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Importance of secondary sources in the atmospheric budgets of formic and acetic acids

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Importance of secondary sources in the atmospheric budgets of formic and acetic acids

Abstract

We present a detailed budget of formic and acetic acids, two of the most abundant trace gases in the atmosphere. Our bottom-up estimate of the global source of formic and acetic acids are ~ 1200 and ~ 1400 Gmol/yr, dominated by photochemical oxidation of biogenic volatile organic compounds, in particular isoprene. Their sinks are dominated by wet and dry deposition. We use the GEOS-Chem chemical transport model to evaluate this budget against an extensive suite of measurements from ground, ship and satellite-based Fourier transform spectrometers, as well as from several aircraft campaigns over North America. The model captures the seasonality of formic and acetic acids well but generally underestimates their concentration, particularly in the Northern midlatitudes. We infer that the source of both carboxylic acids may be up to 50% greater than our estimate and report evidence for a long-lived missing secondary source of carboxylic acids that may be associated with the aging of organic aerosols. Vertical profiles of formic acid in the upper troposphere support a negative temperature dependence of the reaction between formic acid and the hydroxyl radical as suggested by several theoretical studies. © Author(s) 2010.

Keywords

budgets, sources, secondary, atmospheric, acids, formic, importance, acetic, GeoQUEST

Disciplines

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Importance of secondary sources in the atmospheric budgets of formic and acetic acids

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In the following, we describe the sources and sinks of FA and AA and their implementation into the GEOS-Chem framework. In this work, the model is driven by the GEOS-5 assimilated meteorology from the NASA Goddard Earth Observing System. The horizontal resolution is degraded here to $4^\circ \times 5^\circ$ and the vertical resolution to 47 vertical layers. The model is run from 2004 to 2008 following a one-year spin-up.

2.1 Emissions

2.1.1 Terrestrial vegetation

Terrestrial vegetation emits both FA and AA (e.g. Kesselmeier, 2001). Emissions by trees are triggered by light and are well correlated with the transpiration rate. In contrast, crops have been reported not to emit detectable amounts of FA or AA (Kesselmeier et al., 1998). FA emissions by plants are related to the C_1 pathway, ethene synthesis and photo-respiration (Kesselmeier and Staudt, 1999). The emission of AA by plants occurs as the result of the hydrolysis of acetyl-coA, a product of the degradation of fats and carbohydrates (Kesselmeier and Staudt, 1999).

We use the Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.1 (Guenther et al., 2006) implemented in GEOS-Chem as described by Millet et al. (2010) to compute biogenic emissions from each GEOS-Chem grid cell (E):

$$E = \gamma \sum \varepsilon_i \chi_i$$

where the sum is over the number of plant functional types with baseline emission factor, ε , and fractional coverage, χ . For both FA and AA, ε are $30 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ for trees and shrubs and $4.8 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ for crops updated on the basis of recent measurements (A. Guenther, personal communication, 2000). The emission activity factor, γ , accounts for the variability in the local environment (e.g., temperature, light, leaf area, soil moisture). In particular for FA and AA:

$$\gamma = \exp(\beta(T - 303)) \gamma_{(other)} \text{ with } \beta = 0.08 \text{ and } T \text{ in K}$$

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where $\gamma_{(other)}$ is described in Millet et al. (2010).

2.1.2 Biomass burning and biofuel

Both FA and AA have been measured in biomass burning plumes (Goode et al., 2000; Christian et al., 2003; Yokelson et al., 2009). We estimate biomass burning emissions of FA and AA from a CO emissions inventory (GFEDv2 (Randerson et al., 2006)) using the emission factors (EF) summarized in Table 1. Emissions from biofuels are calculated in the same way using the CO emission inventory from Yevich and Logan (2003).

We note that the emission factors used in this study are generally smaller than the ones reported by Andreae and Merlet (2001) for FA but larger for AA. These changes reflect the very large variability in the reported emission factors.

2.1.3 Fossil fuel

Emissions of FA and AA from motor vehicles were first measured by Kawamura et al. (1985). Here we estimate fossil fuel FA and AA from CO fossil fuel emissions (Duncan et al., 2007) scaled by the emission ratios derived by Talbot et al. (1988) at the Hampton Roads Bridge Tunnel (Virginia): 2.1×10^{-4} FA per CO and 4.2×10^{-4} AA per CO.

2.1.4 Agricultural emissions

Large emissions of acetic acid are associated with intensive animal farming (from both cattle and cattle waste (Shaw et al., 2007)). Ngwabie et al. (2008) used the correlation between AA and ammonia to derive emission factors (2×10^{-3} – $0.2 \text{ gC}/\text{gNH}_3$ and a global estimate of AA emissions from cattle (4–17 Gmol/yr). Using an emission factor of $0.1 \text{ gC}/\text{gNH}_3$ and the anthropogenic emissions of ammonia (Bouwman and Hoek, 1997) located on agricultural lands, we estimate the global soil emissions of AA to be $\sim 40 \text{ Gmol}/\text{yr}$.

Ethanol, which has nearly the same molecular weight as FA, is a major emission of cattle farming. This makes it difficult to quantify the emissions of FA by proton transfer

Here we update the photochemical oxidation mechanism of isoprene, a non methane hydrocarbon which accounts for $\sim 30 - 50\%$ of biogenic emissions (Guenther et al., 2006), to include sources of FA from products of its photooxidation with OH: hydroxyacetone, glycolaldehyde and isoprene nitrates (Butkovskaya et al., 2006a,b; Paulot et al., 2009, cf. supplementary materials). Ozonolysis of methylvinylketone (MVK) and methacrolein (MACR), two major products of isoprene photooxidation, are also known to yield FA (Aschmann et al., 1996; Grosjean et al., 1993). In contrast, isoprene photochemistry has long been thought to be an insignificant source of AA (Jacob and Wofsy, 1988). Recent experimental evidence suggests, however, that the photooxidation of hydroxyacetone produces significant amounts of AA (Butkovskaya et al., 2006b) at low temperature. Isoprene is also a significant source of peroxy acetyl radical (PA), which reacts with HO_2 to yield AA with a yield of 15% (Hasson et al., 2004; Dillon and Crowley, 2008).

The OH-oxidation of methylbutenol (MBO), a volatile organic compound emitted in large quantities by coniferous trees (Harley et al., 1998), also yields glycolaldehyde and hydroxymethylpropanal (HMPP), a precursor of acetone (Carrasco et al., 2006), and thus of AA via PA. MBO ozonolysis has also been shown to yield FA as well as acetone and HMPP (Carrasco et al., 2007).

The OH-oxidation of various monoterpenes has been reported to produce FA. However, the yield remains very uncertain. For instance, reported FA yields from the OH-oxidation of α -pinene range from 7% (Orlando et al., 2000) to 28% (Larsen et al., 2001). Yields greater than 50% have been reported for limonene (Larsen et al., 2001). Ozonolysis of various monoterpenes also yields FA and AA (Lee et al., 2006). Monoterpenes are lumped into one species, MONX, in the GEOS-Chem chemical mechanism. We adopt a FA yield of 15.5% for the reaction of MONX with OH and a FA (AA) yield of 7.5% (8%) for its ozonolysis.

The OH-oxidation of acetaldehyde, whose sources include large emissions from the terrestrial and marine biosphere (Millet et al., 2010), is an important source of AA via $\text{PA} + \text{HO}_2$.

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2.2.2 Marine precursors

Ozonolysis of marine biogenic emissions has been suggested to provide a source of FA and AA in the marine atmosphere (Arlander et al., 1990; Sanhueza et al., 1996; Baboukas et al., 2000).

In this study, we include monthly marine emissions of isoprene, acetaldehyde, ethene and larger alkenes. Acetaldehyde marine emissions (~ 1.3 Tmol/yr) are from Millet et al. (2010) and isoprene sources are from Arnold et al. (2009) (top-down estimate : 28 Gmol/yr). Emissions of ethene (162 Gmol/yr) and larger alkenes (164 Gmol/yr) are inferred from isoprene emissions using the flux ratios observed by Broadgate et al. (1997).

2.2.3 Anthropogenic/biomass burning precursors

In addition to fresh emissions from biomass burning or anthropogenic sources, production of FA and AA within fire plumes has been measured in many (Goode et al., 2000; Gao et al., 2003; Yokelson et al., 2003; Herndon et al., 2007) but not all instances (de Gouw et al., 2006). Here, we include formation of FA and AA from the photooxidation of acetylene (Hatakeyama et al., 1986), ethene and propene (and higher alkenes).

Anthropogenic inventories for CO are described by Bey et al. (2001) and biofuel emissions by Yevich and Logan (2003). Recent updates of these inventories are described by Millet et al. (2010). Emissions and photooxidation of acetylene, propene and ethene, which are precursors of FA and AA, were recently included or updated by Fu et al. (2008). In addition we include biomass burning emission of hydroxyacetone and glycolaldehyde (Fu et al., 2008), two precursors of FA and AA.

2.3 Sources not treated

Graedel and Eisner (1988) estimate that emissions of FA from formicine ants could exceed motor vehicle and biomass burning emissions. The overall contribution of

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θ is given by the Hill-Langmuir equation:

$$\theta = \frac{\frac{K}{N_{max}}[X]_g}{1 + \frac{K}{N_{max}}[X]_g}$$

where K (cm^{-1}) is a temperature dependent partition coefficient: $K = \alpha \times \exp(\beta/T)$ with $\alpha_{FA} = 5.8 \times 10^{-11} \text{ cm}^{-1}$, $\alpha_{AA} = 1.0 \times 10^{-10} \text{ cm}^{-1}$ and $\beta_{FA} = 6500 \text{ K}$, $\beta_{AA} = 6600 \text{ K}$ (Crowley et al., 2010).

2.4.4 Dust

Field measurements have identified formate and acetate on collected mineral aerosols (Lee et al., 2000; Lee et al., 2002; Russell et al., 2002; Falkovich et al., 2004). Falkovich et al. (2004) found that formate and acetate were the most abundant mono carboxylic anions in dust particles and that their uptake was facilitated at higher relative humidity (RH).

Consistent with these observations, efficient uptake of carboxylic acids on various components of dust (Usher et al., 2003) has been measured: FA on clay (montmorillonite) (Hatch et al., 2007) and CaCO_3 (Al-Hosney et al., 2005); AA on SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ (Carlos-Cuellar et al., 2003) and CaCO_3 (Prince et al., 2008). Increased water enhance the capacity of the mineral dust to take up carboxylic acids (Al-Hosney et al., 2005; Hatch et al., 2007; Prince et al., 2008) but does not change the accommodation coefficient (γ) significantly.

Surface saturation needs to be explicitly treated as it severely reduces the efficiency of this removal mechanism (Hatch et al., 2007). Accounting for the saturation limit, Hatch et al. (2007) estimated that up to 40% of gaseous AA could be removed during a dust storm.

In GEOS-Chem, dust is carried into four different size bins. Here we use emissions from the dust entrainment and deposition (DEAD) scheme (Zender et al., 2003; Fairlie et al., 2007). From Hatch et al. (2007), we use $\gamma_{FA} = 4 \times 10^{-4}$ and $\gamma_{AA} = 3 \times 10^{-4}$

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for $\text{RH} < 30\%$; $\gamma_{FA} = 5.4 \times 10^{-4}$ and $\gamma_{AA} = 14 \times 10^{-4}$ for $\text{RH} \geq 30\%$. The dependence of surface saturation (S in $\text{mg}(\text{acid})/\text{g}(\text{dust})$) on RH is approximated by fitting an exponential to Hatch et al. (2007) measurements: $S_{FA} = 2 + 4.7 \times (1 - \exp(-8.6 \times 10^{-3} \times \text{RH}))$ and $S_{AA} = 2 + 5.8 \times (1 - \exp(-2.6 \times 10^{-2} \times \text{RH}))$. Heterogeneous degradation of FA (Al-Hosney et al., 2005) and AA (Prince et al., 2008) to CO_2 is not represented but may further enhance the uptake of FA and AA.

2.5 Simulated distribution

2.5.1 Formic acid

The total source of formic acid in the model is about 1200 Gmol/yr (Table 3). This is about twice as large as previous estimates (Ito et al., 2007; von Kuhlmann et al., 2003). Modeled FA sources are dominated by photochemical production from the oxidation of biogenic precursors. More than a third of the FA photochemical source stems from glycolaldehyde and hydroxyacetone via the Butkovskaya's mechanism (Butkovskaya et al., 2006a,b). These sources were not included in previous estimates and account for much of the difference (Table 3). Other important sources include isoprene ozonolysis (14% of the photochemical production) and monoterpenes photooxidation (6%). Acetylene is the dominant non-biogenic precursor (6.5%).

Over three quarters of FA photochemical production is derived from isoprene photooxidation, many aspects of which remain uncertain. In particular, it is worth noting that the mechanism recently proposed by Peeters et al. (2009) results in large modifications of the distribution of isoprene photooxidation products determined from chamber experiments (including hydroxyacetone and glycolaldehyde). If correct, this could significantly affect the modeled budget of FA. Nevertheless, despite our incomplete knowledge of isoprene photooxidation, its representation in the GEOS-Chem mechanism is much more explicit than for most other biogenic volatile organic compounds. This probably results in an overestimation of the importance of isoprene as a precursor for FA as the photooxidation of other biogenic volatile organic compounds, such as the

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different monoterpenes, is much more simplified.

Direct emissions of FA are small (~15%) and dominated by terrestrial vegetation and biomass burning. Emissions from vehicles do not contribute significantly to the modeled FA budget, consistent with observations from de Gouw et al. (2005). Our modeled
5 FA budget suggests, however, that more than 90% of FA is composed of modern carbon globally (Table S2). This percentage is lower in the northern mid and high latitudes, though FA is still predicted to be largely dominated by modern sources (Table S2), consistent with isotope studies in Europe (Glasius et al., 2001).

The enhancement in FA (Δ FA) in aged biomass burning plumes and its correlation with Δ CO has frequently been used to derive emission factors from ground or
10 satellite based observations (e.g. Paton-Walsh et al., 2005; Rinsland et al., 2007; González Abad et al., 2009). Our study suggests that FA is rapidly removed from the boundary layer by wet and dry deposition, so that little FA emitted or formed in the boundary layer is advected over long distances or transported into the free troposphere.
15 Therefore Δ FA observed in aged plumes is unlikely to represent direct emissions, as commonly assumed, but rather the production of FA from the photooxidation of biomass burning emitted precursors. Thus, Δ FA cannot be used, in general, to derive emission factors far away from emission regions.

FA sinks are dominated by depositions. Dust is not a significant sink globally but can
20 result in a large decrease of acids in the vicinity of large deserts.

The modeled atmospheric lifetime of FA is 3.2 days, consistent with previous estimates (Chebbi and Carlier, 1996). The lifetime of FA in the boundary layer is about 1.6 days (excluding transport to the free troposphere).

The FA atmospheric mass is highest in the tropics (~60% of the global burden Table
25 S2) as a result of large biogenic and biomass burning emissions (Fig. 1). Modeled mixing ratios in the Northern midlatitudes are low and follow the seasonal cycle of biogenic emissions.

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2.5.2 Acetic acid

The total source of acetic acid is about 1400 Gmol/yr (Table 3). Emissions of AA account for about one third of AA sources. The difference with FA stems from much
5 larger direct emissions from biomass and biofuel burning. Secondary production from anthropogenic sources or biomass burning is small. AA production has, however, been observed in biomass burning plumes. For instance, Yokelson et al. (2003) observed Δ AA/ Δ CO increase by as much as 9% in some biomass burning plumes and noted that the secondary production of AA exceeds the measured direct emissions. This
10 observation cannot, however, be generalized since other plumes did not exhibit production of AA (de Gouw et al., 2006; Yokelson et al., 2009, and references therein). Yokelson et al. (2009) also noted that the growth of FA and AA in the Yucatan biomass burning plumes cannot be accounted for by the photochemistry of their known precursors, pointing to unidentified high molecular weight precursors. The importance of these precursors as a source of FA and AA will be investigated in section 4.2.

Photochemical production is dominated by the reaction of PA with HO₂ (53%) and other peroxy radicals (24%), with isoprene photochemistry and acetaldehyde oxidation
15 the primary sources of PA. Our estimates are consistent with those of von Kuhlmann et al. (2003) and Ito et al. (2007) but much lower than the estimate by Baboukas et al. (2000). von Kuhlmann et al. (2003) pointed out that this is the result of the very high
20 branching ratio for the production of AA from PA+HO₂ assumed by Baboukas et al. (2000), inconsistent with values reported in recent laboratory experiments (e.g. Dillon and Crowley, 2008).

Similar to FA, deposition is the major sink of AA. Because AA is less soluble than
25 FA and because its oxidation by OH is faster and has a negative temperature dependence, photooxidation of AA is much more important than for FA and contributes to the significantly shorter lifetime of AA in the atmosphere: 2.3 days (1.7 days in the boundary layer). AA is predicted to primarily consist of modern carbon globally (Table S3). The distribution follows patterns similar to FA with a stronger influence of biomass and

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the model. In these regions, FA production may be promoted by seasonal biotic emissions from cattle and crop farming (Karl et al., 2009) associated with elevated ozone due to anthropogenic activities. The anthropogenic contribution to FA is predicted to be low at both sites (less than 5%) consistent with the seasonal profile of FA and previous isotope measurements in Europe (Glasius et al., 2000; Glasius et al., 2001).

We note that Barcroft data must be interpreted cautiously as the complicated topography of the region is not resolved in the model. In particular summer FA total columns show evidence for boundary layer incursions which are not captured at the coarse resolution used in this study. However, CH₂O seasonality is surprisingly well-captured in the model despite a low-bias in the summer (Fig. S6). Therefore, meteorology alone is unlikely to explain the large discrepancy between the model and the data over this site, and sources from the Central Valley (150 km to the west of Barcroft) are likely underestimated.

Missing biomass burning precursors

Evidence for a large but more localized and seasonal biomass burning source of FA can be found in the Wollongong and La Réunion records (Figs. 3a and 4a). In La Réunion, FA peaks in October. This peak is also observed in CO and CH₂O FTS measurements at the same location and is associated with biomass burning in Southern Africa (CO) and Madagascar (CO and CH₂O) (Vigouroux et al., 2009). In Wollongong, the anomalously high FA total column measured in December 2006, the largest on the record, is also associated with biomass burning, since (a) it clearly precedes the biogenic peak in FA observed in other years, (b) very large bush fires burned over 1 million acres from December 2006 to January 2007 in the Victorian Alps ~450 km southwest of Wollongong, and (c) anomalously high CO and HCN columns are recorded during the same time period (Fig. S5). This is consistent with the work of Paton-Walsh et al. (2005) who reported a significant correlation between aerosol optical depth and FA at the same site during bush fires from 2001 to 2003 and inferred that biomass burning could result in a strong enhancement in FA total column at this site.

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The model captures the timing of the biomass burning contribution to the FA column well but underestimates FA during biomass burning periods. The coarse resolution of the model is likely to contribute to this discrepancy due to the dilution of biomass burning plumes. However, the systematic discrepancy on a multi-year average at La Réunion may also indicate missing biomass burning sources of FA.

The discrepancy for marine sites (cruise – Fig. 5 and Paramaribo – Fig. 4d) also hints at a missing biomass burning source of FA. Air masses affected by biomass burning emissions are known to be advected aloft from Africa to South America and their impact has been measured over Paramaribo during the dry season from August to November (Peters et al., 2004; Petersen et al., 2008). High CO measured in the tropics during cruises is also well correlated with FA ($R = 0.64$, Fig. S10). The lifetime of FA is, however, incompatible with a large contribution of directly emitted FA to the FA total column over Paramaribo (transport time from Africa to Paramaribo has been estimated at 10 days by Peters et al. (2004)) and suggests a missing long-lived precursor from biomass burning. Sources of FA and AA from marine emissions are also likely to be underestimated since the model predicts surface concentrations which are 2 to 5 times lower than measurements made during cruises by Arlander et al. (1990) and Baboukas et al. (2000).

A local source in the polar regions

FA and AA account for a large fraction of the water-soluble organic carbon (gas+particle) over snow in polar regions (Anderson et al., 2008). Better constraints on the budget of FA and AA in these regions may help understand the large variations in FA and AA observed in the ice core record in the last 100,000 years (Legrand and De Angelis, 1996). These variations have been tentatively attributed to changes in the biosphere or biomass burning activity in boreal regions (Fuhrer and Legrand, 1997; Eichler et al., 2009).

Measured FA over Thule is about one order of magnitude lower than in Wollongong (Fig. 3b). The largest FA total columns are measured in the summers of 2004 and

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2008. Both these periods are characterized by exceptional biomass burning in boreal regions (in North America in 2004 and in Asia in 2008) (Giglio et al., 2010), consistent with the hypothesis that FA anomalies may reflect large biomass burning events. In the absence of local sources, the modeled FA column is dominated by transport. This is reflected in the modeled vertical distribution of FA peaking in the free troposphere. The model predicts a strong seasonal cycle with maximum during the boreal summer, corresponding to the largest biogenic and biomass burning emissions. The model underestimates FA total column by a factor of 2 to 5. This discrepancy may in part reflect insufficient biomass burning emissions (Andreae and Merlet, 2001). We also note that the model predicts very low concentrations of FA at the surface (~ 10 pptv). This is in sharp contrast with the measurements of Anderson et al. (2008) which report ~ 1 ppbv of water-soluble organic carbon (primarily FA and AA) over Summit at 1.5 m above the snow. This discrepancy between model and observation in Thule may thus reflect missing local sources. Indeed, Dibb and Arsenault (2002) reported surface concentrations of FA and AA measured in the Arctic could not be sustained by transport alone but required a large source from snow photochemistry.

Missing winter sources

Mid latitude and low altitude sites (Bremen, Wollongong) show larger relative biases between the model and the data during the winter (Figs. 3a and 4b). This may point to large missing anthropogenic sources of FA (Talbot et al., 1988). Alternatively leaf decay may also contribute to the FA in the winter months (Kesselmeier et al., 1998). A missing biogenic contribution would be consistent with isotope measurements which showed that FA and AA are primarily made of modern carbon even in the winter (Glasius et al., 2001).

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3.1.2 ACE-FTS

The Atmospheric Chemistry Experiment (ACE) is a Canadian satellite that was launched by NASA on 12 August 2003. FA is measured by high spectral resolution (0.02 cm^{-1}) FTS operating from 2.2 to $13.3 \mu\text{m}$. Using solar occultation, the altitude profile of temperature, pressure and various chemical compounds, including FA, CO and C_2H_2 are determined between 85°N and 85°S . Here, we are using version 3.0 of the ACE-FTS Level 2 data product.

Rinsland et al. (2006) and González Abad et al. (2009) have used the ACE-FTS spectra to retrieve mid and upper tropospheric FA. Even though most FA is located at low altitude and thus cannot be observed by ACE-FTS, these upper atmospheric profiles provide insights into the sinks, sources and transport of FA.

Figure 6 shows the average distribution of FA measured by ACE-FTS from 2004 to 2008. FA is highest from 10 to 50°S , probably reflecting large biogenic sources. The Northern hemisphere exhibits lower FA mixing ratios on average. FA mixing ratios decrease rapidly with altitude and away from the source region. High mixing ratios observed at high altitudes in the Southern Hemisphere may indicate efficient transport of FA or, more likely, its precursors from the boundary layer to the free troposphere.

The model captures mid tropospheric FA in the tropics and Southern mid latitudes relatively well. It is biased low north of 40°N (Fig. 7a), mirroring the low modeled concentration of FA in the planetary boundary layer (Fig. 1) and consistent with the large underestimation of FA total column over Bremen. The model is biased high south of 50°S . This region experiences among the lowest concentrations of FA and it is unclear how significant this discrepancy is.

The model greatly underestimates the measured vertical gradient of FA in the free troposphere, underestimating FA at low altitude and overestimating it at high altitude (Fig. 7a). The correlation plot between FA and CO reveals possible reasons for this discrepancy (Fig. 7b). The model overestimates FA at low CO (40 to 60 ppbv) which primarily reflects the high bias of the model at high altitude where most of the ACE-

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FTS measurements are taken. ACE HCN measurements (not shown) imply that air masses with CO mixing ratios greater than 160 ppbv are strongly influenced by fresh biomass burning emissions. This is in part captured by the model which shows a strong enhancement of FA in this regime. The largest discrepancy is found for values of CO ranging from 120 to 150 ppbv. These air masses exhibit a weak biomass burning signature and are primarily located in the lower free troposphere at high northern latitudes. These air masses may be affected by boundary layer air, carrying high mixing ratios of FA or its precursors of biogenic or anthropogenic origins. Alternatively, they may be associated with aged biomass burning, which would support the existence of long-lived biomass burning precursors of FA.

3.2 Aircraft measurements by mass spectrometry

From the previous section, large sources of FA appears to be missing in the Northern Hemisphere mid latitudes. Here we present data from several aircraft missions over North America to gain insights on these missing sources. We use measurements from the Intercontinental chemical transport experiment (INTEX-B/IMPEX April to May 2006 with a focus on the transport of pollution from Asia to the United States over the Pacific (Singh et al., 2009)), the Second Texas Air Quality Study (TexAQS II – August to October 2006 (Parrish et al., 2009)), the Intercontinental Transport and Chemical Transformation experiment (ITCT 2k4 campaign over the Northeastern United States (Fehsenfeld et al., 2006)) and the Aerosol, Radiation and Cloud Processes Affecting Arctic Climate study (ARCPAC 2008 over Alaska (Warneke et al., 2009)). FA and AA were measured by Chemical Ionization Mass Spectrometry during INTEX-B (Crouse et al., 2006)) and AA was measured by PTRMS during ITCT 2k4, ARCPAC 2008 and TexAQS II (de Gouw and Warneke, 2007). Even though FA was not measured during these missions, it can be expected to correlate very well with AA (e.g., $R = 0.9$ for INTEX-B).

The model underestimates AA and FA in all missions, consistent with total column observations in the Northern mid and high latitudes (Bremen and Thule). Missions

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closer to large biogenic or anthropogenic sources (ITCT 2k4 and TexAQS II) exhibit a smaller discrepancy than INTEX-B (impacted by aged Asian pollution) or ARCPAC 2008 (impacted by biomass burning). This suggests a large missing long-lived precursor of FA and AA. Consistent with this hypothesis, air masses exhibiting a strong Asian pollution signature (as defined by Dunlea et al. (2009)) exhibit a marked enhancement in FA and AA mixing ratio over other air masses sampled over the Pacific (Table 4). Since FA and AA emitted or formed in Asia are expected to be washed out as air is lifted out of the boundary layer, this enhancement hints at a secondary production of both acids. The correlation of FA with the organic fraction of the aerosols ($R = 0.83$, Fig. 8), which are predominantly of secondary origin (Dunlea et al., 2009) is consistent with this hypothesis. Similarly, in ARCPAC 2008, a strong correlation of AA with black carbon ($R = 0.86$) and the organic content of the aerosol ($R = 0.82$) hints at missing sources of AA from biomass burning.

Unrepresented precursors of FA and AA could also account for some of the discrepancy in INTEX-B (e.g. Sinreich et al., 2010). The discrepancy in the marine boundary layer for both acids is similar to the one reported by Baboukas et al. (2000) in the Atlantic ocean. Modeled marine sources of FA are a negligible fraction of FA photochemical production ($\sim 2.5\%$) reflecting the low emissions of FA precursors. This is not true for AA as acetaldehyde emissions from marine sources are large, resulting in $\sim 8.5\%$ of AA production over the ocean. The marked maximum in FA total column in the tropics is, however, consistent with an important role of transport from the continents (Fig. 5).

INTEX-B measurements over the California Central Valley (Table 4) also confirm that cattle and/or crop farming is accompanied by very large mixing ratios of FA and AA (5 times greater than in Asian plumes and 10 times greater than in the Pacific free troposphere). In contrast with measurements taken over the Pacific, AA appears to be produced/emitted more efficiently than FA in this environment.

Comparisons between the model and the data show lower discrepancies for TexAQS II and ITCT 2k4 (~ 2 - $3x$, Figs. 9a and 9b). Correlations with anthropogenic markers

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(benzene: $R = 0.5$ for TexAQS II, $R = 0.75$ for ITCT 2k4; methoxyperoxyacetylnitrate: $R = 0.85$ for ITCT 2k4) suggests a source of AA may be associated with anthropogenic processes.

3.3 Summary of model-measurement comparisons

- 5 The comparisons between measurements and model results have revealed that:
1. the model captures FA concentration and seasonality in regions with large biogenic emissions (ACE-FTS in the tropics, Wollongong, La Réunion)
 2. FA and AA concentrations are largely underestimated when biomass burning (ARCPAC 2008, ACE-FTS, La Réunion) or anthropogenic influences (Bremen, INTEX-B) are strong. However, even in these instances, FA and AA seasonality
10 (Bremen) suggests that a large fraction of FA and AA is associated with emission and photooxidation of biogenic compounds.
 3. Sinks, in particular dry deposition may be overestimated in the model. Deposition velocity for FA and AA have been measured over forested regions and range from
15 0.6 to 1.3 cm/s (Hartmann et al., 1991; Helas et al., 1992; Kuhn et al., 2002). The model predicts deposition velocities from 1 to 2 cm/s in the measurements regions (Fig. S11).
 4. The rapid decrease in FA with altitude in the upper troposphere is not captured by the model.
 - 20 5. FA and AA are greatly underpredicted in polar regions and in Northern midlatitude regions impacted by anthropogenic activities.

These observations are consistent with major secondary sources of FA and AA missing in the model. In the following, we use a series of sensitivity runs to examine the criteria a secondary source of FA and AA must meet to help bridge the gap between the model

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and the data. The reference simulation described in this section is referred to as R1 hereafter.

4 Sensitivity study

4.1 Biomass burning injection height

- 5 As a default in GEOS-Chem, biomass burning emissions are solely released in the boundary layer. However observations have shown that major fires can inject emissions well above the boundary layer (e.g. de Gouw et al., 2006; Vigouroux et al., 2009). Several modeling studies have also shown that observations of CO and aerosols downwind of fires could be best explained when a large fraction of the fire emissions is released above the boundary layer (e.g. Turquety et al., 2007). Injection of FA/AA or their precursors outside of the boundary layer is of great importance in their budget. Indeed a fast transport of carboxylic acids out of the boundary layer increases their lifetime
10 by reducing the dry deposition sink and results in a large increase in their net lifetime. This in turns results in enhanced transport of FA and AA on larger scales. Furthermore biomass burning has been associated with a reduction of low-level precipitation (e.g. Andreae et al., 2004) which may further increase carboxylic acid lifetime.

Several studies have associated enhancements of FA in the free troposphere to biomass burning (González Abad et al., 2009). Here we examine whether injection of biomass burning emissions outside of the boundary layer can help bridge the gap
20 between between model and observations at high CO. We use two different scenarios. In the first one (R2a), 60% of the biomass burning is emitted in the boundary layer while 35% is emitted in the mid troposphere (from the top of boundary layer to 400 hPa) and 5% in the upper troposphere (400 hPa to 200 hPa). In the second scenario (R2b), we adopt one of the scenarios used by Turquety et al. (2007) to investigate biomass burning over North America with 40% of the biomass burning emissions in the boundary
25 layer, 30% in the mid troposphere and 30% in the upper troposphere. Since our

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goal is to examine the sensitivity of free tropospheric FA to biomass burning injection height, modifications of the injection height are applied globally, an important simplification (Val Martin et al., 2010, and references therein). Furthermore we assume that EF for FA and AA are independent of the biomass burning injection height. This is another important simplification since (a) the injection of biomass burning in the free troposphere strongly depends on the fire intensity, and (b) EF for FA and AA exhibit some correlation with the modified combustion efficiency (MCE), an indicator of the combustion type (flaming or smoldering). Therefore, a more quantitative study of the importance of biomass burning in the FA and AA budget would require an explicit description of the relationship between MCE and EF as well as MCE and injection height.

Both scenarios lead to an enhancement of FA in the mid troposphere (by 10% for R2a (not shown) and by 35% for R2b; Fig. 7a panel B). The increase is especially large at high CO, greatly reducing the discrepancy between the model and the measurements (Fig. 7b). This is remarkable since biomass burning emissions of FA and its precursors account for a relatively small fraction of FA sources in the model. This disproportionate effect highlights the strength of boundary layer sinks of FA which greatly hinder its transport to the free troposphere. The increase in FA induced by both scenarios is, however, insufficient to bridge the gap between the model and the data in the lower troposphere. In particular, it has no effect on the modeled FA in air masses with CO mixing ratios ranging from 120 to 150 ppbv. This is not surprising if these air masses are associated with aged biomass burning, as FA sinks (photooxidation and wet deposition) are faster than for CO. In contrast, the injection of FA into the free troposphere significantly amplifies the discrepancy between the model and the measurements in the upper troposphere. The very long lifetime of FA in the upper troposphere is responsible for this strong sensitivity. In R2b, FA is increased by almost 50% in the upper troposphere compared to the reference run, resulting in large discrepancies for CO between 40 and 120 ppbv (Fig. 7a).

These observations suggest that the distribution of FA in the free troposphere is only sensitive to biomass burning injection height for fresh biomass burning plumes. As

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FA is removed from the free troposphere faster than CO, the correlation between FA and CO across the whole CO range can only be sustained if the photooxidation of long-lived unrepresented compounds (i.e., poorly soluble and reactive) produces FA. However, if such a source exists, the observed vertical gradient of FA indicates a large sink is missing from the model in the upper free troposphere.

4.2 Secondary source of FA and AA and organic aerosol aging

The positive correlation of FA and AA with submicron organic aerosol observed in several aircraft campaigns (Fig. 8) hints at a possible relationship between FA and AA production and aerosol aging, i.e., processes affecting aerosol composition.

Aerosol composition is very dynamic as evidenced by the positive correlation between the oxygen to carbon ratio and the residence time of aerosols (DeCarlo et al., 2008; Capes et al., 2008). Near sources, aging is thought to be dominated by gas-phase oxidation of semivolatiles (a), while, for longer residence time, heterogeneous oxidation (b) may become important (DeCarlo et al., 2008; George et al., 2008). The combined evolution of the oxygen to carbon ratio and of the hydrogen to carbon ratio during aerosol aging was recently showed to be consistent with the formation of carboxylic groups (Heald et al., 2010). This is not inconsistent with (a), even though we are not aware of direct evidence for the formation of either FA or AA from the photooxidation of semivolatiles. In contrast, laboratory experiments provide ample evidence for the volatilization of FA and AA (b) following the photolysis of aerosols (Walser et al., 2007; Pan et al., 2009) as well as their heterogeneous oxidation by O₃ (Eliason et al., 2003; Park et al., 2006) and OH (Eliason et al., 2004; Molina et al., 2004; Vlasenko et al., 2008). As heterogeneous oxidation operates on relatively long time scales (\lesssim 4 days (George et al., 2008)), it could help account for observations during INTEX-B and at Paramaribo. It appears, however, to be too slow to provide a large source of FA and AA near emission centers (DeCarlo et al., 2008).

Comparison between the data and the model suggests global sources of FA and AA may be underestimated by up to 50% for both acids, i.e., an additional \sim 2 TmolC/yr.

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Estimates for the global flux of carbon from the photooxidation of aerosol range from 4 to 16.5 TmolC/yr (Kwan et al., 2006), suggesting FA and AA volatilization would need to account for a very large fraction of this flux (10-50%). However this estimate does not account for the probably large dynamic exchange of matter between the gas and aerosol phases driven by semivolatile volatilization and photooxidation (Robinson et al., 2007; Kroll et al., 2009; Jimenez et al., 2009).

Proper evaluation of the role of aerosol aging as a source of FA and AA requires detailed modeling of aerosol evolution (e.g., following the framework presented by Jimenez et al. (2009)) informed by additional laboratory measurements. This is beyond the scope of this paper. Here, we do not explicitly model secondary organic aerosol but use organic aerosol (OA) to generate a diffuse source of FA and AA associated with aerosol aging (scenario R3). In GEOS-Chem, OA represents both emitted OA (primarily from biomass burning with an important contribution of anthropogenic sources in the Northern midlatitudes) and a small and simplified secondary production from the condensation of low volatility compounds from biogenic and anthropogenic sources (Park et al., 2003). The largest global source of organic aerosol is biomass burning globally. We assume that every collision of OH with OA results in the production of one molecule of FA and one molecule of AA. This results in an increase in the source of FA and AA by 320 Gmol/yr, about ~25% (~0.95 TmolC/yr). This reaction does not represent a physical process (OA is not lost via this reaction) but is meant to provide a diffuse source of FA and AA correlated with OA.

This large additional FA source greatly improves the agreement with La Réunion. The mean FA concentration increases by almost 60% in October (Fig. 10a). Similarly, the anomalously high FA measured in December 2006 in Wollongong is much better reproduced in the model with this hypothetical aerosol source (Fig. 10b). We note that it has little effect on the FA total columns for the other years, underlining the exceptional intensity of the 2006 bush fires. For both sites, a similar increase in biomass burning emissions of FA would not result in such a large improvement. This is because the lifetime of organic aerosol is longer than the lifetime of FA. This is evident in the com-

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parison with the cruise measurements where a very large increase is observed in the tropics, reflecting the enhanced transport of FA biomass burning precursors away from their source regions (Fig. S12). Other locations impacted by biomass burning such as Thule see large increases in FA or AA though this remains insufficient to bridge the gap between model and measurements.

In the GEOS-Chem simulations used in this study, organic aerosol sources are dominated by biomass burning. Because of the lack of a proper representation of secondary organic aerosol (SOA) in our simulation, it is not surprising the discrepancy remains very large in locations where organic aerosols are dominated by SOA from biogenic or anthropogenic sources (e.g., Bremen (Fig. S13), INTEX-B). Future work will focus on assessing the role of semivolatiles as a source of FA and AA. In particular, the interaction between biotic emissions (biogenic and agricultural) and anthropogenic activities need to be properly represented, as it has been shown that this interaction could result in enhanced secondary aerosol formation (de Gouw et al., 2005; Weber et al., 2007; Goldstein et al., 2009). If SOA aging is indeed a source of FA and AA, this could help explain the biogenic signature of FA and AA in polluted regions (seasonality and isotopic composition), as well as the similar magnitudes of Wollongong and Bremen FA total columns despite very different isoprene sources.

4.3 Temperature dependence of FA OH-oxidation

The ACE-FTS comparison revealed a high bias of the model in the upper troposphere. At these altitudes, wet deposition becomes small and FA sink is dominated by the reaction of OH with FA.

To examine the sensitivity of the FA profile to the temperature dependence of its reaction with OH, we use the temperature dependence derived theoretically by Galano et al. (2002) for the acidic (k_1) and formyl channels (k_2) and scale it to match the experimental rate of FA + OH determined at room temperature. The resulting rate

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Table 1: Biomass burning emission factors for FA and AA (in g per kg of dry matter). Emission factors from Andreae and Merlet (2001) are indicated in parentheses.

	Savanna	Tropical	Boreal	Biofuel ^a
FA	0.18 (0.7)	0.42 (1.1)	0.80 (2.9±2.4)	0.22 (0.13)
AA	1.58 (1.3)	3.11 (2.1)	4.05 (3.8±1.8)	4.97 (0.4–1.4)

^a Derived from open-cooking.

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Table 2: Soil emissions of formic and acetic acids at $T_{\text{soil}} = 30^{\circ}\text{C}$ in $\text{nmol}/(\text{m}^2\text{s})$ for different land types.

Land Type ^a	Formic Acid		Acetic Acid	
	wet	dry	wet	dry
Agriculture (not Rice)	1.8×10^{-1}	–	1.1×10^{-1}	–
Agriculture (Rice)	5.9×10^{-3}	–	3.5×10^{-3}	–
Conifer and other deciduous	1.47×10^{-2}	4.9×10^{-3}	8.8×10^{-3}	2.9×10^{-3}
Desert	0	0	0	0
Drought deciduous	2.9×10^{-2}	8.9×10^{-3}	1.8×10^{-2}	5.4×10^{-3}
Grassland	1.8×10^{-1}	5.9×10^{-2}	1.1×10^{-1}	3.6×10^{-2}
Tropical rain forest	1.3	1.9×10^{-1}	7.7×10^{-1}	1.2×10^{-1}
Tundra	2.4×10^{-2}	8.2×10^{-3}	1.5×10^{-2}	5.0×10^{-3}
Woodland	8.3×10^{-2}	3.2×10^{-2}	5.0×10^{-2}	1.9×10^{-2}
Wetland	1.5×10^{-3}	–	8.8×10^{-4}	–

^a Wang et al. (1998)

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Table 3: Modeled global budget of atmospheric formic and acetic acids (2004–2008 average). Previous estimates are indicated in parentheses.

	Formic acid ($\tau = 3.2$ days)	Acetic acid ($\tau = 2.3$ days)
Total Sources (Gmol/yr)	1232 (674 ^a , 587 ^b)	1424 (1250 ^a)
Photochemical production	1055	976
	(370 ^a , 435 ^b)	(1250 ^a , 700 ^b , 2000 ^c)
Biogenic	917 ^d	955 ^d
Anthropogenic + Biomass burning	138	21
Emissions	177 (304 ^{a,g} , 217 ^b)	448
Anthropogenic	3.5	7
Biofuel Burning	6.5	114.5
Biomass Burning	32.5	187
Cattle	39.5	39.5
	(25 – 100 ^{f,g})	(4.2 – 16.8 ^f)
Soil	39	57
Terrestrial vegetation	56	43
	(125 ^h , 33 – 166 ⁱ , 20 – 130 ^j)	(25 ^h , 17 – 83 ⁱ , 10 – 33 ^j)
Total Sinks (Gmol/yr)	1233	1426
Photochemical	229.5	413
Dry deposition	536	522
Wet deposition	437.5	451.5
Dust	30	39.5

^a von Kuhlmann et al. (2003) ^b Ito et al. (2007) ^c Baboukas et al. (2000) ^d Neglect biomass burning contribution to hydroxyacetone and glycolaldehyde ^e Sum of biomass burning and biogenic emissions ^f Ngwabie et al. (2008) ^g $\text{C}_2\text{H}_5\text{OH} + \text{HCOOH}$ ^h Lathière et al. (2006) ⁱ Wiedinmyer et al. (2004) ^j Kesselmeier et al. (1998)

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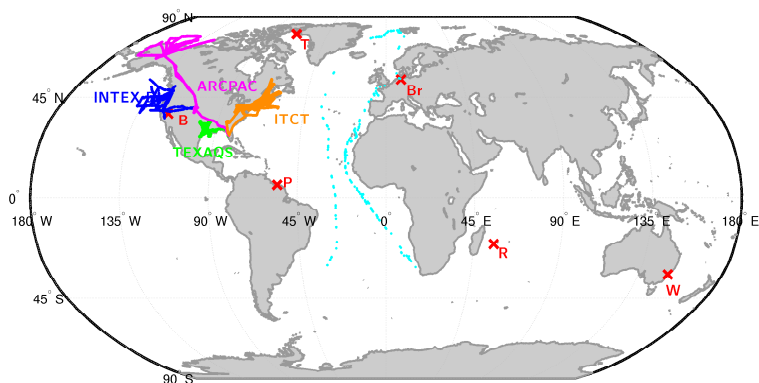


Fig. 2: Locations of the measurement sites used in this study. Red crosses: FTS ground stations (B: Barcroft, Br: Bremen, P: Paramaribo, R: La Réunion, T: Thule, W: Wollongong). Cyan dots: ship cruises. Blue, Magenta, Yellow and Green dots: aircraft missions flight tracks.

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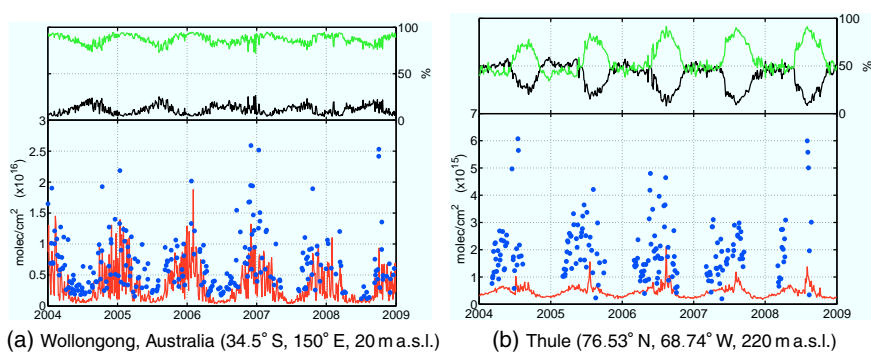


Fig. 3: Upper panel: modeled contribution of biogenic sources (green : emission + photochemical production) and biomass burning (black: emissions + photochemical production) to FA total column. Lower panel: modeled (red) and measured (blue) FA total column. Measurements and model are averaged over a two day time period.

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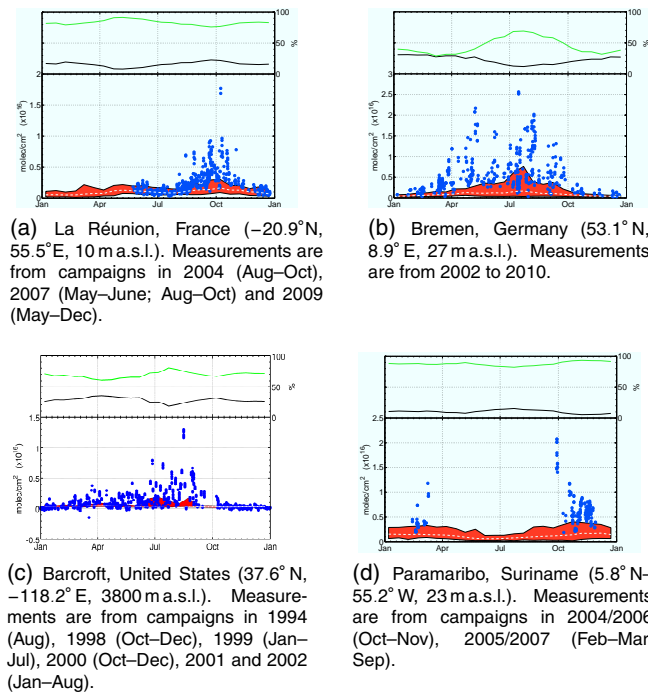


Fig. 4: Upper panels: same as Fig. 3. Lower panel: comparison between modeled and measured FA total columns. Individual total column measurements are indicated with blue dots. The 2004–2008 model range is indicated by the red shaded area and the model mean by the white dashed line.

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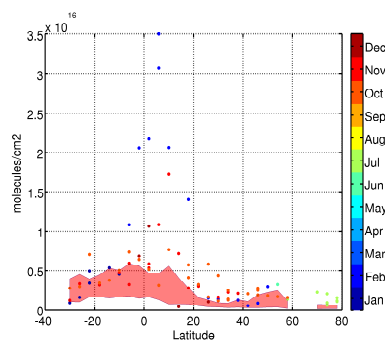


Fig. 5: Monthly FA total column measured during cruises in the Atlantic ocean in 1996, 1999, 2000, 2002, 2003 and 2005 (dots). The 2004–2008 model monthly mean range is indicated by the red shaded area.

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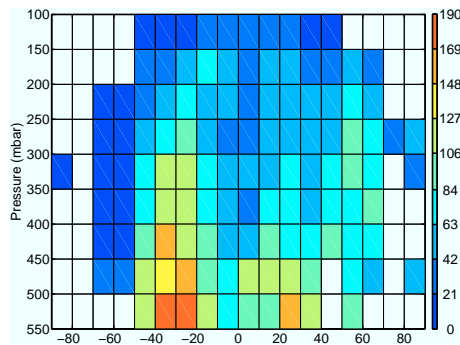
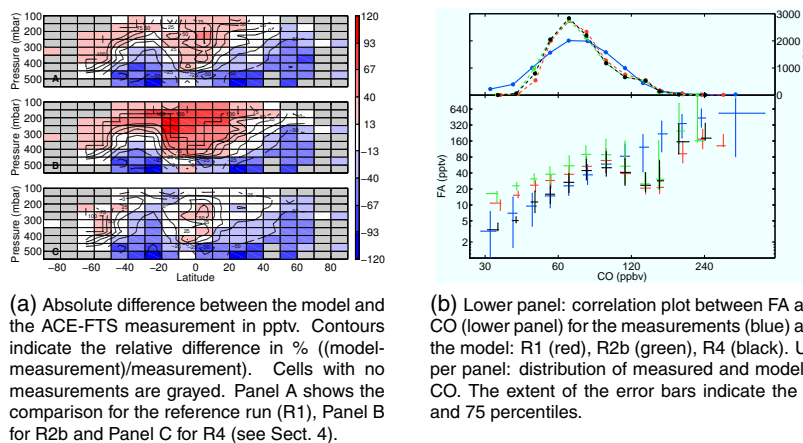


Fig. 6: Average distribution of FA (pptv) measured by ACE-FTS from 2004 to 2008. Measurements are binned in 10° latitude 50 mbar bins. Only bins with more than ten measurements are considered.

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(a) Absolute difference between the model and the ACE-FTS measurement in pptv. Contours indicate the relative difference in % ((model-measurement)/measurement). Cells with no measurements are grayed. Panel A shows the comparison for the reference run (R1), Panel B for R2b and Panel C for R4 (see Sect. 4).

(b) Lower panel: correlation plot between FA and CO (lower panel) for the measurements (blue) and the model: R1 (red), R2b (green), R4 (black). Upper panel: distribution of measured and modeled CO. The extent of the error bars indicate the 25 and 75 percentiles.

Fig. 7: Comparison of ACE-FTS FA measurements with the modeled FA distribution. The model is sampled at the location and time of the ACE-FTS measurement.

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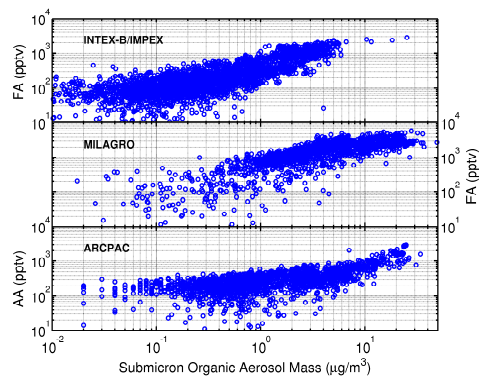


Fig. 8: Correlation plots between the organic content of the aerosol and FA/AA

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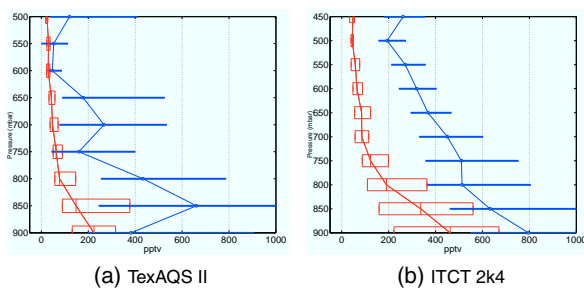


Fig. 9: Comparison between measured (blue) and modeled (red) vertical AA profiles. The box (thick line) extent represents the 25% and 75% percentiles.

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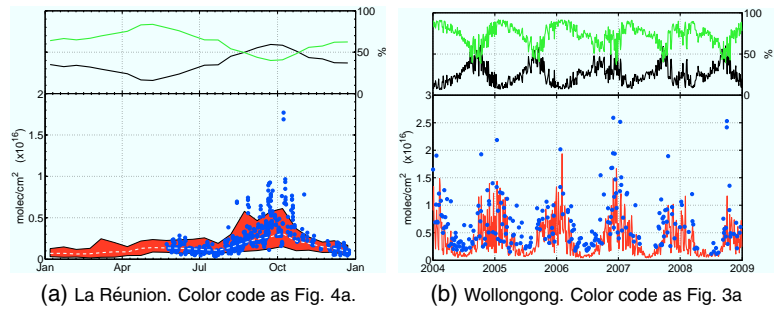


Fig. 10: Effect of a diffuse source of FA from aerosol aging (dominated by biomass burning, R3) on FA total column.