

Reviewer #2

The author sincerely thanks the reviewer for a careful and insightful review of the manuscript. Responses to specific comments are presented below in italics.

Rev#2: overall comments: In the abstract, the author states "Model results of isoprene profiles and fluxes are found to be consistent with previous measurements made at the simulated site and with other measurements made in and above mixed deciduous forests in the Southeastern United States". This statement is not strongly supported by the presented results. Measurement data for isoprene fluxes are not presented in the main body of this manuscript. In Figure 7 there is comparison of measured isoprene mixing ratios at different heights, compared to model predictions. It is difficult for the reader to fully realize the abstract's assertion concerning profiles as some measurements differ from the model predictions for the same elevation from a factor of 3 to >6. The degree to which the model is reasonably consistent with measurements requires an understanding of the bNO_x for each measurement. If the measurement data was color coded the same as the model predictions for bNO_x, this would provide insight as to whether the dependence in model predictions of isoprene vertical profiles to bNO_x is supported by field measurements, and in fact if BVOCs are reasonably represented by the modeling system.

Response: *The reviewer's core points here are well taken. Measured isoprene fluxes for WBW have been added to Figure 8a for comparison with modeled values and additional discussion has been added in Section 4 on this topic. Additionally, discussion of NO_x mixing ratio measurements of Fuentes et al. (2007) have been added to this Section. As noted in more detail below for another reviewer comment, NO_x mixing ratios measured during July 1999 at WBW typically ranged from 2-6 ppbv within and just above the canopy. From Figure 6, it can be seen that this corresponds roughly between the bNO_x = 5 and 30 ppbv experiments. From Figure 7b it can then be seen that the model results are relatively consistent with the measurements of both Fuentes et al. (2007) and Baldocchi et al. (1995). Additional comparisons with Andronache et al. (1994) for western Alabama and Wiedinmyer et al. (2005) for the Ozarks are necessarily more qualitative since the author does not have access to the detailed data from these measurements. Thus, as originally pointed out in the text, modeled surface concentrations and concentrations aloft from ACCESS for WBW are not inconsistent with measurements from both Andronache et al. (1994) and Wiedinmyer et al. (2005).*

Andronache, C., Chameides, W. L., Rodgers, M. O., Martinez, J., Zimmerman, P., and Greenberg, J. (1994) Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States, Journal of Geophysical Research, 99, 16989-16999.

Baldocchi, D., Guenther, A., Harley, P., Klinger, L., Zimmerman, P., Lamb, B., and Westberg, H. (1995) The fluxes and air chemistry of isoprene above a deciduous hardwood forest, Philosophical Transactions of the Royal Society of London A, 350, 279-296.

Fuentes, J. D., Wang, D., Bowling, D. R., Potosnak, M., Monson, R. K., Goliff, W. S., and Stockwell, W. R. (2007) Biogenic hydrocarbon chemistry within and above a mixed deciduous forest, Journal of Atmospheric Chemistry, 56, 165-185.

Wiedinmyer, C., Greenberg, J., Guenther, A., Hopkins, B., Baker, K., Geron, C., Palmer, P. I., Long, B. P., Turner, J. R., Petron, G., Harley, P., Pierce, T. E., Lamb, B., Westberg, H., Baugh, W., Koerber, M., and Janssen, M. (2005) Ozarks Isoprene Experiment (OZIE): Measurements and modeling of the "isoprene volcano", Journal of Geophysical Research,

Rev#2: The statement at the end of the abstract "...canopy which may have an impact on the relative magnitude of SOA formed through aqueous- versus gas-phase pathways as a function of anthropogenic influence..." is due to the fact that predicted biosphere fluxes of water-soluble organic compounds (that form SOA in laboratory experiments) is dependent on simulated NO_x values. This is central to the author's point, but is never explicitly stated.

Response: *The abstract has been modified in the revised manuscript to address this shortcoming.*

Rev#2: The literature search presented in the introduction is extensive, but difficult to connect to the abstract's objective related to aqueous and aerosol phase chemistry. The articles presented here are arguably the important and relevant literature for describing the physics of sub-canopy flux, and it is clear the author understands this body of work. It is difficult for the reader to keep track of the important chemical details regarding differences in development of model chemistry and its application because a synthesis of key details affecting critical uncertainties is not identified, in particular related to gas and/or aerosol phase chemistry. Further, the introduction is largely a discussion regarding canopy focused on differences in tree type (loblolly pine plantation, idealized forest, different types of real forests) and oxidants (NO_x and OH). The author states, "most previous investigations have focused on gas-phase chemical processes and the effect of BVOC emissions.... multiphase modeling and measurement studies of forest- atmosphere exchange are needed to....", but then describes how this work also only considers gas phase chemistry. The author's contention that the relative importance of aqueous versus gas phases processes for SOA formation is important, is not strongly linked to the previous discussion in terms of chemistry or physical nature of the studied environments.

Response: *The author disagrees with the reviewer's comments in this section. The work described here is intended as only a first step in a continuing process to gain a better understanding of the role that forests play in the production of SOA. The first version of the modeling system described here is indeed gas-phase-only, but the long-term intent is to create a model which can simulate the aerosol phase as well and potentially also simulate aqueous-phase processes as might be important for within-canopy fogs or cloud interception in high-altitude forests. The goal of this manuscript is to document the first version of ACCESS (i.e., a gas-phase-only version), but to also lay out a rationale for going beyond previous canopy chemistry modeling efforts (which have all been gas-phase-only) and create a multiphase modeling system. As such, a brief review of previous canopy chemistry modeling efforts is provided, NOT with the intent of synthesizing or reconciling their results across different canopy morphologies, tree species or environmental conditions, but simply to illustrate that all previous efforts have been focused on gas-phase chemistry (primarily related to ozone formation) and that the ACCESS modeling system builds upon these previous efforts. A brief discussion is then provided of recent recognition within the atmospheric chemistry community that BVOC fluxes from forests are important not only for ozone but are also important in SOA formation and that multiphase modeling studies are needed because of the apparent importance of aqueous-phase pathways in addition to gas-phase pathways. The last paragraph of the Introduction states clearly that ACCESS is being created as a multiphase model, but that this manuscript reports on a "preliminary gas-phase-only version of the model". In response to the reviewer's concern, however, the author has modified the Abstract in the revised manuscript to clarify the purpose and direction of this work.*

Rev#2: detailed comments: The author explains in detail how several BVOS are included in the chemical mechanism(s). However in the emissions used in the modeling exercises here, only isoprene emissions are considered. Discussion as to why this is suitable for the area being studied needs to be justified. What are the effects and specific limitations of neglecting a large fraction of the total emissions?

Response: *The BVOC species other than isoprene mentioned in the model description were included because this modeling system is intended to be applied to a wide range of forest canopies with multiple species emissions. The isoprene-dominated WBW application simply provides an initial test case for the model. The lack of significant terpene-emitting tree species in the biomass density census of Kardol et al. (2010) (referenced in the 1st paragraph of Section 3) for Walker Branch Watershed (WBW) strongly suggests an isoprene-emission-dominated canopy. Additional confirmation that the WBW forest canopy is isoprene-emission-dominated is provided by the measurements of Fuentes et al. (2007), who noted that α -pinene and d-limonene concentrations were two to three orders of magnitude smaller than isoprene during their measurements in July 1999. In response to the reviewer's concerns, the terpene measurements of Fuentes et al. (2007) have been referenced in the first paragraph of Section 3 in the revised manuscript to provide further confirmation that WBW is isoprene-dominated and that the neglect of other BVOC emissions is reasonable in this case.*

Fuentes, J. D., Wang, D., Bowling, D. R., Potosnak, M., Monson, R. K., Goliff, W. S., and Stockwell, W. R. (2007) Biogenic hydrocarbon chemistry within and above a mixed deciduous forest, Journal of Atmospheric Chemistry, 56, 165-185.

Rev#2: In the model description it is noted that there is a 60 sec integration time step for sub- canopy processes. Has the author performed sensitivity studies that demonstrate this time step is sufficient? The discontinuity in soil NO_x emissions at 30 deg. C, suggests some possibility of instability.

Response: *Yes, during model development sensitivity studies were performed to gauge the impact of the overall model time step. These experiments indicated that a 60 second overall model time step is sufficient. The reviewer should keep in mind that each process (i.e., emissions, background mixing, dry deposition, chemical transformation and vertical transport) is integrated separately over this time step with its own individually appropriate sub-time-step. For example, vertical transport is integrated with a sub-time-step of 0.5 second, while the time step for the chemical transformation integration is chosen adaptively for each species by the VODE software package based on a specified error tolerance.*

Rev#2: As the author notes, anthropogenic influences on biogenic SOA have been mentioned in the literature (e.g., Hoyle et al applies the idea to forests in Finland). Murphy et al., (2008) and Carlton et al. (2010) describe anthropogenic NO_x effects on biogenic SOA specifically to the Eastern U.S. Would the model results presented here support or contradict those findings applied to the same area the author studies here?

Response: *In general, the results reported here are consistent with the previous results cited by the reviewer. However, as the reviewer points out in another comment below, the most directly comparable previous result is that of Ervens et al. (2008). As noted in that reply, we will include mention of that work in the last paragraph of Section 4 in the revised manuscript.*

Rev#2: On page 24783 (and elsewhere in the paper) there is description of how model-

prescribed NO_x is changed, but prescribed ozone is not. Can the author explain why this is a realistic and valid test? In isoprene dominated areas, one would expect that ozone formation (and concentration) is NO_x-limited. Changes in NO_x inputs would be expected to have an impact on predicted ozone mixing ratios, both for the initial boundary conditions.

Response: *For the preliminary investigation reported here, background NO_x mixing ratios, which were slowly mixed into the modeled column, were varied over each experiment while background O₃ mixing ratios were held constant. As can be seen in Figure 6, the steady-state NO_x and O₃ vertical profiles in the column respond to the simulated chemical environment. As background NO_x values are increased, O₃ values respond accordingly, resulting in generally higher values and a more reactive environment. Data of Fuentes et al. (2007) (Figure 6b in that work) were used to select the value of 60 ppbv of O₃ as a reasonable background concentration during the measurements made at WBW during July 1999.*

Rev#2: page 24786 ... the author describes debate in the literature regarding isoprene oxidation in high and low NO_x environments. Is 'low-NO_x' an appropriate description of the area studied here?

Response: *During the July 1999 measurements of Fuentes et al. (2007), NO_x mixing ratios were typically found in the range of 2-6 ppbv, with some values as high as 23 ppbv and some as low as 1 ppbv. For the lowest background NO_x experiment (bNO_x = 0.1 ppbv), simulated NO_x values are < 0.05 ppbv. Although the actual measured NO_x at WBW in July 1999 probably does not fall into the "low-NO_x" (NO_x << 1 ppbv) category, the lowest value bNO_x experiments result in regimes that certainly might be classified that way, especially in terms of how isoprene oxidation chemistry proceeds in those regimes. As noted by Reviewer #1 and discussed further in the revised manuscript, there is considerable uncertainty in the mechanistic details of HO_x chemistry related to isoprene in the regime where NO_x << 1 ppbv. However, given that WBW is not typically a "low-NO_x" environment, this uncertainty should not substantially change the conclusions drawn from this work.*

Rev#2: page 24788. In what ways are Walker branch and the Ozarks similar, is it in terms of isoprene dominance or in terms of NO_x, ozone and vertical mixing structures also?

Response: *Although NO_x, ozone and vertical mixing would be expected to be somewhat similar between WBW and the Ozarks (i.e., rural southeastern U. S. during summer), the primary similarity is an oak-dominated canopy that produces strong isoprene emissions. The parenthetical aside "similar to WBW" has been moved within the sentence to make this point clearer.*

Rev#2: table 2.... more water soluble products at higher NO_x. It is very interesting to note, that despite a variety of differences in the applied models, this finding is consistent with Ervens et al., (2008), GRL, who found that for a given set of conditions, when the VOC:NO_x ratio is lower (e.g., higher NO_x conditions) a larger fraction of the total organic gas phase carbon is more water soluble.

Response: *Thanks to the reviewer for pointing out this similarity in findings. A citation to and discussion of the Ervens et al. (2008) result has been included in the last paragraph of Section 4 in the revised manuscript.*

Rev#2: figure8 - isoprene can be chemically produced?

Response: *Thanks to the reviewer for pointing out this mistake in labeling. Figure 8 has been modified to remove the term "production" from the caption and figure label.*

Rev#2: Can the canopy height be added to the vertical profile plots?

Response: *Yes. In the revised manuscript, all profile plots contain a horizontal line denoting the level of the canopy top.*