Atmos. Chem. Phys. Discuss., 10, 925–945, 2010
www.atmos-chem-phys-discuss.net/10/925/2010/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Observational constraints on the global atmospheric budget of ethanol

V. Naik[1,2,*], A. M. Fiore[3], L. W. Horowitz[3], H. B. Singh[4], C. Wiedinmyer[5], A. Guenther[5], J. A. de Gouw[6,7], D. B. Millet[8], P. D. Goldan[6,7], W. C. Kuster[6], and A. Goldstein[9]

[1]Woodrow Wilson School, Princeton University, NJ, USA
[2]Program in Atmospheric and Oceanic Sciences, Princeton University, NJ, USA
[3]Geophysical Fluid Dynamics Laboratory, NOAA, Princeton, NJ, USA
[4]NASA AMES, Moffett Field, CA, USA
[5]NCAR, Boulder, CO, USA
[6]NOAA Earth System Research Laboratory, Boulder, CO, USA
[7]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[8]Department of Soil, Water and Climate, University of Minnesota, St. Paul, MN, USA
[9]University of California at Berkeley, Department of Environmental Science, Policy and Management, CA, USA

*now at: High Performance Technologies Inc./Geophysical Fluid Dynamics Laboratory, NOAA, Princeton, NJ, USA

Received: 20 December 2009 – Accepted: 29 December 2009 – Published: 18 January 2010

Correspondence to: V. Naik (vaishali.naik@noaa.gov)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Energy security and climate change concerns have led to the promotion of biomass-derived ethanol, an oxygenated volatile organic compound (OVOC), as a substitute for fossil fuels. Although ethanol is ubiquitous in the troposphere, our knowledge of its current atmospheric budget and distribution is limited. Here, for the first time we use a global chemical transport model in conjunction with atmospheric observations to place constraints on the ethanol budget, noting that additional measurements of ethanol (and its precursors) are still needed to enhance confidence in our estimated budget. Global sources of ethanol in the model include 5.0 Tg yr^{-1} from industrial sources and biofuels, 9.2 Tg yr^{-1} from terrestrial plants, ~0.5 Tg yr^{-1} from biomass burning, and 0.05 Tg yr^{-1} from atmospheric reactions of the ethyl peroxide radical ($C_2H_5O_2$) with itself and with the methyl peroxide radical (CH_3O_2). The resulting atmospheric lifetime of ethanol in the model is 2.8 days. Gas-phase oxidation by hydroxyl radical (OH) is the primary global sink of ethanol in the model (65%), followed by dry deposition to land (25%), and wet deposition (10%). Over continental areas, ethanol concentrations predominantly reflect direct anthropogenic and biogenic emission sources. Uncertainty in the biogenic ethanol emissions estimated at a factor of three may contribute to the 50% model underestimate of observations in the North American boundary layer. Furthermore, current levels of ethanol measured in remote atmospheres are an order of magnitude larger than those explained by surface sources or by in-situ atmospheric production from observed precursor hydrocarbons in the model, suggesting a major gap in understanding. Stronger constraints on the budget and distribution of ethanol and other VOCs are a critical step towards assessing the impacts of increasing use of ethanol as a fuel.

1 Introduction

The use of bio-ethanol (ethanol derived from biomass) is currently being promoted as a renewable fuel that will alleviate dependence on fossil fuels and combat global warming. Future increases in ethanol emissions may impact the oxidizing capacity and the ozone-forming potential of the atmosphere (Singh et al., 2001). High levels of ethanol have been measured in the boundary layer in urban (ranging from 0.4 to 240 ppbv) (Grosjean et al., 1998; Nguyen et al., 2001; Millet et al., 2005), rural (0.04–0.4 ppbv) (Millet et al., 2004, 2006), and remote (0.02–0.2 ppbv) (Singh et al., 2001) atmospheres. While ethanol-gasoline blended fuels have been advocated for reducing carbon monoxide emissions (Poulopoulos et al., 2001), their combustion also increases ambient levels of acetaldehyde and peroxyacetyl nitrate (PAN) (Tanner et al., 1988; Knapp et al., 1998; Jacobson, 2007), both of which are toxic and contribute to ozone pollution. Ethanol may also act as a precursor to secondary aerosols (Blando and Turpin, 2000). A robust understanding of regional and global budgets of ethanol is necessary to evaluate the air quality and climate impacts of projected future increases in ethanol emissions.

A preliminary analysis of the global ethanol sources based on aircraft measurements in March–April 2001 over the North Pacific off the coast of Asia suggests that biogenic emissions (calculated as a residual after subtracting other sources from the total estimated global ethanol source) are the largest contributors to ethanol abundances, followed by equal contributions from anthropogenic emissions, biomass burning, and atmospheric production (Singh et al., 2004) (Table 1). In contrast, measurements off the coast of New England in July–August 2002 suggest that the ethanol source is largely anthropogenic with a small biogenic source but no secondary source from atmospheric production (de Gouw et al., 2005). These studies highlight uncertainties in our understanding of the contribution of each source of ethanol to its global atmospheric distribution. Here we apply a global model in an attempt to synthesize and interpret available observations of ethanol from several regions around the globe.

2 Model and experiments

We simulate the global atmospheric distribution of ethanol accounting for its estimated sources and sinks in the MOZART-4 chemical transport model (Emmons et al., 2009). Meteorological fields are from the NCEP Global Forecast System (GFS) for July 2003 to December 2004 at a horizontal resolution of 1.9° latitude × 1.9° longitude with 64 vertical levels; the first six months of the simulations are used for model spin-up and results are analyzed for the final year. A previous simulation of MOZART-4 with a similar configuration was evaluated with aircraft measurements of ozone and its precursors over the Northeastern United States in summer 2004 during the Intercontinental Chemical Transport Experiment – North America (INTEX-NA) and was found to resolve boundary layer ventilation as indicated by the model skill at capturing the observed campaign-mean vertical profiles of carbon monoxide, ethane, and other hydrocarbons (Horowitz et al., 2007). In the BASE simulation, we use the POET emission inventory for the year 2000, which includes anthropogenic ethanol emissions of 5.0 Tg yr^{-1} of which 3.2 Tg yr^{-1} come from industrial sources and 1.8 Tg yr^{-1} from biofuels (biomass-derived fuels used for transportation) globally (Olivier et al., 2003). We updated the spatial distribution of these emission estimates by first dividing the world into 10 regions and calculating the mean ethanol production in each region based on the country-wise ethanol production statistics provided in the Renewable fuels Association Ethanol Industry Outlook (2006). We then scaled the POET emissions for each region with respect to the regional production assuming that 10% of the ethanol produced is emitted into the atmosphere (Fig. 1a and 1b). We directly simulate the spatial and temporal distribution of biogenic emissions as a function of vegetation-specific emission factors, temperature, and leaf area index, following the approach described by Guenther et al. (2000, 2006):

$$\text{Emission} = \text{EF} \times \gamma_T \times \gamma_{\text{LAI}} \quad (1)$$

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 (see supplementary information: http://www.atmos-chem-phys-discuss.net/10/925/2010/acpd-10-925-2010-supplement.pdf). We calculate monthly mean emissions offline using average emission factors, leaf area index and hourly air temperatures, and apply them in the model to obtain an annual global biogenic source of 9.2 Tg yr^{-1} shown in Fig. 1c. This estimate is uncertain by more than a factor of three as the emission factors are based on measurements in one ecosystem applied globally (see supplementary information http://www.atmos-chem-phys-discuss.net/10/925/2010/acpd-10-925-2010-supplement.pdf). Biomass burning emissions of 0.5 Tg yr^{-1} are also from the POET inventory (Fig. 1d) except over North America during summer 2004 where we use a daily emission inventory (Turquety et al., 2007). Biomass burning ethanol emissions in both inventories are obtained by applying ethanol emission ratios with respect to carbon monoxide for combustion of different types of biomass (Andreae and Merlet, 2001). We include in our BASE simulation tracers of ethanol tagged by each of the four emissions sources (industrial, biofuel, biogenic and biomass burning).

Atmospheric production of ethanol occurs via reactions of the ethyl peroxide radical ($C_2H_5O_2$; produced from oxidation of ethane by OH) with other organic peroxy radicals under relatively low NO_x (=NO+NO_2) conditions. Previous work estimated this secondary source of ethanol by scaling the global atmospheric source of methanol based on the atmospheric abundances and lifetimes of methane and ethane, precursors to methanol and ethanol, respectively (Singh et al., 2004). We improve upon this earlier methodology by explicitly simulating the atmospheric chemistry of ethanol including the self reaction of $C_2H_5O_2$ Reaction (R1) and its reaction with the most abundant organic peroxy radical, methyl peroxide (CH_3O_2) Reaction (R2):

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

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

We use the recommended kinetic data in the literature for Reactions (R1) (Sander et al., 2006) and (R2) (Villenave and Lesclaux, 1996) and the ethanol yields are as

suggested by Madronich and Calvert (1990). About 99% of the atmospheric source of ethanol in the model is from Reaction (R2), which primarily occurs in the lower (600 hPa to surface) tropical marine troposphere. Together, these reactions provide a secondary ethanol source of 0.056 Tg yr^{-1} in the model, accounting for less than 1% of the total source of ethanol.

Atmospheric sinks for ethanol in the model include gas-phase oxidation by the hydroxyl radical (OH), dry deposition, and wet scavenging. We apply the OH-oxidation reaction rate constant $k=6.9\times10^{-12}\exp[-230/T]$ recommended by Sander et al. (2002) with an uncertainty of ~20% at a temperature of 298 K. Gas phase oxidation accounts for about 65% of the atmospheric loss of ethanol (Table 1). Because of its capacity to form strong hydrogen bonds, ethanol is highly soluble in water and can therefore be removed by precipitation. Wet deposition is calculated using the temperature-dependent effective Henry's Law coefficient which is taken to be $H=(1.94\pm0.13)\times10^{2}\exp[(6274\pm241.6)(1/T-1/298)]$ based on a compilation of measurements of the gas-liquid partition coefficient for ethanol (Warneck, 2006). In the absence of information on the dry deposition velocity of ethanol, we assume its deposition velocity is the same as that for methyl hydroperoxide (global mean velocity over land of 0.13 cm s^{-1}) and because its water-solubility is similar to that of methanol, we apply a deposition velocity over oceans equal to that of methanol (global mean velocity of 0.08 cm s^{-1}) (Jacob et al., 2005). Dry deposition and wet scavenging account for 25%, and 10% of the total global loss, respectively.

3 Results and discussion

The BASE simulation yields a global mean ethanol burden of 0.1 Tg and a mean atmospheric lifetime of 2.8 days (Table 1). The global annual mean boundary layer (0–2 km) concentration of ethanol in the model is 33 pptv. Our estimate of the global source of ethanol (15 Tg yr^{-1}) is within the previously estimated range (8–17 Tg yr^{-1}) (Singh et al., 2004). Similar to the previous source estimate, biogenic emissions account for

the largest fraction of emissions (63%) in our inventory; however, we estimate larger contributions from anthropogenic sources including biofuels (34%), and smaller contributions from biomass burning (3%) and atmospheric production (<1%) (Table 1). High ethanol concentrations (200–1600 pptv) are simulated (Fig. 2) over regions with high emissions from vegetation (North and South America, Africa) and from anthropogenic sources (North and South America, Europe, Asia). Concentrations typically decrease by a factor of 5–10 from the surface to mid troposphere, reflecting the importance of surface sources and the short lifetime of ethanol. The simulated ethanol concentration over the remote oceans is less than 10 pptv with little vertical gradient.

Large-scale aircraft campaigns and field experiments conducted over the last decade have contributed to our understanding of the atmospheric distribution of OVOCs, including ethanol. Typical urban mean ethanol concentrations of 2–3 ppbv (Pittsburgh and Granite Bay) (Millet et al., 2005) are 1–2 orders of magnitude higher than the 0.05–0.1 ppb measured in rural (Chebogue Point and Trinidad Head) (Millet et al., 2004, 2006) and remote regions (remote Pacific Ocean) (Singh et al., 2001). To assess the degree of consistency between atmospheric measurements and our understanding of the sources and sinks of ethanol, we compare the ethanol concentrations from our BASE simulation with mean observed values below 2 km from four aircraft field campaigns (Singh et al., 2001, 2004, 2006, 2009), two ship-based surface measurement campaigns (de Gouw et al., 2005; Warneke et al., 2005), and four site-specific ground measurement stations (Millet et al., 2004, 2005, 2006) (Fig. 3). These ethanol measurements are mainly limited to the North American region, with the exception of two aircraft campaigns. We focus mostly on large-scale aircraft measurements as our global-scale model is not expected to resolve urban airsheds and these provide greater spatial coverage, sampling downwind of Asia and over the remote southern Pacific in addition to North America. The BASE simulation consistently overestimates the ship measurements; our tracers tagged by ethanol sources indicate that industrial emissions are the primary source of ethanol (~70%) off the coast of the Northeastern US, suggesting that surface industrial emissions in the model are probably too high

upwind of the measurement cruise track. The BASE simulation also overestimates surface ethanol concentrations measured at coastal sites (Trinidad Head, Chebogue Point) while underestimating values measured in areas influenced by urban emissions, except in Pittsburgh during winter. Finally, the simulation consistently underestimates aircraft observations in the boundary layer and this underestimate worsens moving from North America to remote oceanic regions (off the coast of Asia and over the South Pacific ocean). The model underestimate of aircraft measurements over North America is not necessarily inconsistent with the overestimate of ship observations along the Northeastern US coast. The aircraft flight tracks cover a much larger area than the ship tracks. In contrast to the ship data, the tagged tracers indicate that industrial and biogenic sources contribute equally to the ethanol concentrations sampled by the aircraft in the lower troposphere (below 2 km) over North America.

We compare the mean vertical distribution of ethanol from the BASE simulation with observed values from the four aircraft campaigns (Fig. 4). Observations and simulated concentrations are averaged in 1 km bins onto the horizontal model grid for the ensemble of the data. Observed mean ethanol concentrations decrease by more than a factor of three near the surface (0.37–0.45 pbbv) to 5 km (0.05–0.11 ppbv) over the Eastern United States (INTEX-NA campaign), and over Mexico City and the Gulf of Mexico (INTEX-B campaign). This decrease is not uniform as higher values are observed at altitudes above 5 km, particularly over Mexico City and the Gulf of Mexico because of strong convective influence. Mean ethanol mixing ratios measured downwind of Asia (TRACE-P mission) also decrease with altitude albeit with a small vertical gradient. A small reversed vertical gradient in mean ethanol concentrations is observed over the remote south Pacific region (PEM-Tropics B mission) with higher values at altitudes above 3 km (0.6–0.1 ppbv) than those near the surface (0.05 ppbv). The BASE simulation underestimates observed ethanol at all altitudes over North America and downwind of Asia by more than 50% and this underestimate worsens to over 100% over the remote southern Pacific. The BASE simulation also underestimates ethanol concentrations measured at the high alpine site Jungfraujoch (Switzerland) (Legreid et al.,

2008) by over 100% (data not shown). As noted in the previous section, MOZART-4 adequately resolves boundary layer ventilation, therefore, this underestimate is unique to ethanol, and is thus unlikely to reflect a problem with the model vertical mixing. A possible explanation of the model underestimate of ethanol in the boundary layer could be a model overestimate of OH radical, however, OH is somewhat lower than the OH distribution of Spivakovsky et al. (2000), consistent with the findings of Emmons et al. (2009). Given the short lifetime of ethanol, additional continental emissions fail to eliminate the strong underestimate over the remote regions. The lack of an observed vertical gradient in ethanol concentrations over the ocean also precludes an oceanic source; reducing the oceanic sink by decreasing the deposition velocity over oceans (0.28 to 0.08 cm/s) does not explain the discrepancy. This inability to simulate high observed mixing ratios in the free troposphere has been shown to occur for acetaldehyde in another global chemical transport model (Millet et al., 2009), indicating a general inconsistency between the observations and our understanding of the budget of short-lived volatile organic compounds.

Current chemistry-transport models are unable to correctly simulate the relatively high OVOC concentrations, particularly aldehydes and alcohols, observed over the remote oceanic regions (Singh et al., 2001; Lewis et al., 2005). While measurements of OVOCs under clean-air conditions in the remote free troposphere are challenging and could be impacted by artifacts (Apel et al., 2003; Northway et al., 2004), it has been hypothesized that a large diffuse source of OVOCs exists in remote regions that is presently missing in the models (Singh et al., 2001). A potential source is the presence of other hydrocarbons that can oxidize to form OVOCs (Singh et al., 2001; Lewis et al., 2005). We conduct an additional MOZART-4 simulation, SYNEOH, with a uniform source of 10 pptv d^{-1} ethanol distributed throughout the troposphere (29.3 Tg yr^{-1}) in an attempt to constrain the magnitude of secondary production that would be necessary to match the observations in remote regions. The total source of ethanol in the SYNEOH simulation is three times that in the BASE simulation, while the burden is increased by a factor of six. Additional ethanol at higher altitudes where the oxidative

loss is slow leads to an increased ethanol lifetime (a factor of two higher than that in the BASE simulation). The SYNEOH simulation does not eliminate the disagreement with the North American ship and ground measurements but improves the large mismatch with aircraft measurements, to a −15% bias over the remote southern Pacific, and a −25% bias downwind of Asia (Fig. 3). Likewise, vertical distribution of ethanol in SYNEOH agrees better with those observed over the remote southern Pacific and downwind of Asia (Fig. 4). This could indicate that direct emission of ethanol is the dominant source of ethanol over populated continental areas, while secondary production is the major source in remote regions where NO_x is sufficiently low to allow ethanol production.

OVOCs, including propanal (C_2H_5CHO) and peroxy propionic nitrate (PPN), are potential precursors of ethanol in the atmosphere. As measured abundances of propanal are approximately an order of magnitude larger than PPN (Singh et al., 2004), we use propanal as an example OVOC to estimate an additional secondary source of ethanol. Propanal oxidizes to produce the peroxy propionic radical ($C_2H_5CO_3$), which can then react with CH_3O_2, other organic peroxy organic radicals, HO_2, or NO depending on the relative concentration of these species (see supplementary information http://www.atmos-chem-phys-discuss.net/10/925/2010/acpd-10-925-2010-supplement.pdf). Reaction of $C_2H_5CO_3$ with CH_3O_2 produces the ethyl peroxy radical that can then react to produce ethanol (via R2). Assuming a mean background tropospheric propanal concentration of 9.8×10^8 molecules cm^{-3} (measured off the coast of Asia by Singh et al., 2004), we estimate that ethanol source from propanal is roughly 0.1 pptv d^{-1} or 0.3 Tg yr^{-1} (see supplementary information http://www.atmos-chem-phys-discuss.net/10/925/2010/acpd-10-925-2010-supplement.pdf). Including additional sources of ethanol from propanal photolysis and reaction with NO_3 add only a small amount (up to 0.1 pptv d^{-1}) to the ethanol source from propanal. Thus, secondary atmospheric production of ethanol from measured precursor hydrocarbons is unlikely to explain the ethanol concentrations observed in remote environments. Further research is therefore needed to fully explore the sources of atmospheric ethanol including the possibility

of sources from aqueous-phase chemistry.

4 Conclusions

Ethanol plays an important role in global tropospheric chemistry; oxidation of ethanol is an important source of acetaldehyde, a highly toxic pollutant and an OVOC for which the budget remains poorly quantified (Singh et al., 2001, 2004). Better constraints on the present-day ethanol budget are essential for evaluating the impacts of future increases in the use of biomass-derived ethanol. We have used available observations in conjunction with a global CTM to examine the global budget of ethanol. In comparison with the previously estimated range of 8–17 Tg yr^{-1} (Singh et al., 2004) for the global source of ethanol, our best estimate is 15.0 Tg yr^{-1} including 5.0 Tg yr^{-1} from industrial sources and biofuels, 9.2 Tg yr^{-1} from terrestrial plants, ∼0.5 Tg yr^{-1} from biomass burning, and 0.05 Tg yr^{-1} from atmospheric in-situ production. Our model yields a global mean atmospheric lifetime for ethanol of 2.8 d, with 65% of the total loss resulting from gas-phase oxidation by OH, 25% from dry deposition to land, and 10% from wet deposition. Our analysis suggests that while surface emissions of ethanol are important for continental areas, neither surface sources nor atmospheric production from measured precursor hydrocarbons explain the ethanol concentrations measured in remote oceanic regions where simulated ethanol concentration is an order of magnitude too low. Further work is needed to understand the large remote oceanic abundance of ethanol and to better constrain the global ethanol budget and distribution. Specifically, better and wider spatial sampling of atmospheric ethanol and its precursors is needed. Laboratory studies should explore the aqueous-phase production of ethanol. Observation-based estimates of the ethanol deposition velocity are also needed for improved modeling of atmospheric losses of ethanol. Additional direct measurements of biogenic ethanol fluxes from a variety of ecosystems will improve confidence in the estimated biogenic source.

Acknowledgements. We thank Michael Oppenheimer for helpful discussions and Erin Czech

for providing INTEX-B data. We are grateful to Hiram Levy and Song-Miao Fan for reviewing an earlier version of this manuscript. V. Naik was supported by the Carbon Mitigation Initiative (CMI) of the Princeton Environmental Institute at Princeton University (http://cmi.princeton.edu) which is sponsored by BP and Ford, and the visiting scientist program in Atmospheric and Oceanic Sciences at Princeton and NOAA/GFDL.

References

Andreae, M. and Merlet, P.: Emissions of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955–966, 2001.

Apel, E. C., Hills, A., Lueb, R., Zindel, S., Eisele, S., and Riemer, D.: A fast-GC/MS system to measure C_2 to C_4 carbonyls and methanol aboard aircraft, J. Geophys. Res., 108, 8794, doi:10.1029/2002JD003199, 2003.

Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature review of plausibility, Atmos. Environ., 34, 1623–1632, 2000.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: results from the New England Air Quality Study in 2002, J. Geophys. Res., 110, D16305, doi:10.1029/2004JD005623, 2005.

Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J.-F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), Geosci. Model Dev. Discuss., 2, 1157–1213, 2009.

Grosjean, E., Grosjean, D., Gunawardena, R., and Rasmussen, R. A.: Ambient concentrations of ethanol and methyl tert-butyl ether in Porto Alegre, Brazil, Mar 1996–Apr 1997, Environ. Sci. Technol., 32, 736–742, 1998.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., and Fall, R.: Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, Atmos. Environ., 34, 2205–2230, 2000.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates

of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, 2006, http://www.atmos-chem-phys.net/6/3181/2006/.

Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J.-F.: Observational constraints on the chemistry of isoprene nitrates over the Eastern United States, J. Geophys. Res., 112, D12S08, doi:10.1029/2006JD007747, 2007.

Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., and Singh, H. B.: Global budget of methanol: constraints from atmospheric observations, J. Geophys. Res., 110, D08303, doi:10.1029/2004JD005172, 2005.

Jacobson, M. Z.: Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States, Environ. Sci. Technol., 41(11), 4150–4157. doi:10.1021/es062085v, 2007.

Knapp, K. T., Stump, F. D., and Tejada, S. B.: Effect of ethanol fuel on the emissions of vehicles over a wide range of temperatures, J. Air. Waste. Manage., 48, 646–653, 1998.

Legreid, G., Folini, D., Staehelin, J., Lööv, J. B., Steinbacher, M., and Reimann, S.: Measurements of organic trace gases including oxygenated volatile organic compounds at the high alpine site Jungfraujoch (Switzerland): seasonal variation and source allocations, J. Geophys. Res., 113, D05307, doi:10.1029/2007JD008653, 2008.

Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Stanton, J., Read, K. A., and Pilling, M. J.: Sources and sinks of acetone, methanol, and acetaldehyde in North Atlantic marine air, Atmos. Chem. Phys., 5, 1963–1974, 2005, http://www.atmos-chem-phys.net/5/1963/2005/.

Madronich, S. and Calvert, J. G.: Permutation reactions of organic peroxy radicals in the troposphere, J. Geophys. Res., 95, 5697–5715, 1990.

Millet, D. B., Goldstein, A. H., Allan, J. D., Bates, T. S., Boudries, H., Bower, K. N., Coe, H., Ma, Y., McKay, M., Quinn, P. K., Sullivan, A., Weber, R. J., and Worsnop, D. R.: VOC measurements at Trinidad Head, CA during ITCT 2K2: analysis of sources, atmospheric composition and aerosol residence times, J. Geophys. Res., 109, D23S16, doi:10.1029/2003JD004026, 2004.

Millet, D. B., Donahue, N. M., Pandis, S. N., Polidori, A., Stanier, C. O., Turpin, B. J., and Goldstein, A. H.: Atmospheric VOC measurements during the Pittsburgh Air Quality Study: results, interpretation and quantification of primary and secondary contributions, J. Geophys. Res., 110, D07S07, doi:10.1029/2004JD004601, 2005.

Millet, D. B., Goldstein, A. H., Holzinger, R., Williams, B., Allan, J. D., Jimenez, J. L., Worsnop, D. R., Roberts, J. M., White, A. B., Hudman, R. C., Bertschi, I. T., and Stohl, A.: Chemical characteristics of North American surface layer outflow: insights from Chebogue Point, Nova Scotia, J. Geophys. Res., 111, D23S53, doi:10.1029/2006JD007287, 2006.

Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. I., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys. Discuss., 9, 24225–24279, 2009, http://www.atmos-chem-phys-discuss.net/9/24225/2009/.

Nguyen, H. T., Takenaka, N., Bandow, H., Maeda, Y., de Oliva, S. T., Botelho, M. M. F., and Tavares, T. M.: Atmospheric alcohols and aldehydes concentrations measured in Osaka, Japan, and in Sao Paulo, Brazil, Atmos. Environ., 35, 3075–3083, 2001.

Northway, M. J., de Gouw, J. A., Fahey, D. W., Gao, R. S., Warneke, C., Roberts, J. M., and Flocke, F.: Evaluation of the role of heterogeneous oxidation of alkenes in the detection of atmospheric acetaldehyde, Atmos. Environ., 38, 6017–6028, 2004.

Olivier, J., Peters, J., Granier, C., Petron, G., Müller, J. F., and Wallens, S.: Present and future surface emissions of atmospheric compounds, POET report #2, EU project EVK2-1999-00011, 2003.

Poulopoulos, S. G., Samaras, D. P., and Philippopoulos, C. J.: Regulated and unregulated emissions from an internal combustion engine operating on ethanol-containing fuels, Atmos. Environ., 35, 4399–4406, 2001.

Renewable Fuels Association: Ethanol Industry Outlook, http://www.ethanolrfa.org/objects/pdf/outlook/outlook_2006.pdf, 2006.

Sander, S. P., Finlayson-Pitts, B. J., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgat, G. K., Orkin, V. L., and Ravishankara, A. R.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14, JPL Publication 02-25, Jet Propulsion Laboratory, Pasadena, 2002.

Sander, S. P., Finlayson-Pitts, B. J., Friedl, R. R., Golden, D. M., Huie, R. E., Keller-Rudek, H., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgat, G. K., Orkin, V. L., Ravishankara, A. R., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, 2006.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., and Snow, J.: Evidence from

the Pacific troposphere for large global sources of oxygenated organic compounds, Nature, 410, 1078–1081, 2001.

Singh, H. B., Salas, L., Chatfield, R., Czech, E., Fried, A., Walega, J., Evans, M., Field, B., Jacob, D., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J., Avery, M., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements of the Pacific during TRACE-P, J. Geophys. Res., 109, D15S07, doi:10.1029/2003JD003883, 2004.

Singh, H. B., Brune, W. H., Crawford, J. H., Jacob, D. J., and Russell, P. B.: Overview of the summer 2004 Intercontinental Chemical Transport Experiment–North America (INTEX-A), J. Geophys. Res., 111, D24S01, doi:10.1029/2006JD007905, 2006.

Singh, H. B., Brune, W. H., Crawford, J. H., Flocke, F., and Jacob, D. J.: Chemistry and transport of pollution over the Gulf of Mexico and the Pacific: spring 2006 INTEX-B campaign overview and first results, Atmos. Chem. Phys., 9, 2301–2318, 2009, http://www.atmos-chem-phys.net/9/2301/2009/.

Tanner, R. L., Miguel, A. H., De Andrade, J. B., Gaffney, J. S., and Streit, G. E.: Atmospheric chemistry of aldehydes: enhanced peroxyacetyl nitrate formation from ethanol-fueled vehicular emissions, Environ. Sci. Technol., 22, 1026–1034, 1988.

Turquety, S., Logan, J. A., Jacob, D. J., Hudman, R. C., Leung, F. Y., Heald, C. L., Yantosca, R. M., Wu, S., Emmons, L. K., Edwards, D. P., and Sachse, G. W.: Inventory of boreal fire emissions for North America in 2004: the importance of peat burning and pyro-convective injection, J. Geophys. Res., 112, D12S03, doi:10.1029/2006JD007281, 2007.

Villenave, E. and Lesclaux, R.: Kinetics of the cross reactions of CH_3O_2 and $C_2H_5O_2$ radicals with selected peroxy radicals, J. Phys. Chem., 34, 14372–14382, 1996.

Warneck, P.: A note on the temperature dependence of Henry's Law coefficients for methanol and ethanol, Atmos. Environ., 40, 7146–7151, 2006.

Warneke, C., Kato, S., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Shao, M., Lovejoy, E. R., Fall, R., and Fehsenfeld, F. C.: Online volatile organic compound measurements using a newly developed proton-transfer ion-trap mass spectrometry instrument during New England Air Quality Study – Intercontinental Transport and Chemical Transformation 2004: performace, intercomparison, and compound identification, Environ. Sci. Technol., 39, 5390–5397, 2005.

Table 1. Global atmospheric budget of ethanol using MOZART-4. Numbers in parentheses show the percentage contribution of each source/sink to the total source/sink of ethanol.

	BASE	SYNEOH	Singh et al. (2004)
Sources (Tg yr^{-1})			
Industrial	3.2 (21%)	3.2 (7%)	2 (16.6%)
Biofuel	1.8 (12%)	1.8 (4%)	
Biogenic	9.2 (63%)	9.2 (21%)	6 (50%)
Biomass Burning	0.47 (3%)	0.47 (1%)	2 (16.6%)
Atmospheric in-situ production	0.056 (<1%)	0.056 (<1%)	2 (16.6%)
Missing Source		29.3 (66%)	
Total Source	14.7	44.0	12.0
Sinks (Tg yr^{-1})			
Oxidation by OH	9.6 (65%)	33.5 (77%)	
Wet Deposition	1.4 (10%)	5.0 (11%)	
Dry Deposition	3.7 (25%)	5.2 (12%)	
Total Sink	14.7	44.0	
Global Burden (Tg)	0.11	0.68	0.12[a]
Atmospheric Lifetime (d)	2.8	5.7	~3.5

[a] Estimated as total source multiplied by the atmospheric lifetime.

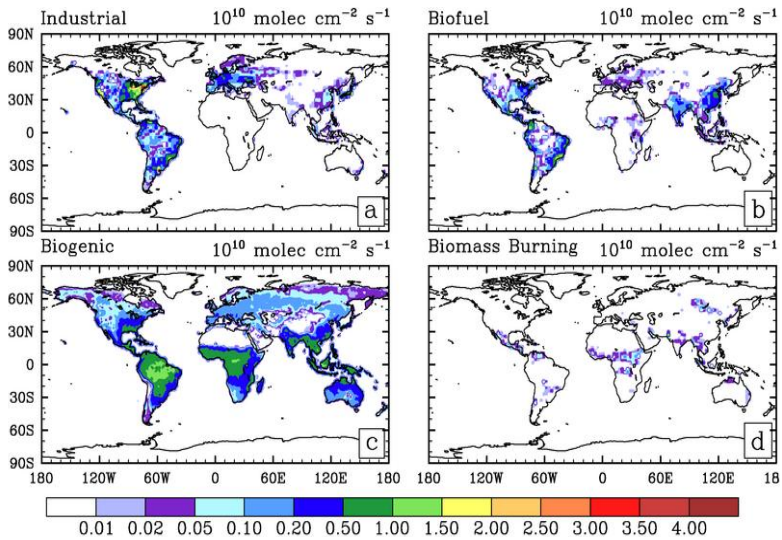

Fig. 1. Annual average emissions (in units of 10^{10} molecules cm^{-2} s^{-1}) of ethanol from different sources: **(a)** industrial, **(b)** biofuels, **(c)** biogenic, and **(d)** biomass burning.

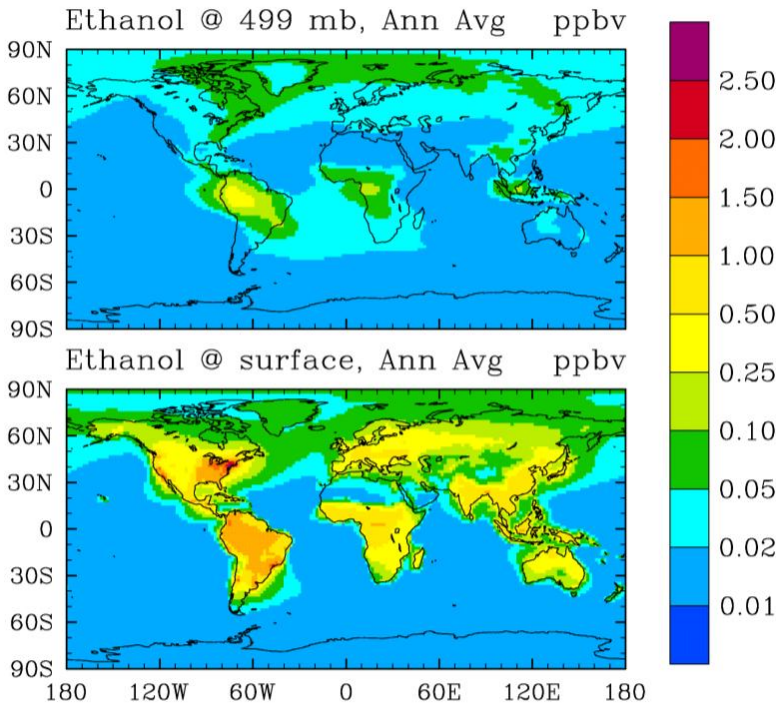

Fig. 2. Simulated annual mean concentration of ethanol near the surface and at 500 mb.

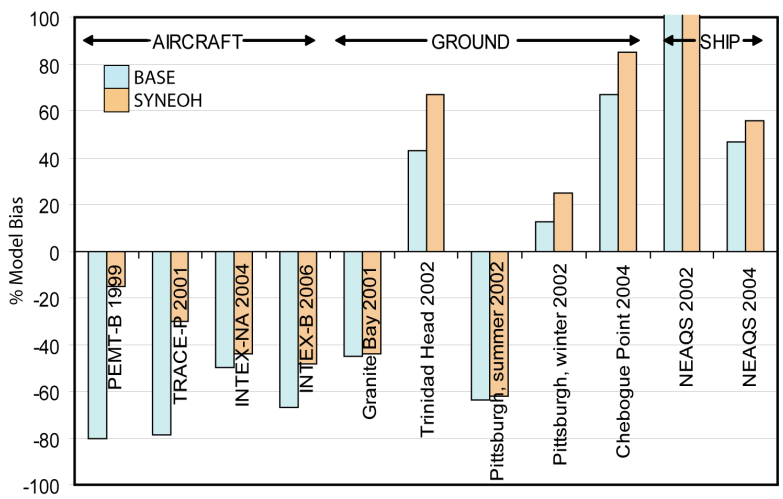

Fig. 3. Comparison of simulated ethanol concentrations with observations from four aircraft field campaigns (below 2 km; PEMT-B over the South Pacific in February–March 1999, TRACE-P downwind of Asia over the North Pacific in March–April 2001, INTEX-NA over the Eastern United States in July–August 2004 and INTEX-B over Mexico City and the Gulf of Mexico in March 2006), four site-specific ground measurements (Granite Bay, California in July–September 2001, Trinidad Head, California in April–May 2002, Pittsburgh, Pennsylvania in July–August and January–February 2002, and Chebogue Point, Nova Scotia in July–August 2004), and two ship-based surface measurements (NEAQS along the Northeastern US coast in July–August 2002 and 2004). Observations are averaged onto the horizontal model grid with a resolution of 1.9°×1.9°. Surface model concentrations are used for comparison with ship-based and ground measurements, while model concentrations are averaged vertically below 2 km for comparison with aircraft measurements.

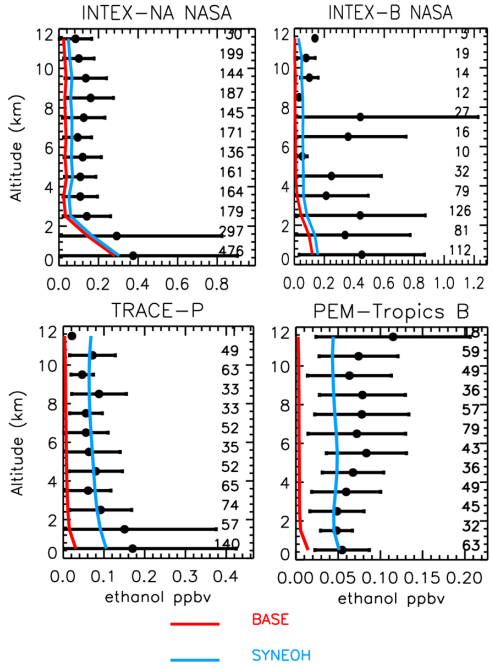

Fig. 4. Mean model simulated and observed vertical profile of ethanol from four aircraft field campaigns (PEMT-B over the South Pacific in February–March 1999, TRACE-P downwind of Asia over the North Pacific in March–April 2001, INTEX-NA over the Eastern United States in July–August 2004 and INTEX-B over Mexico City and the Gulf of Mexico in March 2006; black, standard deviations in horizontal lines). Observations and modeled values are averaged in 1 km bins onto the horizontal model grid. Note the different x-axis scales in each panel.