Atmos. Chem. Phys. Discuss., 14, C3227–C3231, 2014
www.atmos-chem-phys-discuss.net/14/C3227/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temporal and spatial variations in rainwater methanol" *by* J. D. Felix et al.

M. Yang (Referee)

reelguy@gmail.com

Received and published: 4 June 2014

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.

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.

Add references for the first sentence of Introduction.

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.

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?

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? -

Is dissolved methanol concentration in rainwater near the surface expected to be in approximate thermodynamic equilibrium with the surrounding gas phase?

p. 1378, line 19. “event basis” repeated

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.

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?

p. 1381, Section 2.5. Suggest replacing “Storm” with “Rain event” in the section heading

p. 1382, line 4. Two significant figures on the average concentration

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.

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?

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.

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?

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 greater gas solubility.

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

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.

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

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.

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

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

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.

p. 1394. Fig. 2. Represent county level biogenic methanol emission in micro-moles/m2/d or other scientific units.

p. 1397, Fig. 5. This plot seems unnecessary.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1375, 2014.