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Temporal and spatial variations in rainwater methanol

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Abstract

This work reports the first detailed analysis of methanol concentrations in rainwater. Methanol concentrations measured in 49 rain events collected between 28 August 2007 to 10 July 2008 in Wilmington, NC, USA, ranged from below the detection limit of 6 nM to 9.3 µM with a volume weighted average concentration of 1.2 ± 0.2 µM. Methanol concentrations in rainwater were up to ∼ 200× greater than concentrations observed in marine waters indicating wet deposition as a potential significant source to marine waters. Assuming these methanol concentrations are an appropriate proxy for global methanol rainwater concentrations the global methanol wet deposition sink is estimated as 20 Tg yr^{-1} which implies previous methanol budgets underestimate removal by precipitation. Methanol concentrations did not correlate with H^+, NO_3^-, and NSS, which suggest that the dominant source of the alcohol to rainwater is not anthropogenic. However, methanol concentrations were strongly correlated with acetaldehyde which has a primarily biogenic input. Methanol volume weighted concentration during the growing season (1.5 + 0.3 µM) was more than double that of the non-growing season (0.7 + 0.1 µM), further promoting biogenic emissions as the primary cause of fluctuating methanol concentrations. Methanol concentrations peaked in rainwater collected between the time period 12:00–06:00 p.m. Peaking during this period of optimal sunlight implies a direct relationship to photochemical methanol production but there are also increases in biogenic activity during this time period. Rain events with terrestrial origins had higher concentrations than those of marine origin demonstrating the significance of the continental source of methanol in rainwater.

1 Introduction

Methanol is the second most abundant volatile organic compound (VOC) in the troposphere where it plays a significant role in atmospheric chemistry by producing O_3, CO, and HCHO and decreasing $^{\bullet}OH$ concentrations. Tie et al. (2003), using a global chemical transport model, reported that methanol emissions produce approximately 1–2 % increase in O_3, 1–3 % decrease in OH, and a 3–9 % increase in formaldehyde. The GEOS-chem 3-D model of atmospheric chemistry indicates that methanol emissions account for 20 % of CO and HCHO production rates during spring and early summer (Hu et al., 2011). Methanol reacting with OH radicals can also lead to primary production of formic acid (Monod et al., 2000) which in turn increases acidification of rain. 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. These various atmospheric interactions and subsequent impacts on atmospheric chemistry have lead to the investigation and quantification of sources of methanol emissions.

Methanol sources are primarily biogenic (e.g. plant growth and plant decay) but there are a wide range of less significant anthropogenic sources including biofuel burning, biomass burning, gasoline additives, vehicle exhaust, solvent use and many other industrial processes (Howard, 1990; Wells et al., 2012). While it is generally agreed that biogenic sources account for the majority of methanol emissions, the actual percentage attributed to biogenic emissions is still under debate (Millet et al., 2008). Global budgets reviewed by Jacob et al. (2005) report a biogenic source range of 63 to 91 % while in a source tracer study at a site in the upper Midwest US up to 70 % of wintertime methanol was attributed to anthropogenic sources (Hu et al., 2011). This anthropogenic contribution may be more substantial in urban areas which are represented by higher methanol concentrations (Heikes et al., 2002) and are less prone to biogenic emissions. Due to the atmospheric lifetime of methanol (5 to 12 days) (Jacob, 2005), emissions from anthropogenic or biogenic sources can travel across regions making it difficult to differentiate between sources.

Earlier efforts have been made to constrain the sources and sinks (primarily OH oxidation) of atmospheric methanol (Heikes et al., 2002; Millet et al., 2008; Wells et al., 2012). These efforts have been predominately based on methanol concentration data consisting of aircraft and surface air analysis leading to wide discrepancies in global methanol budget models which in turn have led to the reported total global methanol source and sink ranging from 75 to 490 $\mathrm{Tg\,yr^{-1}}$ and sink 40 to 570 $\mathrm{Tg\,yr^{-1}}$, respectively (Galbally and Kirstine, 2002; Heikes, 2002; Jacob, 2005; von Kuhlmann et al., 2003; Singh et al., 2000a; Tie, 2003). There is currently a paucity of condensed phase methanol concentration data and its role in the global biogeochemical cycling. In fact, there are currently no detailed studies of methanol levels in precipitation. This uncertainty has resulted in a wide range in the predicted wet depositional methanol flux of 4 to 50 $\mathrm{Tg\,yr^{-1}}$ (Galbally and Kirstine, 2002; Heikes, 2002; Jacob, 2005; von Kuhlmann et al., 2003; Singh et al., 2000a; Tie, 2003).

The purpose of the current study was to define the ranges and patterns of variation in the abundance of rainwater methanol including such factors as the influence of air mass back trajectory on concentrations. To gain better insight into the possible anthropogenic and biogenic origins of methanol, concentrations were also intercorrelated with a variety of other rainwater components as well as season. Data generated in this study is requisite to the generation of the first total global wet deposition sink of methanol based on measured aqueous phase concentrations.

2 Materials and methods

2.1 Sample collection

Wilmington rainwater samples were collected on an event basis on the campus of the University of North Carolina at Wilmington (UNCW) from 28 August 2007 to 10 July 2008 on an event basis ($n = 49$ events). The collection site at UNCW is a large open area of approximately 1 ha and is made up of a turkey oak, long leaf pine and wire grass community. This area is typical of the inland coastal area of southeastern North Carolina. The site (34°13.9′ N, 77°52.7′ W) is approximately 8.5 km from the Atlantic Ocean. Due to the close proximity of the collection site to the laboratory, methanol analysis or filtration and refrigeration of samples can be done within minutes of collection, which reduces the possibility of compositional changes between the time of collection and analysis. If it wasn't possible to analyze the rain samples within 2 h, they were frozen immediately and stored in a −80 °C freezer. Event rain samples were collected using Aerochem-Metrics (ACM) model 301 automatic sensing wet/dry precipitation collectors containing 4 L Pyrex glass beakers that were pre-cleaned by combusting at 450 °C for 4 h to remove organic impurities. Rainwater concentrations are reported as volume-weighted concentrations with volume-weighted standard deviations (Topol et al., 1985). This is the mathematical equivalent to mixing all rain within a specified time period together and reporting the analytical result for that composite sample.

2.2 Formaldehyde and methanol

Formaldehyde concentrations in rainwater samples were determined by derivtization with 2,4-dinitrophenylhydrazine followed by separation and detection by HPLC (Kieber et al., 1999). Samples and standards reacted with 2,4-dinitrophenylhydrazine for one hour in the dark forming a hydrazone, which was separated from interfering substances by HPLC and quantified by UV detection at 370 nm. Derivatized samples (100 µL) were injected onto a reversed phase Luna 100 mm × 4.60 mm 3 μ C18 Phenomenex column with a 100 Å pore size at 10 °C. The mobile phase was a 1 : 1 mixture of 0.1 % trifluroacetic acid (TFA) in acetonitrile and 0.1 % TFA in DIW at a flow rate of 1.00 mL min^{-1}.

Methanol was determined on a second aliquot by oxidation of the alcohol to formaldehyde via alcohol oxidase obtained from the yeast *Hansenula* sp. (Kieber et al., 2013). The enzyme was prepared by dissolution of 100 units of alcohol oxidase in 5 mL of 0.1M potassium phosphate buffer (pH 9.0). The sample (1000 µL) was combined with 10 µL of buffer, 100 µL of an enzyme working reagent (0.18 units mL^{-1}) and allowed to react at 40 °C for 40 min before addition of 10 µL of DNPH. The concentration of methanol was determined after HPLC analysis by the difference in formaldehyde concentration in samples with and without added enzyme. This method has a detection limit of 6 nM and a precision of 2 % RSD.

2.3 Reagents and standards for methanol analysis

Alcohol oxidase (100 units) from the yeast *Hansenula* sp was purchased from Sigma (St. Louis, MO). Water was purified using a Millipore Q-water system (Millipore Corp., Bedford, MA) and used to prepare all solutions. Reagent grade 2,4-dinitrophenylhydrazine (DNPH) was purchased from Sigma (St. Louis, MO), triply recrystallized from acetonitrile and kept refrigerated in the dark. Acetonitrile (HPLC grade, Burdick and Jackson, Muskegon, MI), 12 M hydrochloric acid (Reagent Grade, VWR International, West Chester, PA), and carbon tetrachloride (HPLC grade 99.9 %, Sigma, St. Louis, MO) were used in preparation and purification of DNPH reagent solution.

Formaldehyde (37.69 % CH_2O, 12.37 % MeOH) and paraformaldehyde (94.19 %, containing no methanol) were obtained from Wright Chemical Company (Wilmington, NC). A 1M formaldehyde stock solution was prepared before each rain event. Methanol (HPLC grade, Burdick and Jackson, Muskegon, MI) and Milli-Q water was used to prepare a 1M alcohol stock solution before each rain event. ACS grade (99.0 %) potassium dihydrogen phosphate and reagent grade potassium hydrogen phosphate (Alfa Aesar, Ward Hill, MA) were used in preparation of all buffer solutions.

2.4 Supporting analyses

Hydrogen peroxide was analyzed at the time of sample collection by a fluorescence decay technique involving the peroxidase-mediated oxidation of the fluorophore scopoletin by H_2O_2 in rain buffered at a pH of 7 with a phosphate buffer (Mullaugh et al., 2012). Organic carbon content in rainwater samples were determined with a Shimadzu TOC 5000 carbon analyzer (Shimadzu, Kyoto, Japan) equipped with an ASI 5000 autosampler (Willey et al., 2000). Inorganic anions (Cl^-, NO_3^-, and SO_4^{2-}) were analyzed using suppressed ion chromatography. A Ross electrode with low ionic strength buffers was used for pH analysis. Organic acid concentrations were measured with a Dionex 4000i/SP ion chromatograph with a SP4290 integrator, Dionex IonPacR AS11 4 mm analytical column, AG11 4 mm Guard column and anion micromembrance Suppressor Model AMMS-11 (Avery et al., 2001).

These supporting data were used to characterize rain events and to evaluate whether the patterns of variation observed for methanol co-vary with any of these analytes. These supporting data also allow comparison with rain collected elsewhere.

2.5 Storm origin definitions

Precipitation events were categorized using air-mass back-trajectories generated using version 4 of the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) developed at the National Oceanic Atmospheric Administration – Air Resources Laboratory (NOAA/ARL 2013). Trajectories were generated using a stand-alone PC version of the model; and calculated using pre-processed gridded horizontal and vertical wind fields generated at 6 h intervals from the National Center for Environmental Prediction's Global Data Assimilation System (GDAS) using the Medium Range Forecast model (MRF) to produce the forecast wind fields. Single back-trajectories were run for each measured precipitation event collected at UNCW starting at the recorded onset of precipitation. Trajectories were run starting at the 500 m level to represent the air-mass near the well mixed boundary layer likely to contribute more heavily to in-cloud processes contributing to wet deposition (Walker et al., 2000). They were then visually categorized based on origin (compass direction) and path (terrestrial, marine, coastal, or mixed). Terrestrial air masses are those whose pathway for the 120 h period preceding the rain event was predominantly over a landmass, and like-wise over ocean for marine types. Mixed trajectories were determined to have the same potential for oceanic as terrestrial influence based on a visual analysis of their pathway (Kieber et al., 2005). Coastal trajectories followed the Atlantic coastline.

GIS shapefiles produced by the HYSPLIT program were used to plot trajectories for each storm type on a US county basemap that portrays size normalized county level biogenic methanol emissions. Methanol emissions used to make the map were from the 2008 National emissions inventory (NEI 2008).

3 Results and discussion

Methanol concentrations for 49 rain events ranged from below the detection limit (< 6 nM) to 9.3 µM with a volume weighted average concentration of 1.2 ± 0.2 µM and a simple average concentration of 1 ± 2 µM. The average concentration is almost 2× the average in rainwater (690 nM) collected at an Arizona site in 1985, the only other known methanol concentration in rainwater (Snider and Dawson, 1985). 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.

3.1 Storm origin

Rain events were classified based on their back trajectory to determine how methanol concentrations were affected by continental influences (Fig. 1). Terrestrial, mixed, coastal and marine storms had volume weighted average methanol concentrations of 1.5 ± 0.5 µM, 1.6 ± 0.2 µM, 0.7 ± 0.4 µM, and 1.1 ± 0.2 µM, respectively (Fig. 1). Figure 2 shows individual storm trajectories plotted over US county-level biogenic methanol emissions. Rain events with terrestrial back trajectories had higher methanol concentrations than those with marine back trajectories which is consistent with previous findings that gas phase atmospheric methanol concentrations reported over land (0.03–47 ppbv) are higher than those reported over the ocean (0.3–1.4 ppbv) (Heikes et al., 2002; Jacob, 2005). This also agrees with global budgets that suggest methanol has a primarily terrestrial biogenic source.

Although storm types with marine influence (coastal, marine) have lower methanol concentrations than those with terrestrial influence, methanol is present in significant amounts. This may be due to several reasons. (1) The ocean can be a source of methanol emissions. Millet et al. (2008) report the ocean as an overall methanol sink but consider the ocean biosphere a large enough source to cause detectable concentrations in the atmosphere. (2) Methanol has an average atmospheric lifetime of (5 to 12) days (Jacob, 2005) allowing for transport of methanol from land masses to oceans. (3) Local scavenging of methanol at the rain collection site would include some terrestrial sources.

3.2 Diurnal variations

Methanol concentrations were further subdivided into 4 time periods in order to examine if concentration underwent short term temporal variations (Fig. 3) similar to what has been observed for others analytes in rainwater at this location (Kieber, 2004; Kieber et al., 2001a, 2001b). Events were excluded from classification if they occurred during more than one time period. Each bar in Fig. 3 represents the volume weighted methanol concentration during the given time period.

Methanol concentrations peaked during time period III (12 p.m.–6 p.m.) with a volume weighted concentration of 2.6 ± 0.7 µM. Peaking during this period of optimal sunlight implies a direct relationship to photochemical methanol production (e.g. the oxidation of methane, and the methylperoxy radical reacting with itself and higher organic peroxy radicals) (Jacob, 2005) but there are also increases in biogenic and anthropogenic activity during this time period. The concentration peak during this time period is consistent with the peak of numerous previous diurnal measurements of methanol flux over varying vegetation and is attributed to light stimulated release of methanol (Bamberger 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).

A ~ 6 fold decrease in methanol concentration between day and night falls within the reported range (0.3 to 7×) of decrease (Jacob, 2005) indicating dry deposition at night and surface uptake. Other possible modes for the nighttime decrease are removal of water soluble gases via dew formation and the advection of “cleaner” marine air to the rain collection site which was suggested as an explanation for lower nighttime concentrations of other rainwater components (e.g. H_2O_2, formaldehyde, formic acid, NO_3^-) at this collection site. (Avery et al., 2001).

3.3 Seasonal variations

The methanol concentration was subdivided into 4 time periods in order to examine seasonal variations in analyte concentrations (Fig. 4). Seasons were defined as winter (1 December–29 February), spring (1 March–31 May), summer (1 June–31 August), and fall (1 September–31 November). The volume weighted average concentration of methanol during the winter and fall rain events were 0.9 ± 0.2 µM and 0.7 ± 0.2 µM, respectively. Since methanol has a stronger biogenic source it is expected to have lower concentrations in the winter months. As with various atmospheric concentration studies (Hu et al., 2011; Jordan et al., 2009; Legreid et al., 2007; Millet, 2005) winter rainwater methanol concentrations are ∼ 1/3 of the summer concentrations and likely have a greater percent contribution from anthropogenic sources. For instance using toluene, benzene, and CO as anthropogenic tracers at a rural Midwestern US site, Hu et al. (2011) estimated up to 70 % of wintertime methanol emissions having anthropogenic origin. It might be expected that fall concentrations would increase due to plant decay but this source is relatively low when compared to reported contributions from the plant growth source (7 to 27 % of plant growth total) (Galbally and Kirstine, 2002; Heikes et al., 2002; Jacob, 2005; Singh et al., 2000b). A possible explanation for lower than expected concentrations of methanol during the fall rain events may be that drought conditions of the previous summer were severe to extreme (NC Drought, 2008) in turn killing vegetation that would have decayed during the fall.

The volume weighted concentration of methanol during the spring and summer months were 1.0 ± 0.3 µM and 2.7 ± 0.9 µM, respectively. Methanol concentrations are expected to increase in the spring as plant growth increases. A slight increase was seen but methanol emissions from vegetation may have been hampered by an unusually dry spring. Methanol concentrations were highest in the summer which was to be expected since summer is during growing season and increasing summer temperatures can lead to exponentially increasing methanol concentrations (Folkers et al., 2008; Hu et al., 2011). The early summer peak in methanol concentration agrees with simulated methanol seasonal cycles and more specifically the monthly rainwater concentration peak in June (3.6 ± 0.9 µM) agrees with the peak seen in several seasonal cycle simulations (Wells et al., 2012).

To further investigate the impact of the biogenic source on methanol rainwater concentrations, rain events were grouped into growing (1 April–30 September) and non-growing (1 October–31 March) periods (Fig. 5). Methanol volume weighted concentration during the growing season (1.5 ± 0.3 µM) was more than double that of the non-growing season (0.7 ± 0.1 µM), further promoting biogenic emissions as the primary cause of fluctuating methanol concentrations.

3.4 Intercorrelation

Formaldehyde, acetaldehyde, rain amount, H^+, NO_3^-, H_2O_2, NSS (non sea salt sulfate), formate, and acetate concentrations were determined in addition to methanol in this study. All rainwater components were analyzed for correlation with each other (Table 1). Methanol concentrations did not correlate with H^+, NO_3^-, and NSS, which suggest that the dominant source of the alcohol to rainwater is not anthropogenic. There was no correlation between methanol and the dissolved organic carbon content of rainwater samples indicating the alcohol make up a variable fraction of the organic carbon pool. Methanol concentrations were strongly correlated with acetaldehyde which has a primarily biogenic input (Millet et al., 2010) suggesting the potential biogenic source for methanol consistent with the higher concentration observed during the growing season (Fig. 5).

There was no correlation of methanol concentrations with rainfall amount (Fig. 6) suggesting it is not simply washed out of the atmosphere at this location but rather is resupplied during a rain event. A possible mode of resupply is transpiration from plants. Rainwater initiates the transpiration stream in plants; methanol being highly soluble is transported in the transpiration stream and is emitted via the stomata (Fall and Benson, 1996; Niinemets, 2003). This methanol emission via transpiration may continue throughout rainfall events and lead to a local resupply that in turn is scavenged by continuing wet deposition. Formaldehyde also does not exhibit washout at this location (Kieber et al., 1999), which the authors attribute to in situ photochemical production from chromophoric dissolved organic matter in rainwater (Southwell et al., 2010). The increase of methanol concentrations during periods of peak sunlight intensity (Figs. 5 and 6) indicates similar photochemical production mechanisms may occur for methanol.

4 Implications

This work reports the first detailed analysis of methanol concentrations in rainwater. The presence of methanol in all rainwater samples analyzed suggests it is a ubiquitous component of precipitation. Rain events with terrestrial origins had higher concentrations than those of marine origin indicating the potential for a significant continental source of methanol in rainwater. Correlation analysis with other rainwater analytes and higher growing season concentrations suggest this continental source is primarily biogenic rather than anthropogenic at this location. The lack of washout behavior implies a mode of methanol resupply during rain events possibly involving photochemical processes or transpiration from plants. Increases in methanol during daytime and summer rain events further underscore the importance of biogenic activity and photochemical production in the biogeochemical cycling of methanol in precipitation.

Methanol concentrations represent 1.5 % of the DOC content indicating it is not a significant contributor to the overall carbon budget in precipitation. The contribution of methanol to DOC is somewhat less than formaldehyde, which accounts for approximately 3 % of the dissolved organic carbon pool in precipitation (Kieber et al., 1999). The lack of correlation with the dissolved organic carbon content of samples suggests that the fraction of DOC that is methanol is also variable.

Methanol levels in rainwater were up to ~ 200× greater than concentrations observed in marine waters (48 to 296 nM) (Dixon et al., 2011) indicating wet deposition as a potential significant source to marine waters. The important role of rainwater deposition of atmospherically enriched analytes such as methanol on oceanic concentrations was demonstrated in an earlier study of hydrogen peroxide on surface seawater at the Bermuda Atlantic Time Series Station. The large increase in surface water concentrations after precipitation events indicated that rainwater deposition was a significant and in some cases the dominant source of hydrogen peroxide to open ocean seawater (Kieber et al., 2001a). It is also likely the rainwater flux of methanol to freshwater systems is episodically significant similar to what has been observed for formaldehyde at this location (Kieber et al., 1999). During the high irradiance summer month's formaldehyde contributes as much as 30 times the resident amount present in freshwater lakes of southeastern North Carolina.

One of the most important uncertainties in the global biogeochemical cycling of methanol is the magnitude of its wet depositional flux. Assuming the annual volume weighted average reported at the Wilmington, NC, USA rain site is an appropriate proxy for global methanol rainwater concentrations and the global annual precipitation volume is $\sim 5.36 \times 10^{17}$ L (Pidwirny 2008), the global methanol wet deposition sink is estimated as $20\,\mathrm{Tg\,yr^{-1}}$. This estimate falls within the theoretical range (4–$50\,\mathrm{Tg\,yr^{-1}}$) produced by many global methanol budget models and is double the reported representative best estimates (9–$12\,\mathrm{Tg\,yr^{-1}}$) (Galbally and Kirstine, 2002; Heikes et al., 2002; Jacob, 2005; von Kuhlmann et al., 2003; Tie et al., 2003). Results of this study are significant because they suggest previous methanol budgets significantly underestimate removal by precipitation. 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.

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Table 1. Intercorrelations between methanol, formaldehyde, acetaldehyde, and various other rainwater components. Bold faced values indicate significance at $p < 0.001$. Asterisk (*) indicates significance at $p < 0.05$. Number of samples equals: 47 for acetaldehyde, nitrate, and sulfate; 27 for formate and acetate; 49 for others.

	CH_3OH	CH_2O	CH_3CHO	NO_3^-	H_2O_2	H^+	NSS	Formate	Acetate
amount	0.057	−0.23	−0.152						
CH_3OH		0.166	**0.464**	0.176	0.307^*	0.085	0.234	−0.142	0.0708
CH_2O			**0.643**	**0.557**	0.373^*	**0.548**	**0.604**	**0.734**	**0.558**
CH_3CHO				**0.442**	**0.506**	0.357^*	**0.699**	**0.609**	**0.779**
NO_3^-					**0.397**	**0.559**	**0.584**	0.371^*	**0.630**
H_2O_2						**0.405**	**0.606**	**0.675**	**0.667**
H^+							**0.760**	**0.722**	**0.687**
NSS								**0.476**	**0.751**
Formate									**0.786**
Acetate									

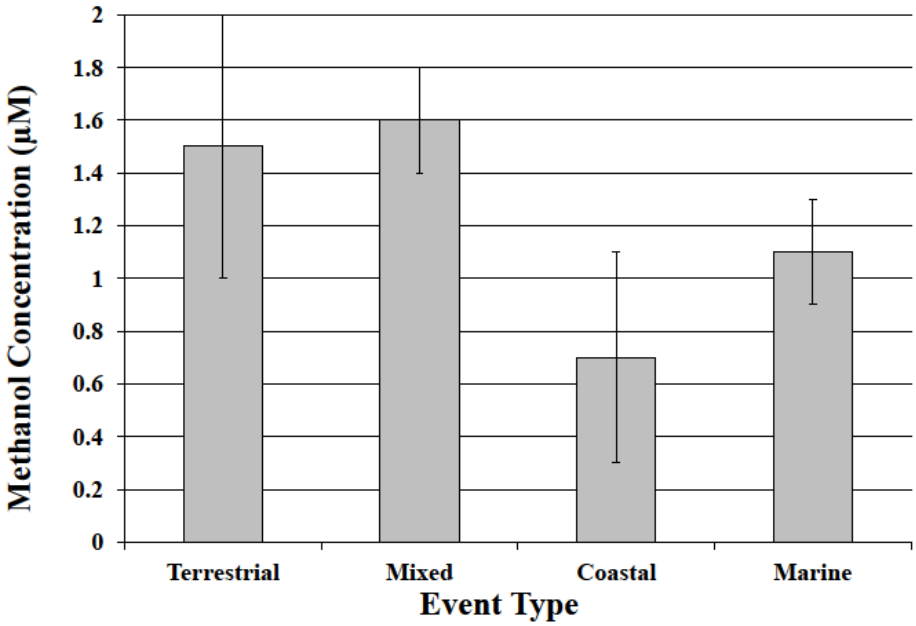

Fig. 1. Volume weighted methanol concentration plotted according to rain event origin.

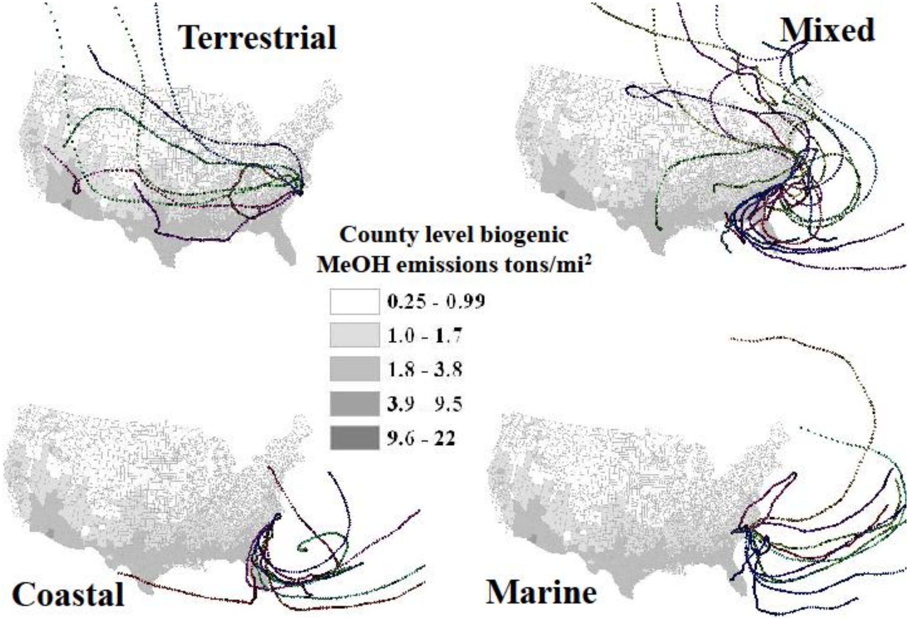

Fig. 2. Rain event trajectories plotted over annual county level biogenic methanol emissions that have been normalized by county size.

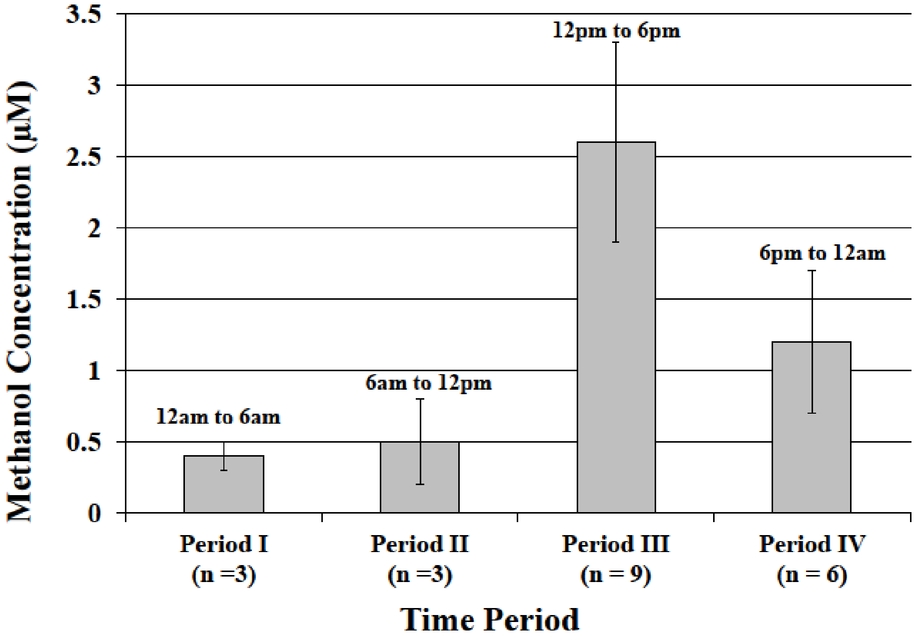

Fig. 3. Diurnal methanol concentrations.

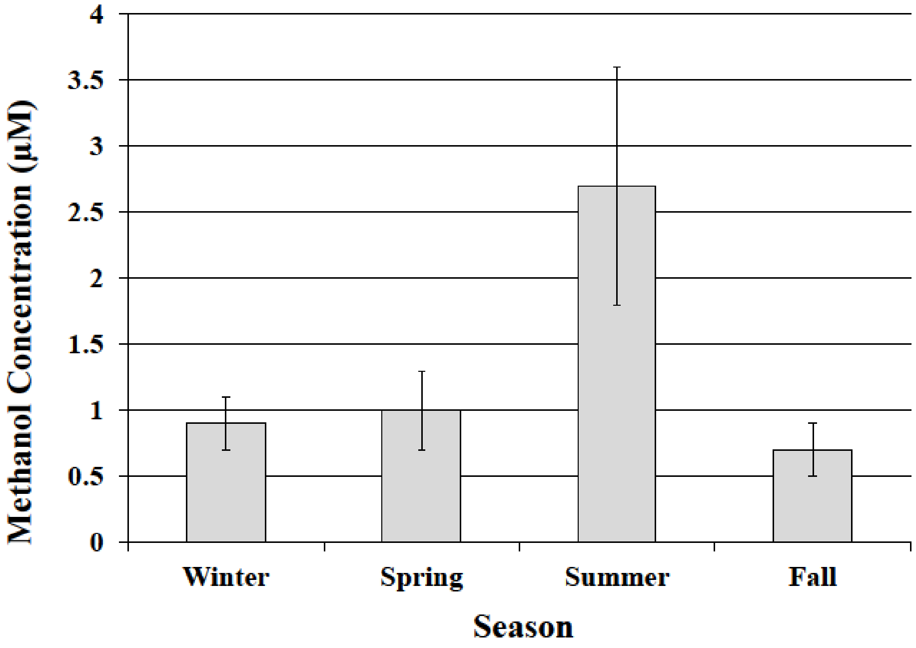

Fig. 4. Volume weighted methanol concentration plotted according to season.

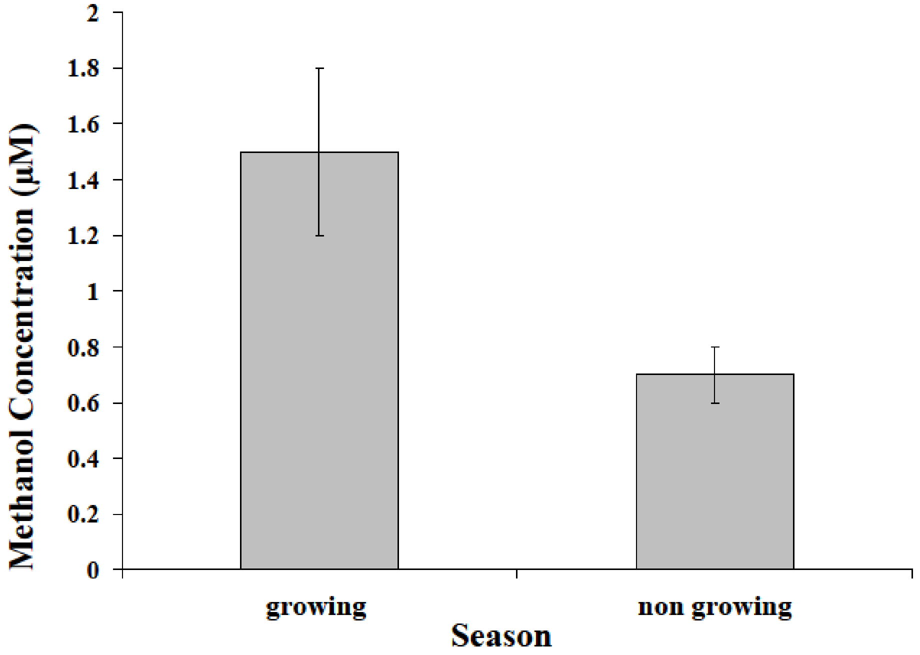

Fig. 5. Volume weighted methanol concentration plotted according to growing/non-growing season.

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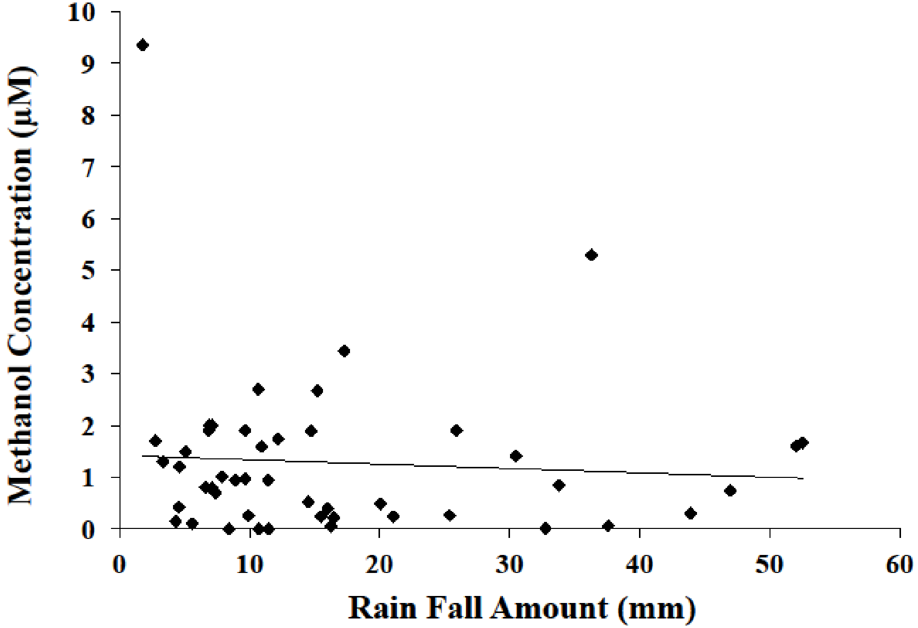

Fig. 6. Methanol concentration vs. rain fall amount for all rain events.