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RESEARCH ARTICLE

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Key Points:

- Formic acid and nitric acid measurements from the winter and summer ClearfLo campaign are reported
- A mean HCOOH concentration of 1.3 ppb is reported, which cannot be accounted for by direct anthropogenic emission and ozonolysis of alkenes only
- The secondary production from BVOC photooxidation could be the dominating source of formic acid in London during summer

Supporting Information:

- Supporting Information S1

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Seasonality of Formic Acid (HCOOH) in London during the ClearfLo Campaign

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Abstract Following measurements in the winter of 2012, formic acid (HCOOH) and nitric acid (HNO₃) were measured using a chemical ionization mass spectrometer (CIMS) during the Summer Clean Air for London (ClearfLo) campaign in London, 2012. Consequently, the seasonal dependence of formic acid sources could be better understood. A mean formic acid concentration of 1.3 ppb and a maximum of 12.7 ppb was measured which is significantly greater than that measured during the winter campaign (0.63 ppb and 6.7 ppb, respectively). Daily calibrations of formic acid during the summer campaign gave sensitivities of 1.2 ion counts s⁻¹ parts per trillion (ppt) by volume⁻¹ and a limit of detection of 34 ppt. During the summer campaign, there was no correlation between formic acid and anthropogenic emissions such as NO_x and CO or peaks associated with the rush hour as was identified in the winter. Rather, peaks in formic acid were observed that correlated with solar irradiance. Analysis using a photochemical trajectory model has been conducted to determine the source of this formic acid. The contribution of formic acid formation through ozonolysis of alkenes is important but the secondary production from biogenic VOCs could be the most dominant source of formic acid at this measurement site during the summer.

1. Introduction

Organic acids, the most abundant being formic acid (HCOOH), are ubiquitous in the troposphere. Formic acid has been found in urban, rural, marine, polar, and remote areas in both the gaseous phase and aerosol phase (Chebbi & Carlier, 1996; Keene & Galloway, 1988; Khare et al., 1999; Le Breton et al., 2012; Yu, 2000) with gas phase concentrations ranging from low hundreds of parts per trillion (ppt) to a few ppb (Paulot et al., 2011). Organic acids contribute to the acidity of precipitation (Andreae et al., 1988; Keene & Galloway, 1988; Keene et al., 1983), well known to be a problem in urban environments. Formic acid acts as a major contributor to cloud condensation nuclei (Yu, 2000). This is a result of their higher hygroscopicity at comparatively low critical supersaturations when formic acid is incorporated into the aerosol (Novakov & Penner, 1993). Hence, formic acid ultimately influences total indirect radiative forcing, a poorly understood effect in the atmosphere (Solomon, 2007).

Despite an understanding of numerous sources of formic acid, relative importance of sources is poorly quantified (Chebbi & Carlier, 1996) and models simulating concentrations in the atmosphere generally underestimate significantly when compared with measured results by factors up to 50 (Ito et al., 2007; Millet et al., 2015; Paulot et al., 2011; von Kuhlmann et al., 2003). Discrepancies between modeled and observed concentrations are partly due to a fundamental shortfall of data (Stavrakou et al., 2012) causing a lack of understanding of processes influencing concentrations. The differences between predicted and measured concentrations of organic acids in the atmosphere have led to many suspecting there are missing source terms which are unaccounted for (Leather et al., 2011). Based on the work of Nguyen et al. (2015), an emission flux on the order of 1 nmol m⁻² s⁻¹ is required during the day to match the discrepancies between modeled and measured formic acid.

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Secondary photochemical production of formic acid, primarily from biogenic precursors such as isoprene, has been shown to be a dominant source of formic acid globally (Neeb et al., 1997; Paulot et al., 2011; Sanhueza et al., 1996; Veres et al., 2011), but the magnitude is highly uncertain. Photochemical production proceeds by the ozonolysis of terminal alkenes, the majority of which are released from vegetation, and the subsequent reaction of Criegee intermediates (e.g., Johnson & Marston, 2008; Leather et al., 2011; Taatjes et al., 2013, 2014; Welz et al., 2012). A detailed list of alkenes that are known to produce carboxylic acids via ozonolysis reactions can be found in Chebbi and Carlier (1996), with isoprene ozonolysis being a dominant source (Paulot et al., 2011). As temperature and light intensity have a strong effect on emission rates of alkenes such as isoprene, the potential importance of seasonality and global location on formic acid production is evident.

Other known sources of formic acid nonexhaustively include primary emissions from biogenic and anthropogenic activity, secondary production via alkene ozonolysis (Sanhueza et al., 1996), acetaldehyde tautomerization to vinyl alcohol, followed by reaction with OH (Andrews et al., 2012; Millet et al., 2015), biomass burning (Andreae & Merlet, 2001; R'Honi et al., 2013), and photodegradation of secondary organic aerosol (Malecha & Nizkorodov, 2016). In urban environments, the photooxidation of enols is also a formic acid source (Archibald et al., 2007). A detailed inventory of known sources can be found in Paulot et al. (2011) with contributions depending on factors such as anthropogenic activity, type, and amount of vegetation and meteorological conditions (e.g., Avery et al., 2001; Jones et al., 2017).

Measured global formic acid concentrations do show seasonal variations, directly correlated with growing seasons (Andreae et al., 1988; Grutter et al., 2010; Keene & Galloway, 1988; Peña et al., 2002) suggesting that terrestrial vegetation is a significant source of carboxylic acids. Rinsland et al. (2004) also showed the importance of seasonality of formic acid production with concentrations between July and September being a factor of 2.5 higher than October through December. This was in good agreement with Talbot et al. (1988) who showed an increase by a factor of 2.7 in the growing season but much lower than that reported from Mount Lemmon, Arizona, where an increase by a factor of 7.5 was observed in summer (Johnson & Dawson, 1993).

Globally, only 10% of total formic acid is said to be produced by fire events or anthropogenic means (Stavrakou et al., 2012). The importance of direct anthropogenic emissions of formic acid during winter in London was shown in the Clean Air for London (ClearfLo) winter intensive observation period (Bannan et al., 2014). The winter study presented no evidence of production from biogenic or secondary photochemical pathways but demonstrated that direct anthropogenic emissions were the dominant source of formic acid at this time and location. High correlations with NO_x , CO, and rush hour periods with formic acid production and no correlation with nitric acid or ozone during the complete winter ClearfLo time series showed that this organic acid was released directly from vehicle emissions (Bannan et al., 2014). Global modeling using the emission factors derived from London during winter suggested that in the northern midlatitudes, around major urban centers, the contribution of formic acid from direct emissions at particular locations (Northern Europe) can reach up to 30% (Bannan et al., 2014). Therefore, it is necessary to establish if the importance of direct anthropogenic emissions to the total formic acid concentration is isolated to just the winter months in London, and likely other mega cities, or if other sources in the summer dominate or at least contribute to the overall concentrations of formic acid at this time.

This study will compare the results of formic acid production from winter (January to February 2012; Bannan et al., 2014) with the summer (July to August 2012) as part of the Clean Air for London (ClearfLo) campaign to assess the importance of seasonality to formic acid production at this location.

2. Experimental

2.1. Site Description

Measurements as part of the ClearfLo summer campaign (<http://www.clearflo.ac.uk/>) were made in North Kensington, London, between 20 July and 19 August 2012. The ClearfLo project aims to provide long term combined atmospheric measurements, resulting in a greater accuracy for future predictions of air quality, specifically within the city of London. Measurements as part of the ClearfLo campaign were primarily taken during approximately 1 month long intensive observations for two periods, one in the winter (January–February 2012) and the second in summer (July–August 2012). The summer measurement period

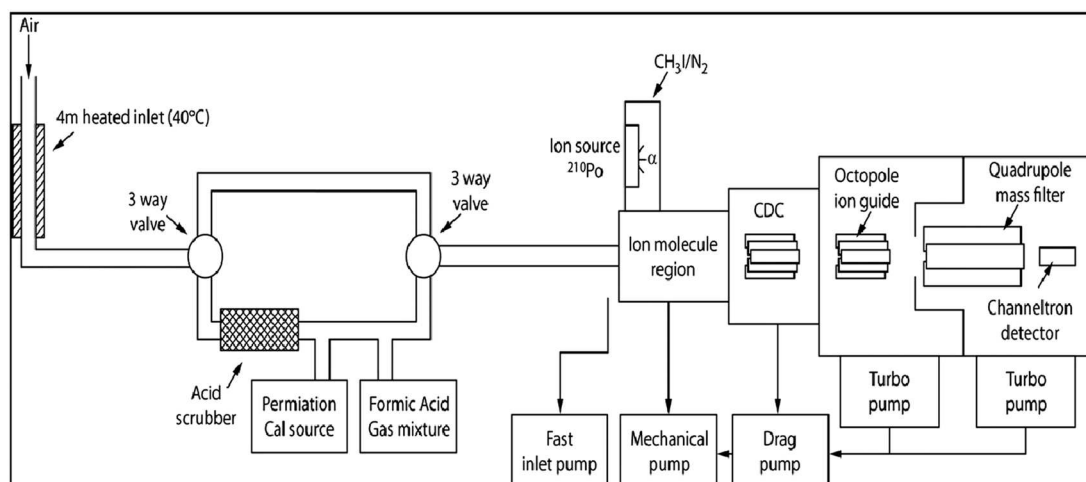


Figure 1. Schematic of the CIMS used in this study.

coincided with the 2012 Olympic Games, providing an opportunity to assess how such a large event in a city influenced important atmospheric species. Also, the site is an air quality monitoring station run by the Automatic Urban and Rural Network (AURN). Information from which can be found in Bigi and Harrison (2010), presenting results between the years of 1996–2008 of CO , NO_x , SO_2 , and PM_{10} . Results from Bigi and Harrison (2010) suggest that this location in North Kensington can be defined as an urban background site.

Detailed site and instrumental descriptions have already been included in Bohnenstengel et al. (2015) and Bannan et al. (2014). The site and instrument set up for the summer are identical apart from minor procedural changes in the running of the CIMS. The site is located at 51.521055°N , 0.213432°W based in the grounds of the Sion Manning School, within a residential area, 7 km west of Central London. The summer measurement period was held during school holidays, so traffic patterns were slightly altered by this but the residential traffic would be unaffected.

2.2. Chemical Ionization Mass Spectrometry

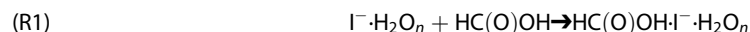
A chemical ionization mass spectrometer (CIMS) was utilized to make measurements of formic and nitric acid as well as other trace gaseous species at a 1 Hz frequency. The CIMS selectively ionizes specific gas phase species using I^- as a reagent gas which is analyzed by a quadrupole mass spectrometer. This system was developed by the Georgia Institute of Technology and has been described by Nowak et al. (2007). The system and calibration set up has also been described by Bannan et al. (2014) and shown in Figure 1. Measurements were made simultaneously with ClNO_2 and N_2O_5 (Bannan et al., 2015). The set up between the winter and summer campaigns was identical to allow continuity of results with only minor procedural changes in the timings of calibrations been changed. Details of which will be described in full in a following section.

2.3. Ionization Scheme

I^- has been used successfully and selectivity as a reagent ion in the CIMS in numerous ground and airborne bases studies (Huey et al., 1995; Le Breton et al., 2012, 2014; Slusher et al., 2004) and was the same ionization scheme used in the winter study to measure organic acids among other species also (Bannan et al., 2014). Specifically, for the Manchester CIMS the methyl iodide reagent ions were produced as previously described by Le Breton et al. (2012), from a gas mixture which comprised 0.5% methyl iodide (CH_3I (99.5%, Sigma-Aldrich), H_2O (0.5%) in N_2 (99.998%, BOC)). The CH_3I mixture and N_2 (99.998%, BOC), at flow rates of $1 \text{ cm}^3 \text{ min}^{-1}$ and 1.5 standard liters per minute, respectively, are passed over the alpha-emitting radioactive source (Polonium-210 inline ionizer, NRDinc Static Solutions Limited) creating an excess of I^- and $\text{I} \cdot (\text{H}_2\text{O})^-$ in the ionization region which react with the species of interest for detection.

The sensitivity of the mass spectrometer is dependent directly on the amount of $\text{I} \cdot \text{H}_2\text{O}^-$ in the system, as it is the $\text{I} \cdot \text{H}_2\text{O}^-$ and not I^- that is the most efficient ionizer of the species such as formic (R1) (Slusher et al., 2004). As illustrated in Le Breton et al. (2014) above a threshold of 1×10^5 counts per second (cps) of $\text{I} \cdot \text{H}_2\text{O}^-$ the

sensitivity to formic acid is independent of relative humidity with the tuning of our system. Throughout the ClearfLO measurement period the average $I \cdot H_2O^-$ was in excess of 4×10^5 cps, well above the threshold required for sensitivity to the independent to changes in water vapor. No normalization was therefore required. This was achieved through the tuning of the ion optics but as H_2O also is added to the ionization mix to this further ensures that the sensitivity of the system is independent to that of fluctuation in ambient relative humidity, as used by Le Breton et al. (2014).



2.4. Formic Acid Calibration, Sensitivity, and Limit of Detection

Formic and nitric acid instrumental backgrounds were determined for 20 continuous minutes every 180 min. These were determined by passing the sample air through densely packed sodium bicarbonate coated nylon shavings, changed weekly, which act as an efficient acid scrubber (Huey, 2007). Twice daily calibrations for formic and nitric acid were also run using a formic and nitric permeation tubes as well as a diluted flow of 0.001% formic acid gas mixture. Instrumental sensitivities for formic and nitric acid were calculated to be 1.2 and 0.84 ion counts s^{-1} pptv $^{-1}$, respectively. The 3σ limit of detection for formic acid during the full campaign was 34 ppt. The same data quality assurance measures described in Bannan et al. (2014) were applied in the summer observation period.

2.5. CIMS Analysis and Data Acquisition

The CIMS continuously monitors 11 mass peaks with a dwell time of 100 ms. Sampling and calibration cycles are averaged to 30 s, from 1 s data. Correlation with meteorological and chemistry data are completed with averaged data over 5 min.

2.6. Photochemical Trajectory Model

A photochemical trajectory model has been used to compare with the measurement suite. The model has been described in detail in previous papers (Johnson, Utembe, and Jenkin, 2006; Johnson, Utembe, Jenkin, Derwent, et al., 2006; Utembe et al., 2005). Meteorological back trajectories derived from the NOAA online trajectory service (http://ready.arl.noaa.gov/HYSPLIT_traj.php) are used to drive the photochemical model (air parcel) that integrates the continuity equation for each chemical species in the model. Pressure, temperature, terrain height, mixed layer depth, relative humidity, and the zenith angle of the Sun are calculated at each time step and are used to calculate kinetic rate coefficients and photolysis rates of the certain species. If the air parcel is in the boundary layer then emissions into the air parcel and dry deposition of certain species out of the air parcel can take place. A species-dependent dry deposition velocity approach was used for dry deposition. More details about the deposition velocities for the gas phase chemical species used in the model can be found in Derwent et al. (1996) and Abdalmogith et al. (2006). The formic acid dry deposition velocity was set to 2.0 cm/s based on von Kuhlmann et al. (2003) study. No allowance was made for the wet deposition of formic acid. The deposition loss of formic acid is crudely represented for in the model which can impact the formic acid prediction in the photochemical trajectory model (PTM) study. Emissions of NO_x , CO , SO_2 , NH_3 , CH_4 , and anthropogenic NMVOCs are taken from the NAEI (<http://naei.defra.gov.uk>) for the UK, CORINAIR (<http://www.eea.europa.eu>), for certain parts of the EU, including Ireland and France and EMEP (<http://www.emep.int>) for the remaining European areas. The biogenic emissions inventory used is based on the work outlined in Simpson et al. (1995). The representation of biogenic VOC emissions has been described in detail elsewhere (Johnson, Utembe, Jenkin, Derwent, et al., 2006). The speciation of the emitted anthropogenic VOC was based on the NAEI, which identifies 650 individual species (Goodwin et al., 2001). The speciation of the total NMVOC emissions into 115 individual hydrocarbons (21 alkanes, 20 alkenes/alkynes including 11 terminal alkenes, 18 aromatics, 16 carbonyls, 17 alcohols/glycols, 12 ethers/glycol ethers, 3 organic acids, and 8 esters) which contribute ~66% of the total NAEI emissions, by mass. The remaining 34% from over 500 hydrocarbons which were emitted in the form of appropriate surrogates with the basis of the chemical class and reactivity. The relative contributions of the individual species to the total emissions can be found in Utembe et al. (2005).

The chemical mechanism used in a photochemical trajectory model (PTM), is the Common Representative Intermediates (CRI) mechanism version 2. The detailed description of the CRI mechanism is given by Watson et al. (2008) with updates highlighted in Jenkin et al. (2008), and the full mechanism is available

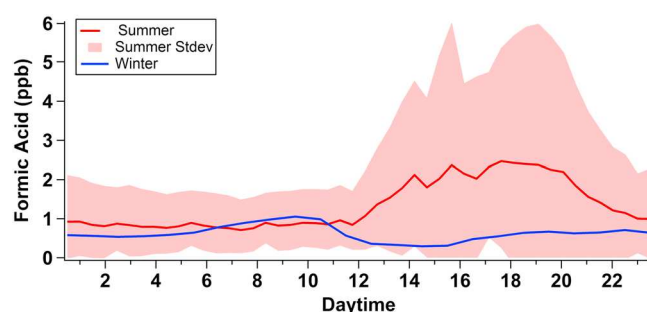


Figure 2. Diurnal average of formic acid in both the summer and winter campaign. Red line indicates the total average for the summer campaign, with the standard deviation of this also showed in light red. For comparison, the winter average diurnal cycle is also shown from Bannan et al. (2014) in blue.

via the Master Chemical Mechanism (MCM) website (<http://mcm.leeds.ac.uk/CRI/>). The rate coefficients specified as a function of temperature and incident light (values taken from either the MCM (<http://mcm.leeds.ac.uk/>) and/or the Jet Propulsion Laboratory kinetic evaluation reports (<http://jpldataeval.jpl.nasa.gov/>), assuming perfect mixing within any given air parcel. The CRI mechanism consists of methane and 115 emitted nonmethane hydrocarbons using 434 chemical species competing in 1,183 photochemical reactions and gives excellent agreement in terms of its ability to produce ozone with the MCM v3.1 over a full range of NO_x levels (Jenkin et al., 2008; Watson et al., 2008). Trajectories are integrated every hour starting 96 h previously to arrive at the measurement point so that a complete time series for the whole campaign can be generated.

2.7. Supporting Measurements

Measurements of NO_x were made using a chemiluminescence instrument (Air Quality Design Inc., USA). Ozone measurements were made using a UV Absorption TEI 49C and 49i (Thermo Scientific) with a limit of detection of 1 ppb. CO was measured using an Aerolaser AL 5002 UV fluorescence instrument which was calibrated using an Air Products 200 ppb CO in air standard that was certified to NPL standards.

Isoprene measurements were made using a dual channel GC-flame ionization detector and was operated by the National Centre for Atmospheric Science (NCAS) Facility for Ground Atmospheric Measurements (FGAM) (now the Atmospheric Measurements Facility (AMF)) with the instrument set up and calibration described in Hopkins et al. (2003) and its deployment during ClearfLO described in detail by Dunmore et al. (2015).

2.8. Dispersion Modeling

Dispersion modeling was carried out using the UK Met Office's Numerical Atmospheric-dispersion Modeling Environment (NAME) dispersion model (Jones et al., 2007); see detail in Bohnenstengel et al. (2015). The NAME dispersion model was used to produce 3-hourly averaged air mass footprints for the campaign period that tracks the air mass origins during the previous 24 h. A count of particle concentration was taken every 15 min during the 24 h period and summed together to create a probability footprint. A regional map over the 24 h domain was used to count the number of particles traveling through predefined regions including UK continental, Atlantic Ocean, the Channel, the North Sea and continental Europe. For each 3-hourly footprint, the total amount of particles counted in each region was translated into a % regional influence (from the total particle count in the whole domain), similar to a residence time in each region.

3. Results and Discussion

Formic acid concentrations during the Summer ClearfLo Campaign, 2012, are shown in Figure S1 in the supporting information. Formic acid concentrations up to 12.7 ppb were observed in this study, a factor of 1.9 greater than the maximum concentration reported during the winter campaign. Concentrations of formic acid were highest on the 23–26 July with peaks of 12.7, 12.5, 10.4, and 7.8 ppb, respectively, concurrent with the 4 days of the highest recorded temperatures. The 26 July had the highest recorded maximum temperature of 32°C, followed by the 23–25 July, all with a daily maximum temperature of over 29°C. NAME modeling analysis for the 22–24 July suggests that the air originated from Northern France and over the English Channel (Figure S2), with a strong south easterly UK influence (with the residence time over the London area increasing significantly toward the 24 July). On the 25 and 26 July the air masses changed quite suddenly, bringing a more northerly air mass from the North Sea area with an East Anglian, UK Midlands, and some Benelux influence. Periods after this include a westerly influence and then again north European influence (but with much more clean Atlantic air in the mix than during the 22–24 period), with Figure S2 providing a visualization for changes in air mass influence throughout the complete measurement period. Concentrations of formic acid rarely dropped below the limit of detection (34 ppt), which only occurred during nighttime hours. Peaks in formic acid occurred between 4 and 6 p.m. local time after which, concentrations dropped significantly following sunset (Figure 2).

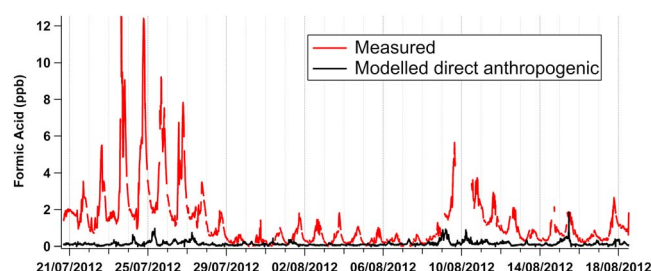


Figure 3. Measured formic acid and calculated formic acid released from vehicle emission based on the NO_x to formic acid emission ratios derived in the winter (Bannan et al., 2014). Vertical lines in the figure indicate mid-night in the time series.

The mean concentration of formic acid measured in summer was 1.33 ppb in comparison with 0.63 ppb reported during winter. The 211% increase in formic acid concentration between seasons indicates that there is either a switch of the types of sources seen or an enhancement of a particular source of formic acid in the summer months. This factor is comparable with the seasonal dependence shown by Rinsland et al. (2004) who saw a 250% increase in formic acid concentrations between summer and winter. The meteorology and chemistry differences between the summer and winter campaigns were considerable. The mean solar maximum for the winter and summer campaigns were measured to be 192 W/m^2 and 534 W/m^2 , respectively, with an average summer temperature of 20°C in comparison with 5°C measured in the winter. Pollution levels, denoted by NO and CO were also substantially smaller during the summer. Such

a considerable change in conditions between the two mirrored campaigns provides an ideal base for a seasonal comparison in sources of formic acid in an urban environment.

Measured winter formic acid (Bannan et al., 2014) presented a strong positive correlation between anthropogenic and pyrogenic emissions such as NO_x and CO, demonstrating a direct anthropogenic emission of this organic acid. In contrast with the winter measurements, there is no relationship between formic acid production and NO_x (Figure S3) or CO during the summer. The average diurnal profiles for the summer campaign are shown in Figure S4 illustrating that there is an anticorrelation between the average diurnal profiles of these anthropogenic and pyrogenic dominated emissions (NO, NO_2 , and CO) and formic acid production. The levels of CO and NO_x are found to be lowest from noon to the afternoon due to the faster oxidation processes. The response of formic acid to oxidative changes are found to be opposite to changes in CO and NO_x (Figure S4), suggesting a strong photochemical source of formic acid. This is not consistent with the winter where definite formic acid rush hour peaks are observed. A change in traffic patterns as a result of the Olympic Games can be ruled out for the altering of the diurnal cycle of formic acid as the vehicle emission tracers, that is, NO_x and CO, still show similar rush hour peaks as in the winter despite lower concentrations seen in summer.

A comparison between the summer and winter diurnal profile is shown in Figure 2. In winter, the values for the average diurnal cycle range between 0.3 and 1.1 ppb and peaks in formic acid concentrations are evident during rush hour periods. Conversely, formic acid production during the summer is peaking during sunlight hours, with an average maximum of 2.8 ppb at 6 p.m. (Figure 2). Concentrations of formic acid in the summer begin to rise soon after 10 a.m. and decrease only after sunset, and an average minimum of 0.8 ppb is reached by midnight. No such rush hour peaks are observed in the formic acid trend during the summer; instead, a correlation with daytime production is seen.

Because of the lack of either observable correlations with anthropogenic trace gas markers (Figure S3) or rush hour peaks in the average diurnal cycle of formic acid (Figure 2), direct anthropogenic emissions can be ruled out as the dominant source in the summer in contrast with the winter study. Using the formic acid emission ratios derived from the winter campaign: $1.22 \times 10^{-3} \text{ ppb}^{-1}$ and $8.35 \times 10^{-3} \text{ ppb}^{-1}$ to CO and NO_x , respectively (Bannan et al., 2014), it is possible to derive a direct anthropogenic emission, as shown in Figure 3.

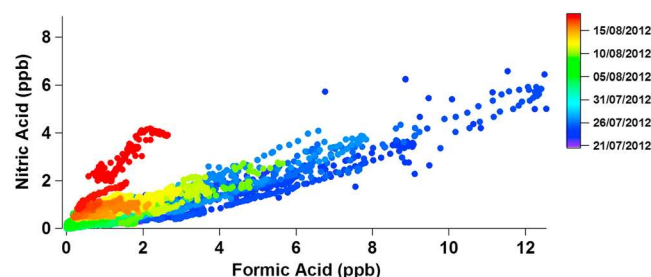


Figure 4. The relationship between formic and nitric acid between the 19 July and 20 August. Color here is depicting time of measurements, with data averaged to a 5 min resolution.

Formic acid concentrations with an average of 0.2 ppb and a peak concentration of 0.73 ppb could be expected from this vehicle source. Direct anthropogenic emissions only contribute 15% to the overall concentrations observed (Figure 3). This would suggest that the summer formic acid concentrations are now being dominated by other sources.

Nitric acid is a secondary photochemical product arising from the reaction between OH and NO_2 and a relationship between formic and nitric acid would suggest the former to be produced via a secondary production pathway (Le Breton et al., 2012, 2014; Veres et al., 2011). The very low correlation between nitric and formic acid throughout the winter campaign ($R^2 = 0.137$), illustrated that secondary production was not a large contributor to formic acid production at that time and location.

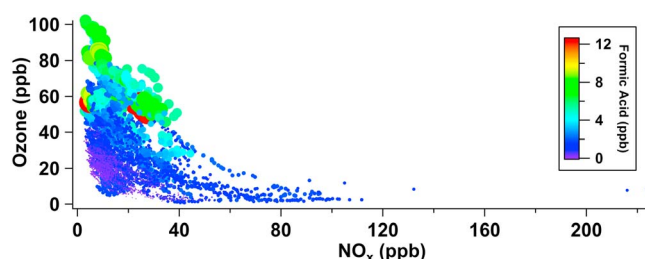


Figure 5. NO_x against ozone concentrations from 20 July 2012 to 20 August 2012. Formic acid concentrations are depicted by both size and color.

This is in stark contrast to the summer campaign where there is a much stronger positive correlation with formic and nitric acid throughout ($R^2 = 0.62$) (Figure 4), suggesting secondary photochemical production of formic acid in summer in this location. There appears to be two gradients for the formic to nitric acid production, one for the majority of the campaign and another on 15–16 August.

The NO_x against ozone, colored by formic acid, plot shown in Figure 5 is in contrast to the correlations observed during the winter campaign (Bannan et al., 2014). During the winter campaign, the highest concentrations of formic acid were observed in periods of high NO_x ,

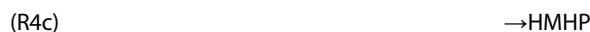
with only very minimal concentrations seen in elevated ozone conditions. However, during the summer measurements, high concentrations of formic acid are observed in the high ozone, low NO_x region. This further indicates a strong switch from the dominance of direct anthropogenic emission of formic acid in the winter to a strong secondary, photochemical production pathway in the summer.

A possible secondary photochemical production of formic acid is via the ozonolysis of a terminal alkene and the subsequent isomerization reaction of the Criegee intermediate. (e.g., Leather et al., 2011; Welz et al., 2012; Taatjes et al., 2008, 2012, 2013). Isoprene is the major VOC emitted by plants (Finlayson-Pitts & Pitts, 2000; Guenther et al., 2006) and ozonolysis of this terminal alkene has been shown to produce large quantities of formic acid (e.g., Neeb et al., 1997). The mean concentration for ozone throughout the summer campaign was 27.8 ppb, in comparison with 0.5 ppb that was seen in the winter. Isoprene concentrations are also significantly larger in the summer campaign with a mean concentration of 0.12 ppb in comparison with the average 0.03 ppb observed in winter. Thus, it is clear that secondary production rates are much more significant in the summer and why no evidence of this production pathway was seen in the winter campaign. Figure 6 shows the secondary production rate of formic acid, that is, $[\text{isoprene}] \times [\text{ozone}]$, in comparison with formic acid, showing the peak formic acid agrees well with secondary production rate via ozonolysis.

Indeed, recently, Welz et al. (2012) suggest that the reaction of Criegee intermediate with the water dimer could be the missing source of formic acid in the atmosphere if it is assumed that the yield from reaction (R4) exclusively forms formic acid.



However, recently Nguyen et al. (2016) have measured the branching ratio for reactions (R3) and (R4) and have shown that there are three possible reaction channels



and reported $F_4(\text{CH}_2\text{O}) = 6\%$ for both (R3a) and (R4a), $\text{HCOOH} = 21\%$ for (R3b) and 54% for (R4b) and $\text{HMHP} = 73\%$ for (R3c) and 40% for (R4c). Sheps et al. (2017) also reported $\text{CH}_2\text{O} = (40 \pm 10)\%$, $\text{HMHP} = (55 \pm 15)\%$, and $\text{HCOOH} < 10\%$ for reactions (R4a)–(R4c), respectively.

Figure 7 shows that a comparison of observed isoprene, O_3 , NO , HNO_3 , CO , and HCOOH levels with PTM, which reproduces the observations moderately well with Pearson r values of 0.36, 0.48, 0.21, 0.46, 0.59, and 0.39 for isoprene, O_3 , NO , HNO_3 , CO , and HCOOH , respectively. The model-calculated concentrations of NO , CO , and HNO_3 are overestimated but do not impact the model formic acid as they are not directly related to the formation of HCOOH . The PTM grossly underpredicts the measured formic acid, despite

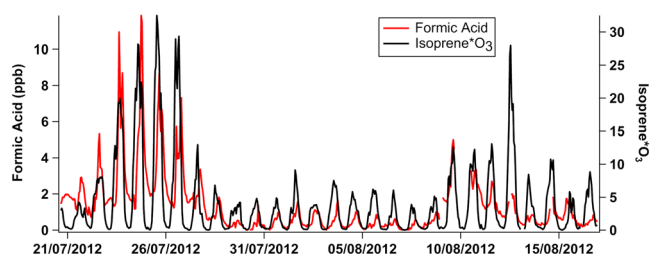


Figure 6. The formic acid time series (red) and [isoprene] \times [ozone]. The 64 min measurement resolution used here, that is, rate of measurement of isoprene. Vertical lines in the figure indicate midnight in the time series.

accounting for known sources such as the ozonolysis of well-defined alkenes (e.g., isoprene, ethene, and 2-methylpropene) and direct emissions from cars. Isoprene is underestimated in the PTM simulation during higher photochemical episode periods because of its highly reactive nature and short lifetime (Utembe et al., 2005) which is reflected in the diel pattern of isoprene in this study (Figure 7a). The formic acid formation is influenced by the sources upwind in the few hours before the measurements; thus, the production from the ozonolysis of isoprene can be underestimated in the PTM. Including (R4) with the branching ratios reported by Nguyen et al. (2016) the PTM simulations of formic acid do improve

compared with the base case (the case where the reactions of CH_2OO with water or water dimer are not considered); moreover, both scenarios (includes (R3) and (R4)) fall far short of the observed formic acid (Figure 7a), and some other formic acid sources are clearly needed in the model.

If CH_2OO reactions are not a significant source of formic acid, what could these sources be? One possible contributor to the missing sources of formic acid is the direct emissions from vegetation. Jardin et al. (2011) and Seco et al. (2007) reported the direct emission of HCOOH from different trees in the range of $0.02\text{--}0.11\text{ nmol/m}^2/\text{s}$ which are very small compared with the emission flux budget of $1\text{ nmol/m}^2/\text{s}$ inferred by Nguyen et al. (2015). We investigated the impact of direct emission sources of formic acid using emission scenarios of isoprene using the PTM. A direct emission of HCOOH to the PTM with temporal profile similar to isoprene emissions does not improve formic acid predictions with a reduction of Pearson r to 0.26 for the ClearLo campaign measurements (Figure 7b) supporting the nonexistence of a significant direct biogenic source of formic acid. The alternative contributor to the sources of formic acid could be secondary production from additional biogenic precursors. Ozone is likely to be strongly correlated with hydroxyl radicals (OH) and isoprene emissions are highly correlated with the emissions of other light-dependent biogenic VOCs.

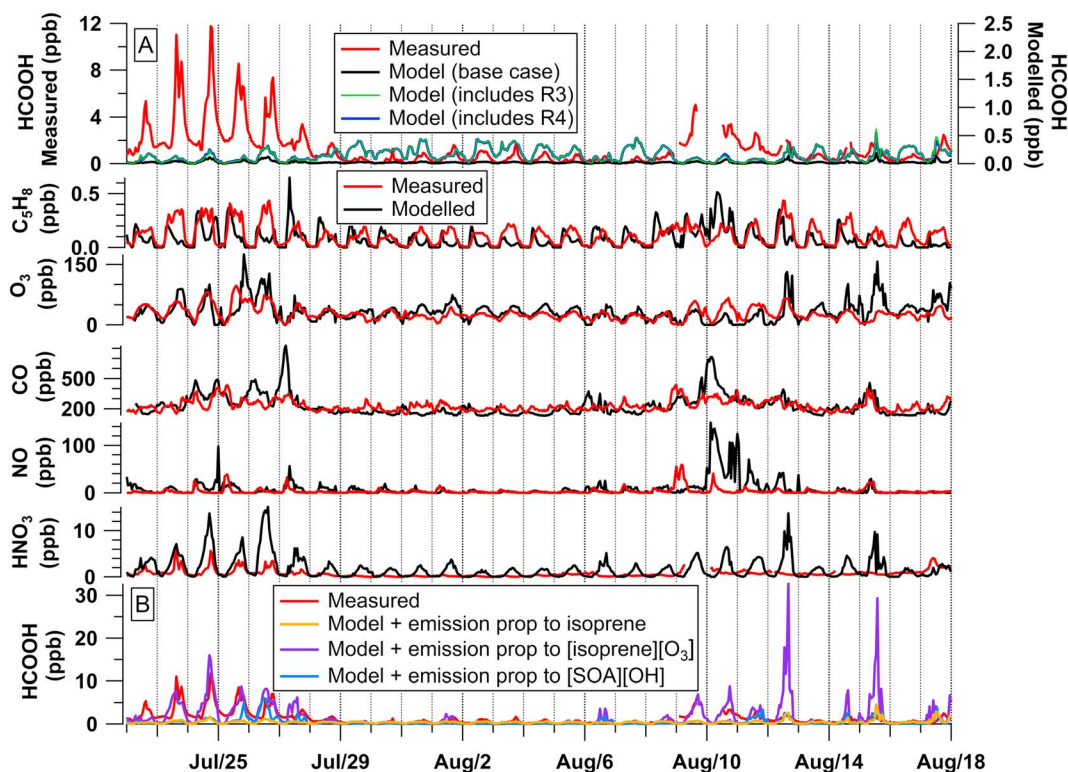


Figure 7. (a) Comparison of measured formic acid, isoprene, O_3 , CO, and NO to PTM model results. The model formic acid including reactions (R3) and (R4) are also shown in the figure. (b) Comparison of formic acid to models that include additional formic acid emission with profile proportional to that of isoprene, [isoprene] \times [O_3] and [SOA] \times [OH]. Vertical lines in the figure indicate midnight in the time series.

We conducted a PTM integration considering the emission scenarios of HCOOH as [isoprene] \times [O₃]. The result (Figure 7b) shows much improved agreement between model and measured HCOOH for the whole campaign with a Pearson r of 0.59 which suggests that a large biogenic emission source of formic acid from the oxidation of unspecified light-dependent biogenic VOCs could be important. A further PTM experiment with HCOOH direct emissions assumed proportional to the product of model secondary organic aerosols (SOA) and OH ([SOA] \times [OH]) slightly improves the model-measurement agreement (Pearson r = 0.42) and so such a source may be important elsewhere but in this environment appears to have a negligible impact.

4. Conclusions

Measurements of formic and nitric acid have been reported from London during the summer months and growing season. Measurements have been made in London under the ClearLo Campaign, which was split into two intensive observation periods, one in the winter (previous study by Bannan et al., 2014) and the other in the summer (this work). The summer campaign coincided with the London 2012 Olympics. From the previous study (Bannan et al., 2014) during the winter campaign, formic acid emissions were shown to be strongly dependent on direct anthropogenic emissions from vehicles. However, in the summer there was little evidence for any anthropogenic emissions of formic acid. Average concentrations of formic acid were over a factor of 2 higher for the complete summer campaign relative to the winter measurements. This is in good agreement with other studies such as Rinsland et al. (2004) who suggest that summer concentrations exceed winter concentrations by 250% and that a strong seasonality in the production of formic acid is seen. The elevated formic acid and positive correlations with HNO₃ and O₃ allude to a strong photochemical production source, but using photochemical trajectory model integrations, ozonolysis of alkenes alone cannot explain such high levels of formic acid. Adding the formic acid emission scenarios as [isoprene] \times [O₃] to the PTM improve formic acid predictions over most of the ClearLo campaign measurements suggesting that the oxidation of unspecified light-dependent biogenic VOCs could be the dominating biogenic source of formic acid.

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