Review 1:

We thank reviewer for useful comments and we revised manuscript based on the comments.

Comment: This manuscript reports measurements of gas phase amines and ammonia in Alabama and Ohio during the summer of 2013. There are relatively few high time resolution datasets that provide measurements of gas phase reduced nitrogen (ammonia, and especially speciated amines) from continental North America, so from that perspective the data are potentially quite interesting. However, the presentation of results in the manuscript is disorganized, and the most relevant complementary data is not presented until the discussion section. In this section, the authors use FTIR and TDCIMS data to show that amines are present in much higher abundance in sub-micron aerosol, compared to the gas phase. This suggests that gas-particle partitioning may play a key role in regulating the abundance of gas phase amines, and this discussion should be prioritized over the correlations with wind direction, CO, isoprene, etc.

RE: Agreed. Gas to particle conversion is the most important finding. We will move particle data to the earlier Section 5, prior to wind direction analysis etc.

Comment: The authors should revise the manuscript to address the following points:

General Comments

Comment: The relatively high levels of particle phase reduced nitrogen calls into question the ability of the gas phase CIMS to discriminate against particle phase ammonium and amines. Based on the inlet schematic presented in the supplementary information, there is no strategy employed to prevent particles from entering the CIMS and potentially volatilizing to generate positive artefacts. What evidence do the authors have that this is not a concern, especially given that the FTIR data suggest that conversion of only 1% of the particle amines could generate a signal equivalent to the measured gas phase amines?

RE: We have tested with different transit times with standard amine vapor produced from permeation tubes, and this did not change the background levels and the concentrations of ambient amines measured with CIMS. So we think even though only 1% of total amines correspond to gas phase amines, this did not affect the sampling issues, substantially. This is perhaps because the time needed for gas to particle conversion or adsorption/desorption may be much longer than the transit time used in this study (less than 0.2 s) and the surface area of the inlet inside wall is really small (so little mass of deposited amines).

Comment: Assuming that the concerns about particle phase artefacts can be addressed, I recommend moving the information about the FTIR, TDCIMS and ion chromatography measurements from pages 16426 -16427 and Figures 11-13 to Section 5, where the other measurements from SOAS are reported. More information about the particulate data would be valuable. Can the TDCIMS data be converted from mass to mass loading (presumably using the volumetric sampling rate?) to better compare the relative amounts of amines in the gas phase and in particles between 40-120 nm? If the FTIR technique only measures primary amines, then it is likely underestimating total particle amines. Do the authors (or the literature) have any insights into what fraction of ambient C1-C6 amines are primary amines?

RE: The TDCIMS data are presented as ions detected per particle mass collected. The purpose for this is to demonstrate that amines compose a smaller fraction of the small particle mass during the late morning and afternoon than in the night. The instrument was not calibrated with amine

standards, so it is not possible to report actual mass loading of amines in the size ranges measured. Even if it were, the nanoparticles measured by the TDCIMS likely represent only a small fraction of the total particle amines and therefore are not suitable for comparing in an absolute way to gas phase concentrations. So the original sentence will change to:

"During SOAS, the TDCIMS measured various amines in particles in the size range from ~ 40–120 nm. The particle amine fractions showed diurnal variations (Fig. 13) opposite to the gas-phase amines 15 (Fig. 3). There were higher fractional levels of aerosol-phase amines (C1–C3) during the night and in the early morning and lower levels from the late morning until the end of the day."

With regard to FTIR data: We were not able to find a good estimate of the primary amine contribution to total amine based on the data we have. The gas or aerosol-phase primary amine fraction of total amine in the atmosphere is currently unknown, but this may be the subject of future study.

Comment: Section 6 presents data collected in Kent, OH, later in the same summer after SOAS, but this section does not really contribute to the analysis of data from the SOAS campaign and seems a bit orphaned in this manuscript. Given that the authors have published other papers that report amine mixing ratios from this site (e.g. Benson et al., 2010; Erupe et al., 2010), I think it would make the paper more cohesive to remove this section and just make the comparison to past datasets reported in the literature. I also recommend removing Figure 9 and related discussions because, given the short lifetime of ammonia against particle uptake and deposition, state-wide aggregate inventory data is unlikely to be representative of the individual source regions for each site.

RE: The purpose of including Kent amine data is to show that (1) the rural sites have lower amines than polluted sites, and (2) this indicates constraint of amines sources from anthropogenic emissions is important and is needed. The previous Yu and Lee, EC 2012 paper shows the winter time amines, and interestingly, we can see from the comparison of this winter and the current summer data that there is a clear seasonal difference due to temperatures, which is also consistent with the general conclusion of the this work. With regard to Figure 9: ammonia lifetimes in the atmosphere are several days, and so the regional scale transport and emissions can be also important. During the same summer in the same year, we saw quite different concentrations of ammonia at these two sites, and that is consistent with higher emissions in Ohio than in Alabama, in general. This was discussed in the text.

Specific Comments
Comment: P 16413, L 6 – 'on a daily basis' makes it sound like the sampling interval was once per day

RE: Change to "every day".

Comment: P 16417, L 10 – What do the values (â´Lij17–40%) refer to?

RE: This is the frequency of new particle formation events. We will change this to "with the frequency of new particle formation from 17-40%".

Comment: P 16417, L 23-25 – Are ethanol clusters used to detect the ammonia and amines, or are they only quantified using BH+? This is mentioned in passing later, but could be clarified here.

RE: In CIMS spectra, we see ethanol monomer, dimers and trimmers for ethanol reagent ions. And for the product ions, we see only BH+ ions. We will add this:

"As shown in CIMS spectra (Figure 1), there were ethanol monomer, dimer and trimmer reagent ions, whereas for the product ions, there were only BH^+ ions."

Comment: P 16419, L 3-4– 'National Institute and Technology' - is this the correct name?

RE: Should be "National Institute of Standard Technology (NIST)".

Comment: Table 1 – NH3 concentrations are given in ppbv, but the unit for the detection limit is probably pptv.

RE: that is right – corrected.

Comment: Table 1 – The detection limits are given for 1 Hz data, but the ambient data appear to be averaged to 20 min. Do the detection limits change for 20 min averages? If they don't improve with signal averaging, then why not?

RE: We have the background mode for 5 min at every 20 min cycle. Because of our sample time is slightly longer than 1 s (actually ~1.2 s), we have 250 data points in each background. We remove 40 data point in the front and 10 data points in the back to remove unstable signals that appear when changing between different modes (from "background" to "ambient" or vice versa). So, 200 points (corresponding to approximately 4 min) are used to calculate the average background. Therefore we do not calculate detection limits for 5 min and 20 min integration. The data shown in time series of all figures in the paper are those further averaged values over 20 min for "ambient" measurement data (in mixing ratio). With the integration time of 1 s, 5 s, 30 s and 60 s, detection limits are calculated and they will be shown in additional tables this will go to Supporting material.

Comment: P16420 – To what factors do the authors attribute the improvement in sensitivity and detection limits compared to past campaigns? The explanation for lower sensitivities of the amines compared to ammonia implies that the amines are more prone to surface adsorption than ammonia, but is that known to be true? Have the authors examined the ion chemistry of the amines carefully to ensure that there is no fragmentation?

RE: The lower detection limits and sensitivities were achieved mainly because of lower background signals and much more stable background signals, independent on ambient RH. Yes, amines are stickier than ammonia, as we can see from their thermodynamics data. This was clear during the calibration. For amines, we had to have really long time (> 20 hr) to "condition" the permeation tube to have reproducible calibration curves. With regard to fragmentation: we have only BH+ ions as the product for all amine isomers we tried. We added this:

"These improvements in the detection limits and sensitivities were mainly because background signals were lower, less variable and independent of ambient RH conditions."

Comment: Figure 2 – It would be useful to indicate the timing and duration of rain events on this Figure since they are referred to in the text.

RE: Done.

Comment: Figures - What is the averaging time for the CIMS data displayed in all of the time series?

RE: 20 min. We will also include this clearly in the text and figure captions.

Comment: Figure 4 – What is the physical basis for the exponential fits provided in the figure panels and why is isoprene included in the figure?

RE: This is based on BVOCs emission rates derived by Gunther et al., 1995, where the authors showed that BVOCs, such as isoprene, have the exponential temperature dependence. We were trying to see if this is the case for amines, similarly to isoprene. In response to this comment and another below, we revised the relevant sentence to:

"Concentrations of C3-amines and NH_3 detected in the Alabama forest showed some exponential dependences on the ambient temperature, like isoprene (Figure 4). Such exponential temperature dependences, as typically found for BOVCs emitted from trees [Guenther et al., 1995], may suggest as some biogenic sources of C3-amines; but there is also caveat in this interpretation, because the temperature dependence was also simply due to the dominant gas-to-particle conversion process, as discussed above."

Comment: Figure 6 – I find the explanation of the data in the related text confusing. It seems that around 14:00 the wind shifted from southerly to northerly and the T, CO and amines all dropped at the same time. This doesn't seem to provide a clear example of amines NOT correlating with SO2 and CO, as indicated in the text.

RE: We have done comprehensive data analysis to see whether amines are correlated to CO and SO2 pollutants in very detail for each day for the entire SOAS campaign. And from this systematic analysis, we found that regardless of wind direction or time of the day (rush hours) or day in the week, there was no any correlation of amines and these pollutants. We will make this more clearly stated in the revision. For the case of the day shown in Figure 6: around 14:00 wind direction changed and CO was dropping, but SO2 were low in the afternoon prior to that time and this did not cause low C3-amines or ammonia. We removed the entire paragraph related to Figure 6 in Sections 5 and 7, but instead, we state now briefly in Section 5:

"We made systematic data analysis for each day of the campaign, and we found that amines and NH_3 concentrations measured in the Alabama forest were not associated with traffic or with transported anthropogenic SO_2 and CO plumes, regardless of wind direction, time of the day (rush hours) or day in the week (e.g., Figure 6)."

Comment: Figure 10 and associated discussion – Given the many reasons that ambient trace gases can have similar diel profiles, the suggestion that the similarity between C3- amines and isoprene can be attributed to biogenic emissions of tri-methyl amine seems quite speculative. Given the strong indication later in the manuscript that ambient volatilization of particle amines can act as a significant source of gas phase amines, I would remove this section.

RE: Agreed - we will remove Figure 10 and will restate: "The exponential temperature dependence of C3-amines, as typically found for BOVCs such as isoprene [Guenther et al., 1995], may suggest as some biogenic sources of C3-amines; but there is caveat in this interpretation, because the temperature dependence was also simply due to the dominant gas-to-particle conversion process at this site, as discussed above."

Comment: P 16424, L7 – Should ppbv actually be pptv for the amine concentrations given here?

RE: Corrected.

P16425 – I suggest changing 'photo-degradation' to 'oxidation' so that it is clear that direct photolysis is not considered an important sink of amines in the atmosphere.

RE: Done.

P16427, L8-12 – I don't understand the discussion about the temperature dependences and thermodynamics here. Presumably it's not just the vapor pressure, but the enthalpy of vaporization that influences the temperature dependence. Furthermore, on P16426, the authors argue that the amines could be taken up into acidic aerosol water, in which case it's the enthalpies of the Henry's Law and acid dissociation constants that should be considered.

RE: These are very interesting comments. In response to these, we actually performed simple enclosure calculations of amines and ammonia in gas and aerosol phases to see their relative differences in gas to particle conversion processes of an amine versus ammonia as the following, and we will include them in the revision.

Consider an ammonia or amine compound A(gas), Henry's law equilibrium:

reaction: A_gas == A_aq

[A_aq] = H_a [A_gas]   (Eq.1)

where H_a is Henry's coefficient. Now consider dissociation followed by reaction:

A_aq + H+ == AH   with K_a = [A_aq][H+]/[AH]   so [A_aq] = K_a [AH] /[H+]
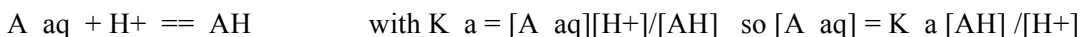
Put into Eq.1:

 [A_gas] / [AH] = K_a / (H_a[H+])   (Eq. 2)

this is the gas to particle ratio for chemical A (neglecting A_aq which is probably very small at acidic pH).

Similarly for another gas, B:

[B_gas]/[BH] = K_b / (H_b [H+])

Take ratio:

[B_gas]/[BH] / [A_gas]/[AH] = (K_b/K_a) (H_a/H_b)   (Eq. 3)

Equation 3 gives the RELATIVE particle/gas partitioning of the two compounds A and B. Now consider A = ammonia, B = some amine:

Henry's law coefficients are similar in general, so assume that H_b/H_a ~ 1, for simplicity.

But pKa is very different: -9.2 for ammonia, -10.6 to -11 for typical alkyl amines. Taking a

difference of 1.6, $K_a/K_b \sim 10^{(-1.6)} \sim 2.5\%$.

So the amine is 40 times (1/2.5%) more likely to be on particles than ammonia. If the ammonia gas/particle ratio is between 1 and 2 (Figure 10), then for the amines the gas/particle ratio should be 2.5% of that, or between 2.5% and 5%. Figure 12 shows this ratio to be between 0.8% and 1.2%, so in pretty good agreement within a factor of 2 which could be easily explained by the ratio of Henry's law coefficients, H_b/H_a, which above we took to be near unity.

So, the much higher particle/gas partitioning for amines, relative to ammonia, is consistent (within a factor of 2) with the amines being stronger bases, and pK ~1.6 lower than for ammonia.

Of course this neglects the effects of salt formation, which is probably likely at pH of 3 at this forest site. So it is not an exactly most accurate calculation, but this still shows the qualitative consistency. We will include the following in the revision:

"We have performed a simple calculation to determine the relative likelihood of gas to particle conversion of an amine versus ammonia. In our calculation, we considered only Henry's Law equilibrium and acid dissociation, and neglected salt formation and other processes. Henry's Law constants are quite similar for an alkali amine and ammonia [Sander, 1999]. But their acid dissociation rates (pKa) are different. So if we take pKa for a typical alkali amine as -10.8, and pKa for ammonia as -9.2 [NIST, 2005], then we can derive the relative gas to particle conversion of an amine compound is nearly 40 times stronger than for ammonia. The ammonia gas to particle ratio is between and 1 and 2 (Figure 10), so according to our calculation, then the gas to particle ratio should be between 2.5% and 5%. Figure 12 shows this ratio to be between 0.8% and 1.2%, so this is consistent within a factor of 2 with the prediction from our simple calculation. These results show that it is reasonable to expect much stronger gas to particle conversion than for ammonia, based on their Henry's Law constants and acid dissociation rates."

Review 2:

We thank reviewers for useful comments and we revised manuscript based on these comments.

Comment: You et al. present CIMS measurements of gas phase ammonia and amines from the SOAS field campaign in Alabama as well as ground base studies in Kent, OH. The measurements represent some of the few higher time resolution measurements of amines available in the literature. While manuscript presents a unique dataset, there are many technical details surrounding this very challenging measurement that need to be resolved. There is no questions that this CIMS detection axis is very sensitive and capable of high time resolution detection of amines and ammonia, however the entire challenging these measurements is in sampling and inlet characterization. If this paper were to be published in ACP, the authors need to make major modifications to the paper and likely conduct a series of laboratory experiments to demonstrate analyte transmission through the entire sampling manifold used during SOAS (and in Kent) at conditions (RH, temp) relevant to these sampling sites.

Beyond the technical shortcomings, there are serious issues in the organization of the discussion section. At present, the specific conclusions of the study are not clear. I would suggest either refocusing the paper on the technical aspects of the measurements and a discussion of the relative ratios of the aliphatic amines measured here. For example, C3/C5 in Alabama is orders of magnitude larger than in Kent. If they have similar loss rates, what does this imply for the primary emission rates for these compounds in the two environments? Simply 0-D box modeling (of both kinetics and gas-particle partitioning) could prove remarkably useful in the interpretation of these preliminary measurements. This is the unique strength of the SOAS data set, as a box model would be very well constrained.

RE: Most of the technical issues raised here were described in detail in our previous papers [Yu and Lee, 2012; Benson et al., 2010]. The current paper intends to show only major improvements made since then and scientific discussions of the ambient data at the two sites. While in the Alabama forest, we saw only C3-amines mainly for most of time. The C5 amines were not present in the Alabama forest except biomass burning periods, so it is not possible to make ratios of C3/C5 there. We plan to build a box model by considering source, deposition, transport, nucleation, coagulation, heterogeneous uptake, salt formation, and photochemical and oxidation processes together, using the SOAS data. Since these two sites have significantly different background aerosol concentrations, different nucleation frequencies, different OH and ozone concentrations, different relatively humidities and temperatures, and different acidities in the aerosol phase, their loss rates are different at the two sites. This is beyond the scope of the current paper and we will publish these results in another paper.

Specific Comments: Page 16415, line 18: This is slightly misleading as the ethanol ion chemistry for detection of NH3 was worked out nearly a decade prior to this (Nowak et al., 2002 JGR). To the best of my knowledge, Yu and Lee linearly applied the technique to the detection of amines.

RE: We restate now: "The ethanol ion chemistry for the detection of NH3 was worked out previously by Nowak and colleagues [Nowak et al., 2002 JGR] and Yu and Lee [2012] linearly applied the same technique to the detection of amines."

Comment: Page 16416, line 2: There are multiple times where the authors state "fast-time response". It would be nice to see some discussion in the introduction of why we need fast-time response measurements for these compounds from ground sites such as this. What is needed? 1Hz, 30 min? The justification for fast-time response from aircraft and ship platforms (or for

measurements via eddy covariance) are clear, but it is not clear what is needed here to answer the science questions posed.

RE: Agreed. We will add the importance of fast time measurements. To identify the source and deposition processes and simulate them in box models, we need fast time response. Figure 7, for example, shows a rapid increase of amines during the burning event, and this short episode was captured because of the CIMS fast time response, and other traditional chromatography methods which takes days or weeks would not be able to catch. Also, Figure 8 shows the abrupt spikes of C4- to C6-amines in Kent, which are different than the C1- to C3-amines and ammonia profiles, and these spikes indicate some local emission sources. These are another example that fast time response instrument is needed even at the ground level to capture those unique profiles of ambient amines. We will add these two sentences:

"These methods are not suitable for capturing temporal variations of amines that rapidly change due to emission and deposition processes, as well as reactions with oxidants and aerosols."

"Detection of such rapid evolution of ambient concentrations of amines was enabled with fast time response CIMS techniue."

Comment: Page 16417, R2: With what certainty can the authors say that this is the ion molecule reaction? It is clear in the mass spectra that they detect amines as BH+, but that does not mean the ion-molecule reaction proceeds through a proton transfer as opposed to a ligand switch followed by collisional dissociation.

RE: We have used standard amine vapor (individually for one compound at a time or mixed together; in the flow tube in the lab and in the field with ambient air) as discussed also in [Yu and Lee, 2012; Yu et al., 2012; Erupe et al., 2011], and the results obtained from these different conditions consistently show that ion chemistry R2 occurs.

Page 16418, Line 1: Were any attempts made to assess the transmission efficiency for amines in this system? While a transit time of 0.17s is short, this does not ensure there is no wall loss? This needs to be accounted for in the discussion. I would assume that mass accommodation of ammonia/amines could be close to one at the wall, especially under the high RH conditions sampled here. What is the number of collisions with the wall in transit? Many other questions also need to be addressed: 1) What is the composition of the three way valve? 2) How does switching from high to low RH for the zero impact any amine that is on the inlet or IMR walls? 3) What is the temperature of the inlet, was it actively controlled? 4) What is the temperature of the IMR? 5) It appears from Fig S1 that the gases for the calibration were added to dry air directly at the inlet to the CIMS, but not to the instrument inlet. Why was this done and what artifacts does this introduce. I find it impossible to believe that adding NH3 or amine to the inlet of the CIMS under dry conditions equates to a standard addition of NH3 or amine to the actual inlet tip under high RH sampling conditions.

RE: Most of these questions came from errors in Figure S1, which did not illustrate correctly what has been actually used. We have revised Figure s1 now and we apologize for these errors. The standard gases were diluted with dry nitrogen gases, but they were eventually merged to the background gases prior to CIMS. We did not see background signals changing with RH, when we tested without the drier using the ambient air. We also did not see any differences in background signals between flowing the indoor air and the ambient air through the scrubber, so for the practical convenience in the trailer, we used room air to generate zero gases for calibration tests. We have tested transmission at different inlet points (thus different times) using the standard

amine gases and we did not see that different transit time also causes different background signals. This is because the transit time is really short. Whether the wall loss will become serious is dependent on time scale of adsorption and desorption and the mass (deposited on the surface of the inlet tubing's inside wall). The three-way valve was made PFA Teflon. The IMR was at 25 C for most of time. The inlet was drilled through the trailer wall and remained at the ambient temperature without active control. We will add these in the revision:

"Our test experiments using the ambient air, without applying the drier, have shown that the drier did not affect the background ion signals. We also confirmed experimentally that the application of the drier did not change the background signals."

"The inlet was drilled through the wall of the trailer at horizontally, in the direction precisely aligned the CIMS inlet. The inlet thus was not shared with other instruments."

Comment: Page 16419, line 25: How many data points were used to calculate the three signal of the background? All of the background determinations for the campaign? Daily values?

RE: We have background mode for 5 min at every 20 min cycle (remaining 15 min is for ambient measurement mode). Our sample time is slightly longer than 1 s (actually ~1.2 s). So we have 250 data points in each background mode. We remove 40 data points in the beginning and 10 data points at the end, to get rid of those unstable signals that occur while switching between different modes (from "background" to "ambient" or vice versa). So, 200 points are used to calculate the background level. Therefore we do not detection limits with 5 min or 20 min integration. Table 1 shows detection limits for 1 s integration time. The data shown in time series of all figures in the paper are those further averaged values over 20 min. With the integration time of 1 s, 5 s, 30 s and 60 s, detection limits are calculated and they will be shown in additional tables which will go to Supporting material (shown below also). The background signals were stable during the entire campaign and in Kent, and they similar to those shown in Figure 1. The mean background signals will be shown in another tables (in Hz and ppt, both) in the Supporting material.

Comment: Page 16419, line 27: The calibration curves are for concentrations that are 2-3 orders of magnitude larger than ambient. What evidence do the authors have that the instrument has a linear response from 1 ppt to 1ppb?

RE: At this moment, we can only provide calibration curves using amines at ppb level, mainly because we don't have low concentrations of standard gases with accurately known concentrations. So and we extrapolate the calibration curve down to ppt but we have no evidence that the CIMS has linear response to over ppt through ppv level. This is one of the issues we will need to explore in the future.

Comment: Page 16420, line 19: This is confusing, why would you expect the background signals to be sensitive to ambient RH if you are drying the air before detection? I presume that the backgrounds are sensitive to RH, but your method of determining this is not adequate.

RE: The conclusion that background signals are not dependent did not come from tests using the drier and came from tests without drier. The drier was applied, in order to prolong the lifetime of the scrubber, after we confirmed that RH does not change the background signals. Without the drier, we tested background signals at different ambient RH conditions at both measurement sites, and we did not see any changes in the background signals with RH. Therefore, using drier does not affect the background signals, which we also confirmed experimentally. We will clarify this in the revision. We will add:

"Our test experiments using the ambient air, without applying the drier, have shown that the drier did not affect the background ion signals. We also confirmed experimentally that the application of the drier did not change the background signals."

Section 3: What was the averaging time that was used to make the measurements? It appears from table #1 that the 1s measurements would be below the detection limit for most all of the Alabama experiment. What is the detection limit for a 20 min sampling period? At what point does signal averaging not improve your detection limit (in many CIMS instruments this can be as short as 30-60 seconds as the sources of error are no longer random), thus requiring frequent background determinations.

RE: Please see our earlier response. As will be seen from additional tables in the supporting material for detection limits as different integration times for all amines and ammonia, we can see detection limits start to level off from 5-10 s.

Comment: Section 3/4: Was the CIMS instrument located on the tower? With an inlet collocated with the other instruments? Or was the instrument on the ground? If so, the inlet must only be through the wall of a trailer? This needs to be expanded on.

RE: The CIMS was located in the trailer at the ground. The air was sampled directly through an inlet drilled through the wall of the trailer, in the exact direction aligned with the center of mass spectrometer detectors and octoples and the CIMS inlet. We did not sample from the tower. The inlet was used only for amine-CIMS, not shared with other instruments. This will be added in the sampling section. We will add:

"The inlet was drilled through the wall of the trailer at horizontally, in the direction precisely aligned the CIMS inlet. The inlet thus was not shared with other instruments."

Page 16422, line 6: What does "within" the CIMS detection limit mean? This is a threshold, the measurement is either below or above. If the measurement is below the detection limit, why are the figures shown? Is the measurement below the 1s detection limit but not the detection limit for a longer integration time? Are the measurement shown 1s?

RE: We will change to "below the detection limit'. The detection limit indicated in Table 1 was calculated from 1 s integration time. The time series in all figures are averaged fro 20 min. We will clarify this in the text and figure captions.