Authors' Response to Anonymous Referee #2

We appreciate the helpful comments of this reviewer which have improved the paper. Our point-by-point responses are embedded below (red) within the referee's original comments (black).

This manuscript summarizes the construction and evaluation of a regional (Canada and USA) atmospheric PAH model. The manuscript adds significantly to the literature on this topic, as there are no other North American regional atmospheric chemical transport PAH models in existence at this time. The authors test the model's ability to simulate both total atmospheric PAH concentrations as well as the distribution of concentrations between the gas and particle phases using two different gas-particle partitioning parameterizations. The evaluation of model ability to predict gas-particle partitioning against observations is not often investigated in similar modeling exercises, further adding the study's novelty. I found no technical corrections to be made (other than perhaps limiting the abstract to one paragraph; in my view, an abstract is too long if it needs to be separated into paragraphs). Therefore, I would like to see the following questions/comments addressed before final publication (i.e., somewhere between minor and major revisions):
Thank you very much for these positive comments. The abstract has been modified as requested.

Please define AURAMS at first use within the main text.
Done as suggested.

Please explain the motivation for the choice of gas-particle partitioning schemes tested (i.e., why was organic matter sorption alone omitted?).
The literature published in recent years has begun to converge toward dual sorption as the preferred approach to partitioning for PAHs (e.g., Lohmann and Lammel, 2004) and away from organic matter sorption alone (Arp et al., 2008). As a result, we did not include an OM sorption model but rather used the dual sorption approach (viz. Dachs-Eisenreich). For the sake of comparison, we also used the more traditional Junge-Pankow approach. It relies on a volatility descriptor (saturated vapour pressure) that is proportional to both K_{OA} and K_{SA}. We were very cautious about increasing the computational load for our model runs and analytical load for the results. Having 2 partitioning expressions instead of one effectively doubled the work and we did not feel justified in adding a third expression, especially since OM sorption is an integral component of the dual sorption approach of Dachs and Eisenreich.

Dry deposition: I would imagine that the cuticle and ground resistances for PAHs are actually quite different from those of acetaldehyde and C3 carbonyls, as they are much larger compounds with greater aromaticity. Can the authors comment on how the scaling factors used may impact results?
The deposition parameters for VOCs are a source of considerable uncertainty in the current generation of air quality models such as AURAMS and this problem is not limited to PAHs. The underlying issue is that there are few, if any measurements, of these parameters upon which to base an air quality model; usually indirect methods of estimating these parameters are used. Unsubstituted compounds are usually assumed to have relatively high resistances while those with carbonyl, acid or nitrate groups have lower resistances (see Zhang et al., 2002, Atmos. Environ. 35:537-560). By that logic, the resistances for PAHs would also be very high. However, based on published reports

of PAH deposition to ground surfaces (e.g., soil, vegetation), we felt that resistances leading to non-zero deposition velocities would be more appropriate. As a result, we use the deposition parameters of acetaldehyde and C3 carbonyls as the best-available homologues. We agree that this is an area of uncertainty and we have added text to this effect to Section 2.1.2.

Since loss via oxidation by hydroxyl radical is a major sink for atmospheric PAHs, can the authors comment on the potential influence of using the same OH reaction rate constant for the four larger PAHs?
OH oxidation is a major sink for atmospheric PAHs in the gas phase; ozone and nitrogen oxides appear to have more effect on the degradation of particulate PAHs (e.g., Masclet et al., 1986, Atmos. Environ. 20:439-446). The larger PAHs are predominantly particulate so we would expect any inaccuracies in the OH loss rate of their gas phase component to have little effect on total airborne concentrations.

Since submission of the draft manuscript, we have identified an error in our reporting of OH loss coefficients. Table S1 has been revised with the k_{OH} values used in the model whose results we have reported.

What is the effect of assuming fully reversible partitioning? What is the justification for this, considering the primary author has previously published data suggesting that the partitioning process may not be fully reversible?
The effect of assuming fully reversible partitioning is not known. It should be noted that some authors' interpretation that partitioning may not be fully reversible has not been elaborated to identify the process(es) by which such full reversibility might be prevented. If irreversible partitioning were occurring in reality but not being modelled, one would expect that modelled particulate fractions would be underestimated relative to measurements. Furthermore, one would expect this effect to be greatest for the highest molecular weight compounds since their fugacity away from the particles to which they'd become sorbed would be the lowest. Our model results do indeed show underestimation of the particulate fraction but such underestimation is greatest for the lowest molecular weight PAHs. As will be discussed in a forthcoming paper, this may be due to underestimated PM mass in AURAMS-PAH rather than the treatment of partitioning per se.

Which particle size bins end up with the greatest fractions of particulate PAH?
We did not assess the distribution of particulate PAH across the aerosol size spectrum. Very few measurement data for PAH particle size distributions were available for our model's spatiotemporal domain and we felt that we would not be able to report results with confidence. We are working on a more detailed analysis of partitioning and particle size distribution issues for a subsequent publication.

I find line 25 of page 18424 to be a bit confusing. Do Jonker and Koelmans report values for sum PAH?
We apologize for the confusing wording. Jonker and Koelmans reported results for individual PAHs. K_{SA} values varied by up to a factor of 47 for individual PAHs on different soots. We have clarified the wording in our revised draft.

Can the authors comment on the possible influences of including snow scavenging?

The absence of gaseous PAH snow scavenging in this run of AURAMS-PAH might be expected to yield overestimated airborne concentrations during snow events. No analysis was conducted to examine seasonal patterns in model performance.

Note that scavenging of particles is included in the model. We have clarified the text to account for this.

Line 5, page 18429: Please specify that annual means are being discussed, rather than "overall means".
We apologize for this ambiguity and have clarified this in our revised draft.

What are some other possible reasons for the smaller temporal RSDs in model results compared to measurements besides temporal variability in emissions? Have OH and/or particle concentrations simulated by AURUMAS been compared to observations within the same model domain, and do the temporal RSDs of these quantities vary less in the model compared to observations as well?
A similar outcome has been seen in studies of particulate matter. Under the AQMEII model intercomparison, the temporal standard deviations of PM_{10} and $PM_{2.5}$ concentrations have been compared to observed values for the year 2006 over all North American stations for AURAMS and a number of other regional air quality models (Solazzo et al., 2012, Atmos. Envrion, 53:75-92). All of the models had smaller temporal SDs than the observations; in the case of PM_{10}, there were smaller by a factor of two on average. We do not know of any comparisons of AURAMs output to measured OH concentrations; the technology to measure OH is still quite new.

Other than missing variability in emissions, a further contributing factor to the small modelled variability might be the loss of true meteorological variability at the regional scale. Small-scale features due to land surface differences and topographic variability induce differences in wind fields, etc., that are not well-represented at a model grid spacing of 42km. We have mentioned this additional source of reduced simulation variability in Section 3.1.1 of our revised manuscript.

Line 17, page 18428: Please use "total concentrations" rather than "values".
We apologize and have replaced the term "values" at several locations in the revised manuscript.

Line 6, page 18429: There are more recent references for particle-reactive BaP (e.g., Poschl et al., 2001, J. Phys. Chem. A; Shiraiwa et al., 2009, Atmos. Chem. Phys.; Kwamena et al., 2004, J. Phys. Chem. A).
Thank you. We have provided a more extensive list of references in our revised draft.

Lines 13-26, page 18429: I would argue that the results in fact DO show that there is a trend toward underestimation of more volatile PAHs, indicating surface volatilization is an important process. The authors state that the results are ambiguous, but in general, the more volatile PAHs are underestimated, the mid-volatility PAHs show little bias, and the low volatility PAHs are overestimated. I would like to see this section rewritten to acknowledge that revolatilization may in fact significantly contribute to atmospheric concentrations.
We initially observed the pattern you describe (see Fig. 3). However, we stand by our conclusion that the findings are ambiguous at this time and must be examined further. Global models that have concluded that volatilization is important (e.g., Lammel et al.,

2009) have observed an effect for fluoranthene, yet our model yields modelled concentrations that are very close to measured values for this PAH. Overestimation of the heaviest PAHs does not support a missing volatilization term. Should such a term be missing, these relatively involatile compounds would be unaffected rather than overestimated. Furthermore, the two overestimated compounds (BaA and BaP) are reactive and largely particulate. Their overestimation could be explained by missing particulate reactivity in the model. We have softened our wording in the revised manuscript to make it clear that we believe this issue is worthy of further examination.

Also, line 13: do the authors mean “water and soil” rather than “air and soil”?
Yes, thank you for pointing out this error. It has been corrected in our revised draft.

It would be useful to have some statement at the end of Section 3.1.1 that hits on the utility of a regional model that simulates concentrations generally within an order of magnitude. What are the model strengths versus other models (e.g., global) that could simulate North American concentrations at more coarse spatial resolutions? Later there is some discussion of finer resolution hopefully providing more accurate results, but can the current version of the model be employed to answer outstanding questions regarding PAHs in North America?
Annual average concentrations are captured very well by our model but it simulates day-to-day variability only within an order of magnitude. The utility of a regional model that simulates annual average concentrations in a manner that is indistinguishable from measurements is of great potential use to a variety of users. For example, health studies aimed at pollutants such as PAHs that exhibit chronic effects need accurate long-term averages rather than predictions of short-term variability. These health studies generally rely on comparatively fine spatial resolution that is incompatible with global modeling.

Particle/gas partitioning is very sensitive to the availability of particulate matter substrate yet gradients in PM are quite steep between urban and rural areas. Such gradients cannot be captured at the global scale. For example, the two global modeling studies capable of simulating PAH concentrations in North America were by Lammel et al. (2009) at ~3°×3° resolution and Friedman and Selin (2012) at 4°×5° resolution. The latter models are approximately an order of magnitude coarser than AURAMS-PAH at 42km resolution and neither describes its performance on a temporally disaggregated scale. Rather, both have aggregated their model and measurement data to monthly and/or annual scales. We have presented an analysis of our model performance that is atypically detailed for PAH modelling studies and more in line with model studies of ozone and PM. For shorter temporal scales, this study has proved successful in identifying shortcomings in the model’s performance and potential areas of improvement.

We have added text to our Abstract and Conclusions to point out this utility.

Deposition: Do any of the measurement stations included in the study provide deposition measurements in addition to concentration? It would be interesting to see how well the model simulates deposition, particularly for the less volatile compounds. This would also help determine whether revolatilization does indeed have a substantial effect on atmospheric concentrations or not (perhaps deposition of volatile PAHs is overestimated compared to particulate PAHs). I ask that the authors please comment

on this.
We agree that an evaluation of deposition performance would be of value. The scope of the study was quite large and we decided to draw the line at examining airborne concentrations only. Had we assessed deposition as well, only measurements from IADN sites in the Great Lakes Basin would have been available. Those measurements provide monthly totals for wet deposition only. We know of no systematic dry deposition data available over our domain for 2002. We are now searching for short-term datasets that may be of use to the assessment of deposition for subsequent model runs.