We thank both reviewers for helpful suggestions and comments that we have responded to below.

Reviewer 2:

This paper gives is well written, and it gives a nice overview of the aerosol and precipitation chemistry in southwestern US. I find it quite interesting, even though it is somewhat speculative, that you maybe can distinguish the difference in sulfate and dust when it comes to their potential as cloud condensation nuclei versus ice nuclei. The conclusion is not surprising as such since it is well known that sulfate act as CCN and that more crystalline particles act as IN, but that you may interpret this from the statistics in the monitoring data is quite neat. Specific comments to the text:

Figure 5 and the text in general: Why is not ammonium included in the IMPROVE data? Is ammonium only measured at selected IMPROVE sites? It is certainly of interest to know the relative contribution of ammonium. The properties of the aerosols are dependent on whether all the ammonium which is available is bound to sulfate or if it is sufficient ammonium to make ammonium nitrate. Ammonium nitrate is not stable and you can have biased nitrate measurements due to l evaporation from the filters. From the precipitation data it seems like it is relatively small contribution of ammonium in the region. Would be nice to have some more discussion on this issue.

Response: Ammonium is not routinely measured in the IMPROVE program, and thus its concentrations are not available at any of the sites for which we used data. We agree with everything the reviewer notes about its importance, but we cannot discuss its data. We do however add text to note that ammonium is not available in the IMPROVE data so other readers won’t have the same question about why it is missing:

“Ammonium is not routinely measured in the IMPROVE program and thus its presence in precipitation are only discussed.”

Page 8624 line 18-22. An additional explanation of higher particulate nitrate concentration in winter is that particulate nitrate winter due to more stable particulate face. NH4NO3 dissociate to NH3 and HNO3 when warm conditions and it is quite common to measure lower concentration in summer especially in warm areas.

Response: The reviewer is absolutely right and we make mention of this important detail:

“Nitrate is a marker for anthropogenic emissions as it often increases in concentration with decreasing mixing height in the winter months and because it is thermodynamically more stable in colder conditions; however, it is also associated with larger particles in the fine mode owing to reactions of HNO_3 (or precursors) with dust and sea salt (Malm et al., 2003; Lee et al., 2004, 2008).”

It would have been nice to include some discussion of the potential artifact problem. It is well know that nitrate (and ammonium) aerosols measurements can be biased due to the gas/particle exchange. However, IMPROVE use a denuder system and may be that the method gives good/accurate measure of nitrate. Are there any studies which has looked at the comparability of the nitrate measurements from IMPROVE with other methods?

Response: The IMPROVE program does indeed use a denuder to remove nitric acid and we make a note of this in the text, in addition to some brief discussion of how nitrate measurements compare to other methods, specifically the advantage of nylon versus Teflon which is a key difference in between methods:

"Nitrate is vulnerable to measurement artifacts and this issue is minimized via the use of an annular denuder (to remove nitric acid, HNO_3) and nylon filters as compared to Teflon to prevent NO_3^- loss via recapture of volatilized HNO_3 (Ames and Malm, 2001; Yu et al., 2005)."

We do not want to provide a very exhaustive review of more studies and details of how nitrate compares between different studies since we feel this will distract readers away from the objectives of the paper.

References

Ames, R. B.; Malm, W. C.: Comparison of sulfate and nitrate particle mass concentrations measured by IMPROVE and the CDN, *Atmos. Environ.*, *35*, (5), 905-916, 2001.

Yu, X. Y.; Taehyoung, L.; Ayres, B.; Kreidenweis, S. M.; Collett, J. L.; Malm, W.: Particulate nitrate measurement using nylon filters, *J. Air Waste Manage.*, *55*, (8), 1100-1110, 2005.

Page 8626, line 4-8. There are high pHs other places than those mentioned here. Typically in areas in where the it is low emission of SO2 and NOx and/or high emissions of dust. Typically in the northern Mediterranean, central Africa, south Asia, Mongolia. You may refer to the regional networks like EANET, IDAF and EMEP. As well as the NADP and CAPMoN of course. You also have regions in US and Canada with lower pH. The publication on Asian data are quite old, and the pH may have changed quite a lot since the nineties due to more sulfuric acid. You may rather to EANET, see data report here: http://www.eanet.asia/product/index.html For European data, you may look at the EMEP database: http://ebas.nilu.no/ African, IDAF data is given in various publications,
I,:

Galy-Lacaux, C., Laouali, D., Descroix, L., Gobron, N., Liousse, C., 2009. Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger). Atmospheric Chemistry and Physics 9, 1579-1595

Response: We thank the reviewer for pointing us to these valuable sources of pH information to help us provide a richer view of how pH varies in different regions. We now update our references and regions to include the United States, Canada, sites within the EANET and IDAF networks, and sites in Europe:

"Examples of regions with higher pH values (> 6) than those in the Southwest, mostly due to alkaline species (e.g. ammonium from agriculture and calcium carbonate from soil dust), are

India (Khemani et al., 1987; Kulshrestha et al., 2005; Mouli et al., 2005), Jordan (Al-Khashman, 2009), Niger (Galy-Lacaux et al., 2009), Spain (Avila et al., 1997, 1998), Israel (Herut et al., 2000), Phnom Penh (Cambodia), Ulaanbaatar (Mongolia) and Jiwozi and Shuzhan in China (EANET Executive Summary, 2011)."

Line 8627 line 17-20. Here again I find the selection of studies used for comparison a bit strange and arbitrary selection. China and Tibet has certainly different source influence than US. Why not just look at US, at least compare to other North American studies in addition. Globally you have a wide range of various relative distributions of ions depending on the main sources in the regions and meteorology.

Response: We add references to more sites for comparison:

"In other regions such as those associated with the Acid Deposition Monitoring Network in East Asia (EANET; EANET Executive Summary, 2011), the Tibetan Plateau, Canada, Spain, India, and Israel, the dominant precipitation cation has been reported to be either Ca^{2+}, Na^+, or NH_4^+ (Avila et al., 1998; Herut et al., 2000; Kulshrestha et al., 2005; Zhang et al., 2007 and references therein; Aherne et al., 2010; Yi et al., 2010; Zhang et al., 2012). Those studies also showed that SO_4^{2-} was the dominant anion, which may be due to significant anthropogenic influence in those studies; the one exception was in western Canada where marine-influenced air promoted Cl^- to be the dominant anion. Calcium and Cl^- were shown to be the dominant cation and anion, respectively, in Jordan rain water (Al-Khashman, 2009). Consistent with our results, Hutchings et al. (2009) showed that NO_3^- was frequently more abundant than SO_4^{2-} in northern Arizona monsoon cloud water; however, they also showed that NH_4^+ was the dominant cation. San Joaquin Valley and Sacramento fog water in California exhibited high nitrate:sulfate concentration ratios (equivalent/equivalent) of 4.8 and 8.6, respectively, due to the influence of agricultural emissions (Collett et al., 2002). It is cautioned again that such comparisons are sensitive to the time span of data collected due to reasons such as varying air quality regulations at different locations and times. Significant changes in the relative amounts of SO_4^{2-} and NO_3^- have been observed in the United States since the 1980s (e.g. Butler and Likens, 1991; Lynch et al., 1995; Nilles and Conley, 2001; Butler et al., 2001; EPA, 2003)."

Page 8629, line13. ". . .dust is the dominant source of SO4" Source? The fact that SO4 comes together with mineral dust is not the same as saying SO4 is from dust . In large part of Asia the main source of sulfate is anthropogenic. Also in the paper by Zhao et al 2011 it is stated that SO4 is at least the latter decades mainly is from anthropogenic sources, i.e. sulfuric acid which attach to mineral dust particles.

Response: We altered our wording to avoid confusion as the reviewer pointed out:

"This link is supported by a large inventory of previous work: (i) measurements in Asia indicate that dust is a significant source of SO_4^{2-}, largely of anthropogenic origin which comes together with dust, in snow and glaciers (Wake et al., 1990; Kreutz et al., 2001; Zhao et al., 2011)"

Page 8630, line 2: “As SO4 and fine soil represent the most abundant PM2.5 constituents”. Well, only if you neglect the carbonaceous fraction. . .

Response: This is a good point, but the latter part of this sentence in question tried to address this issue but maybe not well enough:
“As SO_4^{2-} and fine soil represent the most abundant $PM_{2.5}$ constituents of interest in this work”

We now revise it to say:
“As SO_4^{2-} and fine soil represent the most abundant $PM_{2.5}$ constituents of interest in this work (excluding other constituents such as carbonaceous species), …”

Page 8632, line 12.
The reference to Spain is an old study, maybe use an updated reference from the same group:

Izquierdo, R., Avila, A., Alarcón, M. (2012) Trajectory statistical analysis of atmospheric transport patterns and trends in precipitation chemistry of a rural site in NE Spain in 1984-2009. Atmospheric Environment 61, pp. 400-408

Response: We have made this change:

“These units are now applied for comparison with documented values in the following regions: Brazil (~ 1.10, Dias et al., 2012; ~ 0.61, Migliavacca et al., 2004; ~ 0.11, Migliavacca et al., 2005); Turkey (~ 0.625, Topcu et al., 2002); Jordan (~ 0.51, Al-Khashman, 2005); India (~ 0.28, Singh et al., 2007); Costa Rica (~ 0.05, Herrera et al., 2009); Spain (~ 0.46 from 1984 – 1993 and ~ 0.94 from 1998 – 2009; Izquierdo et al., 2012); Mexico (~ 1.03; Baez et al., 2007); and numerous sites in Asia including in China, Japan, the Philippines, Thailand, Vietnam, Malaysia, and Hong Kong (~ 0.36 – 1.14, Yeung et al., 2007).”

At this site as well as many places in Europe, nitrate is getting relatively more important (even though the absolute concentration do decrease many places) to sulfur. At this Spanish site the NO3:SO4 is 1:1 the latter period. Also here it would be nice to include more North American (NADP+ CAPMoN) studies, and not somewhat arbitrarily global studies. The regional differences in NA are also large.

Response: The reviewer indeed is correct that nitrate may be getting more abundant in a relative sense over time compared to sulfur. We add more references to discuss this with a focus on North America. We note that there was limited discussion in the CAPMON literature as compared to data published for the United States.

“With regard to periods of data collection, it is critical to note that at least in North America, more significant reductions in SO_2 as compared to NO_x over recent decades likely bias intercomparisons of NO_3^-:SO_4^{2-} ratios between different studies (e.g. EPA, 2003; Kvale and Pryor, 2006). Measurements in the eastern United States have pointed to reductions in precipitation sulfate unlike nitrate since the 1980s (e.g. Butler and Likens, 1991; Lynch et al., 1995; Nilles and Conley, 2001; Butler et al., 2001)."

Page 8635, line 12. Include reference to NTN/NADP trends done by others, i.e:

Christopher M. B. Lehmann and David A. Gay (2011) Monitoring Long-Term Trends of Acidic Wet Deposition in US Precipitation. PowerPlant Chemistry 2011, 13 (7). 2011

Her it seems like nitrate actually has a had significant increase in the South-Midwest

Response: We have made the references to NTN/NDAP trends reported by others:

"Previous analyses of NADP/NTN over the United States between 1985 and 2002 showed general increases in ammonium, reductions in sulfate, and mixed changes in nitrate depending on location (Lehmann et al., 2005); furthermore, reductions in sulfate have been shown to be more significant as compared to nitrate (Lehmann et al., 2011)."

Page 8637, line 8. "Other regions" is here very undefined and too general. Surely there are other regions with lower nitrate to sulfate that observed in this study, especially in Asia where sulfate is dominating. But you have many examples of the opposite. Several places in Europe and Africa nitrate is the dominating anion

Response: We decided to remove this bullet point to address this comment. The line in question now reads:

"(v) The precipitation NO_3^-:SO_4^{2-} ratios in this study exhibit the following features: (ii) higher in precipitation samples as compared to $PM_{2.5}$; (ii) exhibit the opposite annual cycle compared to the particulate NO_3^-:SO_4^{2-} ratio; and (iii) are higher in snow relative to rain during DJF. Multiple explanations are discussed that require more detailed investigation, including partitioning of gaseous NO_3^- precursors (i.e. HNO_3) to rain and snow."

Referee #3

Specific Comments and Questions
In Table 1, could you also include the states in which the national parks or monuments are located? They are indicated in Fig. 1, but would also be useful in the table.

Response: We have made this change to Table 1.

I was surprised that Grand Canyon National Park was not included among your sites. Any reason? To my knowledge, both aerosol and wet-deposition measurements were recorded there as well during this time period.

Response: A major reason we chose not to examine Grand Canyon data is that the NADP/NTN site is not as perfectly co-located with the IMPROVE site as compared to the other sites we chose and displayed in Table 1. To be more specific, the NADP/NTN site at Grand Canyon is positioned at 36.0586° latitude, -112.184° longitude, with an altitude of 2071 m (http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=AZ03&net=NTN). The IMPROVE site is at 35.9731° latitude, -111.9841° longitude, and 2267 m (http://vista.cira.colostate.edu/DatawareHouse/IMPROVE/Data/AEROSOL/Help/IMPROVELocTable.txt). Thus, we do not make any changes to the manuscript to address this comment.

Could you comment on why you chose 3 days for the HYSPLIT back trajectories and 10 m AGL? (I am more accustomed to authors using 100, 500, and 1500 m AGL.)

Response: We chose 3 days as we think it is a fairly good time scale to represent characteristic seasonal trajectories for the sites chosen. We chose 10 m AGL to try to mimic where the aerosol samplers were positioned, which are very close to the surface. 100 m AGL would be unrealistic for the surface sampling stations. We do not anticipate significant changes between 10 m and 100 m AGL. Thus, we do not make any changes to the manuscript to address this comment.

The HYSPLIT back trajectories typically include the Phoenix area (Maricopa and Gila Counties), yet you make no mention of anthropogenic sources of pollutants from this region. (Hutchings et al., 2009 suggested that the Phoenix metropolitan area had influenced cloud chemistry in Flagstaff.)

Response: The reviewer raises a good point. We added the following text:

“The majority of the back-trajectories include the Phoenix metropolitan area, which have previously been linked to enhanced levels of anthropogenic species (e.g. sulfate, lead, copper, cadmium) in cloud water more than 200 km to the north in Flagstaff, Arizona (Hutchings et al., 2009).”

Biomass burning is mentioned on several occasions in a general way, but Arizona is well-known for extensive prescribed burning (mostly in early Spring and late Fall) and catastrophic fires (e.g., the Rodeo-Chediski fire in 2002). Was there any evidence that those events impacted the OC levels in the aerosol data?

Response: It is certainly the case that biomass burning impacted OC levels in the aerosol data, but extracting the relative amount contributed by such prescribed burns and catastrophic fires over the long time periods we are examining is outside the scope of our study. A reason it is outside the scope of the study is that we want to stay focused on intercomparing precipitation and aerosol data, and we do not have access to OC in the precipitation data. This is an important topic though that warrants further attention in future work. We do not make any changes to the manuscript to address this comment.