Response to Reviewers

We thank the reviewers for their careful reading of our manuscript. The response to both reviewers is included in this document. To facilitate the review process we have copied the reviewer comments in italics. Our responses are in regular font after each comment. We have responded to all the referee comments and made changes to our paper (in bold text).

Response to Reviewer #1

R1.0) This manuscript describes results from gas and particle measurements made during the two-month long BEARPEX campaign in 2007. The measurements were made at a remote location in the Sierra Nevada Mountains, although it received transport from urban locations, as well. A suite of measurements are presented, including primary and secondary gas-phase species as well as AMS measurements and SOA molecular markers measured by the TAG instrument. Factor analysis is performed using the TAG data and three factors are identified, which together explain 77% of the variance in the total organic aerosol concentration. Overall, interesting diurnal and seasonal behaviors are observed at the site. The manuscript is well written, and well-organized, and is recommended for publication after the following comments are addressed:

Overall Comments:

R1.1) The identification of Factor 3 (Local light-driven emissions and oxidation products) seems highly uncertain. First, there are only two markers used to identify this Factor, compared to 10 each for Factors 1 and 2. Second, both of these compounds are assigned a 'medium' 'Uncertainty of compound identification'. As the authors state, most condensed-phase isoprene oxidation products are not detected by the TAG – how much uncertainty is there in the identification of this factor, and assigning its source as oxidation products of light-driven emissions? To what extent does this factor fully represent all of the 'Local light-driven emissions and oxidation products' in the aerosol?

Perhaps we were overstretching a little with our assignment of this factor as representative of all light driven emissions being that the two components loading into this factor are both related to methyl chavicol and its oxidation. We have renamed this factor in the paper as 'local methyl chavicol emission and oxidation'. We are confident in this assignment due to the good MS library matches for methyl chavicol and 4-methoxybenzaldehyde (both 95 %) and the similarity in the time trends and diurnal profiles to gas phase measurements of both methyl chavicol and methyl butenol (MBO), which are known to be locally light and temperature driven emissions from the pine trees.

R1.2) Factor 2 is identified as Oxidation products of temperature-driven local biogenic emissions, yet this factor appears to be anti-correlated with temperature: this seems very counter-intuitive. Additionally, Figure 4 indicates that pinonaldehyde concentrations were higher during the cold period than during the warm period, supporting the anti-correlation with temperature. How are these derived from local temperature-driven emissions, then? One brief sentence is given to explain this behavior, with the

explanations being either nighttime oxidation, or transport of aged biogenic emissions. Although similar monoterpene diurnal profiles were observed in Bouvier-Brown et al. (2009), significantly more discussion is needed. There are a number of studies that report higher nighttime monoterpene concentrations that appear to be due to a mechanism that is not temperature-driven (e.g., Simon et al. (1994); Hakola et al. (2000); Janson et al. (2001)). Could something similar be happening here?

The reviewer raises an interesting point especially with respect to the higher observed abundances of 'pinonaldehyde' and 'nopinone' (which are two of the major components loading onto this factor) during the later cooler part of the campaign. We feel that it would be appropriate to rename this factor "oxidation products of monoterpene emissions", which eliminates any confusion due to the anti-correlation with temperature. It is our understanding that the higher concentrations of monoterpenes reported at night and in the early morning during BEARPEX, and most likely in the other studies highlighted by the reviewer, are due to temperature driven emissions into a very shallow nighttime inversion layer. The maxima occur at these times when temperatures are warm enough to induce emissions and both oxidation and vertical mixing are slow so concentrations increase in this shallow layer near the ground, as reported by Bouvier-Brown et al., (2009) as well as many previous papers from this site (e.g., Lamanna and Goldstein, 1999). The reviewer suggested adding a sentence to explain the behavior of the monoterpene oxidation products observed in the particle phase by TAG. However, there is already a sentence on lines 22 – 24 of page 17093 that explains that the observed diurnal profiles of compounds loading onto this factor were likely a combination of both nighttime oxidation and downslope transport of aged biogenic emissions. As we state in the paper it is unclear what mechanism is leading to the higher abundance of the monoterpene oxidation products in the particle phase under cooler conditions at night and also later in the campaign but this is something that requires further study as it is important to understand in order to correctly model the contributions of monoterpene oxidation products to SOA.

R1.3) It is surprising that levoglucosenone, rather than levoglucosan, is used as one of the tracers for biomass burning emissions? Can the authors discuss this point? In the Williams et al. (2006) paper, levoglucosan is identified as a compound that the TAG can quantify – was levoglucosan correlated with levoglucosenone (especially during the periods of highest biomass burning influence)? If it is hypothesized that levoglucosan underwent oxidation during transport (as several recent studies suggest), then providing levoglucosan/levoglucosenone ratios would be extremely interesting.

Levoglucosan was not detected during BEARPEX and was likely below the detection limit of the instrument for the duration of the campaign. As such we are not able to look at ratios of levoglucosenone to levoglucosan, which we agree would be very interesting. Williams et al., (2010) reported levoglucosenone in the absence of levoglucosan in Riverside, California. They also showed that levoglucosenone loaded onto identified SOA factors as well as the identified biomass burning factor (Fig. 6 of Williams et al. 2010), suggesting that its presence in the aerosol was likely related to a combination of atmospheric processing of biomass burning and direct emissions. Levoglucosenone has

been reported to form from levoglucosan through dehydration and isomerisation reactions during the pyrolysis of cellulose (Lin et al., 2009) so it is not possible to rule out a direct emission source. We have rewritten lines 14 – 16 on page 17092 and added additional text to clarify the observations of levoglucosenone and the absence of levoglucosan in our measurements. These lines now read:

"Levoglucosan, a known biomass burning marker (Simoneit et al., 1999), was not detected during BEARPEX and was likely below the detection limit of the instrument. Williams et al., (2010) also reported levoglucosenone in the absence of levoglucosan in Riverside, California and reported that levoglucosenone was associated with the identified SOA factors as well as the identified biomass burning factor (Fig. 6 of Williams et al. 2010), suggesting that its presence in the aerosol was likely related to a combination of atmospheric processing of biomass burning and direct emission. Levoglucosenone has been reported to form from levoglucosan through dehydration and isomerisation reactions during the pyrolysis of cellulose (Lin et al., 2009). As such it is not possible to rule out direct emission from biomass burning as a source of levoglucosenone. However, it seems likely that levoglucosenone is predominantly an oxidation product of levoglucosan, which would support the aged influence of this source."

R1.4) The discussion and results of the organosulfates adds little to the manuscript. I.e., the quantified organosulfates contributed less than 1% of OA mass, yet substantial discussion (and 2 of the 8 figures) is dedicated to this topic (Section 3.7). Figure 7 has very little practical value – it could be removed from the manuscript, or at the very least should be moved to the supplemental. Another manuscript (Worton et al., (2011)) is promised on this topic: Figure 7 is out of place here, but may fit better in that paper. Since the finding of a correlation between OA and CO is significant here (and is given appropriate discussion in the manuscript) move Supplemental figure S3 from the supplemental to the main paper.

We disagree that the discussion and results of the organosulfates adds little to the manuscript. They are interesting tracer compounds and illustrate the differences in behavior between the hot and cold periods of the monoterpene and isoprene oxidation products, which is a key finding in the manuscript. While the 16 compounds we quantified contributed less than 1 % to the OA mass many more were detected that have not been calibrated due a lack of authentic standards and to difficulties with the structural sensitivity of the electrospray technique that prevents assigning calibrations based on available standards. We agree that Figure 7 would probably be better suited in the supplementary information and that Figure S3 would be better in the main manuscript, and we have modified the paper accordingly.

Specific Comments
R1.5) Provide the actual measurement dates in the abstract

The dates of the campaign have been added to line 4 of the abstract.

R1.6) Abstract, line 16: Methyl chavicol is not well known to many in atmospheric chemistry: a brief clarifier here identifying its source(s) would be helpful

The reference to methyl chavicol has been reworded to read "**The oxidation of methyl chavicol, an oxygenated terpene emitted by ponderosa pine trees, contributed**…."

R1.7) Abstract, line 17: "…during both identified meteorological periods." At this point, the periods have not been defined, and they are only vaguely defined later in the abstract.

The wording "during both meterological periods." on line 17 of the abstract has been replaced with "**throughout the campaign**." Also, we have added additional text which better defines the different meteorological periods. Lines 14 – 16 now read:

"Concentrations of isoprene oxidation products were larger when temperatures were higher **during the first half of the campaign (August 15th – September 12th)** due to more substantial emissions of isoprene and enhanced photochemistry."

and lines 17 - 19 now read:

"In contrast, the abundances of monoterpene oxidation products in the particle phase were greater during the cooler conditions **in the later half of the campaign (September 13th – October 10th)**, even though emissions of the precursors were lower."

R1.8) Abstract, pg. 17073, ln. 28: "…evidence for the likely importance of aerosol sulfate in spite of neutralized aerosol." Perhaps the neutral aerosol is the reason for the low contribution of organosulfates to the total OA? (comment applies to Section 3.7 as well)

It is possible that the reason for the low contributions of organosulfates to total organic aerosol was due to neutralized aerosol at the site. Another possibility for why the contribution of organosulfates was small was because we only reported measurements of 16 compounds that we could quantified. There is still a lack of good authentic standards for the majority of these compounds so quantification for some of these components is uncertain. We have added some additional text to both the abstract and section 3.7 that highlights both of these possibilities. In the abstract, page 17073, line 27 – page 17074, line 4 now reads:

"Observations of organosulfates of isoprene and α-pinene provided evidence for the likely importance of aerosol sulfate in spite of neutralized aerosol although acidic plumes might have played a role upwind of the site. This is in contrast to laboratory studies where strongly acidic seed aerosols were needed in order to form these compounds. These compounds together represented only a minor fraction (< 1 %) of the total OA mass, **which may be the result of the neutralized aerosol at the site or because only a small number of organosulfates were quantified.** The low contribution of organosulfates to total OA suggests that other mechanisms….".

In section 3.7, page 17096, lines 4 – 5, now reads:

"In total, these 16 compounds contributed, on average, < 1 % to the OA mass. **This minor contribution maybe a result of the neutralized aerosol at the site or because only a small number of organosulfates were quantified due to a lack of authentic standards.**"

R1.9) Pg. 26, ln. 26: the Robinson et al. (2007) and de Gouw et al. (2011) references should not really be put in the same group as the Goldstein and Gallbally (2007) reference, since the Robinson et al. (2007) and de Gouw et al. (2011) studies identify IVOCs and SVOCs collectively as SOA precursors.

We have rewritten lines 24 - 26 on page 17074 to separate out the references as suggested by the reviewer. These lines now read as:

"(1) as yet unidentified precursor species not included in traditional models (Goldstein and Galbally, 2007), including semivolatile and intermediate volatility compounds, SVOC and IVOC, respectively (Robinson et al., 2007; de Gouw et al., 2011)…".

R1.10) Pg. 17097, ln. 20: provide inlet height

The height of the AMS inlet, 25 m, has been added.

R1.11) Pg. 17080, ln. 18: is sample volume not 0.81 m3?

The sample volume has been corrected to read 0.81 m^3.

R1.12) Pg. 17085, ln. 21: "A small discrepancy (~20%) might be expected from the differing size cuts…" citation needed

We have inserted the following citation: Alves et al. (2000) into the text on line 20, page 17085.

R1.13) Pg. 17086, ln. 4: "…30% non-fossil" seems reasonable, but provide a citation

References to Hildemann et al., (1994) and Hodzic et al., (2010b) have been added.

R1.14) Pg. 17089, ln. 19-20: "…which may temper the statement that most of the OA is derived from biogenic sources." Not necessarily: lifetimes of gases and particles are different. This may be a reflection of the regional background, and the relative daily production in relation to that regional aerosol.

We have rewritten lines 17 – 22 on page 17089 from "In contrast to the gas-phase tracers shown in Fig. 3, the diurnally averaged OA concentrations changed by less than a factor of 2 throughout the day during both the hot and cold periods, which may temper the statement that most of the OA is derived from biogenic sources. However, as we will

show in this paper there are multiple components to BSOA whose contributions change not only diurnally but also seasonally." to now read:

"**In contrast to the gas-phase tracers shown in Fig. 3, the diurnally averaged OA concentrations changed by less than a factor of 2 throughout the day during both the hot and cold periods. As we will show in this paper there are multiple components to BSOA whose contributions change not only diurnally but also seasonally**.".

R1.15) Pg. 17095, ln. 9-11: specifically, which compounds could not be detected in injections of liquid standards?

We have added which specific compounds (nopinone and methyl chavicol) that could not be detected from injection of liquid standards on line 10 of page 17095.

R1.16) Figure 4: the aspect ratio of all of the left hand panels are very poor: either improve the aspect ratio, or delete these panels from the figure.

We have adjusted the aspect ratio of all the left hand panels in Figure 4 to make the x-axis wider and also reduced the date range from 08/15/07 – 10/10/07 to 09/06/11 – 10/10/07 to improve the visual characteristics of the plots.

Technical Corrections:

R1.17) Pg. 17082, ln. 25: Herckes misspelled

The spelling of Herckes has been corrected.

References
de Gouw, J. A., Middlebrook, A. M., Warneke, C., Ahmadov, R., Atlas, E. L., Bahreini, R., Blake, D. R., Brock, C. A., Brioude, J., Fahey, D. W., Fehsenfeld, F. C., Holloway, J. S., Le Henaff, M., Lueb, R. A., McKeen, S. A., Meagher, J. F., Murphy, D. M., Paris, C., Parrish, D. D., Perring, A. E., Pollack, I. B., Ravishankara, A. R., Robinson, A. L., Ryerson, T. B., Schwarz, J. P., Spackman, J. R., Srinivasan, A., and Watts, L. A.: Organic aerosol formation downwind from the Deepwater Horizon oil spill, Science, 331, 1295-1299, 2011.

Hildemann, L. M., Klinedinst, D. B., Klouda, G. A., Currie, L. A., and Cass, G. R.: Sources of urban contemporary carbon aerosol, Environmental Science & Technology, 28, 1565-1576, 1994.

Hodzic, A., Jimenez, J. L., Prevot, A. S. H., Szidat, S., Fast, J. D., and Madronich, S.: Can 3-D models explain the observed fractions of fossil and non-fossil carbon in and near Mexico City?, Atmos. Chem. Phys., 10, 10997-11016, 2010b.

Lin, Y. C., Cho, J., Tompsett, G. A., Westmoreland, P. R., and Huber, G. W.: Kinetics and Mechanism of Cellulose Pyrolysis, J. Phys. Chem. C, 113, 20097-20107, 10.1021/jp906702p, 2009.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 10.1126/science.1133061, 2007.

Williams, B. J., Goldstein, A. H., Kreisberg, N. M., Hering, S. V., Worsnop, D. R., Ulbrich, I. M., Docherty, K. S., and Jimenez, J. L.: Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds, Atmos. Chem. Phys., 10, 11577-11603, 2010.

Lin, Y. C., Cho, J., Tompsett, G. A., Westmoreland, P. R., and Huber, G. W.: Kinetics and Mechanism of Cellulose Pyrolysis, J. Phys. Chem. C, 113, 20097-20107, 10.1021/jp906702p, 2009.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmospheric Environment, 33, 173-182, 1999.

Williams, B. J., Goldstein, A. H., Kreisberg, N. M., Hering, S. V., Worsnop, D. R., Ulbrich, I. M., Docherty, K. S., and Jimenez, J. L.: Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds, Atmos. Chem. Phys., 10, 11577-11603, 2010.

Alves, C. A., Pio, C. A., and Duarte, A. C.: Particulate size distributed organic: Compounds in a forest atmosphere, Environmental Science & Technology, 34, 4287-4293, 10.1021/es000028a, 2000.

Response to Reviewer #2

R2.0) This paper presents results from extensive measurements at a rural site impacted by fires, longer-range transport of urban emissions and regional and local sources of biogenic emissions. The data set is unique and it is analyzed in a number of ways. The results are of interest and of significant value and add to a growing body of information on sources of the organic aerosol. The paper should be published after consideration of possible issues raised below.

Specific Comments:

R2.1) The authors are commended for doing an assessment of the filter sampling artifacts by comparing filter OC with AMS OC. Despite the very large disparity (filter 3 times higher than AMS), which is attributed to gas absorption on the filters, the 14C data is still used as if the problem did not exist? Can the authors justify the use of the 14C data given their belief that it is severely impacted by positive artifacts?

Previous work has shown that their might be a significant non-zero intercept when comparing online and filter based techniques that may account for some of this disparity. Peltier et al. (2007) compared OC measured by a particle into liquid sampler (PILS) coupled to a total organic carbon (TOC) analyzer and a sunset labs EC/OC technique and reported a non-zero intercept of $0.6 - 1.7$ $\mu gC\ m^{-3}$. Offenberg et al. (2007) also reported a systematic offset of about 1 $\mu gC\ m^{-3}$ when sampling semi-continuously using filters and this offset had the greatest influence for small air volumes. With the high flow rates of

the high volume (Hi-Vol) sampler this offset would likely be < 10 % of the measured signal. We accept that there are positive artifacts on the filters from gas phase adsorption but assume that the ^{14}C content of the adsorbed carbon is similar to that of the aerosol, which is why we continue to discuss the data in the manuscript. We have added the following text to the manuscript stating this assumption on page 17085, line 23:

"**We do not have information on the 14C content of the gas phase compounds adsorbed onto the filters and in the absence of this information our analysis assumes that the 14C content of the adsorbed gas phase compounds was similar to that of the aerosol.** ".

R2.2) The calculation of urban contribution to non-fossil carbon seems highly speculative (paragraph before section 3.3), it seems a value of 30% is just adapted from other studies conducted in very different locations with likely very different emissions. Is there not sufficient chemical speciation data to at least do a simple calculation to (source apportionment) to justify this correction.

We agree but feel that a full source apportionment is beyond the scope of this paper, especially considering that the actual value has a very minor impact on the inferred biogenic fraction of aerosol carbon, i.e, using a value of between 10 – 50 % still yields a 'biogenic' fraction of between 70 – 80 %. However, we have modified our language to remove a fixed value of ~30 % non-fossil urban source with a range of 10 – 50 %. Page 17086, lines 2 – 7 now read:

"**It is likely that this also includes non-negligible contributions from non-fossil urban sources, which can roughly be estimated as follows: the fossil fraction is 0.16 and by assuming urban emissions were 10 – 50 % non-fossil (Hildemann et al., 1994; Hodzic et al., 2010b), then (0.1/0.9)*0.16 = 0.02 and (0.5/0.5)*0.16 = 0.16 so a range of 0.02 – 0.16 likely represents the non-fossil urban fraction. Therefore, if 0.02 – 0.16 of the 0.84 is from pollution sources, then 0.68 - 0.82 remains that is presumably from biogenic sources.**"

R2.3) Page 17087, estimates on the contribution of BVOC oxidation to CO. Given the host of gas and aerosol organic speciation done at this site are there any long-lived (few days) anthropogenic tracers that could be compared to CO to support the estimated biogenic CO?

Measurements of isopentane (a tracer for mobile combustion emissions) were made and are well correlated to CO after the CO data had been filtered for windspeeds > 1 m/s (to remove influence from the onsite propane generator) and acetonitrile < 0.175 ppb (to remove influence of biomass burning). We compared the ratio observed to that determined for fresh emissions in the source region (Sacramento). The absence of deviations from this correlation supports the suggestion that biogenic sources of CO at Blodgett were small. We added the plot of isopentane to CO in the supplementary material (Figure S4) and added the following text to the manuscript:

CO was also well correlated to isopentane (Figure S4; supplementary information). The upwind source region ratio of isopentane to CO was calculated from isopentane measurements made in the summer of 2001 at Granite Bay and from CO measurements from the California Air Resources Board Del Paso Manor monitoring station (http://www.arb.ca.gov/aqd/aqdcd/aqdcddld.htm) (see Murphy et al., 2007) and is shown in Figure S4. A lower ratio of isopentane to CO would be expected downwind due to differing atmospheric loss rates (isopentane $k_{OH} = 3.6x10^{-12}$ cm^3 molecules^{-1} s^{-1} versus CO $k_{OH} = 1.4x10^{-13}$ cm^3 molecules^{-1} s^{-1}) (Atkinson and Arey, 2003; Atkinson et al., 2006) and atmospheric dilution during advection from the Central Valley to the Blodgett site. Dillon et al., (2002) showed that at the peak impact of the urban plume the air at Blodgett Forest was characterized as a mixture of ~32 % from the urban core and ~ 68 % from the relatively clean background. They also reported an average daytime OH concentration of $1x10^7$ molecules cm^{-3} for the transect between Sacramento and Blodgett in 2001. The best fit trend to the 2007 data presented here was with an OH concentration slightly lower than that reported by Dillon et al., (2002), which would be expected considering the substantial decreases in NO$_x$ emission in this region between 2001 and 2007 (LaFranchi et al., 2011). The absence of large deviations from this correlation supports the suggestion that biogenic sources of CO at Blodgett were small. The observed correlation between CO and OA at Blodgett Forest indicates a possible coupling between SOA and something emitted concurrently to combustion derived CO, e.g., NO$_x$ and/or SO$_2$.

R2.4) Beginning of Section 3.5, here I assume the authors are referring to PM2.5 TAG data, not gas phase data. Also, it is not clear why the data were corrected based on filter data, (i.e., particle phase = ambient -filtered ambient). I assume filtered ambient is: a filter upstream of the TAG, under the assumption gases pass through the filter and particles collected on the filter do not evaporate. Clarify in the text. Why not place a gas denuder upstream to improve this difference method.

To clarify that in section 3.5 that we are now talking about particle phase markers measured by the TAG instrument we have rephrased the beginning of the first sentence so it now reads:

"**The particle phase molecular marker compounds measured by the TAG instrument in PM2.5** were predominately secondary in nature (or their decomposition products, see below) …..".

To clarify what a filtered ambient run is with TAG we have rephrased the end of the first paragraph in section 3.5 to read:

"**To determine the contribution of gas phase adsorption to the surfaces heated during the thermal desorption cycle the air flow was alternated between two separate paths, one with a teflon filter (Zefluor 2.0 μm, Pall Corp.) inline to remove particles. This so called 'filtered ambient' run can be subtracted from the 'ambient' run to give particle phase signals (i.e., particle phase = ambient – filtered ambient)**

to produce relative abundance particle phase timelines for each compound."

The reviewer asks why we did not place a gas phase denuder upstream instead of the filter. At the time we collected the aerosol by inertial impaction and humidified the particles to minimize particle bounce and as such using a denuder was not an option. However, we have now changed our sample collection methodology and routinely use a multi-channel charcoal denuder which has shown excellent efficiency for adsorption of gas phase components in the intermediate volatility and semi-volatile range. A manuscript showing this modification to the TAG system is currently being prepared and will be published soon.

R2.5) Bottom of page 17091 regarding the lack of isoprene SOA tracers in TAG data. This appears to be a significant limitation. A brief discussion of the influence this has on the reported conclusions should be discussed (if there is any) and maybe included in the Abstract and Conclusions.

We do not believe that the lack of observable isoprene tracers with the TAG affects the conclusions of the manuscript. It does affect the ability to assign quantitative numbers to the identified sources/factors from the factor analysis as has been done previously (Williams et al. 2007; 2010) and as a result we did not attempt this in our manuscript. The offline filter analysis provides insights into the behavior of some of the isoprene oxidation products, though obviously higher time resolution would be preferred. We are continuing to modify and develop the TAG instrument in order to detect and quantify these components in the future.

R2.6) It does not appear that gas phase species were included in the factor analysis. Why not?

A factor analysis for gas phase compounds had already been reported for this site by Lamanna and Goldstein (1999), and as we were focusing on the particle phase markers we chose not to include the gas phase compounds in the factor analysis we presented in the manuscript. Including the gas phase compounds into the factor analysis does not dramatically change the results. The same three factors are observed although one of them is split into two with one of them including the biomass burning markers, acetonitrile and levoglucosenone. Two additional factors with only gas phase compounds loading on them were also observed which represent monoterpene and anthropogenic emission sources. Following the reviewers suggestion we have now chosen to include the combine gas phase and particle phase markers factor analysis in the paper and have added additional text describing the additional factors:

Factor 2: Oxidized urban emissions
This factor accounted for ~15 % of the variance and included most of the same compounds that loaded into factor 1 with the exception of the biomass burning markers, levoglucosenone and acetonitrile, which were absent from this factor. OA from the AMS measurements also loaded into this factor, again consistent with the substantial contribution of SOA to OA.

Factor 4: Monoterpene emissions

All the terpenes included in the factor analysis loaded onto this factor which accounted for ~10 % of the variance. The diurnal variation of α-pinene (Figure 4) was representative of this factor and showed the highest concentrations at night when continuing temperature driven emissions accumulated into a shallow boundary layer due to weak vertical mixing. The lowest concentrations were during daytime when vertical mixing was the strongest. This factor compared well with the "temperature (not light) dependent biogenic emissions" factor identified by Lamanna and Goldstein (1999).

Factor 5: Anthropogenic emissions

Only the gas phase compounds isopentane, n-pentane, toluene loaded substantially into this factor which accounted for ~8 % of the variance. The temporal pattern of isopentane (Figure 4) was representative of this group and showed increasing concentrations throughout the day maximizing in the late afternoon consistent with transport of primary pollution from the Central Valley below. This factor compared well to the "anthropogenic emissions" factor reported by Lamanna and Goldstein (1999).

Also, we have modified Table 2 to include the gas phase compounds. The new table is below:

Compound Name (molecular formula)	CAS registry number	Uncertainty of compound identification	Loadings (values < 0.4 omitted)					
			F1	F2	F3	F4	F5	F6
benzene (C_6H_6)	71-43-2	low	0.94					
acetonitrile (CH_3CN)	75-05-8	low	0.92					
levoglucosenone ($C_6H_6O_3$)	37112-31-5	low	0.88					
1-(3H)-isobenzofuranone ($C_8H_6O_2$)	87-41-2	low	0.87					
AMS organics	-	-	0.84	0.50				
triacetin ($C_9H_{14}O_6$)	102-76-1	medium	0.78					
methylethylketone (C_4H_8O)	78-93-3	low	0.78					
1H-indene-1,3(2H)-dione ($C_9H_6O_2$)	606-23-5	low	0.76					
3-methyl phthalic acid ($C_9H_6O_3$)	37102-74-2	low	0.74	0.59				
acetone (C_3H_6O)	67-64-1	low	0.72	0.50				
acetaldehyde (C_2H_4O)	75-07-0	low	0.71	0.47				
4-methyl phthalic acid ($C_9H_6O_3$)	4316-23-8	low	0.68	0.50				
toluene (C_7H_8)	108-88-3	low	0.67				0.62	
phthalic acid ($C_8H_6O_4$)	88-99-3	low	0.67	0.59				
benzoic acid ($C_7H_6O_2$)	65-85-0	low	0.57	0.80				
isoprene (C_5H_8)	78-79-5	low	0.52	0.57				
methanol (CH_3OH)	67-56-1	low	0.51	0.54				
1H-isoindole-1,3(2H)-dione ($C_8H_5NO_2$)	85-41-6	low	0.47	0.75				
2-methyl-3-buten-2-ol ($C_5H_{10}O$)	115-18-4	low	0.46	0.42				0.41
methylvinylketone (C_4H_6O)	78-94-4	low	0.41	0.86				
methacrolein (C_4H_6O)	78-85-3	low		0.82				
benzoic acid, 2-hydroxy methyl ester ($C_8H_8O_3$)	119-36-8	medium		0.56	0.44			
1-methyl-4-(1-methylethenyl)- benzene ($C_{10}H_{12}$)	1195-32-0	medium			0.97			
p-cymene ($C_{10}H_{14}$)	99-87-6	medium			0.95			

Compound	CAS	Level						
pinonaldehyde ($C_{10}H_{16}O_2$)	2704-78-1	medium			0.92			
4,7-dimethylbenzofuran ($C_{10}H_{10}O$)	28715-26-6	low			0.88			
nopinone ($C_9H_{14}O$)	24903-95-5	medium			0.87			
cuminic aldehyde ($C_{10}H_{12}O$)	122-03-2	medium			0.85			
p-methyl acetophenone ($C_9H_{10}O$)	122-00-9	medium			0.81			
1-cyclohexene-1-carboxaldehyde ($C_{10}H_{14}O$)	1192-88-7	medium			0.62			
α-pinene ($C_{10}H_{16}$)	80-56-8	low				0.90		
β-pinene ($C_{10}H_{16}$)	127-91-3	low				0.86		
limonene ($C_{10}H_{16}$)	138-86-3	low				0.84		
benzaldehyde (C_7H_6O)	100-52-7	low	0.48			0.75		
n-pentane (C_5H_{12})	109-66-0	low					0.88	
isopentane (C_5H_{12})	78-78-4	low					0.80	
isopropanol (C_3H_8O)	67-63-0	low				0.43	0.48	
methyl chavicol ($C_{10}H_{12}O$)	67-63-0	medium						0.88
methyl chavicol ($C_{10}H_{12}O$)	140-67-0	low						0.81
4-methoxybenzaldehyde ($C_8H_8O_2$)	123-11-5	medium						0.66

Importance of Factors								
Sum square loadings			11.2	6.9	6.1	3.9	3.0	2.3
Proportion of variance			0.28	0.15	0.17	0.10	0.08	0.06
Cumulative variance			0.28	0.45	0.60	0.70	0.78	0.84

R2.7) Discussion on aerosol acidity: In several sections the role of aerosol pH becomes important and the authors state that the aerosol was neutral based on an AMS ion balance. Based on this type of analysis it seems highly uncertain to claim a neutral aerosol because the AMS is not a comprehensive measurement of ions and there is an uncertainty associated with the ions it does detect. Thus it is very possible the aerosol has a pH significantly below 7. Also, the authors are assuming a completely internally mixed aerosol since everything is reported as a bulk analysis. pH could vary with particle size and between particles.

The reviewer raises several points regarding aerosol acidity, to which we respond sequentially:

1) The reviewer states that the pH of the aerosol may be lower than 7. This may indeed be the case, but we did not state otherwise in the manuscript, and the strong dependence of organosulfate formation on pH occurs at much lower pH. We use an empirical measure of aerosol acidity, the imbalance between the measured anions and cations, as a surrogate of the free H^+ concentration, which is directly comparable to the conditions used in the laboratory studies. This measure of acidity is correlated to the aerosol pH as discussed in Zhang et al. (2007), although the estimates of pH become very uncertain under conditions of neutralized aerosol.

This ion balance for BEARPEX is shown in Figure 8 of Farmer et al. (2011, http://www.atmos-meas-tech.net/4/1275/2011/amt-4-1275-2011.pdf), which is consistent with neutralized aerosol within the precision and accuracy of AMS measurements. E.g. this can be compared with neutralized aerosols at other locations in e.g. with Figure 11 of Docherty et al. (2011, http://www.atmos-chem-phys-discuss.net/11/6301/2011/acpd-11-6301-2011.pdf) and Figure S6 of Aiken et al. (2009, http://www.atmos-chem-phys.net/9/6633/2009/acp-9-6633-2009-supplement.pdf), vs. Figure 10 of Zhang et al. (2005, http://www.agu.org/pubs/crossref/2005/2004JD004649.shtml) which shows acidic and neutralized aerosols at different times. During BEARPEX these ions were found to be well balanced at all times, which is typical of continental sites away from strong SO_2 sources.

Under conditions when the AMS reports neutralized aerosols such as in BEARPEX, the inorganic sulfate is in the form of ammonium sulfate. The important contrast here is with the laboratory studies (Surratt et al., 2008; 2010) already cited our ACPD paper where "the presence of highly acidic sulfate seed aerosol being of critical importance to their formation" (e.g. P17097 L14-15) and "none of these products were observed in the absence of highly acidified sulfate seed aerosol" (e.g. P17098 L12-13). In the experiments of Surratt et al., the "highly acidic aerosols" were as acidic as ammonium bisulfate and sometimes sulfuric acid, while ammonium sulfate aerosols were not conducive to the formation of organosulfates. The presence of such highly acidic aerosols would be obvious in the AMS data, and is not typical of continental sites away from very large SO_2 sources.

2) The reviewer mentions the uncertainty of AMS measurements. However the relative uncertainty in the balance of anions and cations is much smaller than the uncertainty in the absolute concentrations, as many of the uncertainty terms are the same for all species and cancel out when taking the ratio. The scatter plots of anions vs. cations when analyzing neutralized species such as pure ammonium sulfate and pure ammonium nitrate are similar to the figures discussed above, e.g. Farmer et al. (2011) for BEARPEX, and very different to the scatter plots observed when analyzing ammonium bisulfate or sulfuric acid.

3) The reviewer questions the influence of ions that the AMS does not detect on the ion balance. Those "refractory ions" are mainly those in sea salt such as Na^+ and Cl^- from NaCl and related species and atmospheric reaction products. Those particles are produced mechanically and thus are dominantly in the supermicron mode which is not sampled by the AMS. Thus they should only perturb the submicron concentrations minimally. In addition, sea salt is expected to be very low at this site due to the distance from the ocean. Finally, if such ions were present in concentrations high enough to confound the AMS ion balance, they would not be expected to be correlated at all times with the ions that the AMS does detect, and they would then produce a substantial degree of scatter in the AMS ion balance graph (Fig. 11 of Farmer et al. 2011). The fact that such scatter is not observed confirms that the influence of refractory ions on the AMS ion balance during this study is small.

4) Finally, the reviewer mentions the possibility that some particles may be neutralized while others are not, i.e. external mixing with respect to acidity. In our experience such external mixing is unusual in continental regions away from large SO_2 sources, as ammonia is present in the gas-phase and rapidly neutralizes aerosol acids. In addition, the AMS size distributions show no evidence of external mixing of the inorganic species.

In conclusion, we feel that the statements made in the paper about aerosol acidity based on the AMS measurements are accurate and justified. We have expanded the sentence on P17084 L12-14 to reflect this discussion as:

"Ammonium and nitrate contributed on average 0.3 µg m^{-3} (~ 7 %) and 0.2 µg m^{-3} (~ 5 %), respectively, and the aerosol was approximately neutralized without excess H$^+$ (Farmer et al., 2011), indicating that the dominant form of sulfate at the site was ammonium sulfate. Refractory ions, AMS uncertainties, or external mixing are judged to contribute little uncertainty to this assessment. The ammonium sulfate at the site contrasts with the highly acidic conditions required to form organosulfates efficiently in previous laboratory experiments (Surratt et al., 2008, 2010) that require sulfate to be in the form of ammonium bisulfate or sulfuric acid."

References

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605-4638, 2003.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 2006.

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A. H., and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, J. Geophys. Res.-Atmos., 107, 15, 4045 10.1029/2001jd000969, 2002.Docherty, K. S., Aiken, A. C., Huffman, J. A., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Worsnop, D. R., Snyder, D. C., Grover, B. D., Eatough, D. J., Goldstein, A. H., Ziemann, P. J., and Jimenez, J. L.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition, Atmos. Chem. Phys. Discuss., 11, 6301-6362, doi:10.5194/acpd-11-6301-2011, 2011.

Farmer, D. K., Kimmel, J. R., Phillips, G., Docherty, K. S., Worsnop, D. R., Sueper, D., Nemitz, E., and Jimenez, J. L.: Eddy covariance measurements with high-resolution time-of-flight aerosol mass spectrometry: a new approach to chemically resolved aerosol fluxes, Atmos. Meas. Tech., 4, 1275-1289, doi:10.5194/amt-4-1275-2011, 2011.

Gentner, D. R., Harley, R. A., Miller, A. M. and Goldstein, A. H. (2009). Diurnal and seasonal variability of gasoline related volatile organic compound emissions in Riverside, California. Environment Science and Technology 43:4247-4252.

Hildemann, L. M., Klinedinst, D. B., Klouda, G. A., Currie, L. A. and Cass, G. R. (1994). Sources of urban contemporary carbon aerosol. Environmental Science & Technology 28:1565-1576.

Hodzic, A., Jimenez, J. L., Prevot, A. S. H., Szidat, S., Fast, J. D. and Madronich, S. (2010). Can 3-D models explain the observed fractions of fossil and non-fossil carbon in and near Mexico City? Atmos. Chem. Phys. 10:10997-11016.

LaFranchi, B. W., Goldstein, A. H., and Cohen, R. C.: Observations of the temperature dependent response of ozone to NO(x) reductions in the Sacramento, CA urban plume, Atmos. Chem. Phys., 11, 6945-6960, 10.5194/acp-11-6945-2011, 2011.

Lamanna, M. S. and Goldstein, A. H. (1999). In situ measurements of C-2-C-10 volatile organic compounds above a Sierra Nevada ponderosa pine plantation. J. Geophys. Res.-Atmos. 104:21247-21262.

Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., Millet, D. B., Goldstein, A. H., and Cohen, R. C.: The weekend effect within and downwind of Sacramento - Part 1: Observations of ozone, nitrogen oxides, and VOC reactivity, Atmos. Chem. Phys., 7, 5327-5339, 2007.

Offenberg, J. H., Lewandowski, M., Edney, E. O. and Kleindienst, T. E. (2007). Investigation of a systematic offset in the measurement of organic carbon with a semicontinuous analyzer. Journal of the Air & Waste Management Association 57:596-599.

Peltier, R. E., Weber, R. J. and Sullivan, A. P. (2007). Investigating a liquid-based method for online organic carbon detection in atmospheric particles. Aerosol Sci. Technol. 41:1117-1127.

Williams, B. J., Goldstein, A. H., Kreisberg, N. M., Hering, S. V., Worsnop, D. R., Ulbrich, I. M., Docherty, K. S. and Jimenez, J. L. (2010). Major components of

atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds. Atmos. Chem. Phys. 10:11577-11603.

Williams, B. J., Goldstein, A. H., Millet, D. B., Holzinger, R., Kreisberg, N. M., Hering, S. V., White, A. B., Worsnop, D. R., Allan, J. D. and Jimenez, J. L. (2007). Chemical speciation of organic aerosol during the International Consortium for Atmospheric Research on Transport and Transformation 2004: Results from in situ measurements. J. Geophys. Res.-Atmos. 112:D10S26.

Zhang, Q., M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, and J.-L. Jimenez (2005), Time- and size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes, J. Geophys. Res., 110, D07S09, doi:10.1029/2004JD004649.

Zhang, Q., J.L. Jimenez, D.R. Worsnop, and M.R. Canagaratna. A Case Study of Urban Particle Acidity and its Effect on Secondary Organic Aerosol. Environmental Science and Technology, 41,3213-3219, doi: 10.1021/es061812j, 2007.