Supplementary Material

Observational Constraints on the Global Atmospheric Budget of Ethanol

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Biogenic Ethanol Emissions

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

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

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

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

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

Production of Ethanol from Propanal

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

$C_2H_5CHO + OH + (O_2) \rightarrow C_2H_5CO_3 + H_2O$ (R3)

$C_2H_5CO_3 + CH_3O_2 \rightarrow 0.7\ C_2H_5O_2 + 0.3\ C_2H_5COOH + 0.7\ CO_2 + 0.7\ HO_2 + O_2 + CH_2O$ (R4)

$C_2H_5CO_3 + HO_2 \rightarrow 0.71\ C_2H_5COOOH + 0.29\ C_2H_5COOH + 0.71\ O_2 + 0.29\ O_3$ (R5)

$C_2H_5CO_3 + NO\ (+O_2) \rightarrow C_2H_5O_2 + NO_2 + CO_2$ (R6)

$C_2H_5O_2 + NO \rightarrow CH_3CHO + HO_2 + NO_2$ (R7)

$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$ (R8)

$C_2H_5O_2 + C_2H_5O_2 \rightarrow 1.6\ CH_3CHO + 1.2\ HO_2 + 0.4\ C_2H_5OH$ (R1)

$C_2H_5O_2 + CH_3O_2 \rightarrow 0.7\ CH_2O + 0.8\ CH_3CHO + HO_2 + 0.3\ CH_3OH + 0.2\ C_2H_5OH$ (R2)

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

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

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

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

$C_2H_5CHO + h\nu \rightarrow C_2H_5O_2 + HO_2 + CO$

$C_2H_5CHO + NO_3 \rightarrow C_2H_5CO_3 + HNO_3$

$C_2H_5CO_3 + NO_3 \rightarrow C_2H_5O_2 + NO_2$

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

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

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Figure S1. Global biogenic emission factors for ethanol at 1º latitude x 1º longitude resolution in units of µg m^{-2} h^{-1}.