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## Biogenic methanol and its impacts on tropospheric oxidants

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[1] We use a global chemical transport model (MOZART-2) to estimate the effects of surface emissions of methanol on tropospheric oxidants. The importance of methanol in tropospheric chemistry is two fold. First, methanol has a relatively large surface emission with an estimated global emission of 70 to 350 Tg methanol/year. The estimated methanol flux is comparable to other major hydrocarbon surface emissions such as isoprene and total monoterpenes, but the chemical lifetime of methanol is several days (in the boundary layer) to a few weeks (in the upper troposphere), which is much longer than the chemical lifetime of isoprene or monoterpenes (For example, the chemical lifetime of isoprene is about 2 hours). With a surface emission of 104 to 312 Tg methanol/year (encompasses estimated uncertainty in methanol emissions), the calculation shows that on average, the inclusion of methanol emission produces approximately 1–2% increase in O<sub>3</sub>, 1–3% decrease in OH, 3–5% increase in HO<sub>2</sub>, and 3–9% increase in CH<sub>2</sub>O globally. The maximum perturbation to the oxidants occurs in the tropical upper troposphere. However, the uncertainty associated with current methanol emission estimates produces significantly different model predictions of tropospheric oxidant distributions. *INDEX TERMS*: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0325 Atmospheric Composition and Structure: Evolution of the atmosphere. **Citation**: Tie, X., A. Guenther, and E. Holland, Biogenic methanol and its impacts on tropospheric oxidants, *Geophys. Res. Lett.*, 30(17), 1881, doi:10.1029/2003GL017167, 2003.

### 1. Introduction

[2] Methods for measuring atmospheric oxygenated VOC (e.g., acetaldehyde, acetone, ethanol, formaldehyde, methanol) have improved substantially over the last decade. Methanol represents about half of the total global emission of oxygenates and nearly 20% of total global VOC emissions [Guenther *et al.*, 1995]. There is considerable uncertainty surrounding global methanol emissions because of the few measurements and limited understanding of the processes regulating emissions. However, previous studies suggest that even the lower methanol emission estimates have the potential for significant impacts on the oxidizing capacity of the troposphere [Heikes *et al.*, 2003]. The main source of methanol production in leaves is from pectin demethylation in cell wall. The result is significant seasonal variations in methanol emissions with peaks in spring and fall for temperate climates. Singh *et al.* [1995] measured significant concentrations of methanol in the free troposphere in the

early and mid 1990s. Biogenic emissions of methanol are now thought to be the major source (>80%) of atmospheric methanol [Heikes *et al.*, 2003]. Although the existence of a substantial global methanol flux is now certain, there are large uncertainties associated with attempts to estimate the magnitude and distribution of this flux.

[3] In this study, we use these uncertainties to conduct a sensitivity study to investigate the impact of biogenic methanol emissions on global oxidant distributions. We used an established global 3-D chemistry and transport model (MOZART-2) with two “realistic” methanol emission scenarios (upper and lower bounds).

### 2. Methanol Global Modelling and Results

[4] A global chemical transport model (MOZART-2; Model for Ozone And Related chemical Tracers, Version 2 [Horowitz *et al.*, 2003]), was used to calculate the global distribution of methanol and its impact on tropospheric oxidants. In its standard configuration, MOZART-2 simulates the concentrations of 63 chemical species from the surface up to the lower stratosphere. The detailed model description of transport and chemistry is given by Horowitz *et al.* [2003].

[5] Methanol reacts with gas-phase OH to produce HO<sub>2</sub> and CH<sub>2</sub>O. These reactions could have an important impact on tropospheric ozone, and are described in Table 1. The net effect of R-1 to R-5 is to convert OH to HO<sub>2</sub>, and finally to enhance O<sub>3</sub> concentrations. Methanol itself can be produced by the oxidation of certain VOCs that produce CH<sub>3</sub> radicals, such as R-6 and R-7. The major chemical reaction to produce methanol through the multiple reaction pathway is R-8. Removal of methanol from the atmosphere occurs via both wet and dry deposition. The wet deposition of methanol is calculated according to its solubility and the amount of rainfall in the model, as described by Brasseur *et al.* [1998]. The dry deposition velocity of methanol is set equal to the velocity of CH<sub>3</sub>OOH [Wesley, 1989].

#### 2.1. Global Distribution and Budget of Methanol

[6] We conducted three model runs including a standard model run with surface emissions of 312 Tg/year (Run-1), a model run without surface emissions of methanol (Run-2), and a model run with surface emissions of 104 Tg/year (Run-3). The global distribution of methanol is based on the study of A. Guenther (A global model of methanol, ethanol, acetone, acetaldehyde, ethene, propene and butene emissions from vegetation, manuscript in preparation, 2003), and the emission of methanol is dependent on land cover (vegetation type), temperature, sunlight, leaf area, and leaf age. Global satellite observations and meteorological databases are used as inputs for the model which predicts hourly emissions with a 0.05 degree × 0.05 degree spatial resolu-

**Table 1.** Methanol Chemical Reactions

(R-1)	$\text{CH}_3\text{OH} + \text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O}$
(R-2)	$\text{CH}_2\text{O} + \text{h}\nu + 2\text{O}_2 \rightarrow 2\text{HO}_2 + \text{CO}$
(R-3)	$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$
(R-4)	$\text{NO}_2 + \text{h}\nu \rightarrow \text{NO} + \text{O}$
(R-5)	$\text{O} + \text{O}_2 \rightarrow \text{O}_3$
(R-6)	$\text{CH}_4 + \text{OH} \rightarrow \rightarrow \text{CH}_3\text{OH} + \text{products}$
(R-7)	$\text{C}_3\text{H}_6 + \text{OH} \rightarrow \rightarrow \text{CH}_3\text{OH} + \text{products}$
(R-8)	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$

Where  $\rightarrow \rightarrow$  indicates a multiple reaction pathway.

tion. Our standard run (312 Tg/year) is based on the best estimate of the study by Guenther. The magnitude of our lower bound estimate (104 Tg/year) is a factor of 3 lower and is approximately equal to the global total predicted by Galbally and Kirstine [2002].

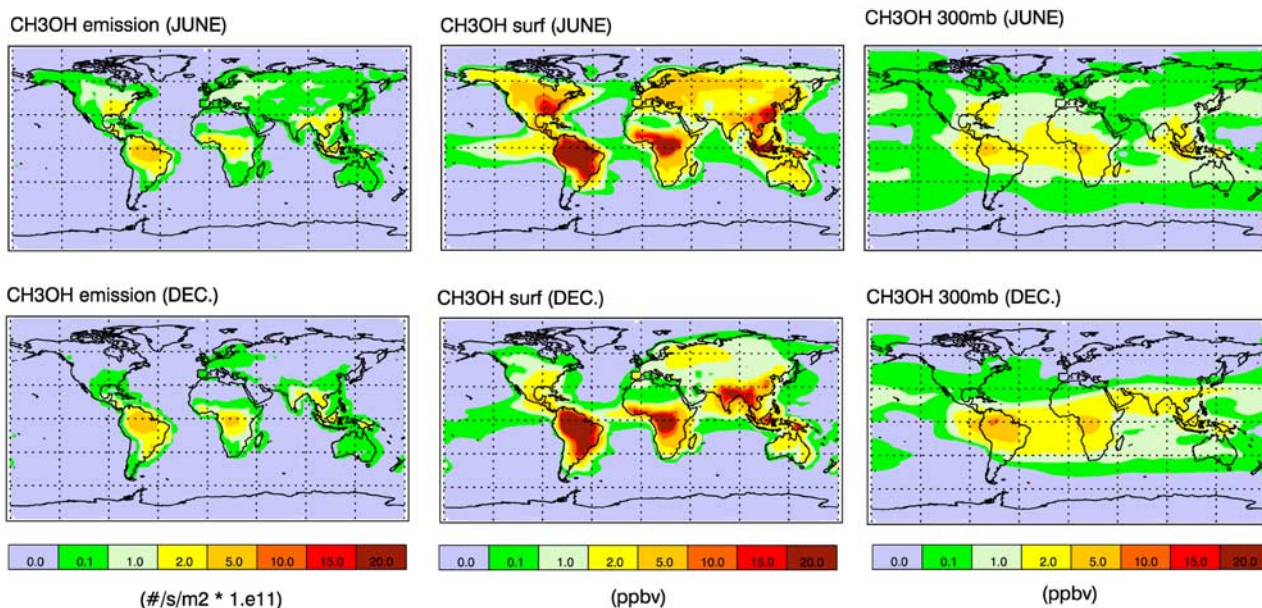
[7] The global methanol distributions calculated by the standard run are shown in Figure 1. There is significant spatial and temporal variation in the global distribution of methanol simulated by the MOZART-2 model. The maximum concentration of methanol ranges from 1 to 20 ppbv at the surface with the highest values occurring in South America, central Africa, southeast US, and Southeast Asia. A significant seasonal variability is predicted for middle to high latitudes. A very small concentration of methanol is predicted for the southeast US in December, and in June methanol concentration increases rapidly in this region with a maximum of 10–15 ppbv. The spatial and temporal variability of surface methanol concentration are strongly correlated to the surface emission. Methanol concentrations are more spread out from the source regions because methanol has a relatively long chemical lifetime (1 to 2 weeks). For example, methanol is transported to the west coast of South America from Amazon region. In the free troposphere (300 mb), a significant amount of methanol is transported from its source region to the upper troposphere due to the convective transport. The maximum concentra-

tion is located in the tropics, and a longitudinal mixing is also evident. By contrast, in middle to high latitudes, the methanol concentrations are very low due to the smaller surface emission and weaker convective transport.

[8] Global observations of methanol are minimal. The existing limited measurements show a strong variability of methanol concentrations in different regions [Heikes *et al.*, 2003]. Observations of methanol mixing ratios in the free troposphere over the Atlantic and Pacific are between 200 and 1000 pptv with a median value of 600 pptv in February [Singh *et al.*, 1995, 2000], similar to modelled methanol concentrations with values, ranging from 100 to 1000 pptv. In the boundary layer over Harvard Forest, the measured methanol concentration ranges from 5 to 15 ppbv in July [Doskey and Gao, 1999], and calculated methanol concentrations around this region range from 5 to 10 ppbv. Mountain forest studies in Colorado report methanol concentrations in August and September that range from 2 ppbv to 4 ppbv [Baker *et al.*, 2001], compared to calculated values of 2 to 5 ppbv.

[9] This study calculates a global methanol budget (Table 2) for comparison to the estimation by Heikes *et al.* [2003]. The annually averaged methanol surface emissions used for the three model runs include 0, 39, and 117 TgC/year (0, 104, and 312 Tg methanol/year). In comparison, the model has annual emissions of 410 TgC of isoprene, 129 TgC of terpene, and 489 TgC of methane [Olivier *et al.*, 1996; Guenther *et al.*, 1995]. Of the total methanol emissions, 92% is due to biogenic sources, which suggests that these natural sources have a significant contribution to the total hydrocarbon emissions.

[10] Chemical lifetime is the second most important factor controlling the methanol budget. The methanol chemical lifetime ranges from one week in the surface to a few weeks in the upper troposphere. The chemical lifetime of methanol is much longer than the chemical lifetimes of



**Figure 1.** Calculated horizontal distributions of methanol surface emissions (upper panels), surface concentrations (middle panels), and concentrations at 300 mb (lower panels) in June and in December, respectively for Run-1, the high methanol emission case.

**Table 2.** Calculated Global Budget of Methanol

	Run1	Run2	Run3
Emissions (TgC/yr)	117	0	39
(Tg/yr)	(312)	(0)	(104)
Trop. Burden (Tg)	4.7	0.48	1.9
Loss (Tg/year)			
Wet dep	50	3.5	16
Dry dep	85	6.0	32
Gas-Chem	149	15.9	59
Chemical Lifetime	12 days (7 days in BL, and 22 days in 10 km)		

a-pinene (less than one hour) and isoprene (a few hours), but is much less than the chemical lifetime of methane (8–10 years). Methanol has limited latitudinal transport unlike methane that is widely spread into the troposphere. Moreover, unlike isoprene and monoterpenes that are limited in the boundary layer of the source regions due to the fast chemical reactions, methanol can be transported from the boundary layer to the upper troposphere. Because methanol chemistry (R-1 to R-5) can convert OH to HO<sub>2</sub> and O<sub>3</sub>, surface emission of methanol contributes to ozone production in the free troposphere.

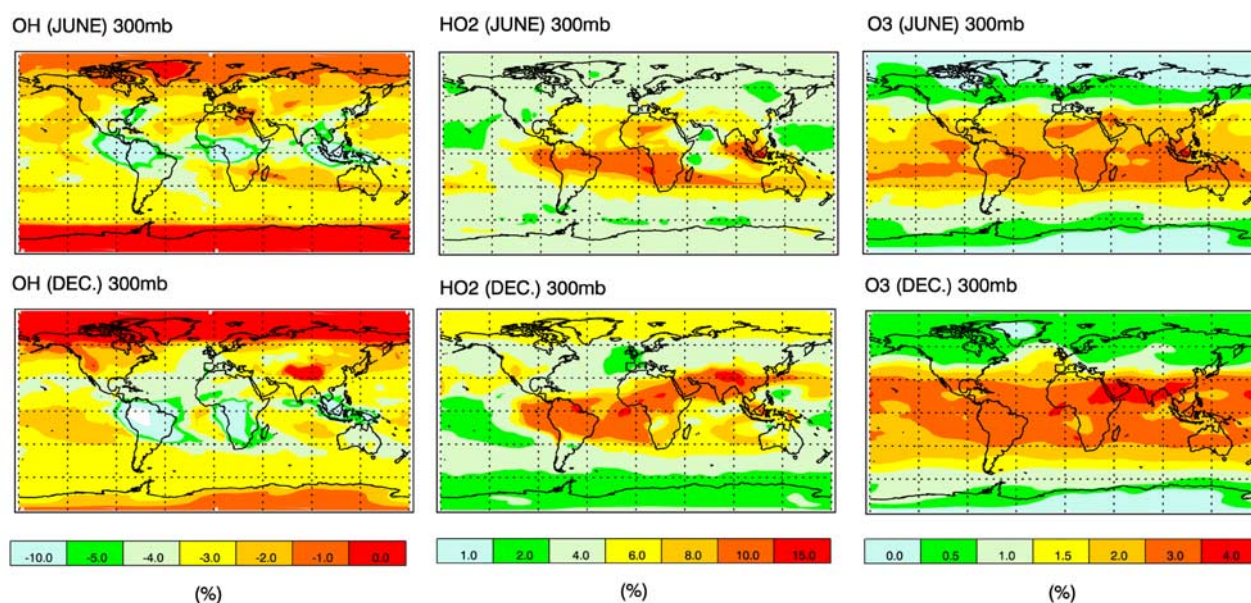
[11] The total tropospheric (from the surface to 100 mb) mass of methanol is estimated to be 4.7 Tg with a surface emission of 312 Tg/year, 0.48 Tg without surface emission, and 1.9 Tg with a surface emission of 104 Tg/year. The 0.48 Tg of methanol without surface emission is due to the chemical production from oxidation of VOCs (R6 to R8), which indicates that 10% (with 312 Tg/year surface emission) to 25% (with 104 Tg/year surface emission) of methanol mass is due to chemical production in the troposphere. The sink terms include dry and wet deposition, chemical destruction, and transport to the stratosphere. Deposition accounts for more than 40% of the total loss. Because methanol is only a slightly soluble species, dry deposition to the surface exceeds wet deposition. The ratio

of dry to wet deposition of methanol is about 1.7. In the calculation, we assume that the deposition velocity of methanol is equal to the deposition velocity of CH<sub>3</sub>OOH, which is a less soluble species than methanol. As a result, the dry deposition may be underestimated in the calculation. Chemical destruction accounts for more than 50% of the total loss. Because the products of chemical oxidation produce O<sub>3</sub> precursors, the calculation above shows that more than 50% of the methanol emitted from the surface will play a role in perturbing tropospheric O<sub>3</sub> chemistry before the methanol is eventually deposited to the surface.

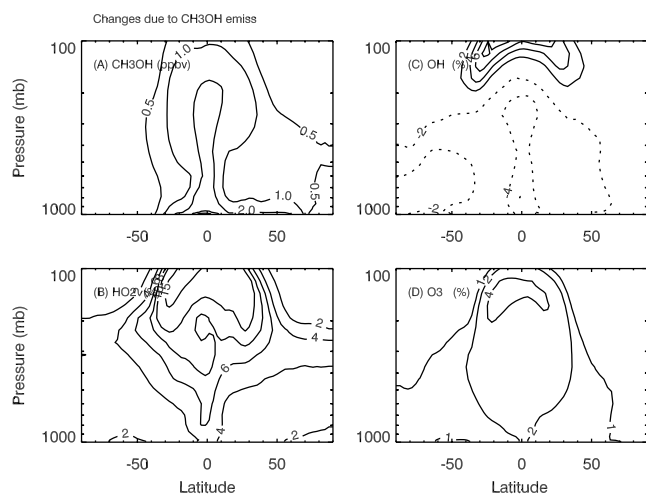
[12] The methanol budget calculated here compares favourably to that of Table 4 of *Heikes et al.* [2003]. Heike et al. calculate a methanol burden of between 3.5 and 6.9 Tg compared to the 1.9 to 4.7 Tg estimated here. They also estimate the gas phase chemical lifetime of methanol to be 18 days based on the calculated global OH distribution by *Bey et al.* [2001] compared to the 12 days calculated here. The difference in lifetime may be partially explained by the use of a calculated global methanol distribution (see Figure 1) while *Heikes et al.* [2003] used a specified methanol distribution (assumed methanol of 600 pptv in the free troposphere, 2000 pptv in the continental boundary layer, and 900 pptv in the marine boundary layer) to estimate the chemical lifetime of methanol. With the same methanol distribution as used by *Heikes et al.* [2003], the estimated methanol lifetime is 16.5 days, which is about 8% different to the estimation by *Heikes et al.* [2003]. This difference may be due to the difference in global OH distributions used in the two estimations.

## 2.2. Impact of Methanol on Tropospheric Oxidants

[13] A large amount of methanol can be transported from the boundary layer into the free troposphere due to its relatively long lifetime (Figure 1), and can impact oxidants in the free troposphere. OH is reduced by 5 to 8% in the tropics. Unlike the surface impacts, the maximum effect of



**Figure 2.** Calculated percentage changes in OH (upper panels) and in O<sub>3</sub> (lower panels) at 300 mb, due to the surface emission of methanol (312 Tg/year) in June and in December, respectively for Run-1 relative to Run-2.



**Figure 3.** Calculated annually and zonally averaged changes in methanol (ppbv, panel A), HO<sub>2</sub> (%), OH (%), and O<sub>3</sub> (%) due to the surface emission (312 Tg/year). The changes are calculated as the concentration in Run-1 relative to Run-2.

methanol on OH at 300 mb is in the centre of the source regions. The effects of isoprene and monoterpenes are limited to the boundary layer due to the fast chemical destruction. HO<sub>2</sub> is enhanced by 8 to 10%, and O<sub>3</sub> is increased by 3 to 4% in the tropics. It also shows that the increase in O<sub>3</sub> is limited to between 30°S and 30°N with a relatively uniform distribution (Figure 2).

[14] The zonally averaged impact of methanol emission on CH<sub>3</sub>OH, OH, HO<sub>2</sub>, and O<sub>3</sub> concentrations shows a significant increase in methanol concentrations in the tropical free troposphere (panel 3A). Zonally averaged HO<sub>2</sub> is enhanced by a maximum of 10 to 15% in the tropical upper troposphere (above 200 mb, panel B). The large increase of HO<sub>2</sub> in the upper troposphere could also be enhanced by the contribution of the photolysis of CH<sub>2</sub>O. As indicated in R-1, the oxidation of methanol produces HO<sub>2</sub> and CH<sub>2</sub>O. With sunlight, CH<sub>2</sub>O is photolysed to produce HO<sub>2</sub> (R-5). The greater actinic flux in the upper troposphere generates a higher rate of photolysis of CH<sub>2</sub>O in the upper troposphere than in the lower troposphere. HO<sub>2</sub> is enhanced in the upper troposphere by both the direct production of methanol oxidation and the photolysis of CH<sub>2</sub>O. Below 200 mb OH is decreased with a maximum reduction of 4% in the tropics (Figure 3C). By contrast, OH is enhanced by 6% in the tropics at 100 mb. In the upper troposphere, OH is sensitive to NO<sub>x</sub> and H<sub>2</sub>O. As shown in Figure 3B, HO<sub>2</sub> concentrations increase significantly in the upper troposphere (partially due to the increase of CH<sub>2</sub>O). As a result, the reaction of HO<sub>2</sub> + NO → NO<sub>2</sub> + OH plays an important role in controlling OH concentration, leading to the enhancement of OH in this region.

[15] The range of methanol emission estimates (104 to 312 Tg/yr) generates significantly different tropospheric OH, HO<sub>2</sub>, CH<sub>2</sub>O, and O<sub>3</sub> concentrations. For example, the changes in OH, HO<sub>2</sub>, CH<sub>2</sub>O, and O<sub>3</sub> decrease from −2.8, 4.8, 8.7, and 1.7% with 312 Tg/yr emission down to −1.0, 1.7, 3.2, and 0.6% with 104 Tg/yr emission because the maximum impact of methanol on the oxidants is in the free

troposphere where the background concentrations of VOCs are small, far from saturating the oxidizing hydrocarbons in this region.

### 3. Summary

[16] Estimates of global methanol emissions range from less than 100 to over 350 Tg CH<sub>3</sub>OH/year. The globally averaged tropospheric impacts of surface methanol emissions (312 Tg/year) were −2.8% for OH, 4.8% for HO<sub>2</sub>, 8.7% for CH<sub>2</sub>O, and 1.7% for O<sub>3</sub>. Smaller surface emissions of methanol (104 Tg/year) had a smaller globally averaged tropospheric impact of −1.0% for OH, 1.7% for HO<sub>2</sub>, 3.2% for CH<sub>2</sub>O, and 0.6% for O<sub>3</sub>.

[17] Methanol plays a significant role in controlling tropospheric oxidants in the upper troposphere and in the tropical marine boundary layer. However, the uncertainty in surface emission estimates of methanol produce significantly different impacts on tropospheric oxidants. Thus, reducing the uncertainties associated with methanol emissions is essential for the study of tropospheric oxidants.

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