

Response to Referee 1 MS No.: acp-2013-933

Replies in bold

We would like to thank referee 1 for a very thorough review. We have made many modifications as suggested by referee 1 and believe they have improved the manuscript greatly. Replies are in bold.

General Comments

This paper provides a summary of the first long-term study of methanol concentrations in rainwater. This summary of the methanol observations may be of aid to modelers in constraining the magnitude of the wet deposition sink of methanol in the temperate Northern Hemisphere. The methodology of this study is carefully presented and the results are complemented by well chosen and well selected Figures. However, in my opinion, the paper will require substantial revision before it can be considered for publication. The authors need to give much more thought about the interpretation of their data and how that can be most effectively communicated to the readers. For the benefit of the authors, I have included a number of Specific Comments primarily related to the Introduction, Discussion and Conclusions. There is also a list of Technical Comments to assist the authors in improving the readability and clarity of the paper.

Specific Comments

1. Abstract: (a) The first sentence of the Abstract is probably correct in stating that this study is the “first detailed analysis”, but it is not the first to measure ‘methanol concentrations in rainwater’, as noted later by the authors on page 1382, lines 5-6.

Reply: We changed the wording to the first comprehensive analysis since the only previous study included limited samples (n=4). We do not state we are the first to measure.

(b) The sentence in lines 18-20 seems contradictory. Even if there is an ‘increase in biological activity’ leading to an enhanced production of methanol, this does not infer a ‘direct relationship to photochemical methanol production’. Also, an increase in production does not necessarily imply a direct relationship.

Reply: Both processes are mentioned because neither can be ruled out. We removed “direct”

(c) The meaning of ‘fluctuating methanol concentrations’ in lines 16-17 is not clear; please clarify.

Reply: Fluctuating was changed to “temporal variations of”

(d) Some other changes might be necessary in the Abstract in response to General Comments later in this review;

2. Introduction: (a) The introduction, although informative, seems unnecessarily long and is focused on aspects that seem only marginally related to the main theme of your paper. It is not clear from the objectives of your paper, why it is important to discuss methanol sources.

Reply: Throughout the paper we discuss methanol sources as a driver for temporal changes so we felt it was necessary to discuss the sources in the introduction. The uncertainty in the magnitude of the sources and sinks emphasizes the need for the data presented in this manuscript.

(b) Given the main theme of the paper, I had expected more background information about the processes that control the concentration of methanol in rainwater, i.e. the physical and chemical processes involved in the entrainment of methanol in clouds and in rainwater. With this in mind, the authors might consider deleting at least the last sentence in paragraph 1, paragraph 2, and the first two sentences of paragraph 3. This would provide the opportunity to include material more relevant to the aqueous-phase.

Reply: As far as we know there is no information regarding the physical and chemical processes involved in the entrainment of methanol in clouds and rainwater. The objective of this paper was to

determine if methanol was ubiquitous in rainwater and discuss temporal and air mass back trajectory influences on concentrations. Hopefully this data will spur further investigation into methanol processing in clouds and rainwater.

3. Introduction, paragraph 3: (a) If the first part of this paragraph is retained, it will require reorganization and clarification. The word ‘constrain’ is not appropriate in the context of sentence 1 (line 26). Further, it is not clear how ‘these efforts’ could have led ‘to wide discrepancies in global budgets’ (lines 26-27)

Reply: Changed “constrain” to refine the estimated quantities of sources and sinks “These efforts” have led to wide discrepancies because the resulting range in global budgets is large.

(b) Sentence 2 needs major revision.

Reply: The sentence was changed in the text to read:

“These efforts have been predominately based on methanol concentration data consisting of aircraft and surface air analysis. The limited number of measurements and the lack of concentration data in the condensed phase lead to wide discrepancies in global methanol budget models, which in turn have led to the reported total global methanol source ranging from”

(c) The first part of sentence 3 is fine, but one can’t have ‘ a paucity . . . of its role’ .. revision is necessary.

Reply: Changed “and its role in the global biogeochemical cycling” to “and a lack of information of methanol’s role in the global biogeochemical cycling.”

(d) In the final sentence, it is not clear to what ‘this uncertainty’ refers. If it refers to the lack of methanol concentrations in precipitation, it is not clear how this would lead to a narrower range of wet depositional sinks.

Reply: It refers to lack of methanol concentrations in precipitation because if one has more knowledge of the wet deposition concentrations you will narrow the range of sink estimates. In other words detailed concentration data is required for an accurate sink estimate.

4. Section 2.4: (a) It might be better to include at least some of the last paragraph in this section at the beginning of the section so that the reader understands what is meant by ‘supporting analyses’.

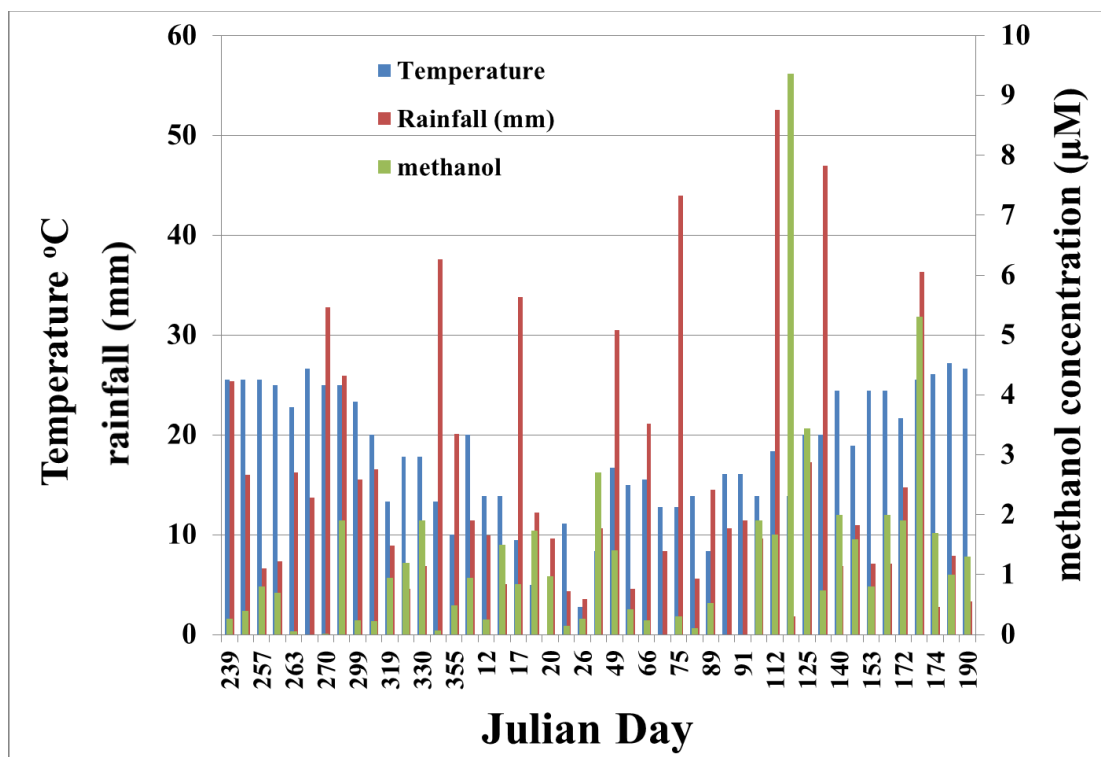
Reply: Last paragraph was moved to the beginning of section 2.4 as requested.

(b) There is no mention of the method used for measuring acetaldehyde (referred to in Section 3.4).

Reply: Method was added as requested.

(c) What meteorological measurements (other than rainfall) were made and how were they measured? Given its important to this study, it would be useful to include a Figure (line or bar chart) showing the times and magnitudes of the rainfall events during the study period. If temperature readings were not made as part of the study, you might consider using data from a near-by meteorological station; these could be shown in the same figure as the rainfall data.

Reply: Other meteorological measurements weren’t made. We have created the suggested figure but believe it is not necessary to add it to the paper. The figure is below.



5. Section 2.5: (a) I may be showing my ignorance about trajectory analysis here, but I wonder why you are tracking air masses rather than clouds, given that clouds are the source of aqueous-phase methanol?

Reply: We are unaware of any programs that provide specific back trajectories for clouds therefore the back trajectories of air masses are currently the best proxy for how clouds move.

(b) In line 26, you refer to a ‘county basemap’. International readers may not be familiar with land division into counties, or what is meant by a ‘county basemap’. Presumably the basemap gives methanol emission fluxes, as shown in Figure 2.

Reply: After “county basemap”, (county is defined as a geological subdivision of a U.S. state) was included as requested.

(c) Also, it would be useful if the units in Figure 2 were given in SI units, or a conversion factor included in the caption.

Reply: Figure two units were changed to SI units.

(d) In line 27, is the inclusion of ‘biogenic’ necessary? It raises the question of how anthropogenic methanol trajectories are portrayed, or how you have distinguished biogenic methanol from anthropogenic methanol. How does the basemap distinguish biogenic methanol from anthropogenic methanol?

Reply: The biogenic emissions are from the National Emissions Inventory 2008 and are defined as emissions from soil or vegetation.

6. Section 3 (lines 1-10): (a) It would be useful to include median concentrations (as well as means). Are the medians similar to the means?

Reply: Median concentration is now included in the text.

(b) There is a very wide range of methanol concentrations for the rain events (noted here and in Fig. 6), yet this variability is not discussed or explained in the paper. This would seem to be quite important?

Reply: The variability in methanol concentrations is driven by a variety of factors including diurnal, seasonal and air mass back trajectory influences which are each discussed in detail in separate sections of the manuscript.

(c) lines: 6-10: In fairness to Snider and Dawson, they acknowledged the inexactness of their precipitation measurements in the Discussion of their paper. I agree that ‘direct comparison to this earlier study should be made with caution’, but I suggest that the last part of the sentence be revised.

Reply: It is important to keep the last part of this sentence intact because it informs the reader who may not be familiar with this earlier study why we are not going through a more in depth comparison. “Direct comparison to this earlier study should be viewed with caution however as the reported blank (625 nM) was very near the reported average concentration and it lacked sufficient analytical sampling frequency (n = 4) to allow for more detailed analysis of temporal or air mass back trajectory influences on methanol concentrations.” We also added a sentence why direct comparison to these 4 samples may not be appropriate because Arizona is in a much more arid region “These are the only other known methanol concentrations in rainwater and may be much lower than the Wilmington average because Arizona is a much more arid region which probably has lower biogenic emissions.”

7. Section 3.1, paragraph 1: (a) There are several problems here that need to be addressed. Firstly, is ‘storm’ synonymous with ‘rain event’, or different? The alternation of these words in this section is confusing for the reader.

Reply: All instances of the wording ‘storm’ were changed to ‘rain event’.

(b) Secondly, and more important, if standard deviations are considered (as they must be), there is no significant difference between the average terrestrial methanol concentration ($1.5 \pm 0.5 \mu\text{M}$) and the average marine methanol concentration ($1.1 \pm 0.2 \mu\text{M}$). Thus, the statement in lines 17-18 is questionable. To assist in this matter, a t-test should be applied to the data and the results included in the paper.

Reply: The following sentence in the next paragraph was re-worded to address this comment: “Although rain event types with marine influence (coastal, marine) have smaller methanol concentrations than those with terrestrial influence, the difference is not significant (ANOVA: p = 0.15, 0.23) and methanol is present in substantial amounts in samples from rain events with coastal and marine origin.”

(c) Also, if marine gas-phase concentrations are an order of magnitude less than terrestrial gas-phase concentrations, how can the marine concentration in this study be so large? I would suggest, without checking the sources, that these values are average value for the whole ocean, and may not be appropriate for comparison to concentrations near the coast.

Reply: To bring attention to this point as requested by the reviewer we included “It should be noted that previous gas-phase methanol concentrations that show greater methanol concentrations over land than over the ocean sampled air over the remote ocean. The aqueous-phase methanol concentrations associated with marine rain events in this study were collected on coastal land, not over the open ocean, so the large concentrations differences seen between gas-phase methanol concentrations collected at a remote marine and terrestrial sites may not be mimicked in this aqueous-phase study.

(d) Thirdly, in comparing gas-phase concentrations with aqueous-phase concentration, one has to be sure that they are in equilibrium and that they are at the same temperature. It is not clear that this is the case here.

Reply: We compare literature gas-phase concentrations with our aqueous-phase concentrations because currently that is the only comparison that can be made with previously reported values.

(e) Fourthly, in the last sentence of this paragraph, I don't think there is sufficient evidence from the concentrations given here to make this statement.

Reply: We address this comment by changing the wording as suggested in the response to (c) above.

(f) There is no problem in including the results of the air trajectory study; but how you interpret them needs to be reconsidered.

Reply: Suggestions are below.

8. Section 3.1, paragraph 2: (a) It might be argued that coastal rain events have a smaller concentration of methanol than mixed samples; however, I suggest (particularly considering the relatively small number of sample analysed) that there is little significant difference between the 4 types of rain events. The question to be posed in this paragraph is why? (1) It seems difficult to argue for an ocean source that is comparable to that on land, if marine gas-phase concentrations are on average an order or magnitude less than terrestrial gas-phase concentrations; (2) methanol can be transported from the continental to the marine atmosphere, but is that consistent with your trajectory analysis for marine and coastal rain events?; (3) local scavenging seems the most likely of the three explanations offered in this paragraph.

Reply: All of these are suggested as possible explanations as we don't know the exact answer. More investigation is needed to know for sure. ANOVA stats are now included.

But before offering an explanation, it is necessary to discuss the physical processes involved: (i) where and how does the scavenging occur; (ii) how stable is the cloud system from which the rain comes? (iii) how long is the air mass in contact with continental air?, and (iv) how long does it take for methanol to equilibrate with rain droplets?; or (v) is the methanol in the rain sample in equilibrium with the atmospheric methanol?

Reply: All of this is beyond the scope of this paper. This information is not in the literature and we hope this work will spur investigation into these questions.

9. Section 3.2, paragraph 1: (a) The last part of the first sentence of this paragraph, following '(Fig. 3)', does not seem related to the first part of the sentence. Based on their titles, the studies of Kieber 2001a and 2002b, do not appear to include measurements 'at this location'. If the latter part of this sentence is retained, the cited studies should be compared with the results of the current study more fully later in the section.

Reply: The Kieber 2001a and 2002b papers were rainwater studies conducted over the open ocean at BATS and in New Zealand respectively as the reviewer correctly assumed from the titles. Within each manuscript rainwater diurnal profiles at these study locations were compared to rainwater diurnal profiles at the Wilmington location which is why the statement "at this location" as presented in the current manuscript is accurate since diurnal profiles of rainwater at the Wilmington site are presented in each referenced paper.

(b) It would seem better to compare the diurnal variation in methanol that you observed in the rain samples with the typical diurnal variation for gas-phase methanol (see paragraph 2).

Reply: This comparison is done in paragraph 2 as suggested.

(c) The last sentence of paragraph 1 would be better included in the caption of Fig. 3.

Reply: Last sentence was included in the caption as suggested.

10. Section 3.2, paragraph 2: (a) There is considerable confusion concerning the interpretation of the results depicted in Fig. 3. In sentence 2, it is not at all clear how you can conclude that the larger methanol concentration in period III was the result of photochemical production of methanol, after earlier in the paper stating that methanol production is ‘primarily biogenic’ – and also that there is a ‘direct proportion’.

Reply: We suggest both as increasing sources during this time period as stated below. The “direct” wording was removed as suggested.

“Peaking during this period of optimal sunlight may result from photochemical methanol production including oxidation of methane and the methylperoxy radical reacting with itself and higher organic peroxy radicals) (Jacob, 2005). The correlation of methanol concentration with light intensity may also result from increases in biogenic and anthropogenic activity during this time period consistent with the peak of numerous previous diurnal measurements of methanol flux over varying vegetation attributed to light stimulated release of methanol (Bam berger et al., 2010; Brunner et al., 2007; Custer and Schade, 2007; Harley et al., 2007; Karl, 2003; Schade and Goldstein, 2002). Daytime light usually brings a temperature increase which is also reported to increase biogenic methanol emissions exponentially (Folkers et al., 2008; Hu et al., 2011).”

(b) Also, are both of the production processes indicated in sentence 2 photochemical? . . . and how much methanol are they likely to contribute?

Reply: All the mentioned processes are increased due to light but we do not consider plant production as photochemical but rather biogenic. An estimate of the production of methanol during the day by a combination of photochemical and biogenic processes could be made but it may be difficult to differentiate between the two.

(c) The latter part of sentence 2 lacks clarity; the ‘biogenic and anthropogenic activity’ is not identified. Are you referring to biomass burning? It seems unlikely that increases in solvent evaporation, for example, could account for the increase in methanol concentration in period III. The authors should reconsider the inclusion of this sentence.

Reply: To clarify as requested “biogenic and anthropogenic activity” was changed to “plant activity and anthropogenic activity (e.g. vehicle use, industrial processes)”

(d) The third sentence of the paragraph is not well worded; I’m not sure what is meant by ‘is consistent with’, or what is meant by ‘varying vegetation’, or what you consider to be the cause of the ‘lightstimulated release’. You might consider what explanation is provided by the referenced authors to account for the observed diurnal pattern in the gas-phase.

Reply: ‘Consistent with’ was changed to ‘corresponds with’ and ‘light stimulated release’ wording was changed to ‘attributed to light causing stomata to open in turn releasing methanol’

(e) Whatever, the reason for the increase in the methanol concentration in period III, it is difficult to assess your arguments without a knowledge of the diurnal patterns of temperature and light intensity during the rain events considered here (it would be helpful if you could provide them). Also, it would be useful to indicate how many of the rain events in the various time periods originated from marine trajectories; did these exhibit similar diurnal patterns to methanol from a terrestrial trajectory?

Reply: Each bar in the diurnal profile represents the volume weighted average of several events that occur during the given time period as pointed out in the preceding paragraph therefore it is not possible to present light intensity and temperature profiles because it varies with each event. There are not enough rain events falling in specified ranges to pull out trajectory trends.

(f) It is important to remember that you are measuring methanol concentration in rainwater, not in the gas-phase of the atmosphere. Rain events in temperate regions are often accompanied by a decrease in temperature, which would increase the solubility of methanol in rain droplets leading to an increase in aqueous-phase methanol, independently of the gas-phase concentration.

Reply: The decrease in temperature would increase the solubility of methanol in rain (Henry's Law) but not significantly enough to warrant investigation into the average temperature over individual rain events.

Using Henry's Law constant, the concentration change between winter and summer due to temperature difference is estimated to be only 5.4%.

11. Section 3.2, paragraph 3: (a) Again in this paragraph, you need to address factors that might lead to reduced methanol concentrations in rain samples collected at night (which are not necessarily the same factors that could affect gas-phase concentrations of methanol). For example, during a rain event, one might expect that wet deposition would exceed dry deposition.

Reply: Wet deposition may not exceed dry deposition if dry deposition was already occurring for an extended period of time before the rainfall event.

(b) It is not necessary, or wise, to list every possible mechanism for 'night-time decrease' that you can think of. Consider what is most likely to explain your results. It is unlikely that you would have 'dew formation' during a rain event. Advection of marine air may have an impact, but this should be easy to test from the air mass trajectories at the time of the rain events. It would also seem likely that if the leaf stomata of plants close at night, biogenic methanol emission would decrease or cease, leading to substantially lower night-time concentrations of gas-phase methanol.

Reply: The most likely cause for lower methanol concentrations at night is a decrease in plant emissions. We included the following in the paragraph "Other than a likely decrease in methanol emissions from vegetation, possible modes for the nighttime decrease..." The 'dew formation' portion of the text was deleted.

(c) Both paragraphs 2 and 3 of this section should be rewritten, with more thought given to factors influencing aqueous-phase methanol concentrations, and whether or not they should be similar to changes in gas-phase methanol.

Reply: Paragraphs were rewritten according to previous comments as suggested.

12. Section 3.3: (a) Examining Fig. 4 suggests that there is no significant difference in methanol concentrations between the fall, spring and winter seasons, but that the methanol concentration in the summer season is significantly greater. Use a t-test as a guide to support or reject this hypothesis.

Reply: T-tests were performed and results are included in text.

(b) Your primary aim in this section should be to (i) summarize the observations; (ii) suggest reasons for seasonal similarities and differences. Do this in a simple and straight-forward manner. The chief observation is that there is an enhanced concentration of methanol in summer rain events. Discuss the reasons for this first. The second important observation is not that there is a smaller concentration of methanol in the rain samples during the other seasons, but rather that in these seasons the methanol concentration it is about a third of that during the summer – still a very significant concentration. Why?

Reply: We never really have a non-growing season Wilmington, NC, just a less active season.

(c) It is recommended that this section be re-written to improve its organisation and clarity. As mentioned earlier, the inclusion of temperature data might be useful (particularly, since methanol emissions seem to be temperature dependent).

Reply: This section was reorganized. The temperature suggestion was addressed in an earlier comment.

13. Section 3.3, paragraph 1: (a) Based on your observations and noted in the previous comment, there seems no reason to group the seasons into winter and fall in paragraph 1, and spring and summer in paragraph 2.

(b) The discussion of the winter/ fall results in paragraph 1 should come after the discussion of summer data, which is currently in paragraph 2.

Reply: The paragraphs were re-ordered as suggested.

(c) Sentence 4, beginning on line 10, is poorly constructed and misleading. It may well be worth pointing out that in the four studies referenced in this sentence, winter concentrations of methanol in the atmosphere are about a 1/3 of those in the summer (you could even supply data from these studies for comparison); but, as currently worded, there seems to be a suggestion in this sentence that the results of these 4 studies determine the results in your study.

Reply: Sentence 4 was changed for clarity as suggested to: “Various previous studies have reported winter gas-phase methanol concentrations to be much smaller than those in summer and these studies suggest a greater percent contribution from anthropogenic methanol sources during the winter (Millet, 2005; Legreid et al., 2007; Jordan et al., 2009; Hue et al., 2011). Rainwater methanol concentrations reported in this current study are consistent with these previous gas-phase methanol results in that winter rainwater methanol concentrations are 1/3 of the summer concentrations.”

(d) lines 13-16: You need to have supporting evidence from your study to argue that the ‘greater percent contribution’ is anthropogenic. It is not reasonable to expect that the results of Hu’s study will automatically apply to your study.

Reply: We state that it is “likely a greater percent contribution from anthropogenic sources.” We are not stating we have conclusive evidence but rather evidence from previous studies and the fact that there is less biogenic activity and steady anthropogenic activity suggest anthropogenic emissions will contribute an increased percentage.

(e) Sentence 6, beginning on line 16, is poorly constructed; if you had first noted that methanol emissions from plant decay is quite small, it would not ‘be expected that fall concentrations would increase’. Also, note that the estimates for plant decay in the studies referenced here are global averages, and may not apply to your location.

Reply: The wording ‘be expected that fall concentrations would increase’ was changed to ‘be expected that fall concentrations would be higher than winter concentrations’. We realize the plant decay estimates may not be directly applied to our location but these are the only current estimates available for comparison.

(f) The argument presented in the last sentence, beginning on line 19, is not convincing.

Reply: The sentence suggests a possible explanation and is not meant to be conclusive which is why is worded “A possible explanation”.

14. Section 3.3, paragraph 2: (a) The expectation of increased methanol concentrations in spring (lines 24-25) should be discussed later in this section, not in paragraph 2.

Reply: It is important to discuss the spring and summer together in paragraph 2 because it is the only logical organization that leads to a discussion of growing and non-growing impacts on methanol concentrations in paragraph 3.

(b) In sentence 3 (line 25), it is not the methanol emissions that are hampered by the dry spring, but rather the rate of plant growth. Are there specific rainfall data to support your statement in sentence 3? Even better, are there any measurements of net primary productivity in the region?

Reply: The sentence “methanol emissions from vegetation may have been hampered by an unusually dry spring.” Was changed for clarity to “methanol emissions from vegetation may have been hampered by a decrease in plant growth due to an unusually dry spring.” A reference to drought conditions was included at the end of this sentence (NC Drought, 2008) as requested. There are no measurements of net primary production in the region.

(c) In sentence 4, beginning line 27, it is more likely that the methanol concentrations were greater in the summer (not because it was ‘during the growing season’) but because gas-phase concentrations of methanol were greater due to more rapid cell growth and/or enhanced temperatures.

Reply: Changed to Methanol concentrations were greater in the growing season due to more rapid cell growth and enhanced temperatures.

(d) The last sentence in this paragraph is difficult to understand, mainly because of the use of ‘agrees’; if the argument presented in this sentence is important, explain it more clearly (even if it takes 2 or 3 sentences).

Reply: “Agrees” was changed to “consistent with” for clarity.

15. Section 3.3, paragraph 3: (a) It is not clear here how the dates for the growing and non-growing periods were obtained. Were they based on NPP measurements or other plant growth experiments? Without supporting evidence, the dates seem rather arbitrary.

Reply: We have deleted the paragraph on growing vs. nongrowing due to the below comment.

(b) That aspect to one side, you are not presenting a new argument here; biogenic emissions were already suggested as a major contributor to atmospheric methanol concentrations earlier in the paper. This paragraph, along with Fig. 5, could be omitted without any loss to the overall argument.

Reply: We have deleted fig 5 and the paragraph on growing vs. nongrowing

16. Section 3.4, paragraph 1: (a) Sentence 3 (line 16): Given the frequent referral to biogenic and anthropogenic methanol in your paper, there is an argument for moving this section to a position earlier in the paper. On the other hand, unless one can estimate the relative percentages of biogenic and anthropogenic methanol, there is little value in distinguishing the two sources of methanol.

Reply: At this time we can’t estimate relative percentages of source contributions. However the lack of correlation with pollution indicators discussed in this paragraph suggest that anthropogenic inputs are not the dominant source of methanol in rainwater at this location.

(b) line 20: an r of 0.46 would not normally be considered as a strong correlation.

Reply: The p value is <0.001 indicating a strong correlation.

(c) The last sentence of this paragraph is rather convoluted, but I gather it is saying that the methanol in the rain water has a primarily biogenic source. I don’t however consider that the correlations in Table 1 provide strong proof for that assumption. If this sentence is retained in the paper, it must be rewritten.

Reply: For clarity the sentence was changed to “Methanol concentrations were strongly correlated with acetaldehyde which also has a primarily biogenic input (Millet et al., 2010).

17: Section 3.4, paragraph 2: (a) Some support for the theory that methanol is replaced via transpiration might come through a comparison of day- and night-time samples (assuming transpiration is much lower at night).

Reply: A comparison between day and night samples is a good suggestion and might support the transpiration argument but because other environmental factors also drive transpiration we have chosen not to include the day and night comparison as supporting information.

(b) Because formaldehyde does not exhibit washout is not evidence for assuming that methanol will, or will not, exhibit washout (lines 3-5). This sentence is best deleted.

Reply: This sentence will be deleted.

(c) The last sentence in this section, which seems to follow from the preceding sentence, makes an assumption about methanol production mechanisms that are unsupported by evidence and are not included in the global budgets for methanol referred to in this study. However, if there is evidence in the literature that methanol is formed by photochemical reactions in rainwater, describe the reactions, and include the reference at the end of this statement. If not, omit the sentence.

Reply: This sentence will be deleted.

18. Section 4: The material in this section is a mixture of implications, discussion, conclusions, and observations from other studies. There may be good reasons for taking this approach, but I would prefer to have a more traditional Conclusion section, with the other relevant material incorporated in the Discussion.

Reply: The implications section was a presentation of conclusions as requested by the reviewer but it also put those conclusions into context with observations from other studies which should be very informative for most readers of ACP.

19: Section 4, paragraph 1: Some of the statement included in this paragraph have been commented on earlier in this review e.g. paragraph 1, sentence 3 (lines 12-14), sentence 5 (lines 16-18), and sentence 6 (lines 18-20). Consideration should be given to these earlier comments.

Reply: We have responded to these comments previously.

20. Section 4, paragraph 2: (a) Include uncertainties with the percentages given in this paragraph.

Reply: Uncertainties have been included as requested.

(b) It is not clear why sentence 2 is included, particularly when the information is from another study. If you wish to compare the methanol content of the rainwater samples with formaldehyde and acetaldehyde, use measurements from this study, which presumably are available. But unless, you have corresponding gas-phase measurements, there doesn't seem to be any purpose in making these comparisons.

Reply: The comparison to formaldehyde was deleted as requested.

(c) Re sentence 3, since you have measurements of methanol and DOC in each sample, the uncertainty in the 1.5% average should indicate the variability, without relying on 'the lack of correlation with DOC'

Reply: The volume-weighted standard deviation was used to report the variability of $1.5 \pm 0.2\%$.

21. Section 4, paragraph 3: (a) The first sentence in this paragraph is relevant to this study, but it doesn't in itself indicate that wet deposition is a significant source in marine waters, since there are many other factors that control the concentration of methanol in the ocean. Revise the sentence.

Reply: There may be other marine sources but 200X greater methanol concentrations in rainwater compared to marine waters indicates that rain is a "potential significant source to marine waters"

(b) It may be of value to discuss some of the other sentences in this paragraph as a lead-up to paragraph 4; but, as a reader of your paper, I would like to see the emphasis placed firmly on 'methanol concentrations

in rainwater'. Unless, you have made methanol measurement in the ocean or in freshwater bodies in this study, the material following sentence 1 has little relevance to the theme of this study.

Reply: As discussed above the goal of this section was to put the methanol rainwater concentrations into environmental context which is why we are describing the implication of methanol in rainwater for biogeochemical settings including bodies of water.

22. Section 4, paragraph 4: (a) I'm not sure that modellers would accept the results of this study 'as an appropriate proxy for global rainwater concentrations', but they might consider it as a first approximation for the mid-latitudes of the Northern Hemisphere when estimating a global wet deposition sink. It would be best to reword this sentence along this line.

Reply: The estimate of global wet deposition flux was included so it could be compared to the global methanol budgets reported in literature. We agree that methanol concentrations in rain will fluctuate globally and have included the following sentence to address this "Additional studies of methanol concentrations in rainwater should be carried out in various regions of the Earth to better constrain the global wet depositional sink of this biologically and chemically labile analyte."

(b) Include an uncertainty for your estimate of 20 Tg yr⁻¹, which includes the uncertainty in your measured concentration and also the uncertainty in global annual precipitation.

Reply: The uncertainty was calculated using the volume-weighted standard deviation and is reported as ± 3.3 Tg yr⁻¹.

(c) One would expect your estimate for a wet deposition sink to be significantly higher because it is relevant only for the location in which it was made. The gas-phase concentration of methanol is much less in the Southern Hemisphere (and also in the Arctic), as is the average annual precipitation. With that in mind, it wouldn't be too difficult to use your methanol concentration to estimate a reasonable global value.

Reply: We have ice core data under review that show early 1900s methanol concentrations as high as 1.5 μ M in the Arctic, so while we do agree the values will vary around the globe, we think this first estimate is a good stepping stone that will be refined with more spatially diverse concentration data. We agree that methanol concentrations in rain will fluctuate globally and have included the following sentence to address this "Additional studies of methanol concentrations in rainwater should be carried out in various regions of the Earth to better constrain the global wet depositional sink of this biologically and chemically labile analyte."

(d) The sentence in lines 19-22 is a little confusing as Tie et al. give only a range with no estimate of the mean; it would be better breaking this sentence into 2 sentences, the first of which compares your estimate to the theoretical range, and the second comparing your value to the global averages.

Reply: The references were rearranged for clarity.

(e) The sentence beginning on line 22 is a bit harsh; your wet deposition sink is much higher because you haven't estimated a wet deposition rate appropriate for the Southern Hemisphere (which is likely to be about half of that in the Northern Hemisphere). Nonetheless, I agree completely with the final sentence of the paragraph.

Reply: The sentence "Results of this study are significant because they suggest previous methanol budgets significantly underestimate removal by precipitation." Was changed as requested to "Results of this study are significant because they suggest previous methanol budgets may be underestimating removal by precipitation."

Technical Comments

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line 4: insert a hyphen between 'volume' and 'weighted'. Check that this is done consistently throughout the paper. **Hyphens added.**

line 7: insert 'by other authors' after 'waters' **Inserted "reported previously in marine waters"**

line 7: insert a comma after 'by other authors'; and replace 'potential' by 'potentially' **Comma was inserted and potential changed to potentially.**

line 7: insert 'of methanol' after 'source'. **Inserted.**

line 8: insert 'that' after 'Assuming' **Inserted.**

line 9: insert a comma after 'concentrations' **Inserted.**

line 9: insert a comma after 'yr⁻¹', and insert 'that' after 'implies' **Inserted.**

line 11: insert 'in rainwater' after 'concentrations', and insert 'significantly' after 'correlate' **Inserted.**

line 12: replace 'suggest' by 'suggests' **Replaced.**

line 14: insert 'The' before 'methanol' **Inserted.**

line 15: replace '+' by '±' **This was ± in the submitted version. We will check on the conversion to the online manuscript.**

line 16: replace '+' by '±' **This was ± in the submitted version. We will check on the conversion to the online manuscript.**

line 18: replace 'between' by 'during' **Replaced.**

line 19: insert a comma after 'production' **Inserted.**

line 21: the adjective 'higher' is used to indicate something that is at a greater elevation.

It is better to use 'larger' or 'greater' in the context of a concentration. Check this throughout your paper. **Higher was changed to greater and lower was changed to smaller.**

line 21: insert a comma after 'origin' **Inserted.**

line 22: replace 'origin' by 'origins' **Replaced.**

line 25: insert a comma after 'troposphere' **Inserted.**

line 26: If the one electron-dot is included in the hydroxyl radical symbol, it should be done consistently throughout the paper. Its inclusion (or exclusion) may be considered optional. **This was made consistent throughout.**

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lines 1-2: insert 'a' before '1-2%' and before '1-3%' **Inserted.**

line 5: including 'radicals' along with 'OH' is redundant **Deleted 'radicals'**

line 5: omit or replace 'primary'. Formic acid is produced by oxidation of formaldehyde following hydrogen abstraction of methanol, and thus the occurrence of formic acid is secondary production.

Primary was omitted.

line 6: insert a comma after '2000)' **Inserted.**

line 7: 'uptake' is a noun, and thus should be replaced by an appropriate verb, perhaps 'adsorb' **Uptake changed to adsorb.**

line 9: insert 'assessing' after 'in' **Inserted.**

line 10: replace 'lead' by 'led' **Replaced.**

line 14: 'biomass burning' could be considered biogenic as it does not require the intervention of humans. **Agreed. Biomass burning can be natural so was deleted from inclusion in anthropogenic sources.**

line 14: not clear to what 'gasoline additives' you are referring, other than methanol itself. If so, 'evaporation of methanol-based fuels' might be better. **The reference is not clear here.**

line 14: omit 'other' **Omitted.**

line 15: The citation for 'Howard, 1990' is not included in your References. Also, it is preferable to use primary sources of this information i.e. studies that have identified these sources (see Wells et al. 2012 for examples). Alternatively, you might say 'as summarized by Wells et al. 2012' **This was changed to as summarized by Wells et al. 2012**

line 15: Note that the word ‘while’ is used to connect two clauses that are coincident in time e.g. “While I am reading, I am making notes”. In this case, replace ‘While’ by ‘Whereas’ **Replaced.**

lines 15-16: replace ‘that’ by ‘that, globally,’ **Replaced.**

line 17: replace ‘debate’ by ‘investigation’ **Replaced.**

line 19: replace ‘while’ by ‘whereas’ or ‘but’ **Replaced.**

line 20: replace ‘This’ by ‘The’ **Replaced.**

lines 20-23: This sentence is not necessary; but, if you wish to include it, I suggest replacing ‘ which are represented by higher methanol . . . ’ by ‘that have higher methanol . . . ’, and add ‘than rural areas’ at the end of the sentence. **The wording was changed.**

line 23: replace ‘Jacob’ by ‘Jacob et al.’ **Replaced.**

line 23-25: This sentence could be confusing. It depends what ‘regions’ you are considering, and how you intend to ‘differentiate’. The sentence needs to be revised in order for a reader to understand the point you are trying to make. **The sentence was changed for clarification. ” Due to the atmospheric lifetime of methanol (5 to 12 days) (Jacob et al., 2005), emissions from anthropogenic or biogenic sources can possibly travel across large continental regions making it difficult to apportion various methanol source contributions to ambient methanol concentrations.**

line 26: omit ‘Earlier’ **Omitted.**

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line 1: insert commas before and after ‘in turn’ **Inserted.**

line 2: omit ‘and sink’. Replace ‘and sink’ by ‘and the sink from’. Omit ‘respectively.’ **Replaced, Omitted.**

line 3: For multiple references, list in chronological order. **Multiple references are now listed in chronological order.**

line 5: replace ‘its’ by ‘their’ **This portion of the text was already changed due to an earlier comment.**

line 7-8: ‘Tg yr⁻¹’ is a measure of emission rate, not flux. **Flux was changed to sink.**

line 15: replace ‘is’ by ‘are’ **Replaced.**

line 16: insert a hyphen in ‘aqueous-phase’ **Inserted.**

line 19: omit ‘on an event basis’, as it is also stated in line 21. **Omitted.**

line 26: better to use past tense in this sentence – replace ‘can’ by ‘could’ **Replaced.**

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line 1: better to terminate the sentence after ‘collection’, and begin the new sentence with ‘This reduces the ..’ **Changed to two sentences.**

line 1: replace ‘time’ by ‘times’ **Inserted.**

line 5: replace ‘combusting’ by ‘heating’ **Combustion is the terminology we traditionally use.**

line 7-8: The citation for ‘Topal et al., 1985’ is not included in your References. **Reference was unneeded and was deleted.**

line 9: delete ‘together’ **Omitted.**

line 11: replace ‘derivitization’ by ‘derivatization’ **Replaced.**

line 12: include acronym ‘(DNPH)’ after ‘2,4-dinitrophenylhydrazine’, as it is used later in line 25 **Included.**

line 18: preferable to replace ‘DIW’ by ‘deionized water’ **Replaced.**

line 20: replace ‘on’ by ‘from’ **Replaced.**

line 24: delete comma after ‘buffer’ and replace with ‘along with’ **Replaced.**

line 28: replace ‘RSD’ by ‘relative standard deviation’ **Replaced.**

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line 9: insert ‘the’ after ‘in’, and also after ‘of’ **Inserted.**

line 14: replace ‘was’ by ‘were’ **Replaced.**

line 17: insert ‘the’ after ‘in’ **Inserted.**

line 22: replace ‘Organic carbon’ by ‘The dissolved organic carbon’ **Replaced.**

line 22: insert 'the' after 'in', and replace 'were' by 'was' **Replaced.**

line 24: 'Willey et al, 2000' is not included in your References **Included.**

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line 10: 'NOAA/ARL, 2013' is not included in your References. Also, be consistent with the punctuation in in-text references; see also line 28 on this page. **Included.**

line 11: delete semicolon after 'model' **Deleted.**

lines 13-14: it is not necessary to include acronyms if they are not used later in the paper **Deleted.**

line 17: it is not usual to include a hyphen in 'air mass', but if including the hyphen, be consistent throughout the paper; cf. line 20 **hyphen deleted**

lines 20-22: omit the final phrase 'and likewise over ocean for marine types' and either include a new sentence to define marine trajectories, or revise the sentence to read 'Terrestrial or marine air masses are those . . . over a landmass or ocean, respectively'. **The wording was changed.**

line 24: insert 'were those that' after 'trajectories' **Inserted.**

line 26: replace 'size normalized county level' by 'size-normalized county-level' **Replaced.**

line 27: insert 'The' before 'methanol' **Inserted.**

line 28: Use upper case for 'Emissions Inventory' **Formatted.**

line 28: 'NEI, 2008' is not included in your References **Reference included**

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line 2: insert 'in the samples' after 'concentrations'; and insert 'the' after 'for' **Inserted.**

line 5: Snider and Dawson's study was conducted in 1982. Changed

line 6: 'Snider and Dawson, 1985' is not cited in your References include **Included**

line 7: insert a comma after 'however' **Inserted.**

line 8: insert a comma after 'concentration' **Inserted.**

line 9: delete 'more' and insert 'variation' after 'temporal' **Deleted. Inserted.**

line 17: replace 'higher' by 'larger' or 'greater' **Replaced.**

line 19: replace 'gas phase' by 'gas-phase' **Replaced.**

line 21: The article cited as 'Jacob, 2005' has a number of authors, and should be written as 'Jacob et al., 2005'. Be sure to correct this throughout the paper, and also in your References **Corrected.**

line 23: replace 'lower' by 'smaller' **Replaced.**

line 24: 'significant' is not the right adjective here. A concentration is significant if it above the detection level. What needs to be considered is whether methanol concentrations in marine air-masses are significantly less or greater than terrestrial types. **Significant was changed to substantial as to not indicate above the detection limit.**

line 25: insert "'in air masses of marine origin' after 'amounts' **"in samples from rain events of coastal and marine origin" was inserted**

line 25: replace the period after 'reasons' by a colon. Also replace 'can' by 'may' **Replaced.**

line 26: insert a comma after 'sink' **Inserted.**

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line 1: use a semi-colon rather than a period after 'atmosphere' **Inserted.**

lines 1-2: remove the parentheses around '5 to 12' **Removed.**

line 2: insert a comma after '(Jacob, 2005)' **Inserted.**

line 2: replace 'oceans' by 'the ocean'. Also, replace the period by a semi-colon. **Inserted.**

line 3: replace 'would' by 'could' **Replaced.**

lines 3-4: since it is the methanol that would contain some terrestrial sources, reword the sentence as 'methanol at the rain collection site could include some methanol scavenged from local terrestrial sources'. **Changed.**

line 6: replace 'Methanol concentrations' by 'The methanol concentrations measured in this study' **Replaced.**

line 6: delete 'further'; and replace 'subdivided' by 'divided' **Deleted. Replaced.**

line 7: replace 'concentration' with 'the concentrations' **Replaced.**

line 7: insert a hyphen between 'short' and 'term', and terminate the sentence after '(Fig. 3).' **Inserted.**

line 8: change 'others' to 'other' **Changed.**

line 10: replace 'volume weighted' by 'average volume-weighted' **Replaced.**

line 12: insert a comma after '6 p.m.)' **Inserted.**

lines 12-13: replace 'a volume weighted' by 'an average volume-weighted' **Replaced.**

line 14: replace 'to' by 'with' **Replaced.**

line 16: insert a comma after '2005)' **Inserted.**

lines 17-20: improve the structure of this sentence. **Wording was changed in a previous comment**

line 19: insert a hyphen between 'light' and 'stimulated' **Inserted.**

lines 19-22: list references chronologically **Multiple references are now listed in chronological order.**

line 21: replace 'brings' by 'produces' **Replaced.**

line 22: include a comma after 'increase' **Inserted.**

line 24: Replace 'A _ 6 fold' by 'The approximately 6-fold' **Replaced.**

line 24: insert 'in this study' after 'night' **Inserted.**

lines 24-26: there may be other causes for a decrease in methanol concentration at night' It does not automatically 'imply' and increase in dry deposition. Also, indicate to what surface uptake you are referring e.g., soil absorption, plant metabolism, etc. **For clarity the wording in these lines were changed to "which could indicate dry deposition at night and adsorption to vegetations and soils."**

line 26: insert "'in the aqueous-phase concentration of methanol' after 'decrease' **Inserted.**

line 27: insert a hyphen between 'water' and 'soluble' **Inserted.**

line 28: Start a new sentence after 'collection site' **Split into two sentences.**

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line 4: replace 'The methanol concentration was' by 'The methanol concentration data collected in this study were' **Replaced.**

line 4: insert 'seasonal' after 'time' **Inserted.**

line 5: insert 'the' after 'in'; and replace 'Seasons' by 'The seasons' **Inserted.**

line 9: replace 'stronger' by 'large'; insert a comma after 'source'; replace 'it' by 'gasphase methanol concentrations'; and replace 'lower' by 'smaller' **Replaced.**

line 10: insert 'when plants are dormant' after 'months' **Inserted.**

line 11: list references chronologically; and insert a comma after '2005)' **Inserted. Multiple references are now listed in chronological order.**

line 13: insert a comma after 'instance' **Inserted.**

line 15: insert 'that' after 'estimated'; and replace 'having' by 'had an' **Inserted. Replaced.**

line 16: insert a comma after 'decay' **Inserted.**

line 17: insert 'of methanol' after 'source'; and replace 'low' by 'small' **Inserted. Replaced.**

line 18: it is not clear to what 'plant growth total' refers.; is it NPP? **Inserted plant growth source total. Refer to references for plant growth source definitions**

lines 18-19: list references chronologically **Multiple references are now listed in chronological order.**

line 20: insert 'the' after 'that' **Inserted.**

line 21: insert a comma after '2008)'; and omit 'in turn' **Inserted. Omitted.**

line 21: The citation for 'NC Drought, 2008' is not included in your References **Reference included.**

line 22: insert 'otherwise' after 'would' **Inserted.**

line 23: replace 'volume weighted concentration of methanol' by 'average volumeweighted concentrations of the methanol observed in this study' **Replaced.**

line 24: replace 'are' by 'were' **Replaced.**

line 26: insert a comma after 'seen' **Inserted.**

line 28: insert in 'rain water' after 'concentrations'; replace 'highest' by 'greatest'; and insert a comma after 'summer' **Inserted. Replaced. Inserted.**

line 29: better to say 'the plant growing season occurs during the summer' instead of 'summer is during growing season' **Changed.**

line 29: insert a comma after 'season' **Inserted.**

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line 2: insert 'the' after 'in'; and replace 'concentration' by 'concentrations' **Inserted. Replaced.**

lines 2-5: this sentence needs re-writing to improve clarity – perhaps expanding it into 2 or 3 sentences **This sentence was clarified in earlier comment.**

line 8: replace 'Methanol volume weighted concentration' by 'The average volumeweighted concentrations of methanol' **Replaced.**

line 9: replace 'that of' by 'those measured during' **Replaced.**

line 10: terminate the sentence after '0.1 μM'; and construct another sentence using the remainder of the information **Changed.**

line 11: 'fluctuation' is not the right choice of word here. **fluctuation changed to “temporal variations of”**

line 15: replace 'correlation with each other' by 'intercorrelation' **Replaced.**

line 16: replace 'suggest' by 'suggests' **Replaced.**

line 17: replace 'alcohol' by 'methanol' **Replaced.**

line 18: insert '(DOC)' after 'carbon' **Inserted.**

line 19: insert 'that' after 'indicating'; replace 'the alcohol' by 'methanol'; and replace 'make' by 'makes' **Inserted. Replaced.**

line 21: insert 'that' after 'suggesting' **Inserted.**

line 22: insert 'is' after 'methanol'; and insert 'of methanol' after 'concentration' **Inserted.**

line 24: insert 'significant' after 'no'; (Table 1 would be a better references than Fig. 6) **Inserted and Inserted Table 1**

line 25: delete 'simply'; and insert a comma after 'location' **Deleted and inserted**

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line 7: Fig. 6 does not support this statement **Figure 6 deleted**

line 11: insert 'that' after 'suggests' **Inserted.**

line 15: replace 'higher' by 'larger' **Replaced.**

line 21: insert a comma after 'content'; and insert 'that' after 'indicating' **Inserted.**

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line 1: insert 'samples measured in this study' after 'rainwater' **Inserted.**

line 2: replace '(Dixon et al., 2011)' by 'by Dixon et al. (2011)' **The format is correct.**

line 2: insert 'of methanol' after 'deposition'; and replace 'potential' by 'potentially' **Inserted.**

line 4: replace 'of' by 'on' **Replaced.**

line 6: include reference at the end of this sentence **Included citation Kieber et al., 2001a.**

line 7: insert a comma after 'significant' **Inserted.**

line 8: insert a comma after 'dominant'; and replace 'to' by 'in'

line 9: insert 'that' after 'likely' **Inserted.**

line 10: insert a comma after 'significant' **Inserted.**

line 11: delete the apostrophe in 'month's', and insert a comma after 'months' **Deleted, Inserted.**

line 13: include a reference at the end of this sentence. **Included citation Kieber et al., 1999.**

line 14: delete 'most'; and replace 'uncertainties' by 'issues' **Deleted, Replaced.**

line 15: insert 'and uncertainty' after 'magnitude'; and replace 'flux' by 'rate' **Inserted and replaced flux by sink**

line 16: replace 'rain' by 'sampling' **Replaced.**

line 17: insert a comma after 'concentrations' **Inserted.**

line 18: 'Pidwirny 2008' is not included in your References. Insert a comma after 'Pidwirny' **Inserted. Reference now included.**

line 18: replace 'global methanol rainwater concentrations' by 'a global average rainwater concentration of methanol' **Replaced.**

line 23: insert 'that' after 'suggest' **Inserted.**

line 25: replace 'earth' by 'Earth' **Replaced.**

line 26: 'labile' means 'subject to change'; this doesn't seem to apply in this context. **Methanol is subject to chemical and biological change.**

Table 1: in title, replace 'between' by 'among' **Replaced.**

Figure 1 caption: insert 'Average' before 'volume-weighted' and change 'concentration' to 'concentrations'. Also, indicate that the error bars represent \pm one standard deviation from the average. **Changes made.**

Figure 2 caption: replace 'county level' by 'county-level' **Replaced**

Figure 3: include a more descriptive caption. Include the last sentence in the first paragraph of Section 3.2. Also, indicate what the error bars represent. **Included.**

Figure 4: include the number of samples in each season. The caption does not seem to represent what has been plotted. It seems that what is plotted is the 'average of the volume-weighted methanol concentrations in each season'. Indicate what the error bars represent. **Changes made.**

Figure 5: insert a hyphen in 'non growing'. Revise the caption as suggested in the comments for Figures 1, 3 and 4. **Figure 5 was deleted.**

Figure 6: replace 'rain fall' by 'rainfall' in both the x-axis title and caption. **Changes made.**