Response to Referee 2 MS No.: acp-2013-933

We would like to thank referee 2 for taking the time to make specific constructive comments and we have modified the manuscript accordingly to improve the quality. Replies are in bold.

Review for “Temporal and spatial variations in rainwater methanol” by Felix et al. 2014.This paper describes a novel set of rainwater methanol concentration measurements made at a terrestrial site. The analytical technique is fairly unique and the measurements seem well made. Methanol concentrations peaked in the daytime and during the growing season, consistent with terrestrial plant emissions. As such, the year-long dataset fills an important data gap. However, the data interpretation and discussion at present seem rather speculative and incomplete. I think the paper can be improved by: - Adding a discussion on the processes in wet deposition. In particular, how do the rainwater concentrations compare to gas phase concentrations at that location or in similar regions? Is thermodynamic equilibrium achieved, why or why not? - Showing the rainwater acetaldehyde concentrations - Stating the limitations/uncertainties in the global wet deposition extrapolation

Specifics
Title It is misleading to use the phase “spatial variations” here, since the measurements were made at a fixed location.
Reply: We originally included “spatial” because of the back trajectory analysis but have now deleted “spatial” for clarity.

Abstract
It seems highly unlikely for rainwater methanol concentrations measured at one terrestrial site to be representative for the entire globe. I suggest removing the “. . .20 Tg/yr. . .” sentence from the abstract. Attributing peak methanol concentrations from 1200 to 1800 to photochemical production seems speculative given the paucity of direct experimental evidence. Most global models show that photochemistry removes methanol faster than produces it.

Reply: We stated the assumption that these methanol concentrations are a proxy for global concentrations and we decided to keep the global wet deposition flux 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 in the discussion 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.”

Instead of implying a direct relationship between methanol concentrations and photochemical production which may mislead the reader, the sentences now read “Methanol concentrations peaked in rainwater collected during the time period 12pm – 6pm. Peaking during this period of optimal sunlight implies a possible relationship to photochemical methanol production, but there are also increases in biogenic activity during this time period.”

Add references for the first sentence of Introduction.
Reply: Millet et al., 2008 was added as a reference.

p. 1377, line 7_9. The role of methanol in aerosol growth is rather speculative and direct evidence rather limited. Suggest removing or softening this sentence.

Reply: At the suggestion of the reviewer, we have deleted "Some studies suggest that sulfuric acid can uptake methanol and contribute to aerosol growth (Kerminen et al., 2004; Van Loon and Allen, 2008) implicating methanol emissions as a factor in air quality and climate change scenarios."

p. 1378, line 1_4. The ranges in total sources and sinks of atmospheric methanol in literature, as summarized by Millet et al (2008), are smaller than stated here. Is a reference missing?
Reply: The range is taken from the review of multiple global budgets reported by Jabob 2005 and the reference is included.

A brief description of processes in wet deposition would be welcomed in this section. For example: - How much of the methanol wet deposition may be due to in cloud scavenging (i.e. rain out), and how much due to below cloud scavenging (i.e. wash out)? This is relevant with respect to the time scale/spatial scale of concern, as well as the vertical profile of atmospheric methanol from the planetary boundary to the free troposphere. - How does scavenging efficiency vary with rain rate or droplet size? –
Reply: The following information is included in the correlation section as requested "There was no significant correlation of methanol concentrations with rainfall amount suggesting it is not simply washed out of the atmosphere at this location". Literature about in cloud/ below cloud scavenging of methanol does not exist and it is not possible with our surface level rainfall data to estimate the relative importance of these processes. Because we cannot quantify these processes we cannot speculate on the vertical profile of atmospheric methanol concentrations. We don't have rain rate or droplet size data so predicting scavenging efficiency with respect to these parameters is not possible at this time.

Is dissolved methanol concentration in rainwater near the surface expected to be in approximate thermodynamic equilibrium with the surrounding gas phase?
Reply: Using Henry's law constants ranging from 140 to 230 (NIST 2014), and a range of atmospheric concentrations of 0.03 to 47 ppb (Jacob et al 2005) the corresponding rain concentration should be 4.2 nM to 10.8 µM. The rain in this study had concentrations in the range of nondetect (<6nM) to 9.9 µM. This suggests that the rain may be in thermodynamic equilibrium in some cases with the atmosphere but disequilibrium can't be ruled out. To address this we have added the following to the paper: "The range in reported gas phase methanol concentrations (0.03 to 47 ppbv (Heikes et al., 2002; Jacob et al., 2005)) and a range of Henry's Law constants (140 to 230 mol /kg*bar) (NIST 2014) were used to investigate if rainwater concentrations are in thermodynamic equilibrium with gas phase methanol. If the rainwater is in equilibrium with the gas phase, the calculated range of rainwater methanol concentrations is 4.2 nM to 10.8 µM. This range is similar to the observed range of < 6 nM to 9.3 µM and suggests equilibrium but disequilibrium can't be ruled out."

p. 1378, line 19. "event basis" repeated
Reply: "event basis" has been deleted

p. 1379, line 4. Is the ACM collector is ventilated to the atmosphere? If so, there would always be a tendency for the collected aqueous methanol to trend towards equilibrium with the air phase by diffusion.
Reply: The ACM collector is not ventilated to the atmosphere.

p. 1379, Section 2.2 & 2.3 This probably has been done, but can be explained in more detail: Have the authors measured the bank concentrations by treating a methanol/formaldehyde-free liquid sample the same way as the rain samples? If so, how large/consistent are the blank concentrations and are they

subtracted from the samples? From our experience, even Millipore Q water contains trace levels of organics. Also, is 2% RSD derived from measuring a specific standard concentration?
Reply: A Milli-Q blank is measured during each analysis and there is a small consistent methanol blank which is subtracted from samples. The following wording was added to the paper to address this point "Milli-Q water is analyzed for methanol during each analysis and the methanol blank concentration is subtracted from the sample." The RSD is measured from several standard concentrations ranging from 0.1µM to 5µM.

p. 1381, Section 2.5. Suggest replacing "Storm" with "Rain event" in the section heading
Reply: All instances of "storm" have been replaced with "rain event" as suggested

p. 1382, line 4. Two significant figures on the average concentration
Reply: This was changed to one significant figure.

p. 1382, line 25. From an autumn transect cruise in the Atlantic, Yang et al. (2013) found that the net air-sea flux of methanol is from the atmosphere to the ocean. Yang et al. (2014) estimated the gross emission of methanol from the ocean, which is likely small.
Reply: The gross emission from the ocean is likely small and the following wording was added to this section to clarify:
"It should be noted that the previous gas-phase methanol concentrations studies that show much greater methanol concentrations over land than over the ocean, sampled air in the remote ocean (Yang et al., 2013). The aqueous-phase methanol concentrations associated with marine rain events were collected on coastal land, not over the open ocean, so it is expected that the large concentrations differences seen between gas-phase methanol concentrations collected at ocean and terrestrial sites will not be mimicked in this aqueous-phase study."

p. 1383, line 1-4. As the authors mentioned, the study site is 8.5 km from the ocean. At a wind speed of 5 m/s, it takes half an hour for wind to transit this distance from the coast, which is comparable to the mixing timescale of the planetary boundary layer. Thus local scavenging seems quite likely. Also, aircraft measurements show significant gas phase methanol concentrations above the planetary boundary layer. Could rainwater methanol also contain some contributions from the higher atmosphere?
Reply: We agree that local scavenging seems likely and have included this with extended discussion noted in previous comment. Contributions could be coming from a higher atmosphere but at this time we don't have significant evidence to suggest that it is.

p. 1383, line 13. But oxidation of atmospheric methanol by OH is probably faster than photochemical production. A higher dissolved concentration during this time period is more likely be due to greater biogenic emission.
Reply: These lines were changed so photochemical production is mentioned as a possibility with emphasis still on biogenic production "Peaking during this period of optimal sunlight implies a possible relationship with photochemical methanol production (e.g. the oxidation of methane, and the methylperoxy radical reacting with itself and higher organic peroxy radicals) (Jacob et al., 2005), but there are also increases in plant activity and anthropogenic activity (e.g. vehicle use, industrial processes) during this time period."

p. 1383, line 24. Dry deposition and surface uptake occur during the day as well. They are just less obvious because of the greater emissions. Is nighttime advection of marine air typical for the collection site? If so, the nighttime dissolved methanol concentrations might be more representative for the marine atmosphere due to a reduced local influence. In fact, instead of grouping rain samples by trajectory, would the sodium content or the NSS:SS ratio be a better indicator for marine air?

Reply: We have included the nighttime advection of marine air as a possible factor for lower nighttime concentrations as it has been suggested as a cause at this collection site but have added text to reiterate that it is most likely due to lower biogenic emissions. The NSS:SS ratio is a good suggestion but back trajectory analysis has been used with success in various previous studies and we believe it is a justifiable approach.

P 1384. Line 16-22. Given the uncertainties and variability in the measurements, the discussion on why the fall concentrations might be lower than winter concentrations seems moot. Furthermore, the rainwater temperature is probably lower in the winter. So one might expect higher dissolved methanol concentrations then due to the greatergas solubility.

Reply: We agree the decrease in temperature would increase the solubility of methanol in rain (Henry's Law) for instance using Henry's Law constant, the concentration change between winter and summer due to temperature difference is estimated to be only 5.4%. This could account for the small difference between fall and winter. In the paper we aren't comparing fall to winter but rather discussing why the fall concentrations aren't as high as one would expect due to possible plant decay emitted methanol.

p. 1385. Line 1-2. Specify that the exponential increase is due to plant emissions.

Reply: For clarity this line was changed to "increasing summer temperatures can lead to exponentially increasing methanol emissions from plants"

p. 1385, Line 13. What are the concentrations of acetaldehyde? In addition to showing the correlation between methanol and acetaldehyde, it would be instructive to show the variation in acetaldehyde at different times/seasons.

Reply: An investigation of acetaldehyde concentrations would be interesting but we chose to focus on the novelty of the methanol concentrations for this manuscript.

p. 1385, line 16. If sulfuric acid takes up methanol, why is there no correlation between methanol in rain and NSS?

Reply: As suggested earlier by the reviewer "role of methanol in aerosol growth is rather speculative and direct evidence rather limited." And we have deleted the portion in the introduction discussing the sulfuric acid uptake.

p. 1385, line 24. Is there any relationship between methanol concentration and rain rate (e.g. in mm/hr) or the size of rain droplets (e.g. drizzle vs. downpour)? Also, a rain event is not fixed in one location, but rather advected with the weather system. The rain measurements were made at a fixed site, rather than following the airmass. Thus the rainfall amount for a given event depends not only on rain rate, but also on how long it took the weather system to pass the collection site. Then it is perhaps not surprising to see a lack of relationship between methanol concentration and rainfall amount.

Reply: This is an interesting idea but we don't have rain rate data or droplet size data to investigate relationships with methanol concentration.

p. 1386, line 7 and line 17. See comment for p. 1383, line 13

Reply: We have changed the wording in several portions of the text to reiterate that the main source of methanol is biogenic but photochemical production is a possibility.

p. 1386, line 21 show range for methanol:DOC

Reply: The following range was added: (range: 0.08 to 14.4%)

p. 1387, line 15-19. The gas phase methanol concentration over land is typically much higher than over the ocean, by often an order of magnitude. If the dissolved methanol concentration in rainwater is in

approximate equilibrium with the gas phase, using measured rainwater concentration from this land site will most likely results in an overestimation of the global wet deposition flux.
Reply: We stated the assumption that these methanol concentrations are a proxy for global concentrations and we decided to keep the global wet deposition flux 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 in the discussion 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."

p. 1394. Fig. 2. Represent county level biogenic methanol emission in micromoles/ m2/d or other scientific units.
Reply: This has been changed to kg/km^2/yr

p. 1397, Fig. 5. This plot seems unnecessary.
Reply: The portion on growing and nongrowing in the text has been deleted along with the figure.

References:
Yang, M., R. Beale, P. Liss, M. Johnson, B. Blomquist, and P. Nightingale (2014) Air–sea fluxes of oxygenated volatile organic compounds across the Atlantic Ocean, Atmos. Chem. Phys. Discuss., 14, 8015-8061, doi:10.5194/acpd-14-8015-2014.
Yang, M., P. Nightingale, R. Beale, P. Liss, B. Blomquist, and C. Fairall (2013) Atmospheric deposition of methanol over the Atlantic Ocean, Proc. Natl. Acad. Sci. www.pnas.org/cgi/doi/10.1073/pnas.1317840110.