1980 J. Aerosol Sci.) so number and volume over our limited sampling time are not significantly affected by physical loss. Iida et al (2008, Conclusion section) report a growth rate range of 15 – 40 nm/hour. Measured growth rates of small particles seem to have the right magnitude to allow growth of Aitken mode particles into the accumulation mode size range, which is what we conclude from our data set. Also some Aitken mode particles may be primary emissions and have a head start diameter wise over freshly nucleated particles. Studies on new particle growth would not rule out a volume growth mechanism for accumulation mode aerosols as in that case large particles would grow faster than small ones.

5. It would seem entirely likely that coagulation is an important mechanism for inclusion into the modeling portion of this study. Coagulation is especially important when (1) high concentrations of particles are present (an Nˆ2 dependence, where N is number concentration) and (2) smaller Aitken-mode particles co-exist with larger accumulation mode particles. Both conditions seem to be present in the current study, and the latter would surely lead to the smearing of the distributions in Fig. 10.

Response: I did not include coagulation because, lacking a source term for ultrafine particles, I am not able to calculate a realistic time evolution for Aitken particles. You are correct that coagulation is favored by an Nˆ2 dependence and a large collection kernel between small and large particles. Coagulation can have a large effect on the size distribution of smaller particles but the total mass of the Aitken mode is small so that (baring extremely rapid turnover of the Aitken mode) mass growth in the accumulation mode must come from the gas phase. I did a back of the envelope calculation using the high number concentration PM sample (age = 0.2 – 0.4). I used the number of particles in a 10 nm bin at the peak of the Aitken mode (5000 cmˆ-3) and a 10 nm bin at the threshold (90 – 100 nm) of the accumulation mode (600 cmˆ-3). Coagulation increased the accumulation mode number concentration by about 1% per hour. As an order of magnitude estimate this should be multiplied by a single digit

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factor to account for transfer from other size ranges. Transfer to particles already in the accumulation mode does not increase the accumulation mode number concentration but would effect the size distribution. I do mention on p1642 that coagulation may play a role in smearing out the double peak of the calculated size distribution in Fig. 10.

6. If the volume distributions in Figs. 6 and 7 are normalized, then no units should be displayed for the y-axis. Response: You are correct. Units have been removed.

7. In general, the grammar and typographic errors are minimal. I did find a few: Pg 1634, line 5: I think the intention is to state "tens of nm," but when I see this I think "10 seconds of nm." Maybe best to just replace it with the word "tens." Response: Changed as suggested. Anonymous Referee #3

The paper presents aerosol number and volume size distributions from measurements made on an aircraft during the MILAGRO experiment in Mexico City. The paper is to some extent a sister paper to the Kleinman et al., 2008 paper which used the same measurement suite to discuss chemical transformations of particulate in the plume of Mexico City and related these to a measure of the photochemical ageing of oxidised nitrogen. The present paper uses the same relationships to investigate how the aerosol umber and volume distributions are transformed downwind of the city. The paper discusses the extreme cases of condensational and volume limited growth of the particulate and is careful to argue the caveats to the approach whilst highlighting the advantages of the simple analysis. The conclusions and behavioural analysis of how an aerosol size distribution changes with age in such a plume and the implications that has on the organic fraction of the aerosol mass are well explained and the paper certainly contributes significant new material. I certainly recommend it for publication in ACP. I do have some comments that I believe would add to the paper.

Page 1624, line 25 and following: Whilst there is a detailed discussed of how Dp was obtained from Dva for the AMS data there is no discussion of how scattering diameter as measured by the PCASP was transformed into Dp. This is important and ought to be discussed and/or referenced as line 16 on page 1629 and the discussion at the foot of page 1630 demonstrate. The independence of the PCASP, AMS and/or DMA regressions will to some extent depend on how this was performed. Response: The determination of Dp for the PCASP and DMA is described in K2008 as indicated on p1624, line 27. I did not repeat the description because it required about 25 lines of text and 3 references. Methods are fairly standard.

Page 1625; line 1 The c ToF AMS acronym has not been defined. Response: definition added in Introduction where term first appears.

Page 1628; line 16-22: AM and PM data are separated to investigate time of day effects. I can imagine that temperature and mixing effects are important diurnally and hence there are differences in time of day no matter where in the plume the measurement takes place. However, one can also envisage that the emission rates into the urban plume also vary diurnally. By segregating the measurements as a function of time no matter how far the measurement is made from source analysing morning and afternoon separately an implicit assumption is made that the diurnal influences on aerosol once formed are much larger than the diurnal variability of the sources. No evidence is given that this is indeed the case as far as I can see. It would be good to see such evidence or if it is not possible a discussion of the assumptions made should be included.

Response: Text added that contributing factors to diurnal differences could be meteorological, emission rates, or nucleation. Diurnal changes in emissions, due for example to different hours of operation of diesel and gasoline powered vehicles, are a concern. Since this paper was written, I have received a preliminary version of SP2 data for G-1 flights in the second half of the campaign (from R. Subramanian and G. Kok of Droplet Measurement Technologies, also worked on by H. Jonsson of Naval Postgraduate School). The ratio of Light Absorbing Carbon (LAC) to CO does not change significantly between the morning and afternoon. As LAC will be emitted preferentially from diesel vehicles and CO from gasoline vehicles, these measurements provide some evidence that diurnal cycles in emissions are not so large that they confuse the interpretation of our results.

Page 1632; line 9: I can how the intercept of the regressions of figure 5 are used to derive background concentrations but I cannot see how the slopes are involved in this analysis. Response: The intercept is the aerosol concentration at zero CO. In order to determine the aerosol concentration at a specified CO (e.g. 130 ppb) the slope and intercept of the least squares line are needed.

Page 1632: line 24-25: The variability in the Aitken mode between day and night appears to suggest that source variability has a major influence, the authors need to comment on this.

Response: The last paragraph in Section 4.4 (now augmented with 2 additional references) contains a discussion of the observed formation of new particles and their growth into the Aitken size range. This is suggested as a contributing factor to the increased numbers of Aitken mode particles in the PM.

Page 1633; lines 17-23: The authors don’t discuss the how the inorganic changes with photochemical age at all. Given that the authors note differences between the AM and PM behaviour of the organic fraction compared to the total volume it would be useful to see the contribution inorganic aerosol are making to the change sin behaviour.

Response: Size distribution graphs as a function of age for inorganic constituents and total AMS volume were not included for the sake of brevity and focus. It was important to show organic spectra to indicate a general similarity with the DMA observations that are the basis for growth calculations. I have modified the discussion of Fig. 8 to indicate that AM and PM organic size spectra have a similar mode diameter and that: Spectra of sulfate and nitrate (not shown) have an AM to PM decrease in mode diameter comparable to that seen in the DMA measurements. Information on the change in inorganic concentration with age is in our previous paper (K2008).

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Page 1634: The near source CO data in table 4 certainly suggest that there is a significant diurnal variability in source strength and hence most likely a significant variation in primary aerosol number than explains some of the Aitken mode number concentration in the plume. The PM data in the far field are likely to be similar air masses to the AM near source data if indeed the paper assumptions are correct and the plume is from the city source only. Can the authors speculate the impact this would have on their AM/PM variations in some of the earlier figures, it may help to interpret the seemingly high ratios in the far field PM data compared to those in the AM. This could be folded into the discussion at this point.

Response: The decrease in near source CO in the PM is largely driven by an increase in boundary layer height which would not affect regression slopes as long as the emissions of aerosols and their precursors are proportional to CO. Data from the SP2 (see above) does not show an AM to PM difference in the ratio of LAC to CO but does not rule out diurnal variations in the ratio of other primary aerosols or precursors to CO. It is suggested in the text that faster daytime photochemistry could play a role in AM – PM differences.

Page 1638; end of page: Whilst extreme cases are discussed, it ought to be pointed out that between these extremes a continuum of vapour pressures exist and therefore characteristic timescales that cover several orders of magnitude. In reality it is unlikely that a parcel in such an environment is ever in full equilibrium across the whole aerosol population. Page 1639; lines 17-18: Coagulation of small particles to the accumulation mode is unlikely to be significant, however the authors should demonstrate that this can be ruled out.

Response: In the statement that equilibrium vapor pressure varies over 10 orders of magnitude, I have added text specifying that so will lifetime. This is implied by the equation in the preceding sentence. Text added to end of paragraph: As ambient aerosol contains a mixture of compounds with a range of volatilities, it is unlikely that full equilibrium is reached across the whole aerosol population. Regarding coagulation, please

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see Response to Reviewer 2, Question 5. I hesitate to add a back of the envelope calculation to the paper and on the other hand there are too many unknowns to do a full calculation on the time evolution of small particles.

Page 1640; lines 27-29: The phrase condensation growth reproduces the main feature of the aging process; namely that increased volume is caused by more particles not larger particles should be qualified. The authors mean that there is an increase in accumulation mode particles. Table 5, I am sure, should also refer to accumulation mode particles but does not. It would be helpful if the authors defined what was meant by accumulation mode when making these statements.

Response: accumulation mode added to line 29. Title of table changed to specify accumulation mode aerosol. Text has been rearranged and modified so that a complete definition of accumulation mode volume and number appears in one place at the end of Sec 4.1.

Page 1641; lines 11-14: Entrainment of residual air containing aerosol aged during the previous day from aloft into the boundary in the morning may also give rise to the presence of near field and far field aged aerosol in the morning and should be mentioned. Response: Entrainment was the mechanism that I had in mind. I have added text making that specific. Over T0, photochemical ages are low and CO concentrations high, so entrainment is potentially more important in the far field.

Page 1642; line 2: It is true that the VMD doesn’t change. However, that is not because the distribution is stationary it is because the increase in diameter of the particles initially in the accumulation mode is offset by the influx of smaller particles into the accumulation mode. The VMD averages these two modes and hence remains close to constant. This should be reflected in the discussion though I see that it is raised in the conclusions.

Response: I believe that the text (page 1642, lines 2-4) Average particle size (VMD) in the accumulation mode remains nearly constant due to an influx of small particles

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from the Aitken mode coupled with lower growth rates for larger particles, already says what you suggested.

Page 1642; line 20: This is the first discussion of inorganic species. It would be good to relate these changes to the organic changes earlier as the difference sin ageing profile between AMS total volume and the AMS organic mass are significant and must be due to the inorganic fraction. Response: Please see response to question about Page 1633, lines 17-23.

Page 1643; line 4: The key point here is that the authors can only measure the net change in organic mass on the particulate. It is highly likely that as the aerosol ages, partitioning to the gas phase as a result of dilution does occur but in this case is smaller than the net condensation presumably resulting from either the formation of lower volatility products in the gas phase or from particulate organic reactions as the air ages. This should be stressed in this discussion.

Response: Text added: Although individual organic species could be evaporating and others condensing, there is no evidence of net organic aerosol evaporation over a time span of ˜ 1/2 to 1 day...

Page 1656; table 5: The number concentrations should be referred to explicitly as accumulation mode number concentrations. Response: Title of table changed to specify accumulation mode aerosol

Page 1659; figure 3 caption vs CO should be per CO as defined in the text as it refers to a specific methodology defined by the authors Response: Changed as suggested.

Page 1660; figure 4: It is conventional that the axis labels appear at the bottom of the lower panel. Response: Incorrect cropping on my part. x-axis scale and label restored.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1621, 2009.