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An estimate of the global budget and distribution of ethanol using a global 3-D atmospheric chemistry transport model STOCHEM-CRI

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Abstract

The atmospheric global budget and distribution of ethanol have been investigated using a global three-dimensional chemistry transport model, STOCHEM-CRI. Ethanol, a precursor to acetaldehyde and peroxy acetyl nitrate (PAN), is found throughout the troposphere with a global burden of 0.024 to 0.25 Tg. The atmospheric lifetime of ethanol is found to be 1.1 to 2.8 days, which is in excellent agreement with estimates established by previous studies. The main global source of ethanol is from direct emission (99%) and the remainder (1%) being produced via peroxy radical reactions. In terms of removal rates of ethanol in the atmosphere, oxidation by hydroxyl radical (OH) accounted for 51%, dry deposition 8% and wet deposition accounted for 41%. Globally there are significant concentrations of ethanol over equatorial Africa, North America and parts of Asia with considerably higher concentrations modelled over Saudi Arabia and Eastern Canada. Through comparison of measured and modelled ethanol data, it is apparent that the underestimation of the source strength of ethanol and the coarse resolution of STOCHEM-CRI model produce the discrepancies between the model and the measured data mostly in urban areas. The increased vegetation and anthropogenic emissions of ethanol leads to an increase in the production of acetaldehyde (by up to 90%) and peroxyacetyl nitrate (by up to 10%) which disrupts the NO_x-ozone balance, promoting ozone production (by up to 1.4%) in the equatorial regions.

Keywords: Global burden; atmospheric lifetime; chemistry transport model; equatorial region; urban areas

INTRODUCTION

Ethanol (C_2H_5OH) is recognized as a minor biogenic volatile organic compound (BVOC) in the atmosphere, which can act as a precursor to acetaldehyde (CH_3CHO), peroxyacetyl nitrate (PAN), and secondary aerosols (Blando and Turpin, 2000; Millet *et al.*, 2012; Suarez-Bertoa *et al.*, 2015). Thus the changing of ethanol concentrations has the potential to affect air pollution by changing the atmospheric composition and chemistry.

Ethanol is emitted directly to the atmosphere from living plants, decaying plants, anthropogenic production, and biomass burning. The biogenic emissions are supposed to constitute the largest fraction of the global source of ethanol (Kirstine and Galbally, 2012; Millet *et al.*, 2010; Naik *et al.*, 2010; Guenther *et al.*, 2012). The oceans may act either as a sink or as a source of ethanol, but fresh water regions may be net sinks of ethanol (Kirstine and Galbally, 2012; Avery *et al.*, 2016). Ethanol is also emitted anthropogenically because of its recent significant use as the biofuel in the fuel industry (Balat and Balat, 2009; Dunmore *et al.*, 2016). The usage of biofuels has been shown to exhibit higher levels of acetaldehyde within regions with high bio-ethanol and it has been suggested that urban levels could increase by up to 650% when 85% ethanol is incorporated into fuel (Sundvor and López-Aparicio, 2014). Jacobson (2007) showed that the incorporation of 85% ethanol in fuel resulted in the elevated levels of ozone and PAN. Within some areas 100% ethanol is used as a fuel source, such as Brazil where 20% of all vehicles run off pure ethanol (Lee, 2013). Photochemical production is another minor source of ethanol in where they are produced by the reaction of ethyl peroxy radicals ($CH_3CH_2O_2$; mainly produced from oxidation of atmospheric species such as ethane) with itself and other higher organic peroxy radicals (RO_2).

$$CH_3CH_2O_2 + CH_3CH_2O_2 \rightarrow CH_3CH_2OH + CH_3CHO + O_2 \quad (1)$$

$$CH_3CH_2O_2 + R^1O_2 \rightarrow CH_3CH_2OH + R^1CHO + O_2 \quad (2a)$$

$$CH_3CH_2O_2 + R^1O_2 \rightarrow CH_3CH_2CHO + R^1OH + O_2 \quad (2b)$$

The loss due to OH oxidation is the main sink for atmospheric ethanol (Atkinson *et al.*, 2006). The other removal processes including dry deposition and wet removal have been previously estimated to account for 23-35% of the total global sink (Millet *et al.*, 2010; Naik *et al.*, 2010). The overall atmospheric lifetimes for ethanol in respect to the gross oceanic uptake, OH, and deposition are approximately 2-10 days (Atkinson *et al.*, 2006; Naik *et al.*, 2010).

There are large regional differences in the atmospheric ethanol concentrations due to the wide variation in biogenic and anthropogenic contributions (Naik *et al.*, 2010). The increasing use of biofuels globally has made ethanol more important to understand how it affects the atmosphere and what implications this has to human health and also to the climate of the earth. Currently, there is uncertainty in emission literature data for

ethanol, which makes it challenging to model global atmospheric ethanol accurately. In this study, we employ STOCHEM-CRI, a 3-dimensional global chemistry and transport model to evaluate the global budget and the global distribution of tropospheric ethanol after considering the updated emission data adapted from Naik *et al.* (2010) and Kirstine and Galbally (2012). This work provides a good indication of the major issues currently residing within the model and the current estimates of atmospheric ethanol.

MODEL DESCRIPTION

STOCHEM used in this study, is a global 3-dimensional Lagrangian Chemistry Transport Model (CTM) first proposed by Collins *et al.* (1997). The model splits the troposphere into 50,000 constant mass air parcels which works offline, incorporating archived meteorological data to determine the transport of these parcels. The archived data has a resolution of 1.25^{o} longitude by 0.83^{o} latitude with 12 uneven vertical levels and includes information on the following: atmospheric temperature, pressure, wind fields, cloud cover, precipitation and atmospheric boundary layer heights. A detailed description of the vertical coordinate, advection scheme, convection and inter-parcel mixing, and boundary layer used in STOCHEM can be found in Collins *et al.* (1997) with updates described by Derwent *et al.* (2008). The chemical mechanism used in STOCHEM, is the common representative intermediates mechanism version 2 and reduction 5 (CRI v2-R5), referred to as 'STOCHEM-CRI' which is uncoupled from the transport mechanism. The detail of the CRI v2-R5 mechanism is given by Watson *et al.* (2008) with updates highlighted in Jenkin *et al.* (2008) and Utembe *et al.* (2010). In this study, CRI v2-R5 mechanism is further updated which consists of methane and 24 emitted non-methane hydrocarbons using 229 chemical species competing in 529 gas phase reactions and 96 photolytic reactions and gives excellent agreement with the MCM v3.1 over a full range of NO_x levels (Watson *et al.*, 2008; Jenkin *et al.*, 2008). The photolysis rate was calculated explicitly for each air parcel. Ideally the model should perform the calculation for each air parcel for every five minutes to match the gas phase chemistry, but to save computational resources and time, the photolysis rate was calculated at a time resolution of one hour, and then linearly interpolated with respect to time to achieve the five minute resolution values which were used in the chemical integration. The surface emissions (e.g. anthropogenic, biomass burning, ocean, soil, vegetation) data employed in the base case STOCHEM model were obtained from the Precursor of Ozone and their Effects in the Troposphere (POET)

inventory for NMVOCs (Granier *et al.*, 2005). Emissions are mapped 2-dimensionally with a resolution of 5^{o} longitude by 5^{o} latitude monthly. Stratospheric tropospheric exchange has been represented by incorporating the movement of ozone and nitric acid into the highest level of the model using wind field data and ozone fields. Lightning and aircraft emissions are accounted for as a three-dimensional emission and distributed regularly between the convective cloud top height and the surface. Dry deposition is one of the removal processes for atmospheric species which is accounted in the model via gravitation movement process over land or oceans, with Antarctica and sea ice being included as an ocean deposition processes and land ice being a terrestrial dry deposition process. The wet deposition is represented by both convective and dynamic scavenging coefficients which are species specific. The coefficients along with both precipitation rates and scavenging profiles are used to determine loss rates of species in an air parcel via this process. The simulation was conducted with meteorology from 1998 for a period of 24 months with the first 12 allowing the model to spin up. Analysis is performed on the subsequent 12 months of data. The three simulations were performed which were based on the scenario in which the model was run with different global ethanol emission values (Table 1). The dry deposition velocities over land and ocean were considered as 1.6 and 3.0 mm/s, respectively which were used in all simulations. Another simulation was performed using the emission class data by Naik *et al.* (2010), with the inclusion of wet deposition parameters such as, dynamic scavenging of 2.0 cm^{-1} and convective scavenging of 3.9 cm^{-1} determined using Henry's law coefficients (Sander, 2015).

RESULTS AND DISCUSSION

Table 2 shows the global budget of ethanol produced by the STOCHEM-CRI. In the base case (Run 1), the atmospheric sources of ethanol (3.2 Tg/yr) are found to be lower than the studies of Naik *et al.* (2010) and Kirstine and Galbally (2012) since vegetation sources were not included in the model. After adding vegetation emissions and extended anthropogenic emissions in the model (Run 2), the estimated source strength of 14.8 Tg/yr and the contribution of direct emission sources of 99% and photochemical production sources of 1% are found which to lie within previous estimations regarding ethanol emissions (Singh *et al.*, 2004; Naik *et al.*, 2010). The global ethanol emissions determined for Run 3 (41.5 Tg/yr) was found to be much higher than Naik *et al.* (2010) and Singh *et al.* (2004) which is due to the model incorporating a much larger flux value

for vegetation. The atmospheric source of ethanol from peroxy radicals for all of the simulations was calculated to be a very small amount of 0.13 Tg/yr. Previous models have shown large variations of the atmospheric sources of ethanol with estimations of 0.06 Tg/yr (Naik *et al.*, 2010), 0.5 Tg/yr (Kirstine and Galbally, 2012), and 2 Tg/yr (Singh *et al.*, 2004). Larger species are capable of producing peroxy radical species which are currently not being accounted for within the model, resulting in an under-prediction for this value. The lack of kinetic data of the reaction between larger peroxy radicals in the model also underestimate the photochemical production of ethanol.

The global sink of ethanol is dominated by OH oxidation (80-88%), with the remaining contribution from dry deposition. However including wet deposition into STOCHEM model (Run 4), the global sink contributions of ethanol accounted for a much larger dependence on wet deposition with a ratio of 51:8:41 for OH oxidation, dry deposition and wet deposition, respectively. Previous models have reported the respective ratios of the losses by OH oxidation, dry deposition and wet deposition as 65:25:10 (Naik *et al.*, 2010) and 75:21:4 (Kirstine and Galbally, 2012). The higher wet deposition loss of ethanol is found in our model study which may be due to using the overestimated scavenging coefficients in the model. The global burden (0.024 to 0.25 Tg) and lifetime (1.1 to 2.8 days) of ethanol found in this study are well within the model results of Naik *et al.* (2010) and Singh *et al.* (2004) (Table 2). The modelled global burden and lifetime of ethanol decrease substantially when wet deposition is added into the simulation (Run 4), which is likely to be due to wet deposition potentially being a large and strong removal process for ethanol.

Figure 1 shows the global distribution profiles for the average concentration of ethanol for base case during June-July-August (J-J-A) and December-January-February (D-J-F). In D-J-F, there is a higher level of ethanol, up to 300 ppt, over North America and Saudi Arabia (Fig. 1b), likely due to the build-up of anthropogenic pollution in these regions. Comparing with D-J-F, the intensity of ethanol is reduced significantly over North America and Saudi Arabia during J-J-A due to the abundances of OH. The higher concentrations of ethanol (up to 300 ppt) are present over Canada during J-J-A, this could be due to the westerly winds resulting in a small proportion of pollution being transported towards the Atlantic. Compared with D-J-F, the OH lifetimes of ethanol in J-J-A are low near the equator due to the higher oxidation of ethanol by OH (Fig. 1c

and Fig. 1d). The spread of biofuel emissions was shown to be higher over North America, South America, India and South-west Asia (Naik *et al.*, 2010) which were reflected in the higher ethanol levels (up to 80 ppt) over North America, India and South-west Asia. South America, from this model, appears to have low emission levels of ethanol, which is unexpected as Brazil is one of the largest biofuel users after the USA and the abundances of vegetation in tropical rainforests (Balat and Balat, 2009). The absence of vegetation and the strong removal processes by OH concentrations (especially in the summer time, D-J-F) in the base case result in lower ethanol concentrations. After including vegetation emission, increased anthropogenic emissions and biomass burning into the model (Run 2), the ethanol mixing ratios were increased to 500 ppt in North America and Saudi Arabia and 300 ppt in tropical South America and Africa (Fig. 1e and Fig. 1f). The high levels of ethanol present over South America and Africa are likely to be produced via vegetation but also due to a large amount of biomass burning occurring within these regions. The year used for the model is 1998, an El Niño year, which causes intensified precipitation along Equatorial Africa during the rainy season (October-November-December) potentially inducing more stress and anaerobic respiration to occur for vegetation with the region (Konecky *et al.*, 2014).

The zonal plot of ethanol shows their highest levels at 30^{o}N-60^{o}N (up to 100 ppt), likely due to larger anthropogenic emissions and at 15^{o}S-15^{o}N (up to 60 ppt) due to the vegetation and biomass burning activity occurring within this region (Fig. 2). The highest observed altitude (9.2 km) with significant ethanol concentrations (up to 30 ppt) is found at 50^{o}N-60^{o}N during J-J-A and 60^{o}N-90^{o}N during D-J-F. Asian pollution plumes could be contributing towards these levels which rise up into the upper troposphere and transport towards Europe (Stohl *et al.*, 2007). There is less ethanol present at the equator during J-J-A compared with D-J-F, which is likely to be due to OH oxidation dominating as there is a large amount of sunlight within this region which speeds up the reaction.

Figure 3 shows the ethanol observation flight data compilation of Naik *et al.* (2010) along with simulated values produced by STOCHEM-CRI for the INTEX-NA campaign conducted in July to August 2004 over eastern USA, INTEX-B campaign conducted from February to April 2001 over the Gulf of Mexico, TRACE-P campaign

255 conducted in March 2001 over the North Pacific, and PEM-Tropics B campaign
256 conducted in March to April 1999 over the South Pacific. The model for all four
257 simulations exhibits an overall similar trend to the observed data, but the mixing ratios
258 of ethanol in the base case have been under predicted considerably in each case. The
259 vertical profile in Figure 3 shows a significant increase in ethanol when the extended
260 vegetation strength and anthropogenic contribution of ethanol is included (Run 2 and
261 3) which brings an improvement of the model in eastern USA, Gulf of Mexico and
262 South Pacific. Pollution from Asia that flows downward towards the Pacific could be
263 responsible for the higher levels of observed ethanol in North Pacific (Stohl *et al.*,
264 2007). A trend of increasing atmospheric concentration of ethanol with altitude over
265 the South Pacific is likely due to convective activity within this region taking pollutants
266 up with it via frontal lifting. The observational errors are relatively higher for all cases,
267 creating a large uncertainty into atmospheric ethanol levels throughout the troposphere,
268 which is due to periodic variations in ethanol emissions and weather phenomena. The
269 difference between the observed and modelled ethanol for all flight campaign data lie
270 within their respective standard deviation. However, the emission class data for the
271 model can be improved by incorporating updated biofuel emissions which could
272 improve the discrepancies between model and observed data.
273
274 Monthly surface model ethanol data was extracted for twenty stations around the globe
275 (Table 3) and then compared with measured ethanol data to evaluate the accuracy of
276 the model (Figure 4). The model ethanol simulated levels from the base case is largely
277 underestimated compared with the measured ethanol for all stations, which may be due
278 to the missing sources (e.g. vegetation) or the underestimating of the biofuel emission
279 in the simulation. The inclusion of vegetation and extended anthropogenic emissions in
280 the model (Run 2) give a better agreement between model and measured ethanol for
281 clean marine and remote environment (e.g. Central Gulf, Masonoro Island, Mace Head,
282 Trinidad Head, and NEAQS).
283
284 The addition of extended vegetation and oceanic emissions (Run 3) has produced a
285 huge improvement between model-measurement discrepancies of ethanol for the rural
286 environment (e.g. Wank, Jungfraujoch, Santa Rita and Mt. Lemmon, Pennsylvania,
287 Nashville). The errors associated with the measured data of Chebogue Point, High
288 Arctic, Pittsburg, Wank, Santa Rita and Mt. Lemmon are significantly high, but with

the modelled data lying within one standard deviation of the mean suggesting the difference is insignificant. The measured ethanol level at Houston and Galveston Bay is much higher than the model ethanol values because the measurement site is close to the downtown Houston making the site well within the urban corridor and the emission of ethanol from this site is from anthropogenic sources which were heavily influenced by industrial emissions (Gilman *et al.*, 2009). Granite Bay, CA is close to the Sacramento urban area and two major highways and one gasoline refiner supplying fuel to the Sacramento area used ethanol instead of methyl-t-butyl-ether during the measurement year (Rubin *et al.*, 2006). The underprediction of ethanol by the model at Houston and Galveston Bay and Granite bay is likely due to the level of anthropogenic emissions being much greater than model used but also due to the resolution of STOCHEM as volume averaging is occurring over such a large scale.

All urban areas (e.g. London, Porto Alegre, Osaka, Mexico City, Pittsburgh, Zurich) show a very large deviation from the simulated concentrations of ethanol likely due to the low resolution of STOCHEM ($5^o \times 5^o$) making it difficult to accurately model highly polluted urban areas which make up only a small fraction of the grid. However due to the large difference in magnitude it is likely that there is a source of ethanol currently being under estimated or not being accounted for, suggesting primarily that anthropogenic emissions (e.g. biofuel) are likely to be much larger than current estimations. The observed ethanol in Porto Alegre are found to be higher than other urban areas due to their use of ethanol fuel in cars. Osaka is a region in where ethanol was not used as a biofuel in the measurement time and showed an observed concentration that was much lower than Porto Alegre. Nguyen *et al.* (2001) study was conducted on a main road through the Osaka city where ethanol may be emitted from some other anthropogenic sources. The industrial and vehicle emissions are the main sources of VOCs in two large metropolitan cities, London and Mexico City. The biofuel has been becoming popular in both UK and Mexico in recent years due to positive impacts on air quality. The UK's gasoline currently contains 5% ethanol and the value is likely to be double by 2020 (Dunmore *et al.*, 2016). The underestimation of the biofuel in the model makes the large discrepancies between measured and modelled ethanol levels in Mexico City and London. There is a large variation in the measured ethanol mixing ratios at two stations (e.g. Jungfaujoch and Zürich) of Switzerland

because Jungfaujoch is located at the 3580 m above from the sea level and has no nearby anthropogenic emission sources, but Zürich is an urban background site which has different nearby anthropogenic OVOC emissions from gasoline and solvent evaporation, residential heating and small industrial enterprises. Higher levels of observed ethanol at both stations of Switzerland in the winter are found which may due to the temperature inversions occurring within the winter months, causing stagnant air pollution to build up. Legreid *et al.* (2007) suggested that 55% of produced ethanol was from combustion in summer as opposed to 41% in the winter, but levels of ethanol are found to be lower in summer due to dominating of the removal processes.

The percentage change of surface mixing ratios of acetaldehyde, PAN and ozone from base (Run 1) to Naik *et al.* (2010) emission scenario (Run 2) and from base to Kirstine and Galbally (2012) emission scenario (Run 3) are shown in Figure 5. The mean surface acetaldehyde mixing ratios have increased by up to 30% in Brazil, Australia and New Guinea after adding vegetation and extended anthropogenic emission (Figure 5a). Further increasing the vegetation and oceanic emissions has resulted in the increment of acetaldehyde up to 90% in equatorial remote region and also in Brazil and New Guinea (Figure 5b). Acetaldehyde is the dominating precursor of the formation of PAN (Fischer *et al.*, 2014), thus an increment of PAN up to 3% from Run 1 to Run 2 (Figure 5c) and up to 10% from Run 1 to Run 3 (Figure 5d) was found over the ocean near acetaldehyde source regions. The increases in ozone are driven by the redistribution of NO_x (decomposition products of PAN) which is found to be largest in remote oceanic regions (Figure 5e). The greatest percentage change up to 0.4% (Run 1 to Run 2) and 1.4% (Run 1 to Run 3) in ozone concentration is found at the surface over the tropical oceans suggested that upon including vegetation and extended anthropogenic and oceanic emissions of ethanol has led to a pronounced effect of the ozone chemistry in this region.

CONCLUSION

In this paper, we used STOCHEM-CRI, a global 3-dimensional chemistry transport model to capture the global distribution and seasonal cycle of ethanol. The global burden of ethanol was found to be in between 0.024-0.25 Tg, matching well with literature. The lifetime of ethanol is 1.1-2.8 days, thus a large amount of ethanol can be transported from the continental boundary layer into the free troposphere which will

have a potentially significant impact on the concentration of oxidants. The photochemical source of ethanol appeared to be lower limit in the study because of the lack of the larger peroxy radical species and their corresponding rate constants in the model. Globally there are significantly higher concentrations of ethanol modeled over Saudi Arabia and Eastern Canada. The highest level of ethanol is modelled at 30^{o}N-60^{o}N and 15^{o}S-15^{o}N. Overall STOCHEM-CRI has under predicted the concentration of ethanol in most of the stations and flight campaigns discussed in the study. The addition of vegetation and extended anthropogenic emissions in the model reduce the discrepancies between modelled and measured ethanol concentrations. The area best modelled using STOCHEM was the marine clean and rural areas was likely due to these area being subject to insignificant amounts of anthropogenic emissions. The values simulated are much lower than observed data for urban areas which could be due to the level of anthropogenic emissions being much greater than used in the model but also due to the resolution of STOCHEM making the areas harder to model accurately as the emissions are measured over such a vast area. The model ethanol level of all flight campaigns lie within one standard deviation of the mean suggesting the difference between model and measurement is insignificant. The addition of ethanol has increased within recent years; the worldwide with global production for 2020 estimated to be over 125 billion litres, compared with only 17.3 billion litres in 2000 (Balat and Balat, 2009). The increasing use of biofuels globally will have an impact in the production of ozone as well as hydroxyl radicals in the remote regions.

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