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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Are biogenic emissions a significant source of summertime atmospheric toluene in rural Northeastern United States?" *by* M. L. White et al.

M. L. White et al.

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We would like to thank both the referees for their helpful comments and suggestions. Many of those suggestions were considered during the process of writing this paper and we appreciate the opportunity to discuss them within this forum. The authors' responses to specific comments are given below:

Anonymous Referee #2, Atmos. Chem. Phys. Discuss., 8, S4125-S4128, 2008.

1. We agree that the extrapolation of biogenic flux rates to a larger scale for comparison to anthropogenic emission inventories is an interesting comparison to make and have added this to the revised version of this paper. To summarize, we have now included biogenic and anthropogenic toluene emission estimates on two larger regional scales:

1) the rural northern New England states of Maine, New Hampshire, and Vermont, and 2) New England as a whole including the more developed states of Massachusetts, Connecticut and Rhode Island.

Extrapolating the coniferous tree and crop flux rates to the forested and cultivated land areas for Maine, New Hampshire, and Vermont yields regional biogenic emission rates of 5 and 0.05 Mg d^{-1}, respectively. This number is approximately 13% of total daily anthropogenic emissions for these states (39 Mg d^{-1}) derived from annual emission estimates in the 2002 EPA National Emission Inventory. Adding the more developed states of Massachusetts, Connecticut, and Rhode Island to these estimates reduces the percentage of biogenic emission to anthropogenic emissions to 7% (6, 0.07, 90 Mg d^{-1} for forest, agricultural, and anthropogenic emissions, respectively, throughout New England).

2. Whether the toluene emissions measured from alfalfa and loblolly pine came from plant production processes or were simply routed through the plant after production in ground water is a question we cannot definitively answer based on our measurements. However, the ^{13}C labeling experiment conducted by Heiden et al. (1999) with sunflower plants in Germany does indicate that plants are capable of toluene production and emission. In that study, sunflowers exposed to isotopically labeled ^{13}CO2 subsequently emitted ^{13}C labeled toluene indicating carbon transfer within plant metabolic processes to produce toluene. Because our study of toluene emissions from loblolly pines and alfalfa exhibited similar diurnal patterns and stress-related enhancements as those observed by Heiden et al. (1999) for sunflowers and Scots pine trees, we feel the biogenic methods of production are most likely similar between the species, as well.

3. Wind direction and speed do shift seasonally at Thompson Farm. During the spring, summer, and fall, wind direction was more variable with a median direction of 210°. During winter, the median direction shifted to 290° reflecting a much more frequent northern influence at Thompson Farm. Wind speeds were also greater during winter months. Mean daytime winter wind speeds were 3.0 $\pm$ 0.1 m s^{-1} compared to 2.0 $\pm$

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0.1 m s^{-1} during the summer months.

However, this seasonal shift in wind direction could not have been responsible for the seasonal enhancements in toluene observed. As we noted in the paper, there was no strong directional influence on toluene mixing ratios during the seasonal enhancements observed at Thompson Farm. Elevated toluene and toluene/benzene ratios were observed in air masses coming from all directions. Furthermore, elevated toluene and toluene/benzene ratios were observed across a range of wind speeds in all seasons ($<$1 to 5 m s^{-1}). Finally, the distinct seasonal relationship observed in seasonal means of toluene, benzene and the ratio of toluene/benzene is preserved when only air masses from the predominant winter northerly direction ($>$270°) are considered (see table below). In all air masses, benzene mixing ratios were at their minimum during the summer months, while minimum toluene mixing ratios were observed in spring. The increase of toluene in summer months resulted in a corresponding increase in the toluene/benzene ratios observed in air masses from all directions.

Means from Wind Direction $>$270° : 2004, 2005, and 2006

	benzene	**toluene**	**toluene/benzene**
winter (n=126)	138 $\pm$ 2	86$\pm$ 3	0.61 $\pm$ 0.02
spring (n=99)	87 $\pm$ 4	48 $\pm$ 3	0.60 $\pm$ 0.04
summer (n=41)	43 $\pm$ 3	60 $\pm$ 8	1.4 $\pm$ 0.2
fall (n=66)	66 $\pm$ 3	62 $\pm$ 7	0.9 $\pm$ 0.1

A discussion of the seasonality of air mass source region influence is now included in section 3 of the revised manuscript (See our reply to Referee#1's comment 5). While this discussion is based on air mass back trajectory simulations rather than wind speed, the conclusions are similar to those presented here.

4. The radius of 20 km was chosen for estimating industrial influence because that

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is the distance of the two closest industrial facilities to Thompson Farm. The next closest toluene emitting facilities are located approximately 80 km away. We actually calculated industrial toluene influence at Thompson Farm with both sets of industrial emissions and found that the smaller radius and two closest facility emissions provided a larger estimate of daily industrial influence (7 pptv d^{-1}) than the larger radius circle (80 km) containing additional, larger toluene emitting industrial facilities (4 pptv d^{-1}). We felt the higher daily influence rate associated with the 20 km radius circle to be the better estimate as the two closest facilities were likely to have a consistent influence on toluene mixing ratios at Thompson Farm.

We also recognize that industrial emissions from even further away are likely influencing toluene mixing ratios at Thompson Farm. Since wind directions were variable and there was no strong directional influence on toluene mixing ratios during the seasonal enhancements, it was not possible to choose a predominant wind direction to back out more distant industrial influences. Instead, we had to assume that industrial influences were part of the background toluene mixing ratios observed at Thompson Farm.

5. A factor analysis of VOC variability at Thompson Farm during summer 2004 has already been done (Chen et al., 2007). In the principal component analysis conducted, high toluene loading was associated with air masses experiencing recent anthropogenic and biogenic emissions. The inability of PCA to separate out these two influences at Thompson Farm indicates that a more complex statistical analysis would not necessarily clarify the biogenic influence on toluene mixing ratios.

6. There was a weaker correlation for the toluene flux rates from the loblolly pine branch enclosure measurements with light (R^2 = 0.46) than there was with temperature (R^2 = 0.73). This correlation largely reflects the similar day/night differences for flux, temperature and light. When only flux measurements made between 6:00 and 19:30 LT were considered, the slope of the linear relationship between light and toluene flux was no longer significantly different than zero (student's t-test, α=0.05).

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7. To account for outlier compression of the data in Figures 1-3, we did change the y-axis scale from linear to logarithmic during the technical corrections to this paper. We feel strongly that it is important to display the original, individual data points that would be obscured by a box and whisker plot. As a result, we have decided to keep the graphs in their current format.

Other Points:

a) Abstract, line 6: We have made the recommended change to the revised manuscript.
b) Page 3, line 10: We have made the recommended change to the revised manuscript.
c) According to the Copernicus Publications Reference Type document provided for manuscript preparation, manuscripts in preparation can be referenced as long as that reference is within a footnote. There is not a prohibition against it. The two papers do not overlap significantly. The Russo et al. manuscript in preparation gives an overview of the more comprehensive VOC data set associated with the Thompson Farm daily canister measurements. Since this paper provides a focused analysis of a subset of those VOC measurements, we feel it is very appropriate to make reference to the more general paper.
d) Page 4, line 9: The seasonal cycle referred to in this line is for anthropogenic emissions, not ambient mixing ratios. As a result, the seasonal cycle being described is not driven by OH as the referee suggested.
e) P. 5, line 6: Since the region described was actually rural containing only one industrial facility, we do not feel that the suggested description of 'toluene-emitting industrial region' is accurate. Despite its clunkiness, the phrase 'regional toluene emitting industrial facility' is a better description of the actual source. f) These references have been added.

Anonymous Referee #1, Atmos. Chem. Phys. Discuss., 8, S6055-S6059, 2008.

1. We believe that incorporating the comparison of biogenic and anthropogenic emission rates extrapolated to the area of New England (see answer to Referee #2 comment

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1) into the revised version of this paper more fully answers the question posed in the title. As a result, we have chosen to keep the original title.

2. The time frame for mandated summertime fuel volatility requirements is now explicitly stated in the second paragraph of section 4 during the discussion of the summer relationship between toluene and i-pentane.

3. We must respectfully disagree with the referee on this point. We did quantify the contribution of seasonal changes in gasoline formulation to summertime toluene enhancements at Thompson Farm in Section 5 of the results and discussion. The referee is incorrect in stating that the summer fuel evaporation estimates given in Table 3 do not reflect summertime results. They are in fact based on the summertime relationships between toluene and i-pentane observed at Thompson Farm each year as well as the summertime enhancement in i-pentane (summer mean 8211; springtime minimum). We also feel that the focus of section 3 is on presenting the seasonal time series while section 4 relates the seasonal pattern to source influences. As a result, relating the seasonal pattern of toluene enhancement to summertime fuel volatility requirement time frame in section 3 is premature. We have more clearly stated the relationship between the summer fuel volatility requirement time frame and the seasonal pattern of toluene enhancement in section 4 as the referee requested.

4. There was no seasonality in sampling times. The average sampling times for each season were as follows: Winter: 12:40 LT, Spring: 12:21 LT, Summer: 12:47 LT, Fall: 12:30 LT. It has now been clearly stated in the methods section that the majority of samples in all seasons were collected between 12:00 and 15:00 LT.

5. The discussion of potential causes for the wintertime increase in benzene and toluene has been expanded to include seasonal changes in boundary layer height and increased wintertime combustion processes. Appropriate references have been added to the discussion. We have also added a map depicting air mass source regions and a discussion of the seasonality of their influence at Thompson Farm to section 3. Previ-

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ous studies of local wind direction measurements at Thompson Farm have shown that they are generally representative of regional wind patterns (Mao and Talbot, 2004). Because we want to eliminate any question that the seasonal pattern represents a seasonal shift in source region, we have based the discussion presented in the revised version of the text on 72 hour back trajectories simulated using the NOAA HYSPLIT transport and dispersion model (Draxler and Rolph, 2003) for each daily sample collection time in the filtered data set.

To summarize the results: during the summer months, the air masses sampled were relatively equally divided between the three different source regions with 37% coming from clean continental area to the northwest, 33% from marine influenced areas to the northeast and east, and 30% from more polluted continental sources to the south and southwest. In contrast, the majority (54%) of air masses sampled during winter came from clean continental source region, 15% from the clean marine influenced area, and 31% from the polluted continental source region. Despite this shift in source region between summer and winter, the actual origin of the air mass had little relationship to the toluene/benzene ratios sampled. More specifically, elevated toluene/benzene ratios were measured in air masses from every source region during the summer months (mean summer toluene/benzene ratios $\pm$ standard error by source region: polluted continental $= 1.5 \pm 0.1$, clean continental $= 1.9 \pm 0.2$, and marine $= 2.0 \pm 0.4$).

6. A map depicting different source regions surrounding Thompson Farm has been included in the revised version. Regarding the referee's question whether the estimate industrial influence at Thompson Farm would be different if a larger radius was considered, please see our response to Referee #2's comment 4.

7. The text has been clarified on page 12293, Section 4, to reflect the significant scatter associated with the background toluene and i-pentane relationships in both 2005 and 2006. Furthermore, we have removed the inference that the planting of alfalfa at Thompson Farm in 2006 was responsible for an increase in ambient toluene in 2006. Our original intent was merely to make the connection between the scatter

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associated with the toluene and i-pentane background relationship in 2006 and the crop planted in the fields that year. We have also clarified that, should corn prove to emit toluene, these emissions could also have influenced the scatter observed in other years, particularly 2005. Regarding the crop plant emission estimates in Table 3, we did clearly state in the first full paragraph of page 12997 that corn rather than alfalfa was planted at Thompson Farm during 2004 and 2005 and that the crop emission estimates relied on the assumption that measured alfalfa emissions were representative of corn as well. We have rephrased this to state more clearly that the crop plant estimates presented in 2004 and 2005 are based on alfalfa flux measurements since corn plants have not been measured for toluene emissions yet. Regarding the estimate of fuel emission influence in 2006, we have stated in the text on p. 12293 (lines 20-25), p. 12294 (lines 6-8), p. 12296 (lines 26-27), and p. 12298 (lines 12-16) that the higher background slope measured in those years (and therefore the high estimate of fuel evaporative emissions) likely reflects the influence of additional sources.

8. Please see our reply to comment 5 as well as to Referee #1's comment 4.

9. Please see our reply to comment 7. We have chosen not to discuss the fact that corn was planted in 2004 and 2005 in the second paragraph of page 12298 as suggested by the referee as that paragraph discusses only biogenic and fuel evaporation estimates for 2006 and the reference is not relevant.

10. A map depicting different source regions surrounding Thompson Farm has been included in the revised version.

11. As we stated within our reply to comment 7, we have stated more clearly that the crop plant estimates presented in 2004 and 2005 are based on alfalfa flux measurements since corn plants have not been measured for toluene emissions yet.

12. Light levels were not measured during the static chamber fluxes. However, all static chamber measurements were made in mid-afternoon (13:00-15:30 LT) on clear days and light levels should not have changed drastically between chamber deployments. As

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we noted in our answer to Referee #2's comment 6, the correlation between light and toluene flux was weak for the loblolly pine measurements. Assuming alfalfa emissions follow the same pattern, we don't think changes in light levels influenced the toluene emissions observed. Chamber temperature was also relatively constant throughout the flux measurements and should not have influenced any variability in the toluene emissions observed.

13. The relationship between loblolly pine toluene and α-pinene fluxes depicted in Figure 6b was shown to point out similarities to the emission patterns of Scots pines observed by Heiden et al. (1999) who noted correlations between toluene and α-pinene emissions for both Scots pine and sunflowers. We did not mean to imply that the similar emission pattern suggested a temperature dependant emission. Instead, our inferral of temperature dependent toluene emissions is based on the actual temperature relationship presented in Figure 6a. We have chosen not to plot the α-pinene fluxes separately because we believe that plotting the two together emphasizes similarities between our study of loblolly pine and that published by Heiden et al. (1999).

Technical Comments:

1. Page 12285, line 3: We have made the recommended change to the revised manuscript.
2. Footnote reference 1: The Copernicus publication department requested the name of the journal to which the manuscript will be submitted in the footnote to meet their formatting standards. It cannot be removed.
3. Page 12287, lines 18-19: We have made the recommended change to the revised manuscript.
4. Page 12288, line 8: We have made the recommended change to the revised manuscript.
5. Page 12289, line 5: We have made the recommended change to the revised manuscript.
6. Page 12289, line 6: This was not actually a spelling error. We intended to describe

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the placement of the collar that was *sampled* during flux measurements, not that the aluminum collar was the *sample*. To avoid confusion, we have clarified this statement during manuscript revision.

7. Page 12290, line 2: The results of the sweet gum measurements (or rather, the lack of results) are referred to in the results and discussion section (p. 12294, lines 26-28). We believe it is important to note that a deciduous species has been sampled for toluene emissions with no results. As a result, this reference to sweet gum (*Liquidambar styraciflua*) measurements will not be removed from the methods section.

8. Page 12292, line 12: We have made the recommended change to the revised manuscript.

References:

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Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., Shao, M., and Wildt, J.: Toluene emissions from plants, Geophys. Res. Lett, 26, 1283-1286, 1999.

Mao, H., and Talbot, R.: O3 and CO in New England: Temporal variations and relationships, J. Geophys. Res., 109, doi:10.1029/2004JD004913, 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12283, 2008.