Atmos. Meas. Tech. Discuss., 4, 5807–5835, 2011 www.atmos-meas-tech-discuss.net/4/5807/2011/ doi:10.5194/amtd-4-5807-2011 © Author(s) 2011. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

Airborne observations of formic acid using a chemical ionisation mass spectrometer

M. Le Breton¹, M. R. McGillen^{1,*}, J. B. A. Muller¹, A. Bacak¹, D. E. Shallcross², P. Xiao², L. G. Huey³, D. Tanner³, H. Coe¹, and C. J. Percival^{1,*}

¹Centre for Atmospheric Science, School of Earth, Atmospheric and Environmental Science, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

²Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

³School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

^{*}currently at: Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration (NOAA), 325 Broadway, Boulder, CO 80305, USA

Received: 5 August 2011 – Accepted: 5 September 2011 – Published: 14 September 2011

Correspondence to: C. J. Percival (c.percival@manchester.ac.uk)

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



Abstract

The first airborne measurements of formic acid mixing ratios over the United Kingdom were measured on the FAAM BAe-146 research aircraft on the 16 March 2010 with a chemical ionisation mass spectrometer using I⁻ reagent ions. The I⁻ ionisation scheme was able to measure formic acid mixing ratios at 1 Hz in the lower boundary layer.

 ⁵ was able to measure formic acid mixing ratios at 1 Hz in the lower boundary layer. In-flight standard addition calibrations from a formic acid source were used to determine the instrument sensitivity of 35±6 ion counts pptv⁻¹ s⁻¹ and a limit of detection of 25 pptv. Routine measurements were made through a scrubbed inlet to determine the instrumental background. Three plumes of formic acid were observed over the UK,
 ¹⁰ originating from London, Humberside and Tyneside. The London plume had the highest formic acid mixing ratio throughout the flight, peaking at 358 pptv. No significant correlations of formic acid with NO_x and Ozone were found.

A trajectory model was employed to determine the sources of the plumes and compare modelled mixing ratios with measured values. The model underestimated formic acid concentrations by up to a factor of 2. This is explained by missing sources in the model, considered to be primary emissions of formic acid of mainly anthropogenic origin and lack of precursor emissions, such as isoprene, from biogenic sources.

1 Introduction

Organic acids are ubiquitous in the gas phase and aerosols, common constituents
 of global precipitation (Keene and Galloway, 1983) and are measured in urban, rural and remote areas (Talbot et al., 1988). The contribution of organic acids to the acidity of precipitation and subsequent effects on aquatic and terrestrial ecosystems has been documented by Keene and Galloway (1986). Formic (HCOOH) and acetic acid (CH₃COOH) can dominate free acidity of precipitation thereby having an influence
 on pH-dependent chemical reactions and OH cloud chemistry (Jacob et al., 1986). Low molecular weight organic salts are present in the fine fraction of aerosols, whose



physical properties, namely hygroscopicity, include relatively low critical supersaturations, allowing for the activation of cloud droplets and subsequently affecting the total indirect forcing (Yu, 2000).

Sources of carboxylic acids include biogenic and anthropogenic primary emissions, e.g. biomass burning (Burling et al., 2010) and in situ production such as hydrocarbon oxidation, though their relative fluxes are poorly constrained (Chebbi et al., 1996). The major sinks of carboxylic acids are dry and wet deposition as a result of their low reactivity towards OH and NO₃. However, the chemical loss via reaction with OH is poorly constrained owing to the uncertainty in the reported rate coefficient (Atkinson et al., 2000). Constrained and reaction (1001) and Hortmann et al. (1001) have above that

- ¹⁰ 2006). Sanhueza and Andreae (1991) and Hartmann et al. (1991) have shown that forests (acetic acid dominating) and particularly savanna regions (formic acid dominating) in Venezuela are strong sources of formic and acetic acid. These are thought to be in part from direct emission by plants, but are dominated by in situ production following ozonolysis of alkenes (Sanhueza et al., 1996) where savanna levels for both species
- peaked around midday with a level of around 1 ppbv. Grosjean (1992) observed high levels of formic and acetic acid at a site in Southern California close to a coastal area, here direct emissions of acetic acid dominated over formic acid by a factor of 2, peaking in the summer at 20.4 and 9.6 metric tons per day respectively. It was also concluded that in situ production was of similar magnitude, with formic acid dominating over acetic
- acid (25.0 and 10.1 metric tons per day during the day rising to 34.5 for formic acid but dropping for acetic acid to 4.3 at night). However, these in situ production rates are based on earlier product data for acid formation from the ozonolysis of alkenes, more recent data (Leather et al., 2011) would suggest that the in situ production has been over-estimated. Preunkert et al. (2007) concluded that in-situ production was the dom-
- ²⁵ inant process for formic and acetic acid production in Europe, based on high altitude measurements.

Johnson and Dawson (1993) carried out ¹³C and ¹⁴C analysis from background sites in the USA and concluded that direct emission of formic acid from C_3 plants was the most likely dominant source. Biomass burning is also a significant source of formic



and acetic acid (Dibb et al., 1996; Keene et al., 2006; Talbot et al., 1999; Zhong et al., 2001). In Sao Paulo, Fornaro and Gutz (2003) concluded that high acetic acid resulted from direct emissions from ethanol fuelled cars, whilst high formic acid came from insitu production. Ocean sources of these acids have been suggested by Baboukas et al. (2000).

Gas-phase concentrations of formic acid in particular have been measured in low ppb ranges (Talbot et al., 1999) and the modelled atmospheric lifetime has been suggested to be 3.2 days (Paulot et al., 2010). Global models under-predict formic acid budgets (von Kuhlmann et al., 2003; Rinsland et al., 2004; Paulot et al., 2010) by up to a factor of 50 in marine locations. Such discrepancies between perceived source

strengths and observed atmospheric concentrations have led many authors to speculate upon the existence of a missing or poorly constrained source term (e.g. Grosjean, 1989; Talbot et al., 1988, 1995; Granby et al., 1997; Rinsland, 2004), and it has been suggested by several of these studies that an unknown anthropogenic, and perhaps

10

secondary source may be responsible, such as higher biogenic emissions during the growing season (Rinsland et al., 2004) and ageing of organic aerosols (Paulot et al., 2010). Also, the oxidation of volatile organic compound (VOC) precursors leading to the production of formic acid has been suggested as a significant source (Arlander et al., 1990), for instance the ozonolysis of ethene, whose emissions have been estimated
 to be 15 Tg yr⁻¹ (Broadgate et al., 1997; Paulot et al., 2010).

Recently Veres et al. (2008), Roberts et al. (2010, 2011), and Bertram et al. (2011) have shown that chemical ionisation mass spectrometry can be used to selectively detect gas-phase acids with a limit of detection below 0.1 ppbv for 1 s measurements of formic acid. The rapid time response of CIMS is particularly well suited for airborne

measurements, and this study focuses on the development of a negative ion chemical ionisation mass spectrometer (CIMS), utilizing I⁻, as a method for the online measurement of carboxylic acids on an airborne platform.



2 Instrument description

2.1 CIMS apparatus

5

Chemical ionisation mass spectrometry (CIMS) was used for real-time detection of formic acid. The CIMS instrument employed here was built by the Georgia Institute of Technology as previously described by Nowak et al. (2007). The schematic in Fig. 1 shows the set up used and operating conditions of the CIMS on board the airborne platform FAAM BAe-146 research aircraft.

The sample air for the CIMS was obtained by sub sampling from the aircraft air sampling pipe (ASP). The ASP is a ram air inlet consisting of a 2" OD stainless steel pipe, which internal surface has been highly electropolished for inertness. Several 1/4" and 3/8" OD Swagelok ports are welded to the ASP and separated by ~ 3.5", providing air to instrumentation in the cabin. Pressure measurements in the ASP were conducted at flight level 27 000 feet with a pitot tube in order to determine the linear air velocity in the ASP during science cruise speed, typically 210 knot aircraft indicated air speed.

- ¹⁵ For an outside static pressure of 344 mb, the ASP static pressure was 406 mb, and its ram air pressure was 427 mb. The derived ASP linear air velocity is $85 \,\mathrm{m\,s}^{-1}$. Given an estimated ASP ID of 45 mm (15.90 cm² cross section), the equivalent volumetric flowrate through the ASP is $135 \,\mathrm{L\,s}^{-1}$. The sub sample passed through a 1/2'' diameter PFA inlet line that entered the CIMS body through a 3/8'' 3-way valve (with internal
- orifice diameter of 0.63 cm, M-Series Solenoid Valve, TEQCOM). A rotary vane pump (Picolino VTE-3, Gardner Denver Thomas) allowed for a fast inlet flow of 131 which corresponded to a residence time of 0.7 s (at standard temperature and pressure) in the total length of inlet tubing. After entering the first section of the flow tube the atmospheric sample entered a sequence of differentially vacuum pumped chambers.
- ²⁵ Initially the sample passed through a 380 μ m diameter sized pinhole to reach the ionmolecule region (IMR) where ionisation occurred at a pressure of 22 Torr, maintained by a dry scroll backing pump (UL-DISL 100, ULVAC Industrial). Here, N₂ at a flow rate of ~1.5 SLM and the ionisation gas mixture of CH₃I/H₂O/N₂ at a rate of 1 SCCM



passed over the ion source (Polonium-210 inline ioniser, NRD inc Static Solutions Limited), producing an excess of I⁻ and I⁻ H_2O ions in the IMR, which then ionised the organic acid molecules in the air sample. The ions then passed through a pinhole of a charged plate, which entered the mass spectrometer section of the instrument, i.e. the

- ⁵ first octopole ion guide chamber which is the collisional dissociation chamber (CDC) where weakly-bound ion-water clusters are broken up to simplify the resultant mass spectrum. The pressure in the CDC of less than 1 Torr was achieved by the use of a molecular drag pump (MDP-5011, Adixen Alcatel Vacuum Technology). After the CDC, the ions passed through the second octopole ion guide, which has the effect of collimat-
- ¹⁰ ing the ions. The octopole chamber was held at a pressure of $\sim 10^{-3}$ Torr which was maintained by a turbomolecular pump (V-81M Navigator, Varian Inc. Vacuum Technologies). Past the second octopole chamber, the ions were mass selected by a quadropole with pre- and post filters with entrance and exit lenses (Tri-filter Quadropole Mass Filter, Extrel CMS). The quadropole section was kept at a pressure of 10^{-4} Torr by a second turbomolecular pump (V-81M Navigator, Varian Inc. Vacuum Technologies). The se-
- ¹⁵ turbomolecular pump (V-81M Navigator, Varian Inc. Vacuum Technologies). The selected ions were then detected and counted by a continuous dynode electron multiplier (7550 M detector, ITT Power Solutions, Inc.).

2.2 Ionisation scheme

The ion-molecule chemistry using iodide ions (I⁻) for trace gas detection has been described by Slusher et al. (2004) and was utilised here to detect organic acids. A gas mixture of methyl iodide, CH_3I , and H_2O in N_2 is used to obtain reagent ions I⁻ and water clusters I⁻H₂O, of which the latter is important for the ionisation of formic acid, forming the acid-iodine adducts as seen in the mass spectrum (Fig. 2). HC(O)OH was ionised by I⁻ via an adduct reaction,

²⁵ $I^- \cdot H_2O_n + HC(O)OH \rightarrow HC(O)OH \cdot I^- \cdot H_2O_n$

which enabled formic acid to be detected selectively at m/z = 173. As the ionisation efficiency is dependent on the presence of water vapour through the production of



(1)

 I^- ·H₂O (Slusher et al., 2004), water vapour was added to the ionisation gas mixture, so as to produce an excess of I^- ·H₂O cluster ions and hence allow operation in the water vapour independent regime.

2.3 Formic acid calibrations, sensitivity and LOD

- Formic acid calibrations were made pre-flight and in-flight. The calibration cycle involves obtaining the formic acid instrumental background by passing the sample air through an acid scrubber which is made of nylon turnings coated with sodium bicarbonate. After an effective zero acid air flow for background determination, a known amount of formic acid from a pressurised gas cylinder is added to this scrubbed air
 flow until a plateau in formic acid signal is achieved. A second background determination
- nation is done before the 3-way PFA valve is switched back to atmospheric sampling mode (Fig. 1). The organic acid gas mixture that was used for the in-flight calibrations of the CIMS was analysed by Flame Ionisation Detection as follows. A liquid standard of the acid (with toluene added) was diluted and then injected directly onto a gas
- ¹⁵ chromatography-flame ionization detector system (GC-FID ADS). The dilution factor was determined by the dilution of the toluene, referenced to a certified Apel_Reimer standard. The in-flight standard was then calibrated against this standard mixture and the formic acid calibration factor was applied to the relative formic acid concentrations during post-flight data processing. The formic acid calibration factor was applied to
- ²⁰ the relative formic acid concentrations during post-flight data processing. During a test flight, the calibration was proven to be invariant with altitude. Calibrations were performed from 50 feet to 3000 feet. The calibration factor for the range of altitudes was within 3 σ of the error calculated from the statistical noise of the calibration signal in the plateau region.
- The sensitivity of the CIMS to formic acid (in units of counts/ppb of formic acid) was calculated as the ratio of the background corrected formic acid calibration counts to the formic acid absolute calibration factor (in units of ppb). For this flight the sensitivity was 35 ± 6 ion counts s⁻¹ pptv⁻¹. The 3σ limit of detection (LOD) for formic acid was



calculated to be 25 pptv. The instrument response time was estimated by adding a known amount of HCOOH to the instrument for a given period of time, as shown in Fig. 3. The instrument has an e-folding time of 1.5 s and a response time, i.e. the time required for a steady state signal to decay to 10% of the initial signal when a background measurement is made (Veres et al., 2008) of 4 s.

Other measurements of formic acid using chemical ionisation mass spectrometry have been reported. Veres et al. (2008) measured formic acid using a negative-ion proton transfer chemical-ionization mass spectrometry (NI-PT-CIMS) utilising the acetate ion ionisation scheme. A limit of detection of 80–90 pptv, a sensitivity of 24 ion counts s^{-1} pptv⁻¹ was achieved and an inlet response time of 1–2 s was reported. The sensitivity and time response of both instruments are comparable; however, the work in this paper utilises the technique on board an aircraft.

Roberts et al. (2010) utilised the same technique for measuring formic acid along with other inorganic acids such as HONO. Although sensitivity is not quoted in this

- ¹⁵ paper, it is reported to be lower than that of HNCO, which is 16 ion counts s⁻¹ pptv⁻¹. Bertram et al. (2011) used a chemical ionization time-of-flight mass spectrometer (CI-TOFMS). A sensitivity of 338 ion counts s⁻¹ pptv⁻¹ and a limit of detection of 0.5 pptv is reported. The increase in sensitivity was attributed to the improved duty cycle of the TOF bases system in conjunction with enhanced transfer optics used in the new
- ²⁰ CI-TOFMS instrument. Reiner et al. (1999) reported aircraft measurements using a triple quadrupole mass spectrometer (TQMS) of formic acid over Germany using ion molecule chemistry, by reacting hydrated CO₃⁻ ions with the atmospheric formic acid. No sensitivities, LOD or time responses were quoted.

2.4 Data logging, capture and handling

5

The CIMS instrument can be set to either to count a set number of masses in sequence, here, eight masses, with a dwell time of 100 ms each yielding a sampling frequency of 1.67 Hz. Alternatively, spectral scans across the whole mass spectrum can be taken, which was done twice during the flight B518 (Fig. 2). The high frequency



formic acid time series was analysed by removing background counts (averaging to 30 s) and calibrating relative counts using the calibration factor obtained during the inflight calibration cycle (averaging to 30 s). The formic acid data capture is 86 % for the whole flight, and 14 % of data loss is a result of the in-flight calibration and background measurements. Data obtained during transit at 10 000 feet are not shown as no calibration was done at this height and calibration altitude independence was only confirmed for heights up to 3000 feet (see above).

2.5 FAAM BAe-146 onboard instruments

5

20

In addition to formic acid data, observations of CO, NO₂ and O₃ are used in the anal-¹⁰ ysis. Nitric oxide (NO) and nitrogen dioxide (NO₂) were measured using separate channels of a chemiluminescence detector and were reported every 10 s with an uncertainty of $\pm 6 \%$ ppbv (Stewart et al., 2008). CO data is reported at 1 Hz using as fast fluorescence CO analyser with an uncertainty of $\pm 5 \%$ (Gerbig et al., 1999). Ozone was measured using a UV Photometric Ozone Analyser at 1 Hz with an uncertainty of ± 3 ppbv (Real et al., 2007).

2.6 Field conditions for flight B518

The 1 Hz formic acid data obtained from take off until landing on flight B518, 16 March 2010 enabled observations of plumes from a variety of sources. The measurements were taken over the North Sea, aiming to intercept pollution plumes from the UK carried by a south-south-westerly wind with a wind speed of 2.8 m s^{-1} . The meteorological conditions for the previous 3 days and the day of the flight were free of precipitation. These conditions favoured the accumulation of carboxylic acids in the vapour phase, since wet deposition would have been kept to a minimum.



3 Analysis and discussion

3.1 Observations of formic acid concentrations

Formic acid mixing ratios ranged from 34.4 pptv, the estimated lower limit of detection, to 358 pptv, as shown in Fig. 4. The mean mixing ratio during the flight was 142.4 pptv, with a 3- σ standard deviation of \pm 71.9 pptv. Comparison to previously reported data is 5 difficult due to its scarcity. Satellite and infrared (IR) measurements have been made, but these are mainly at altitudes greater than 2 km. Zander et al. (2010) reported total vertical column abundances of formic acid above the Jungfraujoch station. This was derived from infrared solar observations performed with a high spectral resolution Fourier transform spectrometer. An average mixing ratio of 110.9 pptv was calculated 10 in the 3.58 to 10.6 km region, with a mean minimum of 46 ppt and a mean maximum of 182 ppt. Satellite based IR measurements have been made to altitudes of 5 km. where mixing ratios of 157 ± 60 have been recorded (Gonzalez Abad et al., 2009). The mixing ratios reported from this study are similar to that observed by IR if the high concentration plumes from London and Humberside are ignored. A decrease in mixing 15 ratios with altitude is observed, which is most likely a consequence of the increasing

distance from direct and indirect sources which results in the dilution of the original plume material and allows time for reactive and depositional loss processes to operate. It is difficult to compare the measurements made here with the current data available due to the possible variances in experimental conditions such as different observational

regions, times, altitudes and also measurement techniques. Bertram et al. (2011) deployed the CI-TOFMS on the R/V *Atlantis* in 2010 during the CalNex campaign. An average concentration in clean marine air was found to be 80 ppt and off shore pollution to be 800 ppt. The concentrations agree well with the

 $_{25}$ observed levels found during flight B518. During the SONEX campaign in 2002, aircraft measurements of formic acid were made and typical formic acid concentrations were reported as 120 ± 65 pptv (Singh et al., 2000), which is similar to data presented in this



paper. However, no further details on formic acid were provided, so no comparison to variability in mixing ratios in and out of plumes can be made.

3.2 Urban plumes

Flight B518 intercepted 3 separate plumes of formic acid over the UK. The different plumes detected during the flight were plumes from London, Humberside and Tyneside, these are labelled in Fig. 4. The London, Humberside and Tyneside plumes had peak concentrations of 358, 311 and 192 pptv respectively. The ability to detect these different source areas demonstrates the utility of the instrument for formic acid detection.

- ¹⁰ The London metropolitan area is densely populated with a high volume of industrial, domestic and transport activity, a known major source of carboxylic acid emissions (Chebbi et al., 1996). Kawamura et al. (1975) observed formic acid emitted directly from motor vehicle exhausts. The high volume of traffic in the Greater London region is likely to be a major source of formic acid.
- Important emissions from anthropogenic sources such as from motor exhausts, from the incomplete combustion of fuel, indicate high levels of formic acid should be emitted from London area (Kawamura et al., 1985). Flight B518 collected data passing through this region. Figure 5 shows the flight track and the concentrations observed on this day. The s-s-westerly wind direction allowed measurements of this plume at an altitude of
- ²⁰ 700 m, 230 km away from the source. With the average wind speed of 2.8 m s⁻¹ on this day, the plume is estimated to have taken around 18 h to reach the location where the CIMS detected it (off the North Norfolk coast). The time series of formic acid concentrations indicates a peak mixing ratio of 358 pptv over this region. No correlations were observed with CO, NO_x and O₃ although NO_x is known to be a marker of traffic and anthropogenic sources. The different formation and loss processes of NO_x and formic
- acid may have different time constants, therefore producing a low correlation. Further knowledge of these time constants is needed to increase the accuracy of the models.



The second plume detected during the flight was from the Humberside region. This is an urban area but with a lower population and industrial activity than London, this is indicated by the lower concentrations observed. North of latitude 53°45′, the average ambient mixing ratio drops to below 100 pptv where as an average concentration before

this was 200 pptv. This low ambient concentration allowed the detection of a plume with a peak of 192 pptv, from the Tyneside region (Fig. 6). Tyneside is expected to be a heavily polluted area similar to that of Humberside and with similar sources as London. The lower mixing ratios found in the Tyneside plume indicates that formic acid sources cannot be categorised simply into anthropogenic pollution. More data are needed to
 identify and characterise important source regions over the UK.

3.3 Altitude profile

The correct altitude profile is essential for satellite retrievals and there inference regarding the photochemistry of formic acid. A vertical profile of formic acid from 800 to 2300 m is shown in Fig. 7. The concentrations increases up to 1200 m peaking at a ¹⁵ concentration of 313 pptv and then fell off with increasing altitude. Low concentrations were observed below 1000 m. Although Baboukas et al. (2000) observed emissions of formic acid from the ocean; net flux measurements are not well known. Emission rates during this flight may have been lower than the deposition rates, causing the observed lower concentrations. At 1000 m, air masses rising from anthropogenic sources will ²⁰ mix and raise the formic acid mixing ratio. A decrease in concentration is observed

- ²⁰ mix and raise the formic acid mixing ratio. A decrease in concentration is observed at 2000 m as this is the top of the boundary layer. For future flights, an Aerosol mass spectrometer (AMS) will be used simultaneously, which will increase our understanding on aerosol and gas-phase partitioning. The profile in Fig. 7 was measured on the edge of the London plume. Due to the possible higher concentrations in the profile
- ²⁵ contributed from the plume, it can still provide information of the gas as a function of altitude, although it may not be typical of an ambient formic acid profile.



Reiner et al. (1999) measured formic acid in the UTLS region from 7–12 km and observed that formic acid concentrations decrease with altitude, which is in agreement with this work. The measured formic acid concentrations ranged from 0–600 ppt with mean concentrations of 59–215 pptv across the measured altitude range.

5 3.4 Trajectory model

20

A trajectory model has been used to estimate formic acid concentrations along the B518 flightpath. The trajectory model used for this purpose has been described in previous papers (Johnson et al., 2006; Evans et al., 2000) and will be only briefly described here. The trajectory model simulates the chemical development in a well-¹⁰ mixed air parcel being advected along multi-day trajectories. The air parcel picks up emissions of NO_x, CO, SO₂, methane, anthropogenic VOC and biogenic VOC when in the boundary layer, which are processed using an appropriate description of the chemical and photochemical transformations leading to the formation of ozone and other secondary pollutants. Dry deposition of species also occurs when the air parcel is in the boundary layer.

Two chemistry modules have been integrated into the trajectory mode: the full Master Chemical Mechanism (MCM v3.1; Jenkin et al., 1997) and the Common Representative Intermediates Scheme (CRIv2-R5; Jenkin et al., 2008; Watson et al., 2008; Utembe et al., 2009, 2010, 2011; Archibald et al., 2010). Trajectories are generated by the Hysplit model and integrated for four days, arriving at a point coincident in time and space with the aircraft flight track (Draxler et al., 2003).

3.5 Comparison between model and measurements

In general, the measurements show that formic acid levels below \sim 500 m are significantly larger than those above \sim 1000 m (Fig. 8). Although the modelled concentrations do not show as large a variation as the measurements, there is a clear negative



gradient with altitude, in keeping with the observations. The model underestimates measurements by a factor of two up to around 2.30 p.m. and from then on agreement between the two is very good (Fig. 8). The sources of formic acid in the model are the reaction of CH₂OO (from ethene ozonolysis predominantly but also other sources such as isoprene) with water and the reaction of OH with acetylene, where the former represents over 95 % of the production and the latter the remainder. Based on the biogenic emission inventory the level of primary emissions from biogenic hydrocarbons into these trajectories is low. The under-prediction early on in the time series could be due to missing direct surface emissions or missing extremely reactive formic acid precursors (e.g. Archibald et al., 2007) such as isoprene. Indeed, inspection of the

- precursors (e.g. Archibald et al., 2007) such as isoprene. Indeed, inspection of the trajectories shows that at around 2 p.m., the aircraft encountered air associated with the plumes from London and Humberside and would have picked up primary surface emissions from combustion sources. Measurements from around 3 p.m. onwards are lower, this is a result of an increase in altitude, where air mass back trajectories sug-
- ¹⁵ gest that direct input from primary surface sources is much weaker. If ozonolysis of terminal olefinic species leads to the formation of CH₂OO (Leather et al., 2011; Taatjes et al., 2008) and the Criegee bi-radical reacts with water to form HCOOH, there may be both anthropogenic and biogenic sources (e.g. isoprene and certain monoterpenes). Inspection of urban isoprene levels from the UK Air Quality (NETCEN) archive (e.g.
- Rivett et al., 2003a, b; Khan et al., 2008) show that typical levels in March are around 60 ppt and not all of this will be of biogenic origin. Using these levels of surface isoprene (higher than those predicted by the emission model) as input into the trajectory model would not generate anywhere near enough HCOOH to rectify the model underprediction that is seen up to around 2.30 p.m. Increasing primary morning emissions of
- HCOOH from an anthropogenic source increases HCOOH in the early afternoon, but has less effect in the late afternoon, consistent with observations. Therefore, based on such a simple analysis, the discrepancy early on is probably due to anthropogenic emissions, most likely direct emissions of HCOOH or possibly (but less likely) emission of fast producing precursors and their reaction with ozone. Therefore, we conclude



5821

that further direct anthropogenic sources are probably responsible for the additional HCOOH observed before 2.30 p.m.

4 Conclusions

The first detailed formic acid measurements by chemical ionisation mass spectrometer (CIMS) onboard an airborne platform are presented. I⁻ ionisation chemistry has been successfully employed for the detection and measurement of trace amounts of atmospheric formic acid. Sensitivity of CIMS to formic acid was 35±6 ion counts s⁻¹ pptv⁻¹ and the limit of detection was 25 pptv.

Mean concentrations formic acid in the UK boundary layer on 16 March 2010 were 142 \pm 72 pptv. Higher concentrations were observed in plumes, which could be linked by trajectory analysis to main urban and industrial centres (London, Humberside and Tyneside regions). Formic acid showed no clear correlation with anthropogenic pollution markers such as NO_x, CO and O₃. The highest formic acid concentrations were measured at lower altitudes which is consistent with predominantly surface emission

- ¹⁵ sources. Formic acid levels as estimated by a trajectory model showed an under prediction of concentrations by up to a factor of 2. This under prediction can be explained by missing emission sources in the model that are considered to be the primary emissions of formic acid (of both biogenic and mainly anthropogenic origin). More measurements and in-depth modelling studies are needed to validate the current chemical
- transport models and help identify and quantify formic acid emission sources. This should also improve understanding of the role of formic acid in chemical cycling in the troposphere. To conclude, the direct measurements of formic acid in the UK boundary layer have shown how variable formic acid levels can be in the horizontal and vertical. The inability of the model to reproduce the observations highlights that further studies
- ²⁵ must aim to improve the understanding and quantification of formic acid sources.



Acknowledgements. The authors would like to thank Alan Knights for analysing the organic acid calibration gas mixture by GC-FID ADS. FAAM staff are also thanked for their assistance in getting the CIMS working onboard the aircraft.

References

10

20

- Andreae, M. O., Talbot, R. W., Andreae, T. W., and Harriss, R. C.: Formic and acetic acid over the central Amazon region, Brazil in dry season, J. Geophys. Res.-Atmos., 93, 1616–1624, 1988.
 - Archibald, A. T., McGillen, M. R., Taatjes, C. A., Percival C. J., and Shallcross, D. E.: On the importance of Ethenol in urban atmospheres, Geophys. Res. Lett., 34, L21801, doi:10.1029/2007GL031032, 2007.
 - Archibald, A. T., Cooke, M. C., Utembe, S. R., Shallcross, D. E., Derwent, R. G., and Jenkin, M. E.: Impacts of mechanistic changes on HOx formation and recycling in the oxidation of isoprene, Atmos. Chem. Phys., 10, 8097–8118, doi:10.5194/acp-10-8097-2010, 2010.
- Arlander, D. W., Cronn, D. R., Farmer, J. C., Menzia, F. A., and Westberg, H. H.: Gaseous oxygenated hydrocarbons in the remote marine troposphere, J. Geophys. Res.-Atmos., 95,
 - 16391–16403, 1990.
 - Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.
- Baboukas, E. D., Kanakidou, M., and Mihalopoulos, N.: Carboxylic acids in gas and particulate phase above the Atlantic Ocean, J. Geophys. Res.-Atmos., 105, 14459–14471, 2000.
 - Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-
- ²⁵ of-flight mass spectrometer, Atmos. Meas. Tech., 4, 1471–1479, doi:10.5194/amt-4-1471-2011, 2011.
 - Burling, I. R., Yokelson, R. J., Griffith, D. W. T., Johnson, T. J., Veres, P., Roberts, J. M., Warneke, C., Urbanski, S. P., Reardon, J., Weise, D. R., Hao, W. M., and de Gouw, J.: Laboratory measurements of trace gas emissions from biomass burning of fuel types from



the southeastern and southwestern United States, Atmos. Chem. Phys., 10, 11115–11130, doi:10.5194/acp-10-11115-2010, 2010.

- Broadgate, W. J., Liss, P. S., and Penkett, S. A.: Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean, Geophy. Res. Lett., 24, 2675–2678,1997.
- ⁵ Chebbi, A. and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, Atmos. Environ., 30, 4233–4249, 1996.
 - Dibb, J. E., Talbot, R. W., Whitlow, S. I., Shipham, M. C., Winterle, J., McConnell, J., and Bales, R.: Biomass burning signatures in the atmosphere and snow at Summit, Greenland: An event on 5 August 1994, Atmos. Environ., 30, 553–561, 1996.
- ¹⁰ Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4. html), NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
 - Evans, M. J., Shallcross, D. E., Law, K. S., Wild, J. O. S., Simmonds, P. G., Spain, T. G., Berrisford, P., Methven, J., Lewis, A. C., McQuaid, J. B., Pilling, M. J., Bandy, B. J., Penkett,
- S. A., and Pyle, J.: Evaluation of a Lagrangian box model using field measurements from EASE (Eastern Atlantic Summer Experiment) 1996, J.A., Atmos. Environ., 34, 3843–3863, 2000.
 - Fornaro, A. and Gutz, I. G. R.: Wet deposition and related atmospheric chemistry in the Sao Paulo metropolis, Brazil: Part 2 contribution of formic and acetic acids, Atmos. Environ., 37, 117–128, 2003.
 - Gerbig, C., Schmitgen, S., Kley, D., and Volz-Thomas, A.: An improved fast-response vacuum-UV resonance fluorescence CO instrument, J. Geophys. Res., 104, 1699–1704, 1999.

20

25

- González Abad, G., Bernath, P. F., Boone, C. D., McLeod, S. D., Manney, G. L., and Toon, G. C.: Global distribution of upper tropospheric formic acid from the ACE-FTS, Atmos. Chem. Phys., 9, 8039–8047, doi:10.5194/acp-9-8039-2009, 2009.
- Grosjean, D. and Seinfeld, J. H.: Parameterization of the formation potential of secondary organic aerosols., Atmos. Environ., 23, 1733–1747, 1989.
- Grosjean, D.: Formic acid and acetic acid emissions, atmossheric formication and dry seposition at 2 southern California locations, Atmos. Environ., 26, 3279–3286, 1992.
- ³⁰ Hartmann, W. R., Santana, M., Hermoso, M., Andreae, M. O., and Sanhueza, E.: Diurnal cycles of formic and acetic acids in the northern part of the Guayana shield, Venezuela, J. Atmos. Chem., 13, 63–72, 1991.

Huey, L. G., Tanner, D. J., Slusher, D. L., Dibb, J. E., Arimoto, R., Chen, G., Davis, D., Buhr,



M. P., Nowak, J. B., Mauldin , R. L., Eisele, F. L., and Kosciuch, E.: CIMS measurements of HNO_3 and SO_2 at the South Pole during ISCAT 2000, Atmos. Environ., 38, 5411–5421, 2004.

Jenkin, M. E., Saunders, S. M., Derwent, R. G., and Pilling, M. J.: Construction and application

- ⁵ of a master chemical mechanism (MCM) for modelling tropospheric chemistry, Abstr. Pap. Am. Chem. Soc., 214, 116-COLL, 1997.
 - Jenkin, M. E., Watson, L. A., Utembe, S. R., and Shallcross, D. E.: A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 1: Gas phase mechanism development, Atmos. Environ., 42, 7185–7195, 2008.
- Johnson, B. J. and Dawson, G. A.: A preliminary study of the carbon isotopic content of ambient formic acid and 2 selected sources – automobile exhaust and formicine ants, J. Atmos. Chem., 17, 123–140, 1993.
 - Johnson, D., Utembe, S. R., Jenkin, M. E., Derwent, R. G., Hayman, G. D., Alfarra, M. R., Coe, H., and McFiggans, G.: Simulating regional scale secondary organic aerosol formation
- during the TORCH 2003 campaign in the southern UK, Atmos. Chem. Phys., 6, 403–418, doi:10.5194/acp-6-403-2006, 2006.
 - Kawamura, K. and Kaplan, I. R.: Determination of organic acids (CrC10) in the atmosphere, motor exhausts, and engine oils, Environ. Sci. Technol., 19, 1082–1086, 1985.

Keene, W. C. and Galloway, J. N.: Considerations regarding sources of formic and acetic acids in the troposphere, J. Geophys. Res.-Atmos., 91, 14466–14474, 1986.

20

- Keene, W. C., Galloway, J. N., and Holden, J. D.: Measurement of weak organic acidity in precipitation from remote areas of the world, J. Geophys. Res.-Atmos., 88, 5122–5130, 1983.
- Khan, M. A. H., Ashfold, M. J., Nickless, G., Martin, D., Watson, L. A., Hamer, P. D., Wayne, R. P., Canosa-Mas, C. E., and Shallcross, D. E.: Night-time NO₃ and OH radical concentrations
- in the United Kingdom inferred from hydrocarbon measurements, Atmos. Sci. Lett., 9, 140– 146, 2008.
 - Leather, K. E., McGillen, M. R., Cooke, M. C., Utembe, S. R., Archibald, A. T., Jenkin, M. E., Derwent, R. G., Shallcross, D. E., and Percival, C. J.: Acid-yield measurements of the gas-phase ozonolysis of ethene as a function of humidity using Chemical Ionisation Mass
- ³⁰ Spectrometry (CIMS), Atmos. Chem. Phys. Discuss., 11, 25173–25204, doi:10.5194/acpd-11-25173-2011, 2011.
 - Nowak, J. B., Neuman, J. A., Kozai, K., Huey, L. G., Tanner, D. J., Holloway, J. S., Ryerson, T. B., Frost, G. J., McKeen, S. A., and Fehsenfeld, F. C.: A chemical ionization mass spectrometry



5825

technique for airborne measurements of ammonia, J. Geophys. Res.-Atmos., 112, D10S02, doi:10.1029/2006JD007589, 2007.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isopropa Science 225, 730, 222, 2000

⁵ prene, Science, 325, 730–233, 2009.

25

- Preunkert, S., Legrand, M., Jourdain, B., and Dombrowski-Etchevers, I.: Acidic gases (HCOOH, CH₃COOH, HNO₃, HCl, and SO₂) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe, J. Geophys. Res.-Atmos., 112, D23S12, doi:10.1029/2006JD008225, 2007.
- Real, E., Law, K. S., Weinzierl, B., Fiebig, M., Petzold, A., Wild, O., Methven, J., Arnold, S., Stohl, A., Huntrieser, H., Roiger, A., Schlager, H., Stewart, D., Avery, M., Sachse, G., Browell, E., Ferrare, R., and Blake, D.: Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic, J. Geophys. Res.-Atmos., 112, D10S41, doi:10.1029/2006JD007576, 2007.
- Reiner, T., Mohler, O., and Arnold, F.: Measurements of acetone, acetic acid, and formic acid in the northern midlatitude upper troposphere and lower stratosphere, J. Geophys. Res.-Atmos, 104, 13943–13952, 1999.

Rinsland, C. P., Mahieu, E., Zander, R., Goldman, A., Wood, S., and Chiou, L.: Free tropospheric measurements of formic acid (HCOOH) from infrared ground-based solar absorp-

- tion spectra: Retrieval approach, evidence for a seasonal cycle, and comparison with model calculations, J. Geophys. Res.-Atmos, 109, D18308, doi:10.1029/2004JD004917, 2004.
 - Rivett, A. C., Martin, D., Gray, D. J., Price, C. S., Nickless, G., Simmonds, P. G., O'Doherty, S. J., Greally, B. R., Knights, A., and Shallcross, D. E.: The role of volatile organic compounds in the polluted urban atmosphere of Bristol, England, Atmos. Chem. Phys., 3, 1165–1176, doi:10.5194/acp-3-1165-2003, 2003a.
 - Rivett, A. C., Martin, D., Nickless, G., Simmonds, P. G., O'Doherty, S. J., Gray, D. J., and Shallcross, D. E.: In situ gas chromatographic measurements of halocarbons in an urban environment, Atmos. Environ., 37, 2221–2235, 2003b.

Singh, H., Chen, Y., Tabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F.,

³⁰ Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Sachse, G., Vay, S., and Kondo, Y.: Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, J. Geophys. Res.-Atmos., 105, 3795–3805, 2000.



- Stewart, D. J., Taylor, C. M., Reeves, C. E., and McQuaid, J. B.: Biogenic nitrogen oxide emissions from soils: impact on NO_x and ozone over west Africa during AMMA (African Monsoon Multidisciplinary Analysis): observational study, Atmos. Chem. Phys., 8, 2285– 2297, doi:10.5194/acp-8-2285-2008, 2008.
- Sanhueza, E. and Andreae, M. O.: Emissions of formic and acetic acids from tropical Savanna soils, Geophys. Res. Lett., 18, 1707–1710, 1991.
 - Sanhueza, E., Figueroa, L., and Santana, M.: Atmospheric formic and acetic acids in Venezuela, Atmos. Environ., 30, 1861–1873, 1996.
 - Talbot, R. W., Dibb, J. E., Scheuer, E. M., Blake, D. R., Blake, N. J., Gregory, G. L., Sachse,
- ¹⁰ G. W., Bradshaw, J. D., Sandholm, S. T., and Singh, H. B.: Influence of biomass combustion emissions on the distribution of acidic trace gases over the southern Pacific basin during austral springtime, J. Geophys. Res.-Atmos., 104, 5623–5634, 1999.
 - Veres, P., Roberts, J. M., Warneke, C., Welsh-Bon, D., Zahniser, M., Herndon, S., Fall, R., and de Gouw, J.: Development of negative-ion proton-transfer chemical-ionization mass spec-
- trometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, Int. J. Mass Spectrom., 274, 48–55, 2008.
 - Von Kuhlmann, R., Lawrence, M. G., Crutzen, P. J., and Rasch, P. J.: A model for studies of tropospheric ozone and nonmethane hydrocarbons: Model evaluation of ozone-related species, J. Geophys. Res.-Atmos, 108, 4729, doi:10.1029/2002JD003348, 2003.
- ²⁰ Utembe, S. R., Watson, L. A., Shallcross, D. E., and Jenkin, M. E.: A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 3: Development of a secondary organic aerosol module, Atmos. Environ., 43, 1982–1990, 2009.
 - Utembe, S. R., Cooke, M. C., Archibald, A. T., Jenkin, M. E., Derwent, R. J., and Shallcross, D. E.: Using a reduced Common Representative Intermediates (CRIv2-R5) mechanism to sim-
- ulate tropospheric ozone in a 3-D Lagrangian chemistry transport model, Atmos. Environ.,
 44, 1609–1622, 2011.
 - Utembe, S. R., Cooke, M. C., Archibald, A. T., Shallcross, D. E., Derwent, R. G., and Jenkin, M. E.: Simulating Secondary Organic Aerosol in a 3-D Lagrangian Chemistry Transport Model using the reduced Common Representative Intermediates Mechanism (CRIv2-R5), Atmos.
- ³⁰ Environ., 45, 1604–1614, 2011.
 - Watson, L. A., Shallcross, D. E., Utembe, S. R., and Jenkin, M. E.: A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 2: Gas phase mechanism reduction, Atmos. Environ., 42, 7196–7204, 2008.



Discussion Paper **AMTD** 4, 5807-5835, 2011 Airborne observations of formic acid M. Le Breton et al. **Title Page** Introduction Abstract Conclusions References Tables Figures Back Close Full Screen / Esc Printer-friendly Version Interactive Discussion

Discussion Paper

Discussion Paper

Discussion Paper

- Yu, S. C.: Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): a review, Atmos. Res., 53, 185-217, 2000.
- Zander, R., Duchatelet, P., Mahieu, E., Demoulin, P., Roland, G., Servais, C., Auwera, J. V., Perrin, A., Rinsland, C. P., and Crutzen, P. J.: Formic acid above the Jungfraujoch during
- 1985-2007: observed variability, seasonality, but no long-term background evolution, Atmos. 5 Chem. Phys., 10, 10047-10065, doi:10.5194/acp-10-10047-2010, 2010.
 - Zhong, Z. C., Victor, T., and Balasubramanian, R.: Measurement of major organic acids in rainwater in Southeast Asia during burning and non-burning period, Water Air Soil Pollut., 130. 457-462. 2001.

10



Fig. 1. Schematic of chemical ionisation mass spectrometer (CIMS) used in this study. Arrows indicate direction of gas flow. Dimensions are not to scale.





Fig. 2. Mass spectrum of CIMS during flight B518, 16 March 2010 at 16:00. Ionisation peaks and formic acid adduct mass are labelled.





Fig. 3. Cycle for background, sampling and calibrations during flight B538.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Fig. 4. Time series of 30 s averaged formic acid observations (left axis) with altitude (right axis) from the 16 March 2011 flight. The London, Humberside and Tyneside plumes have been labelled. Sections of the flight where there are backgrounds, calibrations and transits are set to zero.



Discussion Paper

Discussion Paper

Discussion Paper



Fig. 5. The FAAM Bae146 flight track on 16 March 2010 over the UK. Formic acid mixing ratios are reverse rainbow colour coded from 0 ppb to 0.36 ppb. Populated urban areas are indicated and labelled.



Fig. 6. Box and whisker plots of total flight data and individual plumes detected during flight B518. Whiskers indicate the 5th and 95th percentile.





Fig. 7. Vertical profiles formic acid and NO_x mixing ratios from an altitude of 800 to 2300 m.









Discussion Paper

Discussion Paper

Discussion Paper