

Supplementary Material

Observational Constraints on the Global Atmospheric Budget of Ethanol

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1 **Biogenic Ethanol Emissions**

2 Laboratory and field measurements suggest that ethanol is produced from fermentative processes
3 in trees in response to a number of environmental stresses including flooding, drought, or high
4 levels of pollutant trace gases (for example, ozone or sulfur dioxide) (Kimmerer and Kozlowski,
5 1982; MacDonald and Kimmerer, 1987). For example, laboratory measurements show enhanced
6 ethanol emissions from flooded trees and grasses over those from non-flooded plants (Holzinger
7 et al., 2000). Field measurements conducted in the Sierra Nevada Mountains show that high
8 levels of ethanol are emitted from ponderosa pine trees (Schade and Goldstein, 2001) and are
9 found to increase after high ozone deposition fluxes (Schade and Goldstein, 2002).
10 Measurements also show that ambient temperature and moisture strongly influence ethanol
11 emissions from ponderosa pine trees (Schade and Goldstein, 2001, 2002). However, since field
12 measurements are scarce, it is not clear whether all green plants emit ethanol by the same
13 mechanism. Furthermore, lack of widespread field measurements makes it difficult to develop
14 models to estimate ethanol emissions on a global scale.

15 Here, we simulate the biogenic ethanol emissions using an approach that combines the
16 procedures of Guenther et al. (2000) and Guenther et al. (2006) with observations reported by
17 Schade and Goldstein (2001,2002). Our emission estimate is meant to provide a first guess about
18 the magnitude, spatial distribution and the potential importance of biogenic ethanol emissions on
19 a global scale. Emissions are calculated as

20 $Emission = EF * \gamma_T * \gamma_{LAI}$,

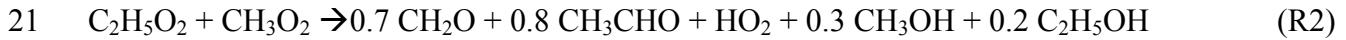
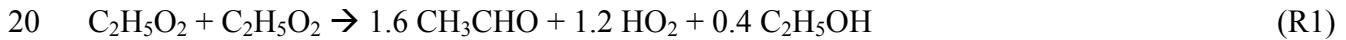
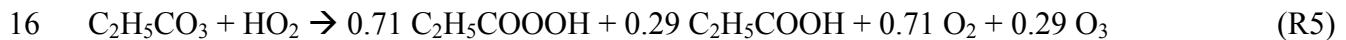
21 where EF is the vegetation-specific emission factor ($mg\ m^{-2}\ hr^{-1}$) for ethanol, γ_T is the
22 temperature dependence for ethanol emission, and γ_{LAI} is the dependence of the emissions on leaf
23 area index. The emission factors (Fig. S1) for ethanol are primarily based on the
24 recommendations of Guenther et al. (2000) except that emissions from coniferous trees are based
25 on measurements at the ponderosa pine plantation in the Sierra Nevada Mountains of California
26 (Schade and Goldstein, 2001, 2002). The minimal set of measurements results in emission
27 factors that are highly uncertain, estimated at a factor of 3. The temperature dependence for
28 ethanol emissions is given by $\gamma_T = \exp[\beta * (Tair - 303)]$, where, β is equal to 0.13 (Schade and
29 Goldstein, 2001) and $Tair$ is air temperature. The dependence of emissions on leaf area index is

1 given by $\gamma_{LAI} = 0.49 * LAI_c / [(1+0.2* LAI_c^2)^{0.5}]$ (Guenther et al., 2006) where LAI_c is the
 2 monthly mean leaf area index derived from MODIS satellite measurements for 2003. The
 3 dependence of ethanol emissions on root flooding or plant stress is not considered here. With the
 4 availability of more information, the calculation of biogenic ethanol emissions has recently been
 5 revised to include the dependence on light and root flooding in MEGANv2.1 (Millet et al.,
 6 2009).

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8 **Production of Ethanol from Propanal**

9 Ethanol is produced when an ethyl peroxy radical ($C_2H_5O_2$) reacts with itself or with other
 10 organic peroxy radicals under low NO_x conditions (R1 and R2 in the main text, repeated below).
 11 Besides ethane, propanal (C_2H_5CHO) and peroxy propionic nitrate (PPN) provide additional
 12 sources of ethyl peroxy radicals in the atmosphere. Ethanol can be produced from propanal by
 13 the following sequence of reactions in the atmosphere.

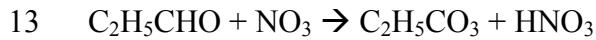
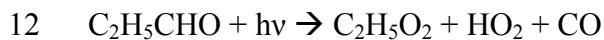


22 The ethanol production rate from the above sequence of chemical reactions is given by
 23 $P(C_2H_5OH) = 0.2 * k_2 [C_2H_5O_2][CH_3O_2]$. The C_2H_5OH production from the self-reaction is two
 24 orders of magnitude smaller and therefore negligible. Since $C_2H_5O_2$ and $C_2H_5CO_3$ are short-lived
 25 radicals, we assume their concentrations to be at steady state. The ethanol production rate is then
 26 given by $P(C_2H_5OH) = 0.2 \times k_3 \times f \times [C_2H_5CHO][OH]$, where

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$$f = \frac{k_2 [CH_3O_2]}{k_4 [CH_3O_2] + k_5 [HO_2] + k_6 [NO]} \times \frac{0.7k_4 [CH_3O_2] + k_6 [NO]}{k_2 [CH_3O_2] + k_7 [NO] + k_8 [HO_2]}$$

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2 We obtain the values of rate constants k_3 , k_4 , k_5 , and k_6 from the Master Chemical Mechanism
3 (<http://mcm.leeds.ac.uk/MCM>), and k_2 , k_7 , and k_8 from Sander et al. (2006). Applying the rate
4 constants at 298 K for average atmospheric conditions with $[CH_3O_2] = [HO_2] = 1 \times 10^8$
5 molecules cm^{-3} and $[NO] = 2.5 \times 10^8$ molecules cm^{-3} to estimate a value of $f = 0.005$. Applying a
6 mean OH concentration (Spivakovsky et al., 2000) of 1.0×10^6 molecules cm^{-3} , mean
7 background tropospheric C_2H_5CHO concentration of 9.8×10^8 molecules cm^{-3} (measured off the
8 coast of Asia), and $k_3 = 1.9 \times 10^{-11}$ at 298 K, yields an estimated ethanol source of up to 0.1 pptv
9 day^{-1} equivalent to a global source of approximately 0.3 Tg yr^{-1} .

10 Additionally, propanal can photolyze and react with NO_3 to provide another source of ethyl
11 peroxy radical which can then produce ethanol via R2.



15 Including these reactions in the above mechanism adds up to 0.1 pptv day^{-1} to the ethanol source
16 from propanal.

17 We note, however, that our calculation depends on the observed value of propanal, which is
18 difficult to measure accurately at low free tropospheric concentrations.

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1 Figure S1. Global biogenic emission factors for ethanol at 1° latitude x 1° longitude resolution in
2 units of $\mu\text{g m}^{-2} \text{ h}^{-1}$.

