Lab and field studies of the kinetics and composition of atmospheric reactive nitrogen and volatile organic compounds

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Abstract

Accurate measurements of ammonia, nitric acid and formic acid are important for achieving a complete understanding of their atmospheric role. Models and measurements of formic acid in the atmosphere continue to show disagreements. Also, the contributions of NMHCs and reactive nitrogen (HNO$_3$ and NH$_3$) to organic and inorganic aerosol formation are important to quantify as gaps in the knowledge of atmospheric aerosols are a source of uncertainty in climate science.

In this thesis, concentrations of ammonia were measured in the atmosphere and the production of formic acid from the ozonolysis of isoprene was measured in the EXTRA (EXTreme RAnge) chamber. Both gases were studied using chemical ionisation mass spectrometry (CIMS). The kinetics of the reactions of sesquiterpenes and terminal alkenes with ozone were studied in the EXTRA chamber using the relative rates technique and GC-FID.

The ozonolysis rate coefficients of a homologous series of terminal alkenes were measured at elevated temperatures and found to be invariant with the carbon number. This led to the conclusion that previous measurements of these rate coefficients were subject to experimental artefacts. The elevated temperature protocol was employed to study the ozonolysis of sesquiterpenes, leading to revisions in $k_{o3}$ for β-caryophyllene and α-humulene of 3 orders of magnitude. It was thus concluded that ozonolysis only accounts for 9-15% of sesquiterpene oxidation in the atmosphere.

A field intercomparison of CIMS for measuring ammonia was conducted wherein CIMS was found to perform well alongside instruments of comparable time response and limits of detection. This thesis also characterised inlet materials used in atmospheric measurements in the first systematic study on the uptake onto inlet walls in a flow tube system coupled to CIMS. It was found that PFA is the preferable material for atmospheric measurements, both for its kinetic qualities and its ready availability and ease of use.

Finally, CIMS was used to measure the yield of formic acid from isoprene ozonolysis as a function of relative humidity. Formic acid yield was found to increase between 0-40% RH to a maximum of 0.18. Using the measured formic acid yields in a global chemistry model leads to an estimate that formic acid production from isoprene ozonolysis is ~9.5 Tg yr$^{-1}$. 
Declaration

I hereby declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Mohamed Ghalaieny
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Dedication

To my family,

My mother Mona Al-Farra who always believed in me even when I doubted myself, my father Baha Ghalayini who challenged me in my life decisions but was supportive regardless, my sisters Basma and Sondos a source of great companionship and wisdom and advice beyond their years.
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First and foremost, thanks go to my supervisor Dr. Carl Percival for giving me the great opportunity to work with him and for helping me secure vital funding. In Carl I was fortunate to have a very hands-on supervisor who was always ready to guide me provided that I lived up to my side of the bargain. Without the consistent support and advice that he provided throughout the highs and lows of the process, both on a personal and professional level, completion would have been exponentially more difficult. Many thanks are due to Carl for imparting to me his great wisdom regarding science and, through his harsh but rigorous comments, forming me into a better writer and researcher.

The time required for research is bought with grants and scholarships; for this I am thankful to the University of Manchester Alumni Fund and the generosity of previous students at our alma mater.

Along the way I was lucky to work closely with two dedicated researchers: Dr Max McGillen and Dr Asan Bacak. I enjoyed being mentored by Max in the early days. Together we came to grips with the trials and tribulations of getting an instrument ready for field work with only a couple of months to spare. However, I learnt the most from Max in his field of choice, kinetics, or as he liked to call it, ‘the sport of kings’. Our work together testing ideas on alkene ozonolysis was path defining. Asan was a great support when I was first forging my own way studying sesquiterpene ozonolysis and then isoprene ozonolysis, always helping me systematically tackle problems in studying temperamental instruments and reaction systems. I owe much to Asan’s help in the final year of writing this thesis and the papers therein.

A debt of gratitude is owed to research technicians both at Manchester University and elsewhere. Messrs, or should that be messers, Alan Lee, Barry Gale, Carl Dixon and Peter Kelly were always at hand to help build and critique whatever unorthodox design was needed for my work, but just as important their collective sense of humour and irreverence were a breath of fresh, if slightly greasy, air during long days in the lab. Thanks also go to Alistair Bewsher. Dave ‘Tech grunt’ Tanner from Georgia Tech for vital tech support crossing time zones during our field work. Alan Knight in Bristol was also extremely helpful in helping me learn the intricacies of GC-FID.

Friends, colleagues and office mates at SEAES and in the wider atmospheric science community deserve special thanks for providing encouraging chats, fun diversions, good advice and sharing experience. Particular thanks go to: James Dorsey, Ann Rowan, Jennifer Muller, Rami Al-Farra, Waheed Akram, Hugo Ricketts, Johnny Crosier, Anna Leavey, Murray Booth, Dan Housely, Kim Leather, Ruth Walmsley, Jamie Whitehead, Chris Lee, Niall Robinson, James Allan and Mike Flynn.

Special thanks go to Jen Kotila for extremely vital proofreading in the final days before submission. Thanks and appreciation are also due to my work colleagues at ICBUW for their extreme understanding while I juggled my new job with wrapping up my overdue PhD.

The PhD process can be a solitary one, particularly in the final months and even more so when coupled with a full time job that lands the student into the twilight zone of evening and weekend writing. As an antidote to this solitude I was fortunate to find a
friend in Sarah who was, like me, coming to the end of her studies and kept me company both in person when working together and equally importantly through entertaining emails filled with good music and wit and caring ‘mother hen’ like advice.
Rationale for submitting this thesis in the alternative format

The research conducted for this PhD could be effectively subdivided into a series of publishable articles, each of which could be completed in sequence independently of the completion of the whole work. Therefore, the alternative format was deemed preferable for this study due to the inherent efficiency of producing five journal articles when compared to presenting the work in a traditional thesis format, which would subsequently require extensive revision prior to further publication in the peer reviewed literature. It is thus beneficial that the thesis be completed in this way and considered quite fortuitous that three of the five research papers presented here have already been accepted for publication.

The presentation of the papers follows the progression of the research itself. The flow chart overleaf shows how the research developed and how the papers are interlinked. The number assigned to each paper represents both the order of presentation in the thesis and the order in which the work was completed.
(above): Flowchart showing the progression of the research contributing to this thesis.

Research paper 1: Inlet Materials Study

Paper 2: CIMS ammonia field intercomparison

Paper 3: Terminal alkene ozonolysis rate coefficients

Paper 4: Sesquiterpene ozonolysis rate coefficients

Paper 5: Formic acid yield from isoprene ozonolysis
1. Introduction

1.1. Atmospheric NMHC

Non methane hydrocarbons (NMHCs) are a diverse and abundant class of trace gases in the atmosphere that have wide ranging roles in plant physiology, atmospheric chemistry and subsequent implications for environmental and human health. The vapour pressure of NMHCs is known to be inversely proportional to their molecular mass when other factors such as functional groups, temperature, surface area and other variables are held equal. In a homologous series of alkenes the vapour pressure is expected to fall with rising carbon number. Therefore higher mass compounds, usually of 12 or more molecules are more likely to exist in the aerosol phase as a result of their lower vapour pressure (Holton et al., 2003). As such, NMHCs are liable to participate in the formation of organic aerosol and to condense readily on surfaces. The formation of aerosol from NMHCs is particularly accentuated upon oxidation as this results in compounds with differing functional groups and structures that can have even lower vapour pressures and therefore leads to enhanced secondary organic aerosol (SOA) formation (Bonn and Moortgat, 2002).

1.1.1. NMHC emissions

Non methane hydrocarbons (NMHC) are a major emission from plants as hormonal regulators (e.g. ethene) or when subjected to stresses (e.g. isoprene or sesquiterpenes). The greater proportion of NMHC in the environment is from natural sources in comparison to anthropogenic sources (Goldstein and Galbally, 2007; Duhl et al., 2008). The burgeoning reliance of modern human society on fossil fuels has also rendered anthropogenic sources of great importance. While natural NMHC emissions exceed anthropogenic sources by a factor of nine (Guenther et al., 1995), the fact that anthropogenic emissions are almost always in close proximity to urban areas means that their environmental and health effects are particularly problematic (Doyle, 2004). Table 1 (Finlayson-Pitts and Pitts, 2000) is an inventory of natural and anthropogenic sources of NMHC and demonstrates the predominance of natural sources by a factor of at least 2.
Table 1: Table of global NMHC emissions by source (take from Finlayson-Pitts and Pitts, 2000).

<table>
<thead>
<tr>
<th></th>
<th>Anthropogenic</th>
<th>Biomass burning</th>
<th>Biogenic – continental</th>
<th>Biogenic – oceanic</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>132</td>
<td>54</td>
<td>310</td>
<td>10</td>
<td>506</td>
</tr>
<tr>
<td>NMHC</td>
<td>98</td>
<td>51</td>
<td>500</td>
<td>30-300</td>
<td>750</td>
</tr>
</tbody>
</table>

While primary emissions of NMHC can be an environmental problem it is their sinks, largely through oxidation by O₃, OH and NO₃ that greatly amplify their deleterious effects. The oxidation of VOCs leads to the formation of photochemical smog, sometimes comprising a harmful mix of particles, respiratory irritants and carcinogens (Doyle, 2004). Photochemical smog formation is also associated with an increase in ground level ozone and OH radical concentrations and an increase in acid rain resulting from the formation of organic acids.

Recent work by Goldstein and Galbally (2007) suggests that there are large unknowns in the number and types of NMHC present in the atmosphere. Through theoretical calculations based on the Belstein chemical database, Goldstein and Galbally (2007) suggest that there are as many as 10,000 unrecorded NMHCs and that the majority of those are likely to be in the higher carbon number. The large number of unknown NMHC contributes to uncertainty in the mass balance of NMHC in the atmosphere, particularly as the anticorrelation between vapour pressure and rising carbon number means that these compounds are likely to be involved in SOA formation. Kinetic studies such as those conducted in this research aim to provide quantitative data to resolve some of these uncertainties.

A key atmospheric role of NMHC is their participation in catalytic processes that form tropospheric ozone, as the cycle in figure 2 shows. VOC oxidation contributes to the formation of peroxy (RO₂) and hydroxy (HO₂) radicals. The reaction of these radicals with NO produces NO₂ which is photolysed to create an oxygen molecule which then creates O₃. The production of ozone shown in figure 1 is considered catalytic in nature because the penultimate step in the formation of ozone, the photolysis of NO₂, returns an NO molecule to the cycle allowing further O₃ production.
Figure 1: The cycle of radical catalysed ozone production (taken from Jenkin, 1998).

The production of ozone can be split into distinct regimes dependent on the levels of NO\textsubscript{x} (NO\textsubscript{x} is defined as the sum of atmospheric NO and NO\textsubscript{2}) and VOCs and is dependent on the fate of the peroxy radical. A NO\textsubscript{x}-sensitive\textsuperscript{1} regime occurs when peroxy radicals are destroyed mainly through self or cross reactions as shown in Reactions (1) and (2)

\begin{align*}
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{HOOH} + \text{O}_2 \quad (1) \\
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \quad (2)
\end{align*}

A NO\textsubscript{x}-saturated\textsuperscript{2} (VOC-sensitive) regime occurs when the reaction of peroxy radicals with NO represents the dominant sink of NO

\textsuperscript{1} In a NO\textsubscript{x}-sensitive regime, concentrations of NO\textsubscript{x} are relatively low in comparison to VOC concentrations, therefore O\textsubscript{3} concentrations change more in response to increased NO\textsubscript{x} concentrations (Sillman, 1999).

\textsuperscript{2} A NO\textsubscript{x}-saturated regime the relative abundance of NO\textsubscript{x} is higher than VOC and therefore O\textsubscript{3} concentrations change more in response to increased VOC additions to the environment (Sillman, 1999).
\[ \text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{RO} \quad (3) \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad (4) \]

and ozone is produced from the photolysis of NO\(_2\). Figure 2 shows a typical \(O_3\) isopleth\(^3\) graph that shows the influence of changing NO\(_x\) and VOC concentrations and more importantly their ratios to one another on tropospheric ozone production and the likelihood of a high ozone episode.

![Image](image.png)

**Figure 2:** A schematic diagram of the ozone isopleth (generated using the US Environmental Protection Agency (EPA) Empirical Kinetic Modelling Approach (EKMA)), illustrating the relationship between the initial concentrations of VOC and NO\(_x\) and the resulting maximum ozone concentration (Taken from Finalyson-Pitts, B.J. and Pitts, J.N., 1986)

Hence, VOCs, which are capable of forming peroxy radicals, strongly influence the total oxidising capacity of the atmosphere\(^4\) by creating \(O_3\) and OH.

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\(^3\) The axes in an isopleth graph denote VOC and NO\(_x\) concentrations, the isopleths (lines of equal concentration) on the graph show the changing nature of \(O_3\) concentrations as the ratio between NO\(_x\) and VOC changes. Isopleths suffer from some limitations such as their sensitivity to changes in chemical mechanisms and VOC composition in addition to sensitivity to initial conditions and difficulties in determining representative VOC/NO\(_x\) ratios. A detailed discussion of the development of ozone isopleth methodology can be found in (Committee on Tropospheric Ozone Formation and Measurement, 1992).

\(^4\) The oxidising capacity of the atmosphere is defined as the total amount of oxidants present in the atmosphere at a given time (Prinn, 2002).
1.1.2. Alkene oxidation

The reactions of alkenes with the OH, O$_3$ and NO$_3$ radicals are their major removal process from the atmosphere. There is a large variety of alkenes present in the atmosphere (Goldstein and Galbally, 2007) and these species have widely varying reaction rate coefficients with respect to the three radicals varying between: $10^{-14} - 10^{-19}$, $10^{-10} - 10^{-11}$ and $10^{-9} - 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) for $k_{O_3}$, $k_{OH}$ and $k_{NO_3}$ respectively (McGillen et al., 2006 and references therein detailed in footnote 5). One or other of the oxidants will dominate as a sink of alkenes depending on variations in concentration and rate coefficients. Table 2 shows the range of concentrations for radical species in the atmosphere by day and night. The low concentrations of OH radical during the night indicate that it will exert the most influence on alkene oxidation during the day and that at night NO$_3$ and to a lesser extent O$_3$ will dominate.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>[daytime] molecule.cm$^{-3}$</th>
<th>[nightime] molecule.cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>$3.94 \times 10^6$</td>
<td>$1.72 \times 10^4$</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>$7.38 \times 10^7$</td>
<td>$2.46 \times 10^9$</td>
</tr>
<tr>
<td>O$_3$</td>
<td>$2.71 \times 10^{12}$</td>
<td>$1.97 \times 10^{12}$</td>
</tr>
</tbody>
</table>

The concentration of O$_3$ is at least five orders of magnitude higher than the other oxidants by day and three orders of magnitude higher by night. This means that it competes by virtue of its abundance, even though the reaction rate coefficients with alkenes are orders of magnitude slower than the corresponding reaction with OH.

A quantifiable measure of a radical species’ influence as a sink for alkenes is the lifetime ($\tau$) of the alkene with respect to the oxidant. $\tau$ is calculated as the reciprocal of the product of the NMHC rate coefficient with respect to the oxidant and the oxidant’s concentration in the atmosphere

$$\tau = \frac{1}{k_{oxidant}[oxidant]} \quad \text{(Eq. 1)}$$

There is never one oxidant present in the atmosphere in any given time, so this calculation of $\tau$ is incomplete. A better determination of $\tau$ would reflect all of the oxidants competing in reactions for a given alkene as follows:
\[ \tau = \frac{1}{k_{O_3}[O_3] + k_{NO_3}[NO_3] + k_{OH}[OH] + k_{X}[X]} \]  
(Eq. 2)

A value calculated for \( \tau \) using the revised equation would be a better determination of the lifetime of a given hydrocarbon with respect to all oxidants in the atmosphere. As such, it would allow for a clearer understanding of the impact of each oxidant on the oxidising capacity of the atmosphere. However, there are still shortcomings in this calculation. Variations in oxidant concentrations, temperature dependency of reaction rates and loss processes of alkenes due to phase changes can all influence \( \tau \) negatively or positively. Although this analysis is an incomplete approximation of the full complexity of the atmosphere, it does serve to sufficiently illustrate the influence of reaction rate coefficients on atmospheric chemistry.

In figure 3, equation 2 is applied to demonstrate the range of atmospheric lifetimes of alkenes attributable to reactions with each of the main oxidants (O\(_3\), OH, NO\(_3\)) during the day and night.

Figure 3: Boxplots of atmospheric lifetimes of various NMHC classes with respect to O\(_3\), OH and NO\(_3\). \( k_{O_3} \), \( k_{OH} \) and \( k_{NO_3} \) taken from references within McGillen et al. (2006).  

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5 Atkinson et al. (2001); Neeb and Moortgat (1999); Treacy et al. (1992); Grosjean and Grosjean (1995); Grosjean and Grosjean (1996); Greene and Atkinson (1992); Khumaganov and Hites (2001); Lewin et al. (2001); Cox and Penkett (1972); Atkinson et al. (1984); Johnson et al. (2000); Cusick and Atkinson (2005); Atkinson et al. (1983a); Greene and Atkinson (1994); Atkinson et al., 1990; Grimmer et al. (1975); Shu and Atkinson (1994); Shorrees et al. (1991); Atkinson (1997); Treacy et al. (1997); Vakhitlin et al. (2003); Atkinson (1986); Ohta (1984); Atkinson et al. (1995); Atkinson and
The maximum and minimum symbolised by the top and bottom whiskers in figure 3 are an indication of the wide range in lifetimes of alkenes in the atmosphere as expected from the range in $k_{\text{oxidant}}$ with respect to alkenes. Using the interquartile range allows a more focussed comparison of the day and night lifetimes of the alkenes. During the day lifetime with respect to O$_3$ and OH appears to be of almost equal importance, but the interquartile range for OH shows that it is in fact of greater influence during the day. During the night it is clear that OH exerts the least influence on alkene lifetime. This is to be expected given its significantly lower concentrations in comparison to NO$_3$ and O$_3$. NO$_3$ exerts the largest influence and O$_3$ retains almost the same role it does during the day.

1.1.2.1. Alkene ozonolysis

The reactivity of ozone with alkenes spans three orders of magnitude. Changes in functional groups and structure have been demonstrated to have a pronounced effect on $k_{O_3}$. Steric hindrance (i.e. physical blocking of reactant molecules) has a strong effect on ozonolysis rates, as was emphasised by McGillen et al. (2008). Structure activity relationships (SARs) can be used to predict reaction rate coefficients based on other physical properties of compounds. SARs constructed for alkenes have utilised knowledge of functional group arrangement, carbon chain length and shape and the number of bonds or functional groups to calculate reaction rate coefficients of alkene ozonolysis (e.g. McGillen et al., 2008; Atkinson, 1987; Calvert et al., 2000) However, it is noted that SARs can only ever be an indication and never a substitute for kinetic measurements.

Ozonolysis is a common reaction in the atmosphere and while it is several orders of magnitude slower than alkene oxidation by OH radical (c.f. $k_{O_3} \sim 10^{-18}$ and $k_{\text{OH}} \sim 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), it is still of great atmospheric significance given the higher concentrations of ozone in the troposphere, as previously discussed. The longevity of ozone molecules into the night also means that ozonolysis participates in important night time alkene chemistry alongside the dominant NO$_3$ radical (Finlayson-Pitts and Pitts, 2000).
**Ozonolysis mechanism**

The ozonolysis of alkenes occurs through 1,3 cycloaddition of an O\textsubscript{3} molecule to the double bond of an alkene. Figure 4 shows the initial steps of ozonolysis leading to the formation of Criegee intermediates which were first postulated to exist by Rudolph Criegee (1949).

![Ozone addition to an alkene double bond and subsequent formation of the primary ozonide and Criegee intermediates (adapted from Calvert et al., 2000).](image)

In figure 4 we see how the breaking of the alkene double bond by ozone addition across the 1,3 positions creates a primary ozonide that is now known to be energy rich. This means that it is capable of undergoing complex unimolecular fragmentation and rearrangement to form carbonyls and carbonyl oxides, known as Criegee intermediates (CIs). The initial reaction energy will be distributed amongst the products in a manner conforming to a Boltzmann distribution. In real terms this means that the CIs created from a given ozonolysis reaction will vary in the amount of energy they have. The energy of a CI and the potential for collisional stabilisation determines its future fate and influences the resulting atmospheric chemistry as reactions (5-9) illustrate.

\[ \text{[CH}_2\text{OO]}^* \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (5)

\[ \rightarrow \text{CO}_2 + 2\text{H} \]  \hspace{1cm} (6)
The reactions above represent only a small portion of the potential role of CIs in atmospheric chemistry, which is elucidated further in the sections below.

**Stabilised Criegee Intermediates (SCIs)**

For CIs to participate in further reactions it is necessary that they are stabilised or they will decompose. Stabilisation of CIs occurs through collisions with surrounding molecules that quench the excess energy that would otherwise cause decomposition as per reactions (5-9). Some CIs are created with a level of energy sufficiently below the barrier for decomposition and are therefore formed as SCI. In their study of the ozonolysis of six alkenes, Kroll et al. (2001) found definite pressure dependence in the yield of OH radicals, with the OH found to form ‘promptly’ upon reaction commencement and fall with rising pressure. The negative pressure dependency of OH yields observed by Kroll et al. (2001) clearly shows the SCI stabilisation with pressure. Raising the pressure of a reaction vessel increases the likelihood of collisions between CIs and surrounding gas molecules, thus transferring excess energy and enhancing stabilisation.

To date, determinations of the yield of SCI ($Y_{SCI}$) from alkene ozonolysis have been based on indirect methods that infer $Y_{SCI}$ by measuring the carbonyl and hydroperoxide products from the reaction of SCI with their atmospheric scavengers (e.g. SO$_2$, NO$_2$, H$_2$O) (Hasson et al., 2001, Rickard et al., 1999). The yield of sulphuric acid from ozonolysis reactions has also been used to infer $Y_{SCI}$ in the work of Hatekayama et al. (1984). While such measurements of $Y_{SCI}$ provide valuable data, they should not be conflated with direct measurements as none currently exist (Welz et al., 2012). Variations in $Y_{SCI}$ are a testament to the challenges in measuring this quantity through indirect means. Rickard et al. (1999) cite interferences from OH reactions as a problem with literature determinations that predate their work, as

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[^6]: Measured using GC-FID or HPLC with fluorescence detection.
evidenced in the disagreement between Schäfer et al. (1997) and Paulson et al. (1998), with regard to the source of OH radicals in indirect determinations of $Y_{SCI}$.

The inherent uncertainty in indirect $Y_{SCI}$ measurements can be illustrated by an overview of measurements of $Y_{SCI}$ for the ozone-ethene system in Table 3 where the yields range from 0.35 – 0.5.

| Yield                  |  |  |  |
|------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| **Su et al. (1980)**   | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Kan et al. (1981)**  | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Niki et al. (1981)** | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Hatakeyama et al. (1984)** | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Horie and Moortgat (1991)** | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Neeb et al. (1997)** | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |
| **Neeb (1996), Neeb et al. (1998)** | 0.38             | 0.37 ± 0.02      | 0.35 ± 0.05      | 0.39 ± 0.053     | 0.42             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              | 0.47             | 0.5              |

The recent work of Drozd and Donahue (2011) used FTIR to infer the yield of SCIs from the ozonolysis of a structurally diverse selection of cyclic and acyclic alkenes. Drozd and Donahue (2011) used hexafluouroacetone (HFA), which was known to be an extremely selective scavenger of SCI (Horie et al., 1999) to infer $Y_{SCI}$ in the ozonolysis of 2,3-dimethyl-2-butene, trans-5-decene, cyclohexene and alpha-pinene as a function of pressure. Recently Taatjes et al. (2012) showed that the rate coefficient of HFA with Carbonyl oxide with HFA is $(3.0 ± 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus if one assumes a similar reactivity for all Criegee intermediates it appears that the assumption of Drozd and Donahue (2011) is appropriate.
Figure 5: The pressure dependence of CI stabilisation inferred by LIF using HFA as a scavenger for SCI. SCI measured from TME in plot (a), cyclohexene (b), trans-5-decene (c) and alpha-pinene (d) (Taken from Drozd and Donahue, 2011).

The $Y_{SCI}$ from Drozd and Donahue (2011) are shown in figure 5. $Y_{SCI}$ was found to display a strong pressure dependence for the linear alkenes but less of one for the cyclic variants. Furthermore, alkenes with a higher carbon number (Alpha-pinene and trans-5-decene) stabilised a higher proportion of SCI at lower pressure; trans-5-decene showed full stabilisation at ~420 Torr. The conclusion of Drozd and Donahue (2011) is that $Y_{SCI}$ is dependent on the structure of the parent alkene and the carbon number. Differences in structure and carbon number influence the capacity of the hot CI to absorb the excess vibrational energy. Longer carbon chains dissipate vibrational energy more effectively given the high number of degrees of freedom afforded by the translational and rotational motion inherent in longer chains of molecules. It is even suggested that for some alkenes CIs can be fully stabilised at 100 Torr (Kroll et al., 2001). The only other work to date on the pressure dependence of alkene ozonolysis was that on the ozonolysis of the monoterpene ocimene by Sun et al. (2011). They question the pressure dependence cited by Drozd and Donahue (2011) but, given the small number of alkenes studied by Drozd and Donahue (2011), it is expected that there will be exceptions to their conclusions. In the absence of direct measurements of $Y_{SCI}$, there will remain significant error and debate on the absolute value of $Y_{SCI}$. Clearly, further work is required and a variety of promising leads exist. Welz et al.,
(2012) suggest that photoionization mass spectrometry (PIMS) offers the chance of directly measuring $Y_{\text{SCI}}$ from ozonolysis for the first time based on their direct observation of CI that were custom created for their experiments on CI reaction rate coefficients (discussed below). Alternatively, Donahue et al. (2011) believe that temperature programmed reaction spectroscopy (TPRS) coupled with FTIR could offer another opportunity for the first direct observation of CI.

**HO$_x$ chemistry**

Even when unstabilised, Criegee intermediates from alkene ozonolysis play a hugely important role in the oxidative capacity of the atmosphere as they influence the amount of free radicals available at any given time. This is particularly true in the case of hydroxyl (OH) and hydroperoxy (HO$_2$) radicals, collectively termed (HO$_x$).

The source of HO$_x$ in the atmosphere varies seasonally and diurnally as it is linked to photolytic processes. For example, in the summer daytime the reactions (10-11) account for the larger proportion of OH radical formation (Emmerson et al., 2005a):

$$\text{O}_3 + hv < 340\text{nm} \rightarrow \text{O}^1\text{D}) + \text{O}_2 \quad (10)$$

$$\text{O}^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (11)$$

Additionally, this similar photolytic process accounts for the formation of HO$_2$ radicals:

$$\text{HCHO} + hv + \text{O}_2 \rightarrow \text{CO} + 2\text{HO}_2 \quad (12)$$

OH production can be derived from reactions (10) and (11) as follows:

$$[O^1\text{D})] = J(O^1\text{D})\times[O_3] \quad (\text{Eq. 3})$$

$$[\text{OH}] = k_{11}[O^1\text{D})]\times[H_2\text{O}] \quad (\text{Eq. 4})$$

where $J(O^1\text{D})$ is the rate of O$_3$ photolysis in reaction (10).
In winter, shorter days and larger solar zenith angles\(^7\) result in less photolysis. It is therefore expected that \(\text{HO}_x\) concentrations would be orders of magnitude less in winter than in summer. In the work of Emmerson et al. (2005b), a photochemical box model based on the version 3.1 of the Master Chemical Mechanism is used to predict \([\text{OH}]\) from ozone photolysis in reaction (10) and subsequent OH production in reaction (11). Field observations during the Pollution in Urban Midlands Atmosphere (PUMA) campaign conducted in the summer of 1999 and winter of 2000 found that \(\text{HO}_2\) and OH concentrations were comparable between the summer and winter. Whereas the box model output found \([\text{OH}]\) to be lower than that measured in winter suggesting that in winter there was a source of \(\text{HO}_x\) not related to photolysis compensating for the reduced solar activity (Emmerson et al, 2005b).

Various researchers have suggested (e.g. Carslaw et al., 2000; Paulson and Orlando, 1996; Faloona et al., 2001) that CIs could be an important source of \(\text{HO}_x\) in the absence of photolytic processes. The accurate measurements of PUMA using LIF of OH are the first proof of this and are important evidence of how crucial CI are ‘plugging’ the gap in \(\text{HO}_x\) production. Figure 6 shows the summer and winter variations in OH sources and sinks with a clear increase in the winter contribution of CI to the production of OH as denoted by the label ‘Criegee decomposition’ in figure 6 (Harrison et al. 2006).

Figure 6: Sources and sinks of the OH radical during the summer and winter periods of the PUMA campaign. A clear increase in OH production from CI is observed. (Taken from Harrison et al., 2006).

\(^7\) The angle between the zenith (i.e. the line perpendicular to the earth’s surface at the point of observation) and the centre of the sun’s disc. In winter, the solar zenith angle is larger meaning that sunlight will pass through more of the atmosphere and thus its intensity will be weaker.
The HO\textsubscript{x} concentrations from the modelling output of PUMA were generally in excellent agreement with the measurements, suggesting that the models had accurately reproduced the mechanisms for HO\textsubscript{x} production in polluted urban atmospheres.

**The fate of Criegee intermediates**

As has been demonstrated above, the fate of CIs has important implications for atmospheric chemistry. Until recently there have only been estimates of reaction rate coefficients for a number of reaction partners with CH\textsubscript{2}OO. All measurements so far have been indirect as there has been no reliable detection method for these species up until now. Due to this any product studies are extremely speculative as the main reaction partner cannot be detected and thus major assumptions are necessary with regard to the value of the rate coefficient. Recently Welz *et al.* (2012) for the first time determined the rate coefficient for the reactions of the simplest SCI, formaldehyde oxide with its key scavengers in the atmosphere:

\begin{align*}
\text{CH}_2\text{OO} + \text{H}_2\text{O} & \rightarrow \text{Products} \quad (13) \\
\text{CH}_2\text{OO} + \text{NO}_2 & \rightarrow \text{NO}_3 \quad (14) \\
\text{CH}_2\text{OO} + \text{SO}_2 & \rightarrow \text{SO}_3 \quad + \text{Products} \quad (15)
\end{align*}

Reactions (13-15) were found to proceed at rates between $7 \times 10^{-12} - 3.9 \times 10^{-11}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. The new quantification of these rapid rate coefficients demonstrates the important role of SCIs in the chemistry of the troposphere and is a departure from the previously estimated rate coefficients for CH\textsubscript{2}OO that spanned nine orders of magnitude as can be seen in table 4.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>value range (cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{H}_2\text{O}}$</td>
<td>$2 \times 10^{-19} - 1 \times 10^{-15}$</td>
</tr>
<tr>
<td>$k_{\text{NO}_2}$</td>
<td>$1 \times 10^{-17} - 1 \times 10^{-13}$</td>
</tr>
<tr>
<td>$k_{\text{SO}_2}$</td>
<td>$3 \times 10^{-15} - 1.7 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
According to the new rate determination for reaction (15), Welz et al. (2012) state that if all SCIs react with SO\textsubscript{2} on a similar scale then SCIs are as important oxidizers of SO\textsubscript{2} as the OH radical. Similar implications are true for the production of the NO\textsubscript{3} radical via reaction (14) with NO\textsubscript{3} concentrations expected to increase by up to 20% or more depending on alkene concentrations.

An important finding of this research is the role of the reaction of SCIs with H\textsubscript{2}O or their water catalyzed transformation into various hydroxy hydroperoxides as in the example of the formation of hydroxy methyl hydroperoxide (HMHP):

\[
[\text{CH}_2\text{OO}] + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{OOH} \quad (16)
\]

\[
\text{HOCH}_2\text{OOH} + \rightarrow \text{HCOOH} + \text{H}_2\text{O} \quad (17)
\]

HMHP subsequently decomposes into HCOOH other products (Gab et al. 1985). Again, placing values on the rate of reaction (13) is pivotal to understanding that the fate of SCIs is critically important with regard to the formation of organic acids in the atmosphere. This process was first postulated by Calvert et al. (1978). It was then confirmed as an important source of carboxylic acids by Martinez and Herron (1981). Now the recent determinations of the SCI reaction rates quantifiably shows this connection.

High ozonolysis yields of HCOOH measured in this work and other studies (Neeb et al., 1997; Leather et al., 2012; Atkinson et al., 1997) in the presence of water vapour are bolstered by the work of Welz et al. (2012), which confirms that the reaction of SCI with H\textsubscript{2}O is a major secondary source of carboxylic acids in the atmosphere.

1.1.2.2. Debate on formic acid sources in the atmosphere

As previously shown in reactions (16-17), the reaction of SCI with water is a potentially important source of formic acid in the atmosphere. The carbonyl oxide (CH\textsubscript{2}OO) is the simplest SCI. Other more complex carbonyl oxides are naturally expected to result in the formation of more complex organic acids in the atmosphere. The focus here is on CH\textsubscript{2}OO because it is one of the most likely products in the
ozonolysis of isoprene (Zhang et al., 2002) and is a key component of this research. In addition to the SCI mediated formation of organic acids, other sources of organic acids are myriad. These include both primary emissions from automobiles and other combustion sources (Kawamura et al., 1985) and secondary formation in the atmosphere (Grosjean et al., 1990a; Neeb et al., 1997; Atkinson et al., 1997). According to Grosjean, (1990b), organic acids can be even more important than inorganic acids with regard to acid deposition (e.g. HNO$_3$, H$_2$SO$_4$). It is also strongly suspected that organic acids, with their low volatility, play an important role as cloud condensation nuclei (CCN) (Kavouras et al., 1998; O'Dowd et al., 2002; Bonn and Moortgat, 2003; Zhang et al., 2004).

Organic acid sources in the atmosphere are complex and there is still uncertainty regarding the relative contributions of the various sources. More field measurements of organic acid concentrations (Le Breton et al., 2012) in conjunction with further laboratory studies of the kinetics of organic acid formation yields would assist in providing closure between models and measurements of organic acids in the atmosphere. At present, models continue to under-predict the global atmospheric concentrations of key acids such as formic acid (Stavroukou et al., 2011; Le Breton et al., 2012).

Razavi et al. (2011) measured global concentrations of formic acid (HCOOH) using the Infrared Atmospheric Sounding Inferometer (IASI) based on the Met-OP satellite. An analysis of the IASI/Met-OP data by Stavrakou et al. (2011) suggests that the annual production of HCOOH is 100-120 Tg per year, a factor of two or three higher than predicted by the IMAGESv2 global chemistry transport model. Figure 8 illustrates the discrepancy between models and measurements in the recent work of Razavi et al. (2011) (Stavarokou et al., 2011). Portion (a) of figure 8 is the global distribution of HCOOH columns in molecule cm$^{-2}$ as retrieved by IASI/Met-OP and portion (b) is the standard output from the IMAGESv2 model. The difference between the model and measurement is clear. The main source of the discrepancy from Razavi et al. (2011) is suggested by Stavrakou et al. (2011) to be either the oxidation of organic aerosols by OH radicals or the photolysis of hydroperoxy-enones originating from isoprene (Peeters and Muller, 2010) in addition to ozonolysis of sesquiterpenes. In portions (c-f) of figure 7 additional model parameters are added to
account for the ‘missing sources’ suggested above. The difference from the measured data becomes progressively less pronounced between (a) and (c-f). However, it is not a perfect representation which suggests there are still sources of formic acid that are unaccounted for.
Figure 7: Monthly averaged HCOOH columns in June 2009 (expressed in 1015 molecules cm$^{-2}$). a, Observed by IASI. b, Simulated by a standard model. c, Simulated assuming the production of HCOOH by the heterogeneous oxidation of organic aerosols by OH. d, Simulated accounting for HCOOH production by the photolysis of hydroperoxy-enones from isoprene. e,f, Inferred from source inversion assuming either a primary(e) or a secondary (f) biogenic HCOOH source (Taken from Stavrakou et al., 2012).

Similarly, back trajectory modelling performed as a comparison of airborne in situ measurements of formic acid by Le Breton et al. (2012) were also less than measured values. The airborne measurements using CIMS measured formic acid concentrations as high as 350 ppt while the back trajectory model at the same point in the time series only predicts ~130 ppt. In this case Le Breton et al. (2012) stress that the discrepancy
is indicative of a large missing source of formic acid such as vehicular combustion or “missing extremely reactive formic acid precursors” such as isoprene or ethene (Le Breton et al., 2012).

Indeed, the model integration of laboratory studies of the formation yields of formic acid from ethene ozonolysis in the recent work of Leather et al. (2012) shows the importance of alkene ozonolysis as a secondary source of formic acid that could contribute to model/measurement closure in the studies cited above (Razavi et al., 2011; Le Breton et al., 2012). Leather et al. (2012) measured a high yield (0.3) of formic acid from ethene ozonolysis at high RH. When integrated into the CRI-STOCHEM (Jenkin et al., 2008; Utembe et al., 2010) global model they were found to increase formic acid photochemical source to as much as 19.2 Tg yr\(^{-1}\), almost double its original value. This important work by Leather et al. (2012) builds upon and confirms similar findings by Neeb et al. (1997) who found yields of formic acid from ethene to be 0.42 at 65% relative humidity.

It is clear that there is still uncertainty regarding the sources of formic (and other organic) acids in the atmosphere. There is also a the vast number of alkenes in the atmosphere, \(\sim 10^5\) according to Goldstein and Galbally (2007), and a high likelihood that a good proportion of these are terminal alkenes with the potential to form organic acids through ozonolysis. Therefore, it is important to probe the formation of organic acids in the ozonolysis of other alkene systems of atmospheric significance (e.g. isoprene) to attempt further closure between models and measurements.
1.2. Reactive nitrogen in the atmosphere

Molecular nitrogen (N\textsubscript{2}) is the most abundant gaseous species in the atmosphere, comprising 78% of gases in the atmosphere. Due to the strength of the N≡N triple bond, not all of this is bioavailable to life forms or free to participate in chemical reactions in the atmosphere without conversion to a less inert form, a process known as fixation or denitrification, that naturally occurs through biotic processes in plants.

More reactive forms of nitrogen, collectively termed N\textsubscript{r}, are ‘fixed’ mainly by biological process and therefore their environmental abundance is limited by these processes. In the past century human activity has resulted in a perturbation in the levels of N\textsubscript{r} in the atmosphere through increased manufacturing, the use of fertilisers, fossil fuel combustion, the cultivation of N\textsubscript{2} fixing crops and biomass burning. Figure 8 is a representation of the nitrogen cycle 100 years ago and in the present era on a European scale. The differences in the quantities of N\textsubscript{r} passing in each part of the system are evidence of the extent to which human activities have changed the nitrogen cycle.

Figure 8: The global nitrogen cycle in the years 1900 and 2000 demonstrating the perturbation caused by anthropogenic nitrogen fixation (Sutton et al., 2011).

The massive perturbation caused to the nitrogen cycle has many associated environmental problems such as acid deposition, eutrophication, contribution to climate change and air quality problems.
1.2.1. Reactive nitrogen species

While reactive nitrogen species exist in the atmosphere only in trace amounts, they attract a great deal of scientific and regulatory attention due to the impacts noted above.

$N_r$ can either be in oxidised form of NO$_x$ (NO + NO$_2$) or NO$_y$ (PAN, HNO$_3$, N$_2$O, N$_2$O$_5$, HONO, NO etc) or in reduced form as NH$_x$ (NH$_3$ and NH$_4$).

Figure 9 shows some important aspects of the $N_r$ cycle with an emphasis on the processes leading to the formation of HNO$_3$, emission of NH$_3$ and the formation of O$_3$. In terms of $N_r$ this study is focused on NH$_3$ and HNO$_3$ chemistry as they both relate to the formation of nitrate aerosols and on the role HNO$_3$ plays in tropospheric O$_3$ production. The following sections present the sources and sinks of NH$_3$ and HNO$_3$, their participation in the formation of nitrate aerosol and the importance of HNO$_3$ as an indicator for tropospheric O$_3$ formation.
Figure 9: The cycle of reactive nitrogen emphasizing the atmospheric chemistry of \( \text{HNO}_3 \), \( \text{NH}_3 \) and \( \text{O}_3 \).

1.2.2. \( \text{NH}_3 \)

As the major gaseous base in the atmosphere, the chemistry of ammonia is relatively straightforward. Table 5 is an inventory of sources of ammonia in the UK and worldwide, emphasising the predominance of primary emissions. As demonstrated in Table 5, sources of ammonia in the atmosphere are predominantly primary emissions from agriculture but also include other sources such as vehicles fitted with 3-way catalytic converters.
Table 5: Global and UK emissions of NH3 represented in Gg NH3-N yr⁻¹. Global data from Olivier et al. (1998), Bouwman et al. (1997) and UK data from DEFRA, 2002, Sutton et al. (2000).

<table>
<thead>
<tr>
<th>Source</th>
<th>Global</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Livestock</td>
<td>20400 (38%)</td>
<td>195 (83%)</td>
</tr>
<tr>
<td>Fertilisers and crops</td>
<td>12600 (23%)</td>
<td>24 (9%)</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>5900 (11%)</td>
<td>-</td>
</tr>
<tr>
<td>Humans/pets</td>
<td>2600 (5%)</td>
<td>6 (2%)</td>
</tr>
<tr>
<td>Oceans</td>
<td>8200 (15%)</td>
<td>-</td>
</tr>
<tr>
<td>Vehicles</td>
<td>-</td>
<td>10 (4%)</td>
</tr>
<tr>
<td>Wild animals</td>
<td>100 (&lt;1%)</td>
<td>5 (2%)</td>
</tr>
<tr>
<td>Other</td>
<td>3900 (7%)</td>
<td>24 (9%)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>53700</strong></td>
<td><strong>264</strong></td>
</tr>
</tbody>
</table>

Sinks of ammonia are wet and dry deposition, and the neutralisation of acidic compounds (e.g. HNO₃, H₂SO₄ and potentially carboxylic acids) in the atmosphere leading to the formation of inorganic and organic aerosol. The formation of ammonium nitrate will be discussed in further detail below.
1.2.3. HNO$_3$

Nitric acid is one of the major inorganic acids in the atmosphere along with sulphuric acid and hydrochloric acid. In contrast to NH$_3$, which has predominantly primary sources, the main source of HNO$_3$ is the oxidation of NO$_x$ in the daytime and NO$_y$ at night.

\[
\begin{align*}
\text{NO}_2(g) & + \text{OH}(g) \rightarrow \text{HNO}_3 & \quad (18) \\
\text{N}_2\text{O}_5(g) & + \text{H}_2\text{O}(g, l) \rightarrow 2\text{HNO}_3(g, aq) & \quad (19) \\
\text{NO}_3(aq) & + \text{H}_2\text{O}(l) \rightarrow \text{HNO}_3(aq) + \text{OH}(aq) & \quad (20) \\
\text{NO}_3 & + \text{RH} \rightarrow \text{HNO}_3(g) + \text{R} & \quad (21)
\end{align*}
\]

Key sources of nitric acid are anthropogenic and related to the combustion of fossil fuels although other sources exist (e.g. lightning strikes). With the predominance of secondary production of nitric acid, its concentrations in the atmosphere are mostly dependent on the specific formation chemistry reactions (18 – 21) outlined in figure 9 above. The fact that HNO$_3$ is formed from the oxidation of NO$_x$ means it has implications for the production of tropospheric O$_3$ and is now known to be an indicator for the conditions that favour O$_3$ formation as will be detailed below.

As with ammonia, major sinks of HNO$_3$ are wet and dry deposition, which contributes to acid deposition. Additionally, an important fate of HNO$_3$ is the formation of NH$_4$NO$_3$ aerosol which has climatic impacts.

1.2.4. Inorganic aerosol formation

The chemistry of ammonia, nitric acid and H$_2$SO$_4$ is strongly related to the formation of inorganic aerosol as seen in reactions (22-23) below:

\[
\begin{align*}
\text{NH}_3(g) & + \text{HNO}_3(g) \rightleftharpoons \text{NH}_4\text{NO}_3(s, aq) & \quad (22) \\
\text{NH}_3(g) & + \text{H}_2\text{SO}_4(g) \rightleftharpoons \text{NH}_4\text{(SO}_4)_2(s, aq) & \quad (23)
\end{align*}
\]
HNO$_3$ competes with H$_2$SO$_4$ for the reaction with NH$_3$. Indeed, for reaction (22) to proceed, H$_2$SO$_4$ concentrations must be low or have been depleted sufficiently by reaction (23) (Nowak et al., 2010). With SO$_2$ levels falling since the 1990s as a result of successful regulatory controls on power plant emissions, the importance of nitrate aerosol formation through reaction (22) has increased (Monks et al., 2009). The reactions forming NH$_4$NO$_3$ are reversible dependent on ambient conditions and have a dissociation constant of $K_p$, a measure of the rate of NH$_4$NO$_3$ dissociation. The aerosol forms if $K_p$ is less than the product of the partial pressure of the NH$_3$ and HNO$_3$ and evaporates if $K_p$ is more than the product of partial pressure.

Both airborne and ground based measurements of NH$_3$ and HNO$_3$ have been conducted with simultaneous measurements of ammonium nitrate and sulphate aerosol (Nowak et al., 2010; Morgan et al., 2010). Such measurements are important in characterising the particle formation processes and the partitioning between the gas and aerosol phase of ammonium nitrate. Quantifying such parameters allows for assessment of the impact of ammonium nitrate aerosol on climate and air quality (IPCC, 2007). Environmental implications of ammonium nitrate aerosol formation relate to aerosol transport and its effect on the radiative balance of the earth. While NH$_3$ and HNO$_3$ can be short lived close to sources because of high reactivity and fast deposition rates, their impacts can spread away from sources through long distance transport of aerosol and in this manner spread the problem of acid deposition and eutrophication transnationally. Ammonium nitrate is a major component of inorganic aerosol with a radiative forcing of $-0.1 \pm 0.1$ W m$^{-2}$. The contribution of ammonium nitrate to the direct aerosol radiative forcing of $-0.5$ W m$^{-2}$ is very uncertain. Ammonium nitrate is also important as a CCN and impacts the indirect aerosol effect, which also suffers from large uncertainties as illustrated in figure 10 showing the
various anthropogenic and natural influences on radiative forcing. The uncertainty in both the direct and indirect aerosol effects is the highest amongst all the radiative forcing terms, testament to the importance of studies into chemical species that partake in aerosol formation.

Figure 10: Radiative forcing (Wm-2) 1970 – 2005 of natural and anthropogenic influences on climate. (taken from IPCC, 2007).
1.2.5. $N_t$ and tropospheric ozone

As previously discussed, in situ tropospheric ozone formation (and accumulation) depends on the photolysis of NO$_x$ produced in an environment with high VOC concentrations.

As a sink of NO$_x$, the formation of HNO$_3$ is thought to lead to the reduction of tropospheric O$_3$ production by acting as a termination step for the O$_3$ production cycle (figure 1):

$$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$$

(24)

It is established that as a sink of NO$_x$, HNO$_3$ can be used as an indicator for whether a NO$_x$-sensitive or VOC-sensitive regime exists. Because of this, knowledge of HNO$_3$ concentrations is important for regulatory controls on O$_3$ production as it impacts both urban and rural air quality. A further source of NO$_x$ discovered relatively recently is the photolysis of NO$_3^-$ deposited in snow covered regions in mid to high latitudes, the phenomenon first observed by Honrath et al., (1999) was noticed because of a seemingly anomalous high rate of O$_3$ destruction within the snow pack.

Milford et al. (1994) established a link between total $N_t$ in the atmosphere and the prevalence of NO$_x$-sensitive conditions. According to Sillman (1995), it is the levels of OH radical that ultimately dictate whether an environment is NO$_x$-sensitive or VOC-sensitive. The ratio of HNO$_3$/O$_3$ is thought to be a good indicator of whether NO$_x$-sensitive or VOC-sensitive conditions prevail and therefore the likelihood of high ozone episodes (Sillman, 1995). Furthermore, Sillman and He (2002) and Sillman and West (2009) show that the ratios of HNO$_3$/H$_2$O$_2$ could also be indicative of VOC-sensitive and NO$_x$-sensitive regimes, thereby providing other valuable metrics to inform O$_3$ control strategies.
1.3. Importance of measurements

As the discussions in the preceding sections show, high quality field and laboratory measurements of the trace species studied are vital for the improved understanding of their environmental chemistry and impacts. A brief survey of current techniques for measuring NMHCs, NH$_3$ and HNO$_3$ follows, along with an overview of the novel CIMS technique used in the work conducted for this research.

1.3.1. Atmospheric measurements overview

Table 6 shows the measurement techniques used so far to quantify the atmospheric incidence of the trace species studied in this research both in the laboratory and in the atmosphere. This is only intended as a brief overview of the technology available. For a full discussion of atmospheric measurement techniques, the reader is referred to Heard (2006). The variation in the time response and limits of detection dictates the utility of the method for airborne measurements, flux measurements and studies of kinetics in the laboratory.

Table 6: Overview of measurement techniques for NH$_3$, HNO$_3$ and NMHCs. Taken from Heard (2006).

<table>
<thead>
<tr>
<th>Species</th>
<th>Analytical Technique</th>
<th>Time resolution</th>
<th>L.O.D (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$/HNO$_3$</td>
<td>Filter packs</td>
<td>1-3 hours</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td></td>
<td>Fourier transform infrared spectroscopy (FTIR)</td>
<td>&gt; 1 minute</td>
<td>4 (NH$_3$)</td>
</tr>
<tr>
<td></td>
<td>Denuders</td>
<td>&gt; 1 hour</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Tuneable diode laser spectroscopy (TDLAS)</td>
<td>0.1 seconds</td>
<td>0.025 (NH$_3$)</td>
</tr>
<tr>
<td></td>
<td>Chemiluminescence (HNO$_3$ only)</td>
<td>10 seconds</td>
<td>0.1 (HNO$_3$)</td>
</tr>
<tr>
<td></td>
<td>Laser induced fluorescence (LIF) NH$_3$ only</td>
<td>5 minutes</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Cavity ring-down spectroscopy (CRDS) NH$_3$ only</td>
<td>5 seconds</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Ion mobility spectrometry (IMS) NH$_3$ only</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Differential optical absorption spectroscopy (DOAS) NH$_3$ only</td>
<td>1 second</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>NMHCs</td>
<td>Chemical ionisation mass spectrometry</td>
<td>1 second</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chromatography (Ion exchange)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid chromatography</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As table 6 indicates, not all of the currently available techniques have the required time response or sensitivity to provide the best measurement of ‘sticky’\(^8\) trace gases such as NH\(_3\), HNO\(_3\) and organic acids. For example, simultaneously measuring NH\(_3\) and HNO\(_3\) with ammonium nitrate (e.g. Nowak et al., 2010; Morgan et al., 2010) requires instruments with fast time response such as CIMS. Similarly, the measurement of the ozonolysis yields of carboxylic acids benefits from a fast response online technique.

### 1.4. Instrument methodology

The following section provides an overview and some detail of each of the analytical techniques used in the course of this research. Some instruments such as CIMS and GC, are afforded more detail than others (e.g. portable aerosol spectrometer and ozone analyser) because they were more important from an analytical perspective and more complex to use and set up.

#### 1.4.1. CIMS

Chemical ionisation mass spectrometry (CIMS) provides the capability to measure various atmospheric trace gases in the atmosphere with high sensitivity and a fast time response (t~1s). The limits of detection for the technique have been demonstrated to be on the order of tens of ppt and even lower. The CIMS method uses a reagent ion to ionise a neutral species. The product ions resulting from this process are then filtered by a quadrupole mass analyser to identify species and determine their abundance by counting the number of ions reaching a detector at the rear of the mass spectrometer. The distinction between chemical ionization mass spectrometry and other mass spectrometry techniques is the use of ion molecule reactions for the selective ionization of compounds of interest in the complicated matrix of ambient air. For example, HNO\(_3\) has been detected in air with CIMS by the following reaction (Marcy et al., 2005) using SF\(_5\) as a precursor

\[
\text{SF}_5^- + \text{HNO}_3 \rightarrow \text{NO}_3^- (HF) + \text{SF}_4
\]  

\(^8\) The difficulties in measuring ‘sticky’ gases are outlined in chapter 2.
It is important when using the CIMS method that the reagent and product ions have sufficient stability on the time scale of the ionization process (i.e. reaction time) to avoid interference from other, often more abundant, atmospheric species. An example of this is when the chosen reagent ion is significantly depleted by reactions with abundant trace species, such as water vapor, the process results in a series of interfering mass peaks arising (Slusher et al., 2001). If the product ion is unstable to reaction with more abundant trace species it might be converted to an ion that doesn’t provide a distinct signature of the species of interest.

A number of CIMS instruments with different ion-molecule reaction schemes have been developed for the measurement of a range of atmospheric species (see Table 7) and are used from both ground stations and mobile platforms, such as aircraft. Most CIMS are equipped with a quadrupole mass filter; in some cases this is an ion trap. These are housed in a differentially pumped high vacuum chambers coupled to an ion source/reactor that operates at pressures ranging from a few Torr to atmospheric pressure. In some instruments, the ion source region is separated from the high vacuum region of the mass spectrometer by a collisional dissociation chamber (CDC) that is maintained at an intermediate pressure (Tanner et al., 1997). The purpose of the CDC is to dissociate weakly bound cluster ions (e.g hydrated ions) to their core ions via energetic collisions. This simplifies the resulting mass spectra. A major improvement in the CIMS technique has been the use of octopole ion guides (Hagg and Szabo 1986) to transmit ions between the intermediate pressure regions and the mass spectrometer. This technique has been used to enhance detected signal levels (Slusher et al., 2004; Crounse et al., 2006; Neuman et al., 2006; Nowak et al., 2006). Analyte ions that are selected to pass through the mass filter are typically detected by an ion multiplier with a gain on the order of $1 \times 10^6$. Amplified pulses corresponding to individual ions are detected with a combination of a preamplifier and discriminator. For this reason, raw CIMS signals are generally reported in ion counts per unit time (typically counts s$^{-1}$ or Hz). The counts s$^{-1}$ data are transformed into relevant units of concentration by a calibration factor derived from a quantified calibration source.
Table 7: A Summary of CIMS reagent ions utilised for ambient measurements of atmospheric trace gases since 1996 (from Huey et al., 1998; Mauldin et al., 1998; Hunton et al., 2000; Leibrock and Huey 2000; Miller et al., 2000; Neuman et al., 2000; Mauldin et al., 2001; Furutani and Akimoto 2002; Hanke et al., 2002; Neuman et al., 2002; Danilin et al., 2003; Sellegrì et al., 2005; Leibrock et al., 2003; Fortner et al., 2004; Slusher et al., 2004; Crounse et al., 2006)

<table>
<thead>
<tr>
<th>Reagent Ion</th>
<th>Detected Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiF$_5^-$</td>
<td>HNO$_3$</td>
</tr>
<tr>
<td>CO$_3^-$</td>
<td>HNO$_3$, SO$_2$, HCN</td>
</tr>
<tr>
<td>SF$_6^-$</td>
<td>HNO$_3$, SO$_2$, HO$_2$NO$_2$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>PAN, PPN, MPAN, N$_2$O$_5$, HCOOH</td>
</tr>
<tr>
<td>CF$_3$O$^+$</td>
<td>HNO$_3$, HCOOH, CH$_3$C(O)OOH, HCl</td>
</tr>
<tr>
<td>SF$_5^-$</td>
<td>HNO$_3$, HCl, ClONO$_2$</td>
</tr>
<tr>
<td>H$^+$(C$_3$H$_6$O)$_2$</td>
<td>NH$_3$</td>
</tr>
<tr>
<td>H$^+$(C$_2$H$_5$OH)$_x$</td>
<td>NH$_3$, DMSO</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>HNO$_3$</td>
</tr>
<tr>
<td>CH$_3$SO$_3^-$</td>
<td>HNO$_3$</td>
</tr>
<tr>
<td>(C$_6$H$_6$)$_2^+$</td>
<td>C$_6$H$_8$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>HO$_2$, HO$_2$+RO$_2$</td>
</tr>
<tr>
<td>H$^+$(H$_2$O)$_n$</td>
<td>VOCs and amines</td>
</tr>
<tr>
<td>Cl$_3^-$</td>
<td>HNO$_3$</td>
</tr>
</tbody>
</table>

1.4.1.1. Georgia Tech Lab and Field CIMS

The same CIMS instrument was used in the field studies of NH$_3$ (chapter 3) and the measurement of formic acid yields (chapter 6), with variations in the setup that will be described in this section. The instrument was designed and built by the Georgia Institute of Technology (GIT) CIMS team. Hereafter the two different configurations of this instrument will be referred to as CIMS-F (field configuration) and CIMS-L (lab configuration). A schematic diagram showing all the major components and differences in the two configurations is shown in figure 11 and will be discussed further below.
Figure 11: Difference in configuration between field configuration CIMS-F (bottom) and lab configuration CIMS-L (top).
1.4.1.1.1. CIMS-F

The CIMS-F was used for the measurement of NH$_3$ as part of an intercomparison of 11 ammonia measuring instruments at the Easter Bush field study site. The Edinburgh intercomparison campaign is described in chapter three, but further details of the instrumental setup, calibration and some data are presented here.

In this configuration ambient air is drawn through the inlet using a pump (Gast) at 19.8 SLM. The inlet is a 5.61 mm internal diameter (i.d.) PFA tube enclosed in a 100 mm long aluminium sleeve. The inlet sleeve is heated by a 50 watt cartridge heater; the heating temperature is controlled by a PID controller (Love Controls Series 35Z) with a K-type thermocouple providing temperature feedback. The airflow into the ion-molecule region is regulated by a 3-way solenoid valve (Teqcom 3/8” M-series solenoid valve). The valve is controlled by the instrument control software to conduct regular background measurements by diverting the airflow through a scrubbing device containing H$_3$PO$_4$ pellets. The pellets produce phosphoric acid when they react with atmospheric humidity which removes NH$_3$ from the gas stream. The CIMS-F was run predominantly with the 3-way solenoid valve set to sample ambient air. However, regular standard addition calibrations were conducted during background measurement cycles by opening an automated solenoid valve allowing the flow of NH$_3$ carried in N$_2$; this was the output of a permeation source described in the calibration section and appendix 1. There is a 0.031” diameter pinhole before the ion-molecule region. The ion molecule region consists of a QF40 fitting with multiple ports for the Po$^{210}$ radioactive source (NRD inc.). The ion molecule region is 165 mm long and is pumped by a dry scroll pump (Varian Tri Scroll).

NH$_3$ was chemically ionised using the protonated acetone dimer as a reagent ion (H’(C$_3$H$_6$O)$_2$). This reacts sensitively and selectively with NH$_3$ to form a cluster ion in reaction 13.

\[
\text{H'}(\text{C}_3\text{H}_6\text{O})_2 + \text{NH}_3 \rightarrow \text{H'}(\text{C}_3\text{H}_6\text{O})_2\text{NH}_3 \quad (R13)
\]
H⁺(C₃H₆O)₂ was generated by combining a 3.2 SLM flow of N₂ with a 1 sccm flow of an SF₆/Acetone/N₂ mixture (Nowak et al., 2010)

A mass spectrometer with a quadrupole mass analyser was used to detect ions. The mass spectrometer had a three-stage differentially pumped vacuum chamber leading to a ceramic channeltron electron multiplier detector (ITT-K & M electronics) with a gain of ~1 x 10⁶. Product ions from the ion-molecule region pass through several stages to reach the detector. Firstly, ions enter the collisional dissociation chamber (CDC), via a 0.076 mm pinhole. The CDC acts to dissociate weakly bound cluster ions (see section 1.4.1). The CDC was held at a pressure of ~28 Torr by a hybrid pump (Alcatel ATH31). After the CDC ions were focused by a charged 3 cm outer diameter (o.d.) and 2.2 mm i.d. stainless steel plate into the second stage, the octopole chamber; the octopole guides the ion beam into the quadrupole mass filter via a charged 3 cm o.d. and 2.2 mm i.d. stainless steel plate. Both the second stage and rear chambers were pumped by individual turbo-molecular pumps (Varian V-81M) backed by a single scroll pump (Varian Triscroll) to reach a vacuum pressure in the region of ~9 x 10⁻⁶ Torr..

Calibration, figures of merit and data analysis

Two independent calibrations were performed for the instrument as described below.

Automated calibrations

The CIMS is calibrated by the output of a permeation tube (see appendix for details). During ambient measurement cycles the permeation output is directed through the Gast mechanical pump. When the green solenoid valve in figure 11 is closed, the output of the permeation tube is directed through the CIMS inlet to perform the standard addition calibrations. A background measurement cycle begins by actuating the 3-way valve, diverting the inflow through a H₃PO₄ scrubber. The background signal was allowed to stabilise for one minute. Calibration additions were performed every hour alternating with background cycles. The use of the solenoid valves allowed for full automation of switches between ambient measurement, background and calibration cycles for the duration of the field campaign.
Data from a typical background/calibration cycle are shown in figure 12

Figure 12: Data showing typical background and calibration cycles for the CIMS-F during the 2008 NH$_3$ intercomparision campaign.

where calibration factors were calculated first by subtracting an average background signal from the average of the final ten seconds of a calibration cycle. The calibration and background cycles used for this calculation are marked in figure 12. A calibration factor is obtained by dividing the difference in signal by the nominal value of the standard addition in ppb. An average calibration factor for the duration of the campaign was found to be 3010 ± 350 Hz ppb\(^{-1}\) (where the error is the 1 $\sigma$ standard deviation of calibration factors). The calibration factor, limits of detection (L.O.D) and other key analytical figures of merit are calculated from the data similar to that in figure 12 and reported in table 8.
Table 8: Analytical figures of merit for the CIMS-L and CIMS-F.

<table>
<thead>
<tr>
<th>Instrument Type of calibration</th>
<th>Instrument Response Time (s)</th>
<th>Calibration Factor (Hz ppb$^{-1}$)</th>
<th>Background (Hz)</th>
<th>Precision (ppb)</th>
<th>L.O.D (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIMS-F Permeation tube</td>
<td>&lt;4.95</td>
<td>3010 ± 350</td>
<td>4262</td>
<td>0.69</td>
<td>3.48</td>
</tr>
<tr>
<td>CIMS-F Cylinder</td>
<td></td>
<td>3439 ± 161</td>
<td></td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>CIMS-L Cylinder</td>
<td>&lt;2.9</td>
<td>2700 ± 288</td>
<td>2749</td>
<td>0.11</td>
<td>1.34</td>
</tr>
</tbody>
</table>

The instrument response time is calculated by fitting an exponential function to the data from the beginning of a background cycle. Typically, the function resulting from the fit is as follows:

$$NH_{3,Signal} = 18076 + 29806e^{-\left(\frac{t-3.3\times10^6}{25}\right)}$$

where $\tau$ is the instrument response time in seconds and is calculated by the curve fitting software. $\tau$ was calculated for background cycles from every day of the Edinburgh intercomparison campaign and found to be < 4.95 seconds as shown in table 8. For comparison, a similar analysis was applied to background measurements in the work done in paper V and $\tau$ was < 2.9 seconds.

Instrument precision is calculated as one standard deviation of the background signal and is reported in the table. The limits of detection are calculated as the sum of the background signal and three standard deviations. The precision of the CIMS-F was consistent between the data set for the entire intercomparison (0.69 ppb) and the cylinder calibration data set quoted in von Bobrutzki et al., (2010) (chapter three) and described below.

The average calibration factor calculated above was applied to the raw data in order to generate concentration time series for comparison with the other instruments in the field campaign. The CIMS data reported in chapter three were also reduced to minute averages to conform to the slower instruments in the comparison.
Cylinder calibration

The cylinder calibration used the more traditional technique of performing multiple standard additions of varying concentrations to produce a calibration curve shown in figure 13. The calibration factor to be applied to arrive at a concentration is the slope of this curve reported in table 8. There is agreement between the calibration factor derived from the cylinder calibration and the ‘spot’ calibrations performed during the measurement campaign.

![Figure 13: Calibration of CIMS-F for NH$_3$ using the cylinder method.](image)

1.4.1.1.2. CIMS-L

The CIMS-L was used to measure formic acid yields within the EXTRA chamber. The set-up and construction of EXTRA is described in chapter six. The CIMS-L is the same instrument used in the NH$_3$ field measurements with a different inlet and ionisation setup. These are highlighted in figure 11 and described below.

The differences in the setup of the inlet are the removal of the background/calibration module and the high flow Gast pump on the inlet. A further difference involved the use of CH$_3$I (methyl iodide) as an ionisation gas resulting in a negative ion-analyte
adduct, thus necessitating that the electron multiplier detector be operated in negative ion counting mode.

HCOOH was chemically ionised by \( \Gamma \). \( \Gamma \) was produced by passing a combined flow of \( \text{N}_2 \) (1.5 SLM) and 0.5% \( \text{CH}_3\text{I}/\text{H}_2\text{O/}\text{N}_2 \) (1 sccm) through a Po\(^{210}\) Nuclecel radioactive source (NRD Inc.). The following ion-adduct reaction describes the ionisation of HCOOH:

\[
\Gamma \cdot \text{H}_2\text{O}_n + \text{HCOOH} \rightarrow \text{HCOOH}\cdot \Gamma + \text{H}_2\text{O}_n
\]

It allows formic acid to be detected selectively at \( m/z = 171.65 \) (Slusher et al., 2004).

The same mass spectrometer with quadrupole mass analyser described in the CIMS-F was used. Some changes in the apertures between the different chambers are described. A sample of the ion molecule gas flow containing reactant ions enters the CDC through a 0.38 mm aperture held at a potential of \( -0.17 \) V to focus charged reactant molecules. In this setup, the CDC was pumped by a molecular drag pump (Alcatel MDP-5011), backed by a scroll pump (ULVAC DISL-100) resulting in a pressure of \( \sim 20 \) Torr. Ions passed through a stainless steel 1 mm aperture at \(-0.36 \) V to reach the octopole ion guide. Ions are further focused by the octopole and then pass through another 1 mm aperture at \(-0.48 \) V to the rear chamber containing the quadrupole mass analyser (ABB Extrel, Merlin) leading to the channeltron electron multiplier detector (Dtech 402A-H) in negative ion counting mode. The octopole and rear chambers were each pumped by a turbomolecular pump (Varian 81-M) backed by the molecular drag pump (Alcatel MDP-5011) resulting in a pressure of \( \sim 9 \times 10^{-6} \) Torr in typical operating conditions.

**Calibration**

In this case the CIMS was calibrated by the addition of quantified dilute solutions of HCOOH in deionised water. The work and results of this calibration are presented and discussed in chapter six but figures of merit have been presented here within table 8. The improvement in the reported L.O.D of 1.34 ppb and precision of 0.11 ppb is noted for the data from CIMS-L, which can be attributed to the fact that the
instrument was used in a lab setting several years after the Edinburgh intercomparison and following improvements in the CIMS instrument.

**Data analysis**

Mass to charge ratios \((\text{m}/\text{z})\) of interest were identified calculated by summing the molecular masses of the ion adduct. Initial mass scans, such as the example shown below, allow the determination of the exact \(\text{m}/\text{z}\) ratio of interest as the mass analyser might have a slight deviation. Such work also allows any interesting peaks to be followed, such as the HMHP peak thought to be at \(\text{m}/\text{z}\) 220 in the mass spectral scan in figure 14. The peak at \(\text{m}/\text{z}\) 220 was found to decrease with time in a way that was anticorrelated with HCOOH, suggesting it could be HMHP. Such mass spectral scans are only taken periodically as sample volume was precious so it was preferred to focus on approximately 5-8 ‘single ion monitoring’ scans that follow several \((\text{m}/\text{z})\) at the same time allowing the study of time series.

![Figure 14: Mass spectral scan comparing the production of formic acid from isoprene ozonolysis at the beginning and end of an experiment and also comparing wet and dry conditions (inset).](image)
1.4.2. Gas Chromatography

A gas chromatograph (GC) is an established analytical technique utilising coated capillary columns to separate and detect the constituents of chemical mixtures. A sample is injected into the column in a flow of inert gas conventionally known as the mobile phase. The separation occurs through the interactions between the flowed sample and the chemical coating on the capillary column walls, known as the stationary phase. The length of capillary columns varies, but typically is tens of metres.

The molecular weight and other properties of substances influence the extent of retardation by interactions with the stationary phase. Because of this, different compounds will emerge from the end of the column at different times. The amount of time taken by a compound to exit a GC column is known as its retention time ($T_r$). For any given compound and GC column, $T_r$ will be constant when temperature and mobile phase flows are unchanged.

GC systems can be coupled to a variety of detectors. The most common are GC with mass spectrometry (GC-MS), GC with flame ionisation detection (GC-FID) and GC with electron capture detection (GC-ECD).

The experiments in chapters four and five used an Agilent HP5970 GC-FID. The capillary columns used were the HP-1 and DB-1 columns for the terminal alkene analysis and a DB-1 column for the SQT analysis. The columns used were non-polar with a dimethylpolysiloxane stationary phase. The GC oven temperature range was varied between 70 – 200 degrees and the carrier gas flow ranged from 0.5-2 ml/min for both experiments.

Samples were mixtures of two analytes in a cyclohexane solution. Individual analytes were identified by their retention time and order of retention. Retention times were previously established by introducing the individual analytes to the GC column separately.

A sample chromatogram from an experiment studying the relative rate for 1-dodecene shows the different peaks for 1-decene and 1-dodecene in figure 15. The area under each peak is a measure of the quantity of each compound in the sample. Successive
chromatograms following ozonolysis were used to provide the data to calculate the relative rate coefficient. The chromatogram in figure 15 shows a relatively advanced reaction as evidenced by the multiple product peaks.

![Figure 15: Chromatogram from the ozonolysis of a mixture of 1-dodecene, 1-decene and cyclohexene showing a variety of product peaks.](image)

As the reaction progressed it was noticed that some products of the ozonolysis were eluting in a way that interfered with the peaks of interest (see ‘compound Y’ and ‘compound X’ in figure 15). GC oven temperature and flow were varied to enhance the separation between the peaks of interest and product peaks in order to accurately obtain the areas used in calculating of the relative rate coefficient. An example of the data used to calculate the relative rate coefficient for 1-dodecene are shown in table 9.

<table>
<thead>
<tr>
<th>Compound of interest</th>
<th>Reference compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak area</td>
<td>Ln(C₀/Cₙ)</td>
</tr>
<tr>
<td>88.2</td>
<td>0</td>
</tr>
<tr>
<td>79.2</td>
<td>0.1076</td>
</tr>
<tr>
<td>69.3</td>
<td>0.2411</td>
</tr>
<tr>
<td>60.1</td>
<td>0.3835</td>
</tr>
<tr>
<td>55.6</td>
<td>0.4614</td>
</tr>
<tr>
<td>46.8</td>
<td>0.6337</td>
</tr>
<tr>
<td>41</td>
<td>0.7660</td>
</tr>
<tr>
<td>32.8</td>
<td>0.9891</td>
</tr>
</tbody>
</table>

Table 9: Sample data for dodecene relative rate determination. C₀ denotes the compound of interest with an unknown rate co-efficient at the beginning of the experiment before ozonolysis and Cₙ signifies measurements undertaken following ozonolysis. R denotes the reference compound used, in this case 1-decene. The same convention is followed regarding subscripts.
The natural logarithm of the ratio of $C_0/C_n$ and $R_0/R_n$ is calculated in the second column for each compound and the values are plotted in figure 16. The slope of the line gives the ratio between the two reaction rate coefficients allowing the unknown reaction rate coefficient for the compound of interest to be calculated.

![Figure 16: Plot of the relative rate coefficient of 1-dodecene to 1-decene.](image)

Data from successive experiments were plotted in a master relative rate plot to give the relative rate coefficient for each of the compounds studied. The slope of the line is the relative rate coefficient and the absolute rate coefficient for the reference compounds was measured in pseudo-first order conditions with the alkene concentration in excess of ozone. The details of the technique are described in chapter four and also in the earlier work of Leather et al. 2010.

**Uncertainties and errors**

Sources of uncertainty and error in GC-FID analysis can arise from physical parameters such as column temperature, carrier gas flow rate, detector temperature and the temperature of the transfer line between the reaction chamber and the column. Sample preparation and injection into the reaction chamber could be a source of variation in the initial concentration of analytes, however when using the relative rates technique (paper III and IV) relative decay of the compound of interest with respect to the reference compound is independent of the initial concentrations.
One standard deviation errors were used as a measure of the uncertainty in the result and obtained from the linear regression of relative rate plots as reported in paper III and IV.

1.4.3. Portable aerosol spectrometer

Portable aerosol spectrometers are commonly used as a rough method of the quantification of aerosol concentration and particle size distributions. The principle of operation of the Grimm (Model 1.018) PAS is the measurement of light scattered off particles. This data can be used to measure the number of particles in each size.

Figure 17 demonstrates the principle of GRIMM operation as taken from the manufacturer’s literature.

![Diagram of portable aerosol spectrometer](image1)

**Figure 157: Principle of operation for GRIMM portable aerosol spectrometer.**

The PAS samples by sucking in ambient air using an internal pump and can measure all aerosols above 0.3 micrometres. The Grimm PAS could not measure nucleation mode aerosol of < 0.01 micrometre in size.

1.4.4. Ozone analyser

The Monitor Labs Ozone analyser (Model 8810) used in this research (paper III, IV and V) operates by using the principles of the Beer-Lambert law which states that the absorption of a beam of light through a gas or liquid is proportional to the
concentration of the constituent of the solution. The monitor labs measured the absorption by ozone at 284 nm.
1.5. Research aims and objectives

The study aimed to investigate the reaction kinetics and composition of ‘sticky’ (low vapour pressure and polar) trace gases (e.g. NH₃, HNO₃, HCOOH, sesquiterpenes) in the atmosphere by:

**Field and laboratory testing of the CIMS for measuring trace gases**

A laboratory study to test the performance of inlet materials for measuring HCOOH and HNO₃ (chapter four) was conducted in addition to a field test of CIMS measurements of ammonia (chapter four).

**Providing improved kinetic measurements of semi-volatile NMHCs**

The rate of the alkene-ozone reaction is not well known for many semivolatile alkenes, some which have large biogenic emissions. The aim above was achieved first by employing an adapted protocol at elevated temperatures to measure the $k_{O3}$ for terminal alkenes (chapter four) and then by applying the new protocol for the measurement of $k_{O3}$ for sesquiterpenes to arrive at an improved determination (chapter five).

**Studying the products of the ozonolysis of alkenes**

The yield of ozonolysis products is an important quantity to know with regard to the atmospheric implications of alkenes. The aim above was achieved by using CIMS and the EXTRA chamber (chapter six) to measure the yield of formic acid from the ozonolysis of isoprene as a function of temperature.
2. Paper I

“Kinetic study of uptake of trace gases onto inlets to evaluate preferable materials for atmospheric measurements”

by


**Status:** *In preparation.*

**Contributions:** Mohamed Ghalaieny conducted the experiments and prepared the manuscript. Max McGillen assisted with experimental setup and Alistair Murray Booth made the contact angle measurements. The work was conducted under the supervision of Carl Percival.
Kinetic study of uptake of trace gases onto inlets to evaluate preferable materials for atmospheric measurements.

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Abstract
The HNO$_3$ and HCOOH uptake onto six flow tube surfaces: PFA, quartz, alumina, Granger’s ® coated alumina, Granger’s ® coated quartz and silane coated quartz was measured using Chemical Ionization Mass Spectrometry over a range of atmospherically relevant pressures from 13-760 Torr; The wall loss rate coefficient measured $k$ at 760 Torr was 0.9 ± 0.1, 2.2 ± 0.1, 8.4 ± 0.6, 6.7 ± 0.2, 4.9 ± 0.4 and 0.8 ± 0.1 s$^{-1}$ respectively. Within experimental error, PFA and silane coated quartz were found to have the same value of $k$. PFA was deemed superior to due to its shorter signal stabilisation time of 132.2 ± 6.4 seconds vs. 451.6 ± 8.7 seconds for silane coated quartz. Furthermore, PFA is readily available commercially and a more practical material for diverse applications. No direct correlation was found between the superhydrophobicity of surfaces and the wall loss rate coefficient.
**Introduction**

Nitric acid and organic acids are trace atmospheric constituents with wide ranging environmental and atmospheric implications. HNO$_3$ influences tropospheric ozone chemistry by acting as a reservoir for reactive nitrogen species (Neuman et al., 1999), it is also an important component of acid precipitation. In the stratosphere HNO$_3$ plays a key role in the formation of polar stratospheric clouds by combining with water to form nitric acid trihydrate and therefore is related to the mechanism of stratospheric ozone depletion (Fahey et al., 1989). Furthermore, HNO$_3$ contributes to the formation of inorganic aerosol through its interaction with bases in the atmosphere (e.g. NH$_3$). Organic acids also contribute to acid precipitation and the formation of particulates in the atmosphere: their low volatility makes them well suited to the formation of secondary organic aerosol (Pandis et al., 1991; Kavouras et al., 1999). Additionally, organic acids are an important precursor of tropospheric ozone and contribute to photochemical smog formation and its associated negative health effects (Doyle et al., 2004).

The quantitative measurement of trace species in the atmosphere is technically challenging; the low atmospheric concentrations of these species, in the ppt – ppb range, and the rapid variations in concentrations requires highly sensitive measurement techniques with a fast time response. Additionally, some trace species, such as HNO$_3$ and NH$_3$, have a tendency to adhere, or adsorb, onto the instrument inlet because of their polar properties. Therefore, high precision quantitative measurements of trace species needs good inlet design incorporating temperature control, rapid flow rates and minimal inlet length. The inlet material also plays a key role in minimising the adsorption of analytes.

Several studies have investigated the adsorption of NH$_3$ to different types of sample inlet materials at various temperatures (Yokelson et al., 2003; Shah et al., 2006; Whitehead et al., 2008; Ellis et al., 2010). Neumann et al. (1999) and Horii (2002) also studied the adsorption of HNO$_3$ onto a variety of materials with varying temperature. Additionally, Yokelson et al. (2003) also observed the inlet responses of organic compounds. All of the inlet studies cited did not probe the kinetics of the reactive uptake onto the inlet materials, but rather studied the difference in analyte
signal with differing inlets.

This is the first systematic kinetic study of the uptake of HNO$_3$ and organic acids onto a variety of commonly used inlet materials. The study utilised the precision and fast response time of Chemical Ionisation Mass Spectrometry (CIMS) to compare the signal of analyte flowed through several laminar flow-tubes constructed from a variety of materials commonly used as inlets in atmospheric measurements.

**Experimental**

*Figure 1 is a schematic diagram of the apparatus used. A conventional flow system with Chemical Ionisation Mass Spectrometric detection of gaseous species was used to study the uptake of HNO$_3$ and HCOOH onto inlet materials.*

![Figure 1: Experimental setup of laboratory Chemical Ionisation Mass Spectrometer, flow tube and moveable injector.](image)

*Figure 1: Experimental setup of laboratory Chemical Ionisation Mass Spectrometer, flow tube and moveable injector.*

Six flow tubes of identical dimensions were constructed from PFA, alumina and quartz. The flow tubes were all 600 mm in length with an internal diameter of 5.61 mm. The alumina and quartz flow tubes were tested in their basic state and also when coated with silane. PFA and quartz were chosen because they are widely used in gas phase atmospheric measurement, alumina was used because its naturally textured surface (see figure 3 below) provided a good means of testing the coating with hydrophobic materials. Full descriptions of the flow tube materials and coating processes can be found in the materials section. A 1/8” PFA sliding injector within
the flow tube was used to vary the contact time between the compound of interest (either HNO₃ or HCOOH) and the flow tube walls. Nitrogen (ranging from 1 to 6 SLM) was used as the main flow and injected at the rear of the flow tube. During experiments the pressure of the flow tube was maintained at 13 – 760 Torr, pumped by a rotary pump (Varian DS 1602). All experiments were conducted at room temperature. Due to time constraints, the study of pressure variation was prioritized over temperature variation as pressure variations were deemed of more importance for the design of inlets for aircraft measurements. Attached to the ion-molecule region was a quadrupole mass spectrometer (ABB Extrel) where ions could be analysed. The CIMS ion-molecule region was constructed from 22 mm o.d. Pyrex tubing. All gas flows were monitored with calibrated mass flow meters (MKS, 1179). The pressures in the flow tube were monitored using a 0–1000 Torr capacitance manometer (MKS, Baratron).

For the uptake of HNO₃ the flow of nitrogen was passed through a permeation device. The permeation device was comprised of a 15 cm permeation tube (KIN-TEK, La-Marque, Texas) constructed from Teflon tubing and placed inside a heating device. The heater was controlled by a PID temperature controller (Watlow). The permeation source temperature was set at 30°C, at this temperature the emission rate of the permeation tube is 61ng/min. The concentration output of permeation tubes are a function of temperature and flow, so the concentration of HNO₃ flowed ranged from 0.003 – 0.02 ppm. For the uptake of formic acid a flow of 100sccm HCOOH was flowed from a cylinder containing a mixture of 0.01% HCOOH in N₂ at 5 Atm.

Uptake experiments were performed by initially establishing a flow of HX (where X =NO₃ or COOH) with the sliding injector positioned past the end of the flow tube. The injector is then moved quickly to an upstream position so that the flow tube wall is exposed to HX. Any uptake on the flow tube wall leads to a drop in HX signal. By varying the length of flow tube exposed, a concentration-time profile of HX signal along the flow tube can be obtained.

HNO₃ and HCOOH were chemically ionised using SF₆⁻ as the reagent ion. To generate SF₆⁻, a 10 slm flow of N₂ was combined with a 1 sccm flow of SF₆ and passed through a ²¹⁰Po Nuclecel ionizer (NRD Inc.). The reagent ion was then carried
into the ion-molecule region through an injector constructed from 6 mm o.d. stainless steel. A fan shaped turbulizer was attached to the end of the inlet to enhance mixing of the reagent ion with the sampled flow from the flow tube. HNO$_3$ and HCOOH were ionized by SF$_6$ via fluoride ion transfer enabling the species to be detected at $m/e$ 82, i.e. the NO$_3$.HF$^-$ ion and at $m/65$, i.e. the HCOO.HF$^-$ ion respectively.

Ions were detected with a quadrupole mass spectrometer in a three-stage differentially pumped vacuum chamber. A sample of the bulk gas flow containing reactant ions is drawn into the front chamber through a 0.6 mm aperture which was held at a potential of −70 V to focus charged reactant molecules. The front vacuum chamber was pumped by a rotary pump (Varian DS402) and held at approximately 2 Torr. The ions were further focused by a 30 mm o.d. and 0.2 mm i.d. stainless steel plate held at −15 V and passed into a second chamber containing the quadrupole mass filter (ABB Extrel, Merlin) and held at a pressure on the order of 10$^{-5}$ torr. A turbomolecular pump (Varian V250) backed by a rotary pump (Edwards E2M8) was used to pump this second chamber. A further turbomolecular pump (Varian V250) was used to pump the rear chamber holding the multiplier assembly. Under typical operating conditions the rear chamber was held at a pressure of approximately 9 x 10$^{-6}$ Torr. Ions were detected using a channeltron (Dtech 402A-H) in negative ion counting mode.

Scanning Electron Microscope (SEM) imagery was carried out using a Phillips FEI XL30 Environmental Scanning Electron Microscope (ESEM). The SEM was operated with the backscatter detector and beam energy of 20 kV.

**Inlet material**

**PFA**

PFA (Perfluoroalkoxy) is used extensively in scientific research because of its inertness. This property makes it particularly suited for work with 'sticky' gases such as HNO$_3$, HCOOH and NH$_3$. Subsequently, losses to the walls of PFA tubing are minimal and the memory effect resulting from repeated sampling is minimised thus reducing sampling artefacts.
**Quartz**

Horri (2002) suggests that quartz coated with silane (1H,1H,2H,2H-Perfluorooctyltriethoxysilane) has a very low interactivity with trace gases. According to Xue et al., (2010) coatings of silane applied to various substrates renders them ‘superhydrophobic’ which in addition to repelling water has had a demonstrable effect on reducing the adsorption of trace gases in atmospheric measurements. A quartz flow tube was tested without coating and was then coated with silane as described in the ‘Hydrophobic surfaces’ section.

**Alumina**

An uncoated alumina flow tube was used to assess the uptake of HNO₃. The Alumina was also studied with a coating of Granger’s waterproof solution. The solution was applied to the tubing in manner described in the section on ‘hydrophobic surfaces’.

**Hydrophobic surfaces**

Evans et al. (2005) have shown that a patterned or roughened surface which has a hydrophobic coating can result in (super-hydrophobic) properties with contact angles to water of in excess of 160° (Roach and McHale, 2007; Shirtcliffe et al., 2011). Figure 2 shows a water droplet on a) a flat surface, b) a hydrophobic flat surface and c) a super-hydrophobic surface having the same surface chemistry as surface b). Figure 2 d) is an electron microscope image of the surface structuring and roughness resulting in the water repellent enhancement. Arranged correctly these surfaces do not allow water droplets to form and remain on the surface and so they offer potential for use as inlet material that operates in high RH conditions. Furthermore, it is postulated that hydrophobic surfaces will be effective in reducing the gas-wall interactions of polar gases in a similar way to how they reduce the interaction of water with their surface.
In our quantitative assessment of acid uptake onto flow tube surfaces, the hydrophobic surface was prepared by first patterning the surface followed by coating with a hydrophobic solution (Grangers’s XT – sprayable garment waterproofer). For quartz tubing this was achieved by sandblasting the inside of the quartz tubes while rotating to ensure the uniformity of the operation. The alumina was used as is because it exhibited an adequately patterned surface when inspected under an environmental scanning electron microscope (ESEM). Figure 3 shows the ESEM images of both surfaces at 4000x magnification.

Figure 2: A water droplet on a) a flat surface, b) a hydrophobic flat surface, c) a superhydrophobic flat surface with the same surface chemistry as surface b), d) is an electron microscope image of the surface structuring and roughness taken from (Shirtcliffe et al., 2004).
a) Alumina  

b) Quartz

**Figure 3**: ESEM image of a) alumina in its normal state, b) quartz after sandblasting. The surface features in a) demonstrate the naturally patterned surface of alumina.

Surface features in the range of 5 to 10 \(\mu\)m are observed for Alumina and in the 10-\(\mu\)m range for quartz. In the case of the silane coating the quartz was not patterned and was simply treated as is, as per the directions in Horii, (2002). The details of the application of hydrophobic coating are described below.

*Granger’s XT spray waterproofer*

The chemical treatment was applied by pouring 50 ml of Granger’s solution™ repeatedly into the flow tube whilst rotating. The flow tube was then heated to 50°C for 50 minutes with a heat gun whilst being rotated to fix the coating onto the surface.

*Silane (1H,1H,2H,2H-Perfluorooctyltriethoxysilane)*

The silane was chosen as per the work done by Horii (2002). The isotopic labeling of the product had no bearing on the choice of material, it was the only product available. Silane was added to 200 ml ethanol and 10 ml deionised water and acetic acid. The ethanol-water mixture was prepared by adjusting its pH to 5 by adding acetic acid, and then 2-5% by weight of neat silane was added to the mixture. The mixture was then stirred for 15 minutes until hydrolysis occurred. The flow tube to be coated is prepared by washing with soap and rinsing in water then drying it thoroughly. The final step is applying the coating uniformly by pouring the solution down the flow tube whilst rotating for between 2 and 5 minutes; the flow tube is then
rinsed in ethanol and left to cure overnight or heated in an oven at 100 °C for 15 minutes.

Materials

The HNO₃ permeation tube was obtained from KIN-TEK (SRT-005.00-2022/30, Lamarque, Texas, USA). It contains trace amounts of sulphuric acid to sequester any water, but the concentration of HNO₃ is greater than 99%. Formic Acid (99%) was obtained from Sigma Aldrich. N₂ was obtained from BOC. PFA was purchased from Swagelok. Alumina was obtained from (HP Technical Ceramics, 99.9% purity alumina tube). Quartz tubing was purchased from the University of Manchester stores.

An overview of the inlet materials used and their treatment prior to experimentation follows. Silane (1H,1H,2H,2H-Perfluorooctyltrioxyisilane; 97%, ACBR.DE). Granger’s waterproof treatment (Granger’s, UK)

Results and Discussion

Figure 4 is a typical HCOOH signal response on contact with increasing lengths of flow tube surface. There is an initial large uptake followed by a stabilisation time to reach a steady state uptake. Multiple experimental runs repeatedly showed the same large initial uptake followed by a recovery to a stable steady state, indicating that the drop in signal immediately following the increased contact time was due to an interaction between the analyte gas flow and the flow tube surface.
The signal average was calculated using the steady state values of HCOOH marked in figure 5. At the steady state the signal was deemed stable and flat, approximately 100-150 seconds after the injector was pulled back for PFA and 400-460 seconds for silane coated quartz. Using the steady state values of HX, a plot of ln HX signal against contact time yielded a straight line, showing that the loss to the surface was first order with respect to [HX] (see figure 5). The slope of the plot in figure 5 is $k^1$, the first order wall loss rate coefficient.
Uptake experiments were repeated several times for a range of pressure conditions from 13 – 760 Torr. The resultant $k^I$ for experiments at 298K on PFA as a function of pressure are shown in figure 6. The data in figure 6 show that $k^I$ first order loss decreases with pressure, as the molecular diffusion is inversely proportional to pressure. The gas stream in the flow tube exhibited laminar flow at all times (Reynolds number < 2300) meaning that the pressure dependent molecular diffusion processes from the gas stream to the flow tube walls were one determinant of the wall loss coefficient.

![Graph showing the inverse of pressure vs. $k$ (s$^{-1}$)](image)

**Figure 6:** The inverse of pressure vs. $k$ (s$^{-1}$) demonstrating the pressure dependence of values of $k$ for PFA.

Figure 7 is a plot of the pressure dependence of the uptake coefficient $k$ for all inlet materials studied. The data indicate a pressure dependence of uptake for all materials as is clear from the slope of the lines in figure 7. The material with the lowest first order wall loss rate $k^I$ was quartz coated with silane and PFA was found to have the second.
Figure 7: Inverse of pressure vs. \( k \,(\text{s}^{-1}) \) for PFA, quartz, alumina, Granger’s ® coated alumina, Granger’s ® coated quartz and silane coated quartz.

However, when considering stabilisation time it was thought that PFA would be a better overall inlet material because it reached the steady state of uptake in less time. Figure 8 illustrates this difference in stabilisation time. Similar time responses have been observed for uptake of HNO\(_3\) on salt surfaces (e.g. Leu et al., 1995). The surface ageing could be as a result of two processes happening, a physical (reversible) and a chemical (permanent) loss. The aim of this paper is not to interpret the loss process on a physical basis, but rather to elucidate which inlet surface has the fastest time response to changes in gas concentrations and to determine which surface produces the smallest overall loss of trace gas. The only way to test the hypothesis of two processes would be to analyze a desorption peak and compare the integrated adsorption and desorption peaks to see what fraction of HNO\(_3\) remained on the inlet surface. As stated, this is beyond the aim of this paper which is to simply elucidate the preferred inlet material.

The data in figure 8 show that PFA and quartz coated with silane had stabilisation times of 132.2 ± 6.4 and 451.6 ± 8.7 seconds respectively, where the error is the standard deviation in time from repeated runs.
PFA is much better in a practical sense given that silane coated quartz only offers only a marginally better uptake coefficient than PFA and that the coating process is laborious in comparison to the easy commercial availability of PFA.

**Contact angle measurements**

The contact angle of a droplet of water was measured for each of the inlet materials using the pendant drop technique. As introduced above, regarding hydrophobic surfaces, the contact angle between a water droplet and a surface is deemed a good measure of the hydrophobicity of the material of which the surface is constructed. Furthermore, given the shared polar nature of water and the acids in question, the hydrophobicity was hypothesised to be an indication of which materials would have higher first order wall loss coefficients \( k^1 \). The data from the contact angle measurements are shown in table 1 alongside the values of \( k \) at 760 torr as a test of this hypothesis.
As expected, the application of coatings to the flow-tubes increases the contact angle confirming that a superhydrophobic surface has been created. However, the increased superhydrophobicity does not translate into reduced wall losses as the data in table 1 show. In fact coated quartz, one of the materials with the highest contact angles, also has a significant increase in wall loss rate from 2.2 s\(^{-1}\) (uncoated) to 4.9 s\(^{-1}\). One explanation of the increased wall losses to superhydrophobic surfaces could be the increased surface area resulting from the patterning of the surfaces by sandblasting. Investigating this phenomenon is beyond the scope of this study, but could be quantified by using the Brunauer, Emmett and Teller (BET) method to analyse adsorption isotherms.

The only studies comparing the effects of adsorption of atmospheric trace gases onto flow tubes of different materials were the experiments of Neuman et al. (1999) and Horii, (2002). The work of Neuman et al. (1999) used CIMS to measure the overall change in HNO\(_3\) signal flowed at a fixed contact time through a variety of inlet materials and Horii, (2002) repeated the work of Neuman et al. (1999) using Tunable Diode Laser Absorption Spectroscopy (TDLAS) to measure the analyte concentrations. Both studies only attempted to quantify the inlet material efficiency by reporting overall percentage loss in HNO\(_3\) signal for a fixed length of inlet material, using identical flow conditions. Table 2 summarizes the experimentally obtained percentage change in HNO\(_3\) concentration observed by Neuman et al. (1999) and Horii, (2002) for the PFA and quartz coated with silane.

### Table 1: Inlet materials studied and their contact angle measurements and first order uptake coefficient at 760 torr.

<table>
<thead>
<tr>
<th>Inlet Material</th>
<th>Contact angle measurement (degree)</th>
<th>wall loss rate coefficient (k) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz coated with Granger’s</td>
<td>112.19 ± 1.17</td>
<td>4.9 ± 0.4</td>
</tr>
<tr>
<td>Quartz</td>
<td>59.43 ± 2.98</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>Alumina</td>
<td>73.83 ± 18.60</td>
<td>8.4 ± 0.6</td>
</tr>
<tr>
<td>Alumina coated with Granger’s</td>
<td>81.96 ± 18.36</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>Quartz coated with Silane</td>
<td>88.38 ± 1.42</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>PFA</td>
<td>94.79 ± 6.96</td>
<td>0.9 ± 0.1</td>
</tr>
</tbody>
</table>
Table 2: The observed reduction in HNO$_3$ signal when flowed through a PFA and quartz inlet coated with Silane in the previous work of Neuman et al. (1999) and Horii, (2002).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta [\text{HNO}_3]$ (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA</td>
<td>-6.25</td>
<td>Neuman et al., 1999</td>
</tr>
<tr>
<td></td>
<td>-31.8</td>
<td>Horii, 2002</td>
</tr>
<tr>
<td>Coated Quartz</td>
<td>-61.45</td>
<td>Neuman et al., 1999</td>
</tr>
<tr>
<td></td>
<td>-16.6</td>
<td>Horii, 2002</td>
</tr>
</tbody>
</table>

Using an atmospherically relevant concentration of ~5 ppb, Neuman et al. (1999) found that PFA only showed a small change in HNO$_3$ signal (-6.25%) in comparison to silane coated quartz (-61.45%). Conversely, Horii (2002) showed that PFA had a higher change in signal (-31.8%) in comparison to silane coated quartz (-16.6%). While the data of Neuman et al. (1999) confirm the results of this study and find that PFA is a preferable material to work with, the work of Horii, (2002) is contradictory. It is not clear why Horii (2002) contradicts both this work and the results of Neuman et al. (1999). However, previous studies do not attempt to quantify the error in the observed loss, furthermore, as stated both of the studies measured the change in HNO$_3$ signal at a fixed contact time. Whereas this work quantified the inlet material in terms of wall loss and found that within experimental error both PFA and silane coated quartz had the same wall loss, however, that PFA showed a better stabilization time. Thus, in terms of ease of use, this work would suggest that PFA should be used as a preferred inlet material. Recently, Ellis et al. (2011) conducted basic tests of a heated and unheated PFA inlet to measure NH$_3$ with a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) and found that PFA had good properties for measuring ‘sticky’ trace gases, again indicating that PFA is a useful inlet material for trace gas studies.

Conclusions and future work

The uptake of HNO$_3$ and HCOOH onto the walls of six flow tubes constructed from PFA, quartz, alumina, Granger’s ® coated alumina, Granger’s ® coated quartz and silane coated quartz was measured using a flow tube-CIMS system. The experiments
were conducted under a range of pressure conditions (13 – 760 Torr) at ambient temperature. Silane coated quartz had the lowest first order uptake co-efficient and PFA had the second lowest. However, PFA was found to have a much faster stabilisation time in comparison to silane coated glass, a property that has important implications for fast time response measurements of ‘sticky’ trace gases. PFA also benefits from being readily available whereas silane coated quartz requires more preparation. Fluouro polymers (e.g. Perfluoroalkoxy (PFA)) have become established as good materials to minimise adsorptive sampling losses and this study conforms to the results of Neuman et al. (1999) and Ellis et al. (2010) that PFA is a good material for use in inlet to measure ‘sticky’ nitrogen species in the atmosphere.

Attempts were made to improve inlet efficiency by generating superhydrophobic surfaces. ESEM and contact analysis confirmed that a superhydrophobic surface was generated, but no correlation was found between hydrophobicity and a reduction in uptake coefficient. In fact, an anti-correlation was observed. The process of generating a superhydrophobic surface produces an increase in surface roughness, as shown by ESEM analysis. The increase in roughness is likely to create an increase in surface area and thus has the potential to increase loss. Further work is required to understand the efficacy of such surfaces to the uptake of nitrogen species.
References for paper I


3. Paper II

“Field inter-comparison of eleven atmospheric ammonia measurement techniques”

by

Kristina von Boburutzki, Mohamed B. Ghalaieny; Max R. McGillen, Carl J. Percival et al.


Contributions: Mohamed Ghalaieny and Max McGillen conducted the field work. The data analysis and manuscript contribution for CIMS work was led by Mohamed Ghalaieny and assisted by Max McGillen. All the work was done under the supervision of Carl Percival. Kristina von Bobrutzki coordinated the project and led the preparation of the manuscript.
Field inter-comparison of eleven atmospheric ammonia measurement techniques

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Abstract. Eleven instruments for the measurement of ambient concentrations of atmospheric ammonia gas (NH₃), based on eight different measurement methods were inter-compared above an intensively managed agricultural field in late summer 2008 in Southern Scotland. To test the instruments over a wide range of concentrations, the field was fertilised with urea midway through the experiment, leading to an increase in the average concentration from 10 to 100 ppbv. The instruments deployed included three wet-chemistry systems, one with offline analysis (annular rotating batch denuder, RBD) and two with online-analysis (Annular Denuder sampling with online Analysis, AMANDA; AirRmonia), two Quantum Cascade Laser Absorption Spectrometers (a large-cell dual system; DUAL-QCLAS, and a compact system; c-QCLAS), two photo-acoustic spectrometers (WaSul-Flux; Nitrolux-100), a Cavity Ring Down Spectrometer (CRDS), a Chemical Ionisation Mass Spectrometer (CIMS), an ion mobility spectrometer (IMS) and an Open-Path Fourier Transform Infra-Red (OP-FTIR) Spectrometer. The instruments were compared with each other and with the average concentration of all instruments. An overall good agreement of hourly average concentrations between the instruments (R² > 0.84), was observed for NH₃ concentrations at the field of up to 120 ppbv with the slopes against the average ranging from 0.67 (DUAL-QCLAS) to 1.13 (AirRmonia) with intercepts of −0.74 ppbv (RBD) to +2.69 ppbv (CIMS). More variability was found for performance for lower concentrations (<10 ppbv). Here the main factors affecting measurement precision are (a) the inlet design, (b) the state of inlet filters (where applicable), and (c) the quality of gas-phase standards (where applicable). By reference to the fast (1 Hz) instruments deployed during the study, it was possible to characterize the response times of the slower instruments.

1 Introduction

Ammonia (NH₃) plays an important role in atmospheric chemistry. It represents the major alkaline gas and is therefore important for the neutralization of acidic gases and the formation of particulate matter (Duyzer et al., 1994; Asman et al., 1998). Deposition of atmospheric NH₃ to ecosystem can lead to effects such as eutrophication and acidification of soils, contributing to forest decline and a decrease in biological diversity (Fangmeier et al., 1994; Sutton et al., 1995; Ferm, 1998). As a consequence, many measurement methods for NH₃ have been developed. Ambient measurement of NH₃ concentrations is difficult due to several factors: ambient levels vary widely, from 5 pptv in remote regions (Janson et al., 2001; Sutton et al., 2001) to 500 ppbv
near sources (Krupa, 2003). Ammonia occurs in gaseous, particulate and liquid phases which add further complexity to its measurement (Warneck, 1988), since the measurement technique should be specific to the gas-phase and not modify the gas-aerosol equilibrium which depends on environmental conditions (Mozurkewich, 1993). In addition, NH₃ is “sticky” and interacts with surfaces of materials, often leading to slow inlet response times (Yokelson et al., 2003). Finally, NH₃ is emitted by people, increasing the potential for sample contamination (Sutton et al., 2000b).

Currently, bulk denuder techniques are the most widely used method for sampling NH₃ and operate by stripping the gas phase NH₃ from the air stream (Ferm, 1979; Keuken et al., 1988). The main disadvantages of this manual sampling method are the low temporal-resolution, and when high-frequency measurements (e.g. hourly) are needed, the manpower required becomes considerable. Moreover, the manual handling, including sample preparation, wet-chemical analysis and sample storage, increase the chances of sample contamination. In the 1980s systems were developed, based on wet effluent diffusion denuder (WEDD) techniques, to collect stripping solution at regular intervals into test tubes (e.g. Keuken et al., 1988), this automated the process of sample preparation and extraction, while still retaining the need for manual off-line analysis. In a next step, in the 1990s these WEDDs and mist chambers were coupled to NH₃ online analysers in the field (Simon et al., 1991; Simon and Dasgupta, 1993; Wyers et al., 1993; Blatter et al., 1994; Erisman et al., 2001).

In parallel, spectroscopic techniques for NH₃ were developed, such as the use of chemiluminescence NOₓ monitors with NH₃ converters (e.g. Breitenbach and Shelef, 1973), Differential Optical Absorption Spectroscopy (DOAS; Gall et al., 1991), Tunable Diode Laser Absorption Spectroscopy (TDLAS; Grisar et al., 1987; Warland et al., 2001) and Fourier Transform Infra-Red spectroscopy (FTIR; Galle et al., 2000). While many of these techniques have been deployed successfully to measure concentrations and emissions downwind of strong sources, it has only been over the past 15 years that spectroscopic techniques have gradually become sufficiently sensitive and robust for field application at typical ambient concentrations (0.1 to 10 ppbv). Approaches more recently applied for NH₃ measurements include photoacoustic spectroscopy (e.g. Harren et al., 2000; Pushkarsky et al., 2002), Chemical Ionization Mass Spectrometry (CIMS; e.g. Norman et al., 2007; Nowak et al., 2007), quantum cascade laser absorption spectrometers (QCLAS; e.g. McManus et al., 2002) and Ion Mobility Spectrometry (IMS; e.g. Myles et al., 2006).

Some experiments have been carried out to compare NH₃ measurement techniques. Wiebe et al. (1990) reported a test of four methods: FTIR, filter-pack, denuders (simple and annular) and a transition flow reactor. Williams et al. (1992) conducted an inter-comparison of five instruments: a photofragmentation/laser-induced fluorescence (PF/LIF) instrument, a molybdenum oxide annular denuder sampling/chemiluminescence detection (MOADS) system, a tungsten oxide denuder sampling/chemiluminescence detection (DARE) system, a method based on citric acid coated denuder sampling coupled with ion chromatographic analysis (CAD/IC), and a method using an oxalic acid coated filter pack sampling coupled with colorimetric analysis (FP/COL). For selection within the Netherlands National Air Quality Monitoring Network (NAQMN) six analysers were studied by Mennen et al. (1996): a wet-annular rotating denuder, a WO₃-coated thermodenuder, a V₂O₅-coated thermodenuder, a DOAS system, a photoacoustic monitor and a chemiluminescence NOₓ monitor with NH₃ converter. In addition, there were smaller inter-comparisons between two instruments: a field study on Tenerife by Milford et al. (2000) included an AMANDA instrument (see below) and a diffusion scrubber flow injection analyzer (DS-FIA). Fehsenfeld et al. (2002) reported a comparison of a CIMS with a citric acid denuder and a molybdenum oxide (MoO₃) converter. Nowak et al. (2006) compared two different CIMS instruments in the field: a NOAA chemical Science Division (NOAA-CSD) apparatus and the Georgia tech (GT) low pressure reactor.

The development of new continuous measurement approaches has motivated two major inter-comparison campaigns in recent years: a laboratory inter-comparison of gaseous NH₃ with seven instruments were performed by Schwab et al. (2007): a TDLAS, a wet scrubbing long-path absorption spectrometer (LOPAP), a WEDD system, an IMS, a photo-acoustic absorption analyzer, and a modified chemiluminescence analyzer. The emphasis of this short inter-comparison was on the accuracy and time-response of these approaches under laboratory conditions while sampling from a common manifold. In addition, Norman et al. (2009) realised an inter-comparison of three instruments at a Swiss grassland site: a modified Proton Transfer reaction Mass Spectrometer (PTR-MS; Norman et al., 2007) and two wet chemistry techniques, based on a horizontal denuder technique (GRAEGOR; Thomas et al., 2009), and a diffusion membrane sampler (AirRmonia; Erisman et al., 2001). Further, Whitehead et al. (2008) made measurements between a QCLAS, a TDLAS and an AMANDA instrument.

The work presented here included eight different atmospheric NH₃ measurement methods implemented in eleven different instruments, focussing on comparison of the techniques under typical field conditions. Ammonia was measured over intensively managed grassland in Scotland, between 20 August and 4 September 2008. The field was fertilised on 28 August 2008 to stimulate emission from the field and test the instrumentation over a wide concentration range, including regimes that are typical for moderately agricultural mixed land use and also near-sources. The aim was to assess instrument performance and characterise the instrument response times. In addition to the description of time-series, we used regression analyses for concentrations over the entire
concentration range and, separately, below 10 ppbv to assess the performance at low concentrations in more detail. Three of the instruments were also used for micrometeorological flux measurements based either on the flux gradient technique (AMANDA, WaSuFlux) or eddy-covariance (DUAL-QCLAS), but these results will be presented elsewhere.

2 Methodology

2.1 Site description

The measurements were made at a micrometeorological field site in Southern Scotland (55°52′N, 3°2′W, 190 m a.s.l.) on an intensively managed grassland area (Easter Bush), located about 1 km to the west of the Pentland Hills with peaks of up to 500 m (see Milford et al., 2001; Whitehead et al., 2008). The Easter Bush site is divided into two fields, each approximately 5 ha, more than 90% of which is covered by Lolium perenne (perennial ryegrass). The dividing line between the fields runs NW to SE, and in the following analysis the fields to the NE and SW of the measurement equipment are referred to as N field and S field, respectively. The Pentland Hills channel the wind so that on average 60% of the wind comes clearly from the S field and 19% clearly from the N field (Milford et al., 2001). Both fields receive the same management and have been used for cattle and sheep grazing in recent years. Easter Bush is an intensive flux monitoring site of the NitroEurope IP measurement programme (Sutton et al., 2007) and has hosted several studies on NH₃ flux measurements (Milford et al., 2001; Whitehead et al., 2008). The inter-comparison experiment took place from 20 August to 4 September 2008 with the instruments placed along the boundary between the two fields (Fig. 1). All instruments were deployed with an inlet height of 1.1 m above ground, with the exception of the DUAL-QCLAS (1.95 m), as this was also used for eddy-covariance flux measurements.

Fertilisation took place on 28 August 2008 on both the N and S field, with 35 kg N ha⁻¹ in the form of urea.

2.2 Environmental conditions during the field experiment

Figure 2 presents the time-series of hourly data of precipitation, temperature and relative humidity. The wind direction and speed are represented by the direction and length of the arrows, respectively. The mean wind speed was around 3 m s⁻¹. Several rain events occurred during the campaign with the maximum amount being 4.9 mm h⁻¹ on 20 August 2008. There was no rain during the fertilisation on 28 August 2008 and therefore no NH₃ was washed into the ground immediately after fertilisation (see Sect. 3.1). The relative humidity never decreased below 58%. The mean temperature was 12.8 °C. Overall, August 2008 was wet in Eastern Scotland, receiving about twice as much rainfall compared with the long-term average (mean since 1961; values for Leuchars; Eden, 2008). This high level of precipitation led to the formation of a “pond” near to the measurement site in the N field. Although the accumulating water was pumped away on several occasions, the associated rotting vegetation is likely to have created an additional and heterogeneous NH₃ source near the instruments, for NE wind directions. The few occurrences of this wind direction were therefore excluded from the regression analysis presented below.

Figure 2 also includes a time-series of NH₄⁺ aerosol in PM₂.₅ measured with a MARGA instrument, similar to GRAEGOR (Thomas et al., 2009), except that it deploys online cation analysis rather than FIA and a PM₂.₅ inlet cyclone, at the Auchencorth EMEP site, 10 km south of Easter Bush. From previous simultaneous measurements, there is close (±20%) agreement between NH₄⁺ concentrations at Auchencorth and Easter Bush. This time-series is included because it is possible that some of the NH₃ measurement techniques deployed here may show some cross-sensitivity to NH₄⁺ aerosol. Ammonium concentrations were below 1 µg m⁻³ except for 30 and 31 August 2008.

2.3 Measurement techniques

The characteristics of the NH₃ measurement systems deployed in the inter-comparison are summarised in Table 1, and can be described as followed.
2.3.1 Wet-chemistry analysers

Two of three wet chemistry instruments deployed (RBD, AMANDA) are based on the denuder principle described by Ferm (1979), whereby gas phase NH$_3$ is stripped from the air stream through diffusion to the denuder glass walls, without collecting the NH$_4^+$ aerosol phase, since gas molecules diffuse quicker than particles to a moistened/acidified tube wall. In a third instrument (AiRRmonia), a diffusion membrane was used to strip the gas phase from the air stream. All three instruments were developed by the Energy Research Foundation of the Netherlands (ECN, Petten, NL). The instruments were housed in weather proof enclosures and placed at the measurement height, with inlets of <0.1 m length.

Annular rotating batch denuder (RBD)

In the RBD instrument (Keuken et al., 1988), air is pumped at 271 min$^{-1}$ through the annulus formed by two horizontal concentric rotating glass tubes (with a diameter of 45 mm) and a 25 cm long HDPE (High Density Polyethylene) inlet (12 mm diameter). The glass tubes are wetted with a thin layer of collecting liquid, which contains 2.0 g l$^{-1}$ NaOH, 3.4 ml l$^{-1}$ >98% formic acid and 0.5 mg l$^{-1}$ thymol as biocide. Ammonia is absorbed into this thin layer of collection solution over a sampling time of 40 min within each hour, after which the sample (10 to 15 ml) is pumped off to an autosampler holding 20 ml test tubes. All samples were analysed for NH$_4^+$ offline on an NH$_3$ Flow Injection Analyser (AMFIA, ECN, Petten, NL), based on analysis by selective ion membrane and conductivity measurement (Genfa and Dasgupta, 2000). For analysis, 0.5 M NaOH solution is added to the sample, resulting in the conversion of NH$_4^+$ to gas-phase NH$_3$ in solution. As the solution then passes a semi-permeable Teflon membrane, NH$_3$ permeates the membrane and is dissolved in a counter stream of deionised water. Here NH$_3$ is re-ionised to NH$_4^+$ and is detected by conductivity (Sutton et al., 2000a; Erisman et al., 2001; Milford et al., 2001). This technique is precise.
and reasonably specific, but it has been shown to be somewhat cross-sensitive to selected amines at high concentrations (Husted et al., 2000). In addition to NH$_3$ it is possible to use the RBD to capture other water soluble inorganic trace gases like HNO$_3$, HCl, SO$_2$ and H$_2$O$_2$ (Keuken et al., 1988), which would need to be quantified by a different analytical technique such as anion chromatography.

### Table 1. Summary of the characteristics of the instruments.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Manufacturer</th>
<th>Air flow rate [l min$^{-1}$]</th>
<th>Used time resolution/used time average [s]</th>
<th>Precision [ppbv]</th>
<th>Range [ppbv]</th>
<th>Accuracy [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBD</td>
<td>Energy Research Foundation of the Netherlands (ECN) (Keuken et al., 1988)</td>
<td>27</td>
<td>2400/3600</td>
<td>0.02</td>
<td>not specified</td>
<td>not specified</td>
</tr>
<tr>
<td>AMANDA</td>
<td>Energy Research Foundation of the Netherlands (ECN) (Wyers et al., 1993)</td>
<td>28</td>
<td>450/450</td>
<td>0.02</td>
<td>0.02–500</td>
<td>not specified</td>
</tr>
<tr>
<td>AiRRmonia</td>
<td>R&amp;R Mechatronics</td>
<td>1</td>
<td>600/60</td>
<td>0.05</td>
<td>0.04–500</td>
<td>±3$^1$</td>
</tr>
<tr>
<td>DUAL-QCLAS</td>
<td>Aerodyne Research, Inc. (ARI) (Whitehead et al., 2008)</td>
<td>15</td>
<td>0.2/60</td>
<td>0.018</td>
<td>not specified</td>
<td>±5$^2$</td>
</tr>
<tr>
<td>e-QCLAS</td>
<td>Aerodyne Research, Inc. (ARI) (McManus et al., 2007)</td>
<td>8.9</td>
<td>1/60</td>
<td>0.05</td>
<td>not specified</td>
<td>±10$^1$</td>
</tr>
<tr>
<td>WaSul-Flux</td>
<td>Hilase Ltd.</td>
<td>4</td>
<td>300–1800/300–1800</td>
<td>0.25</td>
<td>0.25–1 000 000</td>
<td>not specified</td>
</tr>
<tr>
<td>Nitrolux-100</td>
<td>Pranalytica Inc. (Cowen et al., 2004)</td>
<td>1.2–1.6</td>
<td>3/300</td>
<td>0.1</td>
<td>0.1–200</td>
<td>±4$^3$</td>
</tr>
<tr>
<td>CRDS</td>
<td>Enviro Sense1000 Analyzer, Picarro (Berden et al., 2000)</td>
<td>1</td>
<td>3/300</td>
<td>0.07</td>
<td>0.07–25</td>
<td>±7$^3$</td>
</tr>
<tr>
<td>CIMS</td>
<td>Georgia Institute of Technology CIMS team (Nowak et al., 2007)</td>
<td>19.5</td>
<td>1/60</td>
<td>0.94</td>
<td>not specified</td>
<td>±4$^4$</td>
</tr>
<tr>
<td>IMS</td>
<td>Bruker Daltonik</td>
<td>0.4</td>
<td>4/60</td>
<td>not specified</td>
<td>Variable, dependent on other substances present</td>
<td>not specified</td>
</tr>
<tr>
<td>OP-FTIR</td>
<td>MIDAC Corp.</td>
<td>n/a</td>
<td>8/120</td>
<td>not specified</td>
<td>not specified</td>
<td>not specified</td>
</tr>
</tbody>
</table>

1. based on manufacturer specification  
2. based on the statistical standard deviations of the reported mixing ratios during calibration  
3. based on the statistical standard deviations (twice) of hourly data, referenced against AiRRmonia inter-comparison dataset  
4. based on the calibration during the experiment

### AMANDA

The technique of NH$_3$ Measurement by ANnular Denuder sampling with online Analysis (AMANDA) was developed by Wyers et al. (1993). The system used here consists of three annular wet rotating denuder inlets, similar to that used in the RBD, located at different heights (0.39 m, 1.07 m, and 2.20 m). Unlike in the RBD, however, the stripping solution (0.5 g l$^{-1}$ NaHSO$_4$ containing 0.2 ml l$^{-1}$ 37% HCHO...
as a biocide) is continuously pumped from the denuders to a common detector block, where the three concentrations are analysed sequentially by the same selective ion membrane/conductivity technique as deployed in the AMFIA. In the denuders a constant liquid level is maintained by the use of an independent peristaltic pump, controlled by a conductivity measurement along the denuder. This particular instrument has been upgraded with a newer detection block, using two conductivity measurements. One conductivity cell monitors the initial conductivity of the deionised water, while a second conductivity cell monitors the NH$_4^+$ content after the membrane exchange. The difference in both readings of the conductivity cells is a measure for the original NH$_3$ content in the sampled air. This approach takes into account changes in the water quality during longer service intervals. The instrument reports one concentration gradient every 7.5 min, but the overall instrument response time is limited by the exchange of the stripping solution within the denuder (see Sect. 3.3 below).

**AiRRmonia**

The AiRRmonia is a further development of the AMANDA technique. As with the AMANDA, it was originally developed by ECN (Energy Research Centre of the Netherlands, Petten, NL), but has been further improved and commercialised (Mechatronics Instruments b.v., Hoorn, NL) to provide a sensitive, easy-to-use NH$_3$ monitor (Erisman et al., 2001). Unlike the RBD and AMANDA, the instrument uses a Teflon membrane to strip the NH$_3$ from the airflow into a deionised water flow. The detection system of NH$_3$ is similar to that of the AMANDA, also using the double conductivity measurement. Precision and stability of this instrument are further improved through the use of syringe pumps for reagents and solutions, which undergo less variation due to changes in pump tubing and temperature than the peristaltic pumps used in the AMANDA. The AiRRmonia inlet consists of stainless steel with a length of 5 cm and a diameter of 3.2 mm.

**2.3.2 Quantum cascade laser absorption spectroscopy (QCLAS)**

QCLAS is an infrared absorption technique that makes use of the rich spectral absorption region in the mid-infrared, in which most species of interest in the atmosphere have resolvable absorption features. Both laser systems used here were produced by Aerodyne Research Inc. (Billerica, MA, USA), and operate with the light source of a thermoelectrically cooled pulsed Quantum Cascade (QC) laser (Alpes Lasers, Neuchatel, Switzerland). Their design was similar to the closed path configuration described by McManus et al. (2002). These lasers scan over a narrow range of wave numbers chosen to contain an absorption feature of the trace gas of interest, which for NH$_3$ is at a wavelength of 10.3 µm.

Both instruments use astigmatic Herriott multipass absorption cells, to increase the effective path length, while providing a fast spot measurement. They operate at cell pressures of around 40 Torr as a balance between minimising line broadening, maximising time response and achieving good sensitivity.

In the data acquisition protocol chosen for this study, the spectra were recorded and averaged over the data acquisition time of one second, with the resulting spectra fitted to known spectral line profiles from the HITRAN (HIgh-resolution TRANsmission) molecular spectroscopic database (Rothmann et al., 1998). In principle, this approach provides an absolute measurement.

**DUAL-QCLAS**

The DUAL-QCLAS uses two separate thermoelectrically cooled pulsed Quantum Cascade (QC) lasers for the potential measurement of two trace gases at different wave lengths. The two beams are brought together (with the pulses separated in time) and directed into either one of two astigmatic Herriott multipass absorption cells where they undergo 238 reflections, before leaving the cell and arriving at a cryogenically cooled HgCdTe infrared detector. The large (51) cell provides an effective path length of 210 m, while the small (0.31) cell provides a path length of 56 m. The large cell is used for higher precision measurement applications whilst the small cell (used here) provides the fast time response required for eddy-covariance flux measurements. Data were recorded at a rate of 5 Hz to be averaged up in post-processing for the purpose of the concentration inter-comparison reported here. Background measurements were made typically every 15 min and background spectra were subtracted from the measurements prior to the wave fit. For this purpose, NH$_3$ free air was generated using a customized Pd/AL$_2$O$_3$ catalyst heated to 300°C, in an attempt to determine the background at a relative humidity as close to ambient as possible. The Pd/AL$_2$O$_3$ catalyst has been shown to have a negligible affect on the water concentration of the background air (Wert et al., 2002). The inlet was a 2 m length of 6.4 mm (OD) PFA tube, which was co-located with an ultrasonic anemometer (model HS; Gill Instruments Ltd., Lymington, UK) for the purpose of flux measurements. A general calibration factor of 1.23 was applied to the DUAL-QCLAS data based on the field based calibration. For more information and studies of the DUAL-QCLAS see Whitehead et al. (2008).

**Compact QCLAS (c-QCLAS)**

The c-QCLAS uses a single QC laser and a single cell with a volume of 0.5 l and an effective path length of 76 m. Air was drawn into the optical cell through a short (<0.1 m) quartz inlet that was heated to 40°C and coated with a hydrophobic siloxyl coating. The inlet contains a critical orifice that drops
the pressure in the optical cell to approximately 45 Torr while keeping a constant flow rate of approximately 91 min$^{-1}$. Following the critical orifice, the flow is split into two branches with 90% of the flow making a sharp turn and being pulled through the optical cell. The other 10% is pulled directly to the pump, relying on inertia to remove more than 50% of particles larger than 300 nm. This design was chosen to minimize surface interactions for gas phase NH$_3$ while reducing possible positive artefacts in the measurements from particle volatilization. The quartz inlet was connected to the optical cell via ~3 m and 9.5 mm PFA tubing. Background measurements were performed every 30 min by flushing the quartz inlet using dry nitrogen. Standard addition calibrations were performed every two hours with a permeation tube standard, added either into ambient air or dry nitrogen. The permeation rate was determined gravimetrically by the manufacturer (Kin-Tek) as 100 ng min$^{-1}$ at 40 $^\circ$C. The rate was confirmed as 100±5 ng min$^{-1}$ at 40 $^\circ$C by passing a flow of permeation tube standard through citric acid filters for 24 h, followed by extraction with deionized water and analysis using ion chromatography.

2.3.3 Photoacoustic spectroscopy

Two instruments measured NH$_3$ concentration using photoacoustic spectroscopy. A light source is tuned to an absorption feature of the target species and molecules are excited to a higher quantum state. Modulating the light source results in a periodic temperature change, giving rise to a periodic pressure change that equates to an acoustic signal if the modulation frequency is in the acoustic range. The intensity of the acoustic signal, which can be detected by a sensitive microphone, is proportional to the concentration of the light-absorbing species (Harren et al., 2000).

Diode laser based photoacoustic system (WaSul-Flux)

This new instrument combines near-infrared photoacoustic spectroscopy with pre-concentration sampling as described in more detail elsewhere (Pogány et al., 2008). The instrument is built into a 48.3 cm 6U temperature controlled instrument box and has an additional waterproof housing. The photoacoustic detection unit consists of a fibre-coupled DFB diode laser light source (FOL1DCWD-A82-19560-A, Furukawa Inc.) with ~40 mW output light power at 1532 nm, and an acoustically optimized photoacoustic cell with an electret microphone (Knowles, EK 3029) for measuring the photoacoustic signal. Ammonia is concentrated from the sampled air by a tungsten (VI) oxide coated preconcentration unit. The instrument has three gas inlets and is therefore suitable for measuring NH$_3$ concentration at three different heights above the ground. The sampling lines were 6 m long Teflon tubes with 8 mm inner diameter, heated to ~50 $^\circ$C by self-regulating heating tape and included filters which were replaced weekly. The pre-concentration time can be adjusted to match the air concentrations. Here the integration time was varied between 15 and 45 min according to the actual concentration. Before fertilization all three inlets were placed at the same height and the reported data are the averages of the three measurements. After fertilization, the inlets were operated in gradient configuration and the reported data represent the measurement of the middle height.

Nitrolux-100

The Nitrolux-100 (Pranalitica Inc., Santa Monica, CA, USA) is an ambient NH$_3$ analyser that uses resonant photoacoustic spectroscopy and a line-tunable CO$_2$ laser to provide continuous or on-demand measurements (Pushkarsky et al., 2003). The excited NH$_3$ molecules undergo collisional deactivation, which converts the absorbed energy into periodic local heating at the modulation frequency of the laser. The resulting acoustic waves are detected with minimal interferences by other compounds at typical concentrations in a non-polluted atmosphere (Cowen et al., 2004). The instrument was originally developed for clean room applications in the semiconductor industry, but has been more widely used for ambient measurements. It is operated with an inlet filter to remove dust and NH$_3$ from a non-polluted atmosphere (Cowen et al., 2004). The instrument is insulated and heated to ~35 $^\circ$C. The inlet was sheltered by an inverted plastic funnel.

2.3.4 Cavity Ring Down Spectroscopy (CRDS)

Cavity Ring Down Spectroscopy (CRDS) is a direct absorption technique, which uses pulsed or continuous light sources and has a significant higher sensitivity than other conventional absorption spectroscopy (Berden et al., 2000). The EnviroSense 1000 Analyzer (Picarro Inc., Sunnyvale, CA, USA) monitors NH$_3$ in air using this approach. Cavity Ring Down Spectroscopy uses a pair of mirrors facing each other. A brief pulse of laser light is injected into the cavity, and it passes back and forth between the mirrors, while a fraction leaks through the mirror. Ammonia absorbs some of the light and thus the amount of light in the cavity decreases faster—it makes fewer passes. A CRDS setup measures how long it takes for the light to drop to a certain percentage of its original intensity, and this “ringdown time” is used to calculate the concentration of the absorbing substance in the gas mixture in the cavity. Like the Nitrolux-100, the Picarro CRDS uses an inlet filter and is calibrated by the manufacturer subsequent (~2 months) to its most recent calibration.

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CRDS was operated with a 4 m and 6.4 mm OD Teflon inlet which was insulated and warmed with heating tape (∼35 °C). Again, the inlet was sheltered by an inverted plastic funnel. For detailed information see Rella (2008).

2.3.5 Chemical Ionisation Mass Spectrometry (CIMS)

Chemical Ionisation Mass Spectrometry (CIMS) techniques use ion-molecule reactions to selectively ionize and detect trace species of interest in ambient air with high sensitivity and fast time response. The CIMS method uses a reagent ion to ionise a neutral species, and the product ion resulting from this process is identified and quantified by a quadrupole mass analyser. The distinction between chemical ionization mass spectrometry and other mass spectrometry techniques is the use of ion molecule reactions for the selective ionization of compounds of interest in the complicated matrix of ambient air. In the system deployed here, NH₃ was detected using H⁺(C₂H₅O)₂ as a reagent ion (Nowak et al., 2007). The configuration of the CIMS deployed here is described elsewhere (Slusher et al., 2004; Neuman et al., 2006; Kim et al., 2007; Nowak et al., 2007). The instrument sampled air though a 0.1 m long and 9.5 mm O.D. PFA inlet, temperature controlled to 40 ± 1 °C. Inlet flow was 19.5 l min⁻¹, with 0.88 l min⁻¹ being subsampled through a 0.65 mm pinhole into the ionization region, where reaction of NH₃ with H⁺(C₂H₅O)₂ proceeds. The instrumental signal was calibrated every hour using a standard addition from a calibrated permeation tube oven and an instrument background was taken hourly.

2.3.6 Ion mobility spectrometer (IMS)

Ion mobility spectrometers separate chemical substances on the basis of velocity of gas-phase ions in an electrical field (Eiceman and Karpas, 1994). Ions are introduced into an electrical field and the time of flight is measured. The sample molecules are first ionized by β-radiation from a 63Ni source. The formation of positive ions is dominated by the proton-transfer reaction (Sunner et al., 1988) from water clusters to substances that have proton affinity higher than water (697 kJ mol⁻¹), which includes NH₃ (854 kJ mol⁻¹). The charged ions are pulsed through a shutter grid into the drift region, where they are separated by mobility and detected at the end of the drift tube by an electrometer. The instrument is not very specific and the NH₃ measurement can suffer from the cross sensitivity of other compounds of similar mobility if they also have a proton affinity greater than water, while the quantification can be compromised by competing ion reactions. More details on the IMS technique are given in Hill et al. (1990) and Bacon et al. (1998). In this field study the commercial ion mobility spectrometer RAID I was used (Bruker Daltonik GmbH, Bremen, Germany). Sampling gas flow was 0.41 min⁻¹ and the sampling line was 2 m non-heated Teflon tubing. Heating was not applied to avoid contamination from the evaporation of NH₄⁺ aerosols, although the response time to the concentration peaks might be improved with a heated sampling line.

2.3.7 Open-path Fourier Transform Infra-Red (OP-FTIR) spectroscopy

Fourier Transform Infra-Red (FTIR) spectroscopy can be used to identify and quantify substances by their molecular absorption of infra-red radiation at specific wavelengths. An open-path configuration permits the estimation of path-integrated average concentrations of a gas species of interest over path lengths of up to 1 km. OP-FTIR has been shown to be a useful tool for the measurement of NH₃ from agricultural sources (e.g. Griffith and Galle, 2000). In the present study, a MIDSAC M4401 portable FTIR spectrometer with Stirling cooled MCT detector module was used in conjunction with a 50.8 cm infra-red (IR) source in a bi-static open-path configuration (path length of 102 to 105 m). Both the FTIR spectrometer and IR source were aligned at 1.3 to 1.4 m above ground. The spectrometer was operated at a resolution of 0.5 cm⁻¹ and eight sample scans were co-added for each spectrum.

Measured spectra were analysed for NH₃ using the NH₃ infra-red absorption features at 968 cm⁻¹ and 932 cm⁻¹ (accounting for interference by H₂O and CO₂ absorption). Concentration retrievals were performed using the MALT software (Griffith, 1996). MALT iteratively computes synthetic spectra (convolved to the spectrometer line shape) from the HITRAN absorption line database (Rothman et al., 1998) until the mean-squared difference between the synthetic and measured spectra is minimised. The resultant concentrations used for the best-fit synthetic spectrum yield the path-integrated NH₃ (as well as H₂O and CO₂) mixing ratios (in ppbv) for the measured open-path.

2.4 Calibration and treatment of aerosol components

The wet chemistry instruments were calibrated weekly with individual liquid standards and a common liquid standard was run on all analytical systems. The CIMS and c-QCLAS were calibrated regularly with their own gas-phase standards. As noted above, the Nitrolux-100 and CRDS were calibrated by manufacturers and operated within the specified calibration intervals. The WaSul-Flux and IMS were calibrated by the operating groups prior to the campaign by comparison against wet-chemistry reference systems.

An inter-comparison calibration (standard addition to ambient air) from a common NH₃ gas cylinder took place during the campaign. The cylinder was a standard of nominally 21 ppmv NH₃ in N₂ (BOC, UK). During the experiment presented here the actual concentration was determined as 20.2 ± 1.4 ppmv by bubbling the gas through acid adsorption solution which was then analysed for NH₄⁺ by flow injection analysis, following the procedure described by
Table 2. Correlation of hourly NH$_3$ concentrations less than 10 ppbv (z=1.1 m) between each instrument and the NH$_3$-ens. Also shown are the bias for the entire data range and the data <10 ppbv, as well as the gas and liquid standard biases for all instruments.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Slope [ppbv]</th>
<th>Intercept [ppbv]</th>
<th>$R^2$</th>
<th>&lt; 10 ppb regression</th>
<th>Overall bias [%]</th>
<th>Gas Std. bias [%]</th>
<th>Liquid Std. bias [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBD</td>
<td>0.89</td>
<td>-0.33</td>
<td>0.85</td>
<td>-20.1</td>
<td>+5.65</td>
<td>+13.37</td>
<td>+2.62</td>
</tr>
<tr>
<td>AMANDA</td>
<td>0.83</td>
<td>-0.08</td>
<td>0.85</td>
<td>+6.2</td>
<td>-0.63</td>
<td>-24.71</td>
<td>+0.85</td>
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<tr>
<td>AiRRmonia</td>
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<td>+0.71</td>
<td>0.81</td>
<td>-12.8</td>
<td>-4.02</td>
<td>-23.2</td>
<td>N/A</td>
</tr>
<tr>
<td>CIMS</td>
<td>0.86</td>
<td>-0.19</td>
<td>0.66</td>
<td>-20.6</td>
<td>-32.1</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>c-QCLAS</td>
<td>0.81</td>
<td>-0.05</td>
<td>0.85</td>
<td>-22.0</td>
<td>+1.27</td>
<td>–</td>
<td>N/A</td>
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<tr>
<td>DUAL-QCLAS</td>
<td>0.42</td>
<td>+3.42</td>
<td>0.52</td>
<td>+2.51</td>
<td>+1.69</td>
<td>–</td>
<td>N/A</td>
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<tr>
<td>WaSul-Flux</td>
<td>0.50</td>
<td>+3.14</td>
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<td>+26.0</td>
<td>+5.10</td>
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<td>Nitrolux-100</td>
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<td>0.87</td>
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<td>-2.90</td>
<td>–</td>
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</tr>
<tr>
<td>CRDS</td>
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<td>IMS</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* After calibration using this gas standard.

Thomas et al. (2009). The concentration range and number of step increases varied between instruments. A similar calibration scheme is described in Schwab et al. (2007). For each instrument a calibration bias from a NH$_3$ gas cylinder and a corresponding measured NH$_3$ concentration (gas std. bias) was calculated (see Table 2). This gas-phase measurement was used only as a check for most instruments, except for the DUAL-QCLAS, for which it provided the primary calibration, yielding a calibration factor of 1.23.

As outlined in the instrument descriptions above, the wet chemistry systems strip the gas phase from the sample stream, while the aerosol phase passes through the sampling system. The c-QCLAS uses a virtual impactor to prevent most of the particles from entering the detection cell. The Nitrolux-100, CRDS and WaSul-Flux employ filters to prevent aerosol components from contaminating the detection cell. This has the potential to lead to artifacts due to aerosol dynamics on the filter. Indeed, the Nitrolux-100 was initially operated with a used filter and reported elevated NH$_3$ concentrations compared with the other instruments (the deviation correlating with temperature), suggesting that the NH$_3$ originated from NH$_4$NO$_3$ volatilisation from the filter. Following replacement of this filter, the Nitrolux-100 measurements were found to agree with the other techniques sharing the same inlet line. The early data were therefore excluded from the data analysis. It appears that, for ambient measurements, the filters provided by the manufacturer have a much shorter lifetime than stated by the manufacturer. The stated lifetime is possibly more appropriate for the clean room applications for which the instrument had originally been developed.

3 Results

3.1 Time-series analysis

Figure 3a and b show the time-series of measured NH$_3$ during the inter-comparison period of all instruments, measured at different temporal resolutions (1 min to 1 h). Different vertical scales were used to present the time-series before (Fig. 3a) and after (Fig. 3b) the fertilisation on 28 August 2008. The NH$_3$ traces from the instruments at their individual time resolution (Table 1) are presented in two groups for increased clarity, separating wet chemistry analysers and spectroscopic techniques. In addition, the wind direction is indicated at the top of Fig. 3a and b. Before the fertilisation (Fig. 3a), there were brief NH$_3$ peaks in the time-series of the DUAL-QCLAS and CIMS of up to 18 ppbv. Except for these individual events, the NH$_3$ level measured by all instruments ranged up to 10 ppbv before the fertilisation on 28 August 2008. After fertilisation (Fig. 3b), NH$_3$ concentrations increased up to 120 ppbv, with such high concentrations continuing until 29 August 2008 around 14:00. The early NH$_3$ peaks and some periods of disagreement coincided with periods when the wind came from the rotting vegetation source in the N field as indicated by the shaded areas in Fig. 3a and b.

Overall, the absolute NH$_3$ concentrations of all instruments revealed the same features and agreed closely with each other. By contrast, the different time resolution of the instruments resulted in slightly different features of the temporal NH$_3$ structure. Of the wet chemistry instruments, the 1 minute data of the AiRRmonia analyser shows additional NH$_3$ variations during the fertilisation peak (29 August 2008), which the AMANDA and RBD failed to capture because of their lower time resolution. Similar differences can be seen in the comparison of the spectrometric techniques.
Fig. 3. Times series of NH$_3$ for all instruments (z=1.1 m) with occurring wind direction for the data (a) before fertilisation and (b) after fertilisation on 28 August 2008. The shaded areas indicate periods during which the wind came from the N field. RBD (red), AMANDA (blue), AiRRmonia (green), Nitrolux-100 (red), CRDS (brown), CIMS (purple), IMS (blue), WaSul-Flux (green), c-QCLAS (cyan), DUAL-QCLAS (orange), OP-FTIR (black).

3.2 Instrument inter-comparison

For the regression analysis data from each instrument was block-averaged to hourly values in order to match the time resolution of the slowest instrument (RBD). In addition, wind directions from the sectors 0° to 150° and 310° to 360° were excluded from the analysis, due to the heterogeneous source from the rotting vegetation in the N field.

Figure 4a–j depict NH$_3$ concentrations from each instrument compared with the ensemble average of made NH$_3$ observations (NH$_3$−ens), together with the results of the linear regression analysis. The NH$_3$−ens was computed as the average over all instruments that were operational at a given time, excluding the OP-FTIR, for which too few data points were available. Additionally, the horizontal error bars on NH$_3$−ens
Fig. 4. Scatter plots showing correlation of hourly NH$_3$ concentrations (z=1.1 m) between all instruments and the NH$_3$-cites screened for wind direction (150–310°). The horizontal error bars calculate the statistical standard error. For AiRRmonia, DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS the vertical error bars mark the estimated accuracy (Table 1). The solid line gives the 1:1 line and the dashed line the result of the axis regression.
show the statistical standard error (SE) of the different readings from the instruments that went into the calculation of each value of NH$_3$-ens. Further, the estimated accuracy for the AirRmonia, DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS (Table 1) is shown as vertical error bars.

Overall, a high correlation between all instruments is observed, with $R^2$ > 0.84. The DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS comparisons with NH$_3$-ens have a slope < 1 (Fig. 4d, e, g, h, i), with the DUAL-QCLAS and the CIMS lowest at 0.67 and 0.80, respectively. The RBD, AirRmonia, WaSul-Flux and IMS comparisons with the NH$_3$-ens have a slope > 1, but have negative intercepts of −0.74 ppbv (RBD) to −0.32 ppbv (IMS) (Fig. 4a, c, f, j). The AMANDA instrument was closest to NH$_3$-ens, with a slope of 1 and an intercept of 0.20 ppbv (Fig. 4b). Relatively high intercepts were observed by the CIMS, CRDS and Nitrolux-100 compared with the other instruments. It is thought that the CRDSs and Nitrolux-100 intercept might be due to a local contamination source which was either on the sampling post, sample tubing (both came from the same batch of tubing) or most likely the inlet filters. It should be noted that for the IMS, only data from before fertilisation and after the fertilisation plume had diminished could be used, because above about 30 ppbv the IMS becomes strongly non-linear due to the consumption of the parent ions and the formation of clusters, which shifts the mobility. The consequence was a reduced dataset, biased towards smaller concentrations.

Accurate measurement of NH$_3$ at typical ambient background levels is more challenging. For this reason, the linear regression for periods when NH$_3$-ens < 10 ppbv was calculated separately (Table 2). The $R^2$ against NH$_3$-ens varied from 0.52 (Nitrolux-100) to 0.90 (AirRmonia). The slope of AMANDA and IMS against NH$_3$-ens were > 1 and all others were < 1, e.g. 0.42 (Nitrolux-100) to 0.95 (CIMS) with intercepts from −0.61 to 3.42 ppbv. The highest intercept values were measured for CIMS, CRDS and Nitrolux-100 and again for the latter two inlet/filter contamination are thought to be the cause.

The bias (%) between two instruments is defined according to Eq. 1, where $m$ is the slope of the regression analysis when forced through zero.  

$$\text{bias} = (m - 1) \times 100$$  

(1)

The biases reported in Table 2 represent the percentage difference of the full range NH$_3$ concentration (overall bias) and the bias derived from concentrations < 10 ppbv (10 ppbv bias). The overall bias for all instruments were reasonably small, ranging from −12.9% (CIMS) to 10.9% (AirRmonia) except for the DUAL-QCLAS, whereas the 10 ppbv biases showed more variability. Also included in Table 2 is the bias of a reading based on a calibration through standard addition from an NH$_3$ calibration cylinder. It turned out not to be easy to provide a common, reliable and portable gas-phase calibration standard suitable for the large range of flow rates of the different instruments. Because these are based on standard additions to ambient air, they only reflect the error on the response (slope) and do not include the intercept. Calibration results were more variable than the slopes derived from the regression analysis and should therefore be treated with caution.

For the wet-chemistry analysers a liquid intercalibration was performed using common 50, 100 and 500 ppbv aqueous standard on the three analytical systems and the outcome is again the regression with the measured percentage difference. For the three wet-chemistry instruments the used liquid standards showed excellent agreement concerning the liquid standard bias (Table 2).

The OP-FTIR was operated manually in the field and the dataset is much reduced compared with the other instruments (9 h). Thus, it is not included in the hourly data analysis. Instead, Fig. 5 compares the OP-FTIR data at 2 min time resolution against the other fast response instruments (c-QCLAS, DUAL-QCLAS and CIMS).

The data of the OP-FTIR agreed best with the DUAL-QCLAS (Fig. 5) with a slope of 0.82 (Table 3), which was reading lower compared to the other instruments (Fig. 4d) with the c-QCLAS providing the best match with the reference here. Further, the regression analysis revealed for the OP-FTIR a high intercept of > 3.74 ppbv compared with all other instruments.

While for graphical representation the analysis of an individual instrument against a common NH$_3$-ens provides a digestible overview over the results, the full information of the inter-comparison is only revealed through correlation between each of the eleven instruments with each other. Tables 4 and 5 show the results of the regression analysis of all hourly data, while Tables 6 and 7 show the results of the regression confined to data points where both instruments reported concentrations of less than 10 ppbv. Each of the four tables contains two separate diagonal parts with information for the instruments. For the top half of the table (grey) the regression provided is the vertical axis (row) against the horizontal axis (column). Concerning the bottom half it switches to horizontal axis (column) against vertical axis (row).

For example, the regression analysis of the RBD against the AMANDA for the entire data range is:

$$\text{RBD} = 0.86 \times \text{AMANDA} + 1.41 \text{ppbv},$$  

\[ R^2 = 0.93, \]  

\[ \text{bias} = -11.1\% \]
while the results of the regression analysis of the AMANDA vs. RBD are not included. Although derived from the regression fit of \( y = ax \), the bias does not always fully represent a clear picture of the combined effects of the average discrepancy between two instruments specify by slope and intercept. For example, due to a lack of data and high intercept values for some instruments, the datasets in these scatter plots showed a distributed appearance and the linear regression line was difficult to draw (Table 8). Thus all four parameters need to be considered when interpreting the performance of two instruments against each other.

For the overall data range the slopes of the AMANDA, AiRRmonia, c-QCLAS, WaSul-Flux, Nitrolux-100 and CRDS varied by \( \pm 20\% \) with each other (Table 4). For the data limited to <10 ppbv the slopes between RBD, AiRRmonia, WaSul-Flux and IMS were all within \( \pm 20\% \) of unity (Table 6). High intercepts were found for correlations of CIMS, Nitrolux-100 and CRDS with all other instruments (Bold numbers in Tables 4 and 6), with values from 1.60 to 6.14 ppbv for the full data range and from 1.22 to 3.92 ppbv for data <10 ppbv. For the full data range, \( R^2 \) values <0.90 were limited for inter-comparisons involving RBD, CIMS or IMS (Table 5). For <10 ppbv, an \( R^2 >0.80 \) was achieved for any comparison between AMANDA, AiRRmonia and c-QCLAS (Table 7). The DUAL-QCLAS (italic numbers in Tables 5 and 7) was biased towards lower values, compared with all other instruments.

Table 8 contains two separate diagonal parts with information and presents a visual support to the results from Tables 4 to 7. The results provided are for the regression of the instrument on the vertical axis (row) against the instrument on the horizontal axis (column) for the entire data range (white).
Table 4. Inter-comparison of linear correlations between each instrument for the entire data range. Slopes are given in the bottom half and intercepts are indicated by the top (grey) of the matrix. Bold numbers indicate noticeable non-zero intercepts (>1.5 ppbv).

<table>
<thead>
<tr>
<th></th>
<th>RBD</th>
<th>AMANDA</th>
<th>AiRRmonia</th>
<th>CIMS</th>
<th>c-QCLAS</th>
<th>DUAL-QCLAS</th>
<th>WaSuFlux</th>
<th>Nitrolux</th>
<th>CRDS</th>
<th>IMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept [ppbv]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>RBD</td>
<td>−</td>
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<td>0.70</td>
<td>3.65</td>
<td>1.17</td>
<td>1.09</td>
<td>0.55</td>
<td>6.14</td>
<td>3.63</td>
<td>0.10</td>
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<td>AMANDA</td>
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<td>−1.08</td>
<td>3.51</td>
<td>−0.62</td>
<td>0.34</td>
<td>−0.86</td>
<td>1.82</td>
<td>2.27</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
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<td>−2.46</td>
<td>0.34</td>
<td>0.57</td>
<td>0.16</td>
<td>2.65</td>
<td>2.93</td>
<td>0.02</td>
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<td>CIMS</td>
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<td>0.65</td>
<td>−3.26</td>
<td>0.38</td>
<td>0.92</td>
<td>1.82</td>
<td>2.27</td>
<td>0.04</td>
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</tr>
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<td>0.83</td>
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<td>0.47</td>
<td>5.73</td>
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</tr>
<tr>
<td>DUAL-QCLAS</td>
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<td>0.69</td>
<td>0.59</td>
<td>0.65</td>
<td>−1.13</td>
<td>2.46</td>
<td>1.82</td>
<td>0.40</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>WaSuFlux</td>
<td>0.90</td>
<td>1.02</td>
<td>1.06</td>
<td>1.00</td>
<td>1.55</td>
<td>−</td>
<td>3.09</td>
<td>3.02</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Nitrolux-100</td>
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<td>0.85</td>
<td>0.97</td>
<td>0.90</td>
<td>0.92</td>
<td>−0.03</td>
<td>−2.22</td>
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<td>CRDS</td>
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<td>0.93</td>
<td>0.83</td>
<td>1.09</td>
<td>1.04</td>
<td>1.60</td>
<td>0.92</td>
<td>1.00</td>
<td>−1.13</td>
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<td>IMS</td>
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<td>0.30</td>
<td>0.93</td>
<td>0.69</td>
<td>1.11</td>
<td>0.95</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Inter-comparison of correlation coefficients and biases between each instrument for the entire data range. Biases are given in the bottom half and correlation coefficients are indicated by the top (grey) of the matrix. Bold numbers indicate high biases (>20%), mainly of the Dual-QCLAS.

<table>
<thead>
<tr>
<th></th>
<th>RBD</th>
<th>AMANDA</th>
<th>AiRRmonia</th>
<th>CIMS</th>
<th>c-QCLAS</th>
<th>DUAL-QCLAS</th>
<th>WaSuFlux</th>
<th>Nitrolux</th>
<th>CRDS</th>
<th>IMS</th>
</tr>
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<tbody>
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<td>R²</td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>RBD</td>
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<td>0.93</td>
<td>0.82</td>
<td>0.87</td>
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<td>0.95</td>
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<td>0.97</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td>AiRRmonia</td>
<td>−1.77</td>
<td>9.41</td>
<td>−3.26</td>
<td>0.94</td>
<td>0.94</td>
<td>0.79</td>
<td>0.75</td>
<td>0.71</td>
<td>0.58</td>
<td>0.82</td>
</tr>
<tr>
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<td>−18.8</td>
<td>−15.6</td>
<td>−26.8</td>
<td>−0.89</td>
<td>0.94</td>
<td>0.79</td>
<td>0.75</td>
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<td>0.58</td>
<td>0.71</td>
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<tr>
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<td>DUAL-QCLAS</td>
<td>−43.4</td>
<td>−29.8</td>
<td>−38.9</td>
<td>−37.7</td>
<td>−33.0</td>
<td>−</td>
<td>0.98</td>
<td>0.97</td>
<td>0.91</td>
<td>0.66</td>
</tr>
<tr>
<td>WaSuFlux</td>
<td>−8.85</td>
<td>−0.3</td>
<td>−9.50</td>
<td>3.19</td>
<td>1.80</td>
<td>48.3</td>
<td>−</td>
<td>0.95</td>
<td>0.95</td>
<td>0.82</td>
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<tr>
<td>Nitrolux-100</td>
<td>−12.4</td>
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<td>−9.83</td>
<td>8.00</td>
<td>2.62</td>
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<td>−0.99</td>
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<td>0.57</td>
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<tr>
<td>CRDS</td>
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<td>−0.2</td>
<td>−10.6</td>
<td>14.7</td>
<td>13.8</td>
<td>86.4</td>
<td>−0.12</td>
<td>0.37</td>
<td>−</td>
<td>0.20</td>
</tr>
<tr>
<td>IMS</td>
<td>14.3</td>
<td>−10.9</td>
<td>10.9</td>
<td>−60.8</td>
<td>−5.58</td>
<td>−19.9</td>
<td>15.2</td>
<td>−51.1</td>
<td>−60.5</td>
<td>−</td>
</tr>
</tbody>
</table>

for the RBD. The AiRRmonia seemed to have the least time delays in the system: $\tau_{95}$ of 14.4±4.0 min closely matched the internal measurement cycle of 10 min.

The IMS derived with $\tau_{95}$=34.9±6.4 min the highest delay with reported data of 3 s, but the limited amount of data qualified this statement. The CIMS and DUAL-QCLAS have similar time responses as the c-QCLAS and this approach is therefore not suitable to characterise them further. They are therefore not listed in Table 9.

4 Discussion

4.1 Overall measurement agreement

The instruments tested in the present study revealed good correlation with $R^2>0.84$ for one hour averages compared with NH$_3$-ens. It should be pointed out, that the regressions show relative performance of the instruments against NH$_3$-ens (Fig. 4a–j) or against each other (Tables 4, 6, 8). They do not demonstrate a functional relationship of a dependent to an independent variable. Thus, a consideration
of an a priori uncertainty would not be appropriate for this analysis. Nevertheless, a possible approach of performing regression analysis by using a least-squares fitting with uncertainties of the data can be found in Cantrell (2008).

The CIMS, CRDS and Nitrolux-100 revealed elevated intercepts compared with the other instruments pointing at a possible contamination of the inlet filters (CRDS and Nitrolux-100), inlets or both. The detected results during this campaign are in line with the studies listed below. Measurements of RBD, AMANDA, AiRRmonia, WaSul-Flux and c-QCLAS were within ±25% for NH₃ concentrations of 10 to 120 ppbv.

It should be noted that, although an attempt was made to eliminate the effect of spatial heterogeneity, emissions from grazed and fertilised grassland are expected to show some variability. It was neither possible (though desirable) for all instrument to sample from a common point (e.g. the wet chemistry instruments do not use an inlet tube, while the OP-FTIR provides a line average), nor was the use of a common inlet in the spirit of this experiment, in which we wanted to test independent systems with the respective inlets as they would have been operated by the different groups in the field. There is some indication that at times, instruments that were located more closely to
Table 8. Linear regression between each instrument for the entire data range (bottom left) and less than 10 ppbv (shaded top right).

<table>
<thead>
<tr>
<th></th>
<th>RBD</th>
<th>AMANDA</th>
<th>AiRRmonia</th>
<th>CIMS</th>
<th>c-QCLAS</th>
<th>DUAL-QCLAS</th>
<th>WaSul-Flux</th>
<th>Nitrolux-100</th>
<th>CRDS</th>
<th>IMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>AiRRmonia</td>
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<td>WaSul-Flux</td>
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Each other (e.g., WaSul-Flux/AMANDA/RBD/AiRRmonia and CIMS/DUAL-QCLAS/c-QCLAS/Nitrolux-100/CRDS) agreed more closely with each other, but this observation was not consistent.

Previous comparison campaigns have already illustrated the challenges involved in measuring ambient NH$_3$ concentrations accurately, especially at low concentrations. The results in the study of Wiebe et al. (1990) showed an agreement within ±30% for NH$_3$ concentration > 1.5 ppbv with time resolution of minimum four hours for the filter packs and the annular denuders. The five instruments compared by William et al. (1992) yielded an agreement of within a factor of two for NH$_3$ concentration > 0.5 ppbv. In detail the CAD/IC and PF/LIF agreed within 15% for NH$_3$ concentration of 0.2 to 5.0 ppbv for a time resolution of 2 to 8 h. The framework of the NAQMN study by Mennen et al. (1996) determined a general applicability for all requirements for air quality monitoring on one hour sampling. Further, the DOAS and the NO$_x$ converter instruments reached $R^2 > 0.9$ compared with the wet-annular rotating denuder, but both were only useful during high NH$_3$ concentration near stacks or stables. In the study by Mennen et al. (1996)
the photoacoustic monitor was eliminated due to high maintenance demands and because of leaving only 1% useful data. During the campaign of Milford et al. (2000) AMANDA and DS-FIA showed an overall difference of 35% for a sampling time of 30 min, but with substantial scatter. Fehsenfeld et al. (2002) reported for CIMS and MoO$_x$ converter method $R^2 > 0.9$ compared with the citric acid denuder (sampling time minimum two hours). The average concentration difference compared with the denuder was 0.8 for the CIMS and 1.75 for the MoO$_x$ converter method. Two CIMS instruments tested during the field study in Nowak et al. (2006) measured $R^2 = 0.71$ and concentration difference of 17% (time resolution one minute) with NH$_3$ concentrations from 0.4 to 0.13 ppbv. Milford et al. (2009) compared measurements with three AMANDA systems and a mini-WEDD system. The NH$_3$ measurements showed good agreement between the instruments (<20% difference) for some periods, but with poorer agreement on some individual days, due to variable performance of the automatic wet chemistry detection systems.

Of particular interest here are the results of the recent laboratory inter-comparison study of Schwab et al. (2007), because it followed a complementary approach (being laboratory based), while including some of the same instrument models tested here. The seven instruments tested during the laboratory comparison agreed within 25% of the expected calibration value. The IMS and Nitrolux-100 yielded biases of ±25% with slower response time than the TDLAS (similar to the QCLAS used here). Further, the wet chemical instruments LOPAP and WEDD worked well in the calibration tests in view of absolute accuracy of measured concentrations, but a disadvantage was the slower time response of the WEDD.

In the recent field inter-comparison of Norman et al. (2009) the slopes of hourly uncorrected data of PTR-MS (an alternative CIMS technique using a different ionisation scheme), GRAEGOR (based on the same collection and analytical technique as the AMANDA, but with lower flow rates) and AiRRmonia ranged between 0.78 to 0.97 for NH$_3$ concentrations from 2 to 25 ppbv. During atmospheric conditions favouring condensation in inlet lines, the PTR-MS underestimated NH$_3$ concentrations. The authors point out the need to put more emphasis on the inlet designs for future campaigns. Whitehead et al. (2008) reported that their concentration measurements from the QCLAS and the AMANDA instrument correlated well, with $R^2 = 0.84$. However, the QCLAS underestimated fluxes by 64% compared with the AMANDA instrument.

### 4.2 Instrument specific issues

While providing a good response to the concentrations, the Nitrolux-100 and CRDS measurements in the present study were subject to a similar high intercept compared with the other instruments. There were two aspects common to these instruments: they shared the same sampling line, which may have been contaminated, but they also both use inlet filters, exchanged infrequently (up to 3 months, according to manufacturers), which may collect NH$_4$NO$_3$ which then could dissociate at low concentrations, providing a (temperature dependent) offset. This process clearly affected the Nitrolux-100 data at the start of the experiment, taken with an old filter, which were discarded from the analysis. This inlet / filter issue may also have affected the regressions of these instruments, especially over the low concentration range, as the intercept may not be stable in time. Apart from this issue, both instruments are convenient to operate as they are both manufacturer calibrated with long service intervals.

The only other instrument using an inlet filter is the WaSul-Flux, which operates on a similar principle as the Nitrolux-100. However, its filter was changed weekly, mimicking the effect of NH$_4$NO$_3$ volatilisation. An attempt was made to investigate the potential of NH$_4$NO$_3$ interference on those instruments that do not remove the aerosol phase. In the c-QCLAS inlet a virtual impactor removes the coarse aerosol fraction. The CIMS does not use a filter and the residence within the heated inlet is 0.1 s and thus, the interference from NH$_4$NO$_3$ volatilisation is expected to be negligible, as noted by Fehsenfeld et al. (2002). Indeed, laboratory tests have shown that NH$_4$NO$_3$ volatilisation only becomes an issue for $T > 325$ K. Filters were not used on the IMS and the DUAL-QCLAS systems either, but the residence time in the analysis cell of the DUAL-QCLAS is of the order of 0.2 s and laboratory tests have found NH$_4$NO$_3$ interference to be negligible. In the wet chemistry systems aerosols are thought to pass the inlet uncollected. Unfortunately, the regional NH$_4^+$ concentration was fairly constant during the campaign (Fig. 2), except for a period which coincided with the fertiliser emission peak of NH$_3$, during which NH$_4^+$ still made a minor contribution to total NH$_3$. As a consequence, the effect of inlet heating (to 50℃) on NH$_4$NO$_3$ volatilisation in the WaSul-Flux inlet could not be investigated.

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**Table 9. Analysis of the response time of AMANDA, RBD, WaSul-Flux, AiRRmonia, Nitrolux-100, CRDS and IMS in comparison to c-QCLAS with corresponding statistical parameters.**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>$\tau_{1/e}$ (min)</th>
<th>$\tau_{50}$ (min)</th>
<th>$\tau_{95}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMANDA</td>
<td>10.7±1.3</td>
<td>7.4±0.9</td>
<td>32.2±3.7</td>
</tr>
<tr>
<td>RBD</td>
<td>28.7±4.2</td>
<td>19.9±2.9</td>
<td>85.9±12.5</td>
</tr>
<tr>
<td>WaSul-Flux</td>
<td>19.1±5.4</td>
<td>13.3±3.7</td>
<td>57.3±16.1</td>
</tr>
<tr>
<td>AiRRmonia</td>
<td>4.8±1.4</td>
<td>3.4±0.9</td>
<td>14.4±4.0</td>
</tr>
<tr>
<td>Nitrolux-100</td>
<td>3.6±0.8</td>
<td>2.5±0.6</td>
<td>10.9±2.5</td>
</tr>
<tr>
<td>CRDS</td>
<td>4.5±1.7</td>
<td>3.1±1.2</td>
<td>13.4±5.0</td>
</tr>
<tr>
<td>IMS</td>
<td>11.6±2.1</td>
<td>8.1±1.5</td>
<td>34.9±6.4</td>
</tr>
</tbody>
</table>

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www.atmos-meas-tech.net/3/91/2010/
The WaSuL-Flux performed well against the other instruments, but has a relatively slow time response (45 min) at the background concentrations. It can achieve a detection limit of 0.25 ppbv at 45 min time resolution (Table 1), which may still not be sufficient for all applications. Work is underway to improve the sensitivity further.

By contrast, the IMS is highly sensitive, but less specific and affected by competing ion chemistries, which makes it applicable only to situations of low NH$_3$ and where no interfering compounds are to be expected. Its comparatively poor performance over the entire concentration range is misleading as concentrations >20 ppbv had to be removed due to saturation. It shows one of the best correlations with the average at the sub-10 ppbv comparison ($R^2=0.87$, Table 2).

Three instruments deployed here (DUAL-QCLAS, c-QCLAS and CIMS) have the potential to provide a fast NH$_3$ spot measurement, of particular interest for aircraft applications and eddy-covariance flux measurements. Although their time response was not characterised here, they clearly provide faster response than the other instruments and previous characterisations has shown response times to be better than 1 s, depending on inlet design (e.g. Whitehead et al., 2008).

The QCLAS technique (like OP-FTIR) in principle provides an absolute measurement of the concentration. However, without calibration, the instruments turned out to significantly underestimate the concentration. The c-QCLAS was calibrated at regular intervals in the field with a permeation tube calibration source, while a regular zero calibration but a one-off span calibration were applied to the DUAL-QCLAS, with average span calibration factors in the region of 1.3 and 1.2, for the two instruments respectively. This difference in the calibration approach is likely to be responsible for the poorer performance of the DUAL-QCLAS during this campaign. In addition, the DUAL-QCLAS was set up for eddy-covariance flux measurements, with a relatively long inlet, which may have added further uncertainty. The DUAL-QCLAS sampled air through a 2 m length of 6.4 mm PFA tubing. Owing to the “sticky” nature of NH$_3$, this can have an impact on NH$_3$ measurements (Shaw et al., 1998; Whitehead et al., 2008). This may therefore partly explain the under-estimate in the NH$_3$ concentration at the peak concentrations. Against this possible approach, it should be noted that the DUAL-QCLAS showed one of the highest $R^2$ values (0.98 for the full dataset), with a small intercept compared with other instruments (Fig. 4d and Table 6), indicating a significant but rather constant slope of ~1.2. By contrast, the c-QCLAS was one the better performing instruments tested here.

The CIMS provides a fast, highly sensitive technique and this was the first field deployment of this particular instrument, which showed more scatter than most instruments. Although, it should be noted that it is uncertain how much of this scatter is natural variability and how much is represented by instrumental noise. The instrument was calibrated hourly and the sensitivity of the instrument was (2.5±0.5) Hz ppt$^{-1}$ 1σ and the 1σ background noise corresponded to 45 pptv. In a subsequent deployment of this instrument (C. J. Percival, personal communication, 2009), which employed a similar inlet design and throughput, large variability in NH$_3$ signal was observed on a second by second basis, such variability was not present in the background and calibration cycles, indicating that the inlet is able to respond to rapid changes in the NH$_3$ concentration associated with different plumes and is therefore capturing real, rather than artificial variability. It appears that, as with the c-QCLAS approach, stability in the instrument response coupled with the need for a reliable zero and span gas-phase calibration source is the limiting factor in improving performance. This is consistent with the observations of Nowak et al. (2007), who reported the need for very frequent background determinations for an airborne CIMS instrument, especially when targeting background concentrations.

The OP-FTIR instrument averages over a path-length of 100 m which possibly limits comparability with the other point measurement techniques. Furthermore, measurements were made over a more limited concentration range. Yet, the comparison with the other fast-response techniques is encouraging (Fig. 5). Like the c-QCLAS, the OP-FTIR should also provide an absolute measurement but reports some of the lowest concentrations. At very low concentrations, instrument noise may exceed the signal from NH$_3$, which may explain the high intercept (>3.74 ppbv) in comparison with other detection methods. Interestingly, both c-QCLAS and OP-FTIR underestimate the concentration when used in absolute (uncalibrated) mode and both rely on the accuracy of the same absorption line information of the HITRAN database.

All three wet chemistry systems used here are based on flow injection analysis using a selective ion membrane, which is known to have some cross sensitivity for some amines (Husted et al., 2000). Although probably unimportant here, they may make a more significant contribution in other situations, e.g. of organic animal manure emissions. Using batch sampling and off-line analysis, the RBD is the most “manual” technique included here. It is surprising that the RBD performed better (compared with the average) at small concentrations than over the entire concentration range (Table 2). This is possibly due to sample carry-over in situations of highly variable concentrations. AMANDA and AirRmonia compared well with each other and, together with WaSuL-Flux and IMS (and closely followed by c-QCLAS), achieved the best agreement with each other over the low concentration range. AMANDA and IMS read somewhat higher than the other instruments. The excellent agreement on the common liquid standard within ±3% (Table 2) indicates that the wet chemistry instruments are stable and easy to calibrate, as long as the collection efficiency can be assumed to be 100% and the flow rates are well established. The wet chemistry instruments have the implicit advantage
that they do not rely on an accurate gas-phase standard or any absorption cross sections. Further, they provide a more robust approach to separating gas and aerosol phase. However, they could potentially suffer artefacts from interfering gas-phase compounds in certain situations.

The WaSul-Flux instrument was compared against an AMANDA in previous measurement campaigns (Pogány et al., 2009), where a correlation coefficient of 0.98 was found between the photoacoustic signal and the concentration readings of AMANDA for concentrations 0 to 120 ppbv, which agrees with the correlation coefficients for NH$_3$-env in this campaign (0.98, Fig. 4f), and the correlation coefficients between WaSul-Flux and the wet-chemistry instruments (0.98 for AMANDA and AiRRmonia and 0.95 for the RBD; Table 5). However, the limit of detection of the WaSul-Flux instrument (0.25 ppbv) is currently higher than that stated for the AMANDA (0.02 ppbv) or AiRRmonia (0.04 ppbv).

### 4.3 Time responses

The additional capture of NH$_3$ variations of instruments with higher time resolution, shown in Sect. 3.1, is consistent with the observations of Norman et al. (2009). The calculated time response for the instruments in Sect. 3.3 showed higher values than stated by the manufacturers (Table 1). This is particularly true for the AMANDA system for which the actual response time was estimated to be 37 min. A similar observation was made for the GRAEGOR analyser, based on the same horizontal annular denuder design, but using a lower liquid flow rate (Thomas et al., 2009). Faster response could be achieved by further minimising the liquid pool in the denuders, or by increasing the liquid flow rate (thereby sacrificing sensitivity). For the AiRRmonia, the calculated time response of 14.4±4.0 min time to obtain 95% of the signal is only slightly slower than the 10 min measurement cycle (Table 1). The same is true for CRDS and Nitrolux-100 with 13.4±5.0 min and 10.9±2.5 min to obtain 95% of the signal, respectively, as compared with instrument recording every 6 s (Table 1). During the study of Schwab et al. (2007), a TDLAS reached a value near 35 ppbv within 6 min, whereas IMS and Nitrolux-100 had the slowest time response of all the instruments investigated in their experiment. The same observations were made during this inter-comparison, where the IMS presented the slowest time response, probably due to the use of internal materials which are not optimised for NH$_3$ measurements.

### 5 Conclusions

This paper reports an inter-comparison of eleven instruments for measuring atmospheric NH$_3$ at ambient concentrations, representing the largest NH$_3$ inter-comparison under typical field conditions to date. The approaches deployed included automated wet chemistry techniques, optical, photo-acoustic and mass spectrometric techniques. There were differences in the concentrations reported, but overall the high correlation with $R^2>0.84$ compared with the average of all instruments used, is very encouraging. The correlation worsens if only concentrations <10 ppbv are considered. Concentrations of RBD, AMANDA, AiRRmonia, WaSul-Flux and c-QCLAS agreed within ±25% for concentrations >10 ppbv. Some reasons for variability were identified: inlet length greatly affects measurement precision and time-response. Where used, inlet filters need to be changed very frequently (e.g. daily to weekly), at much shorter intervals than stated by some manufacturers. Instruments based on chemical ionisation mass spectroscopy and quantum cascade laser absorption spectroscopy need to be calibrated or at least zeroed frequently, and the provision of a reliable gas-phase calibration source in the field determines their measurement accuracy. Wet chemistry instruments show good long-term stability, are housed to operate with very short inlets and the liquid part of the system is easier to calibrate. They provide a reliable differentiation between gas-phase NH$_3$ and aerosol NH$_4^+$, which could not be validated for the other instruments during this study. For future inter-comparisons using all inlets at a single sampling point should be attempted, bearing in mind the logistic constraints when working with a large number of sizeable instruments. Not all instruments tested here are suitable for accurate measurements at concentrations <1 ppbv, while the application of ion mobility spectroscopy is limited to low concentrations (<20 ppbv) and conditions with no competing pollutants. Despite, recent advances in technologies, the continuous measurement of NH$_3$ remains a challenging and costly enterprise, in terms of capital investment or running costs or both.

### Acknowledgements

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Edited by: J. Stutz
References


4. Paper III

“Determination of gas-phase ozonolysis rate coefficients of C8–14 terminal alkenes at elevated temperatures using the relative rate method”

by

Max R. McGillen, Mohamed B. Ghalaieny and Carl J. Percival

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Contributions: Max McGillen conceived and designed the experimental setup. Mohamed Ghalaieny conducted the experiments. All authors contributed to the manuscript and the work was conducted under the supervision of Carl Percival.
Determination of gas-phase ozonolysis rate coefficients of C_{8–14} terminal alkenes at elevated temperatures using the relative rate method

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The rates of ozonolysis of a suite of terminal alkenes ranging from C_{8–14} are determined in the gas phase at an elevated temperature of 395.9 ± 1.2 K and a pressure of ~650 Torr using the EXTreme RAnge chamber (EXTRA). Rates are found to be invariant with carbon number, whilst literature measurements conducted under ambient conditions exhibited an increase in rate coefficient after 10 carbon atoms. These earlier findings appear to contradict the intuitive notion that the inductive effect is a short-range process operating over a maximum distance of a few carbon atoms. These new measurements support the hypothesis that operating under ambient conditions, kinetic measurements of condensable species can be influenced adversely by heterogeneous processes and should therefore be treated with caution.

Introduction

Emission of non-methane hydrocarbons (NMHCs) into the atmosphere has far-reaching consequences for air quality, oxidative capacity, and climate change and has been subjected to several recent reviews.4–6 Whereas the atmospheric behaviour of lower-molecular weight NMHCs has been well characterized, the higher molecular weight species are less well understood.7 Notwithstanding their low vapour pressures under ambient conditions, long-chain hydrocarbons have been observed to partition readily into the gas-phase in Earth’s atmosphere.8 Since the dominant pathway for their removal is through oxidation, in order to understand the atmospheric fate of these species it is important to know the rate with which they react with atmospheric oxidants such as hydroxyl radicals, nitrate radicals and ozone.

Under standard laboratory conditions, low vapour pressure compounds can be difficult to handle in the gas phase, since, inevitably volume : surface area ratios of reactors and trace gas introduction systems are high in comparison to the atmosphere, as are the concentrations involved. These conditions may lead to wall loss9–11 and subsequent uncertainties in gas-phase concentrations—and also the participation of the condensed phase in reactive systems.12 There are various methods that are employed for tackling these problems, the most common of which is to conduct experiments in very large reactors, thus maximizing the volume : surface area ratio. However, it appears that for low vapour pressure compounds such as terminal alkenes above C_{10}, even large reactors may generate rate coefficients which are apparently influenced by heterogeneous chemistry. Conversely, this study broaches the problem by conducting experiments at a temperature of 395.9 ± 1.2 K and heating all gas lines and inlets, and in doing so, aims to minimize partitioning to the condensed phase.

Experimental

Experiments were conducted in the dark in the 123 L Teflon-coated EXTRA chamber, described in detail elsewhere.13 The typical starting pressure of a given experiment was 650 Torr of oxygen free nitrogen (BOC), approaching 760 Torr of a nitrogen/oxygen mixture with subsequent O_{3} additions. The temperature was maintained at 395.9 ± 1.2 K throughout.

Prior to the injection of reactants, the chamber was held at ~0 Torr and ~396 K for at least 2 h, allowing the chamber to be baked out adequately. The reference compound (1-decene) and the alkene of interest were injected simultaneously into an evacuated chamber in a solution of cyclohexane, which acted as a thinning agent aiding injection by a microsyringe, a diluent and an OH scavenger. The cyclohexane solution was injected into the chamber through a septum into a round bottom flask, which was maintained at 338.4 ± 1.7 K. The contents were allowed 10–15 min to evaporate into the chamber before heated nitrogen was passed...
through the flask filling the chamber to \( \sim 650 \) Torr and carrying off any residual reactants in the flask and lines.

Chamber contents were sampled into a 100 \( \mu \)L stainless steel loop \( via \) a 30 cm, 1/8" PFA Teflon \(^{\circ}\) line, at a sample rate of 13 scm. The loop and sample line were kept at \( \sim 360.5 \pm 2.3 \) K and 338.7 \( \pm \) 1.7 K, respectively, and were allowed a 5 min conditioning period prior to injection onto the column in order to reduce spurious contributions of monitored alkene reactants from previous samples.

Relative concentrations of the reference and the alkene of interest were measured by gas chromatography with flame ionization detection (GC-FID). 1-Octene, 1-nonene and 1-undecene were injected onto a 30 m DB-1 column (0.320 mm i.d. and 1 \( \mu \)m film thickness), the GC oven was varied between compounds from 75–150 °C and column flow was in the range of 1.2–2.0 scm. The less volatile compounds 1-dodecene, 1-tridecene and 1-tetradecene were injected onto a 30 m HP-1 column (0.320 mm i.d. and 0.25 \( \mu \)m film thickness) with temperatures varying between 70–170 °C and column flow held at 1.8 scm.

The initial measurement in each experiment was performed with no O\(_3\) present. Subsequent measurements were made following the injection of between 500 and 4000 cm\(^3\) O\(_3\)/O\(_2\), where O\(_3\) was present at ppm level mixing ratios into the chamber produced using a discharge-based ozone generator (BMT 802N, BMT Messtechnik GmbH). After each O\(_3\) injection, O\(_2\) was injected at 2 slm in order to flush remaining O\(_3\) out of the lines and promote mixing in the chamber.

Rate constants were measured using the relative rate technique \( e.g. \) ref. 14 where the decay of an alkene was determined relative to the decay of a reference compound with a known rate constant, affording the calculation of the absolute rate constant of the alkene using the following expression:

\[
\ln \left( \frac{[alkene]_t}{[alkene]_0} \right) = \frac{k_1}{k_2} \ln \left( \frac{[reference]_t}{[reference]_0} \right)
\]

where \([alkene]_t\) and \([reference]_t\) represent the starting concentrations of the alkene of interest and the reference compound (1-decene), respectively, and \([alkene]_0\) and \([reference]_0\) represent their concentrations after some reaction time has elapsed. Since these measurements were conducted in a rigid, leak-tight vessel with no volume change during ozone addition and since sampling volumes were negligibly small, the effects of dilution can be discounted in this case and are therefore not considered in the expression above.

The rate constant for the reference compound, 1-decene, was determined absolutely at 395.9 \( \pm \) 0.5 K. The rate constant was measured in the EXTRA chamber under pseudo-first-order conditions by monitoring the decay of ozone with a Monitor Labs UV Ozone analyser, in this determination the concentration of 1-decene was held in excess of ozone at all times. The concentration of 1-decene used varied between 0.9 and 4.0 ppm. The pseudo-first-order technique is explained in more detail by Leather \textit{et al.} (2010).\(^{13}\)

All terminal alkenes studied were commercially available and were used without further purification, notably 1-octene (98%, Aldrich), 1-nonene (98%, Aldrich), 1-decene (99.5%, Fluka), 1-undecene (95%, Fluka), 1-dodecene (95%, Aldrich), 1-tridecene (99%, Alfa Aesar), 1-tetradecene (99.8%, Fluka) and cyclohexane (99%, Fischer Scientific).

**Results and discussion**

The rate coefficient for the reference compound, 1-decene, was determined using the absolute method, and a value of \( 7.35 \pm 0.33 \times 10^{-17} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) was obtained at 395.9 K. The 2nd-order plot containing each of the 1st-order determinations is shown in Fig. 1.

In all cases, relative rates were measured against the decay of 1-decene. The results are displayed in Fig. 2 and summarized in Table 1.

![Fig. 1](image1.png) 2nd-order plot of 1-decene measured at 395.9 \( \pm \) 1.2 K. 1\( \sigma \) error bars obtained from the linear regression of the first-order plots.

![Fig. 2](image2.png) Relative rate plots of this work. For clarity, offsets on the y-axis have been applied to all but the 1-octene trace.
It is apparent from Table 1 that within the experimental error, all relative rates measured in this study are almost identical. This contrasts with values reported at room temperature, which are shown in Fig. 2 and Table 2. It can be observed from Fig. 3, discounting the anomalously large rate coefficient obtained for 1-heptene by Atkinson et al. (1982),\(^{15}\) that up until C\(_{10}\), ozonolysis rate coefficients are invariant with carbon number. From C\(_{12}\) onwards large departures from this trend are observed. In order to compare the results of this study with literature measurements made at room temperature, an activation energy has been derived from the difference in rate coefficient between the average literature determination of 1-decene and the absolute rate coefficient of this study, leading to a value of 19.83 kJ mol\(^{-1}\), this has been applied to all alkenes studied in this work. This appears to be a valid assumption as the experimentally determined activation energies for the terminal alkene homologous series reported in the literature are invariant within the experimental error.\(^{16}\) It is acknowledged that this is not best practice, since the Arrhenius literature measurements and SAR estimates of ozonolysis rate coefficients at 298 K plotted against carbon number.

(SARs) predict no change in rate coefficient across the terminal alkene homologous series from C\(_{5}\) onwards (see Fig. 2).\(^{17,18}\) The SAR of McGillen et al. (2008)\(^{17}\) rationalized this effect based partly upon PM3 and B3LYP calculations, which found that the total Mulliken charge, and therefore reactivity of the olefinic carbon atoms, changes negligibly after a substituent chain length of 1; and partly from the insensitivity of the SAR to the inclusion of steric calculations past a chain length of 3. This treatment of the steric effect accords with the generally telescopic behaviour of the steric effect as observed previously.\(^{16}\) EPI Suite predicts rate coefficients based upon the SAR of Atkinson and Carter (1984);\(^{20}\) it will therefore predict the same rate coefficient for each member of the terminal alkene homologous series since it is degenerate with respect to the identity of the R group.

It is interesting to note that ambient chamber experiments on the partitioning of terminal alkenes to the condensed phase appear to show a sharp inflection after 12 carbon atoms

<table>
<thead>
<tr>
<th>Compound</th>
<th>This work(^a)</th>
<th>Literature in units of 10(^{-17}) cm(^3) molecule(^{-1}) s(^{-1})</th>
<th>SAR(^b)</th>
<th>SAR(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>0.968(^d)</td>
<td>0.968(^d)</td>
<td>1.41</td>
<td>1.2</td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.928(^d)</td>
<td>0.928(^d)</td>
<td>0.96</td>
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<tr>
<td>1-Pentene</td>
<td>1.07 ± 0.04,(^e) 0.92 ± 0.05,(^e) 0.96 ± 0.16,(^e) 0.87 ± 0.02(^e)</td>
<td>0.75</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1-Hexene</td>
<td>1.11 ± 0.03,(^e) 1.08,(^e) 1.21 ± 0.28,(^e) 1.02 ± 0.06,(^e) 0.97 ± 0.14,(^e) 0.96 ± 0.02,(^e) 0.898 ± 0.054,(^e)</td>
<td>0.75</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1-Heptene</td>
<td>1.73 ± 0.19,(^e) 0.94 ± 0.04,(^e) 0.92 ± 0.03,(^e) 1.10,(^f) 1.05 ± 0.07(^f)</td>
<td>0.75</td>
<td>1.2</td>
<td></td>
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<tr>
<td>1-Octene</td>
<td>1.01 ± 0.01</td>
<td>1.25 ± 0.04,(^g) 1.01 ± 0.04(^g)</td>
<td>0.75</td>
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<tr>
<td>1-Nonene</td>
<td>0.99 ± 0.02</td>
<td>0.75</td>
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<tr>
<td>1-Decene</td>
<td>0.80 ± 0.14,(^g) 1.11 ± 0.05(^g)</td>
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<td>1-Undecene</td>
<td>1.03 ± 0.02</td>
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<td>1-Dodecene</td>
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<td>0.75</td>
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<td>1-Tridecene</td>
<td>0.96 ± 0.05</td>
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<tr>
<td>1-Tetradecene</td>
<td>0.97 ± 0.05</td>
<td>0.75</td>
<td>0.75</td>
<td>1.2</td>
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</tbody>
</table>

\(^a\) Based on room temperature normalized data and the 1\(\sigma\) errors are obtained from the linear regression of the relative rate plots at 395.9 K.\(^9\) SAR prediction from McGillen et al. (2008).\(^17\) SAR prediction from EPI Suite (2009).\(^18\) \(^d\) Recommended value at 296 K (Calvert et al., 2000).\(^4\) \(^f\) Japar et al. (1974)\(^24\) / Tracy et al. (1992).\(^25\) \(^g\) Grosjean and Grosjean (1995)\(^26\) / Avzianova and Ariya (2002).\(^16\) / Adeniji et al. (1981).\(^27\) / Atkinson et al. (1982).\(^15\) / Mason et al. (2009).\(^12\) / Cadle and Schadt (1952).\(^28\)
and the fraction of a given alkene remaining in the gas phase decreases rapidly thereafter.\textsuperscript{11} It is also apparent that the response time and wall losses of compounds that readily absorb to Teflon\textsuperscript{6} surfaces (e.g. nitric acid) are improved greatly at higher temperatures.\textsuperscript{21} Similarly in this study it was found during the development of the experimental protocol that unless all components of the reactor and sampling system were heated, unacceptable memory effects were observed when sampling the larger terminal alkenes. Therefore, even though this study does not speculate upon the mechanism by which gas-phase species may adhere to Teflon\textsuperscript{6} surfaces, be it a simple phase change or a more complex mechanism such as through interaction with Eyring “holes” (e.g. ref. 22), it can be observed that increasing the temperature of the reactor and inlet diminishes the ability of the walls to act as reservoirs for less volatile species.

Experiments involving the oxidation of heavier (C\textsubscript{$\geq$}10) terminal alkenes have produced unusual results previously, in the example of McGillen \textit{et al.} (2007),\textsuperscript{23} a sharp increase in observed 2nd-order loss rates at and above a carbon number of 10 could be attributed to heterogeneous chemistry. However given that these experiments were conducted in turbulent conditions, reaction with the walls in this case is unlikely. There is still the possibility that a loss process associated with particle formation may have been responsible for the observed loss rates. The experiments undertaken in this present study were undertaken at elevated temperatures, to ensure that partitioning to the aerosol phase does not occur. The profiles of total rate coefficient against carbon number look appreciably different depending on whether OH, NO\textsubscript{3} or O\textsubscript{3} is the oxidant. It must be acknowledged that there are major differences in the mechanism by which each of these reactions proceed. For example, the study of McGillen \textit{et al.}\textsuperscript{23} on the reactions of the hydroxyl radical with terminal alkenes attributed the increase in reactivity of the larger alkenes to an increasingly important hydrogen abstraction channel. Clearly for ozonolysis reactions there is only one possible reaction channel and thus the change in reactivity throughout the terminal alkene homologous series could only result from a change in inductive or steric effects or else a long-range interaction engendered by a change in carbon chain length. It therefore remains that if the inflexion in rate coefficient observed for the reaction of, for example, O\textsubscript{3} with terminal alkenes under ambient conditions is an experimental artifact, then the difference in behaviour observed between each of these oxidants may result from secondary processes associated with the very different product distributions of these reactions.

\section*{Conclusions}

Ozonolysis rate coefficients were determined for the terminal alkene homologous series from C\textsubscript{8-14}. The measurements conducted at 395.9 ± 1.2 K were found to be invariant and therefore confirm that the rate with which these species react with ozone does not change significantly as a function of sidechain length. When normalized to the room temperature data, these results are in good agreement with literature determinations for 1-undecene, but in disagreement with the work of Mason \textit{et al.} (2009)\textsuperscript{12} for C\textsubscript{12-14} compounds, where the enhancement in rate coefficient observed in that study is likely to relate to heterogeneous chemistry as was suggested previously. It is therefore apparent that alkenes possessing vapour pressures less than or equal to that of 1-dodecene are likely to be problematic for the conventional chamber apparatus operated under ambient conditions. Relative ozonolysis rates are provided for 1-nonene and 1-undecene for the first time, as is the absolute rate coefficient of 1-decene at 395.9 ± 1.2 K. In each case good quality relative rate plots were generated from the EXTRA chamber, and it is intended that this experimental methodology will be applied to probing the reactivity of atmospherically important low vapour pressure compounds of biogenic origin such as the sesquiterpenes and heteroatomic unsaturated volatile organic compounds.

\begin{thebibliography}{1}
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\end{thebibliography}
23 M. R. McGillen, C. J. Percival, D. E. Shallcross and J. N. Harvey, 
5. Paper IV

“Determination of gas-phase ozonolysis rate coefficients of a number of sesquiterpenes at elevated temperatures using the relative rate method”

by


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Contributions: The experiments were conceived and conducted by Mohamed Ghalaieny. Asan Bacak assisted with the experimental setup. Max Mcgillen assisted in data analysis and interpretation. All the authors above contributed to the manuscript. Damien Martin, Simon O’Doherty and Alan Knights assisted with setup of instrumentation. Dudley Shalcross provided modelling for atmospheric implications of the work. The work was conducted under the supervision of Carl Percival.
Determination of gas-phase ozonolysis rate coefficients of a number of sesquiterpenes at elevated temperatures using the relative rate method

Mohamed Ghalaieny, a Asan Bacak, a Max McGillen, i Damien Martin, b Alan V. Knights, b Simon O’Doherty, b Dudley E. Shallcross b and Carl J. Percival a

Introduction

The effects of non-methane hydrocarbons (NMHCs) emissions into the atmosphere encompass issues of air quality,1,2 oxidative capacity of the atmosphere,3,4 and climate change.5,7 Long-chain hydrocarbons, such as biogenic volatile organic compounds (BVOCs), have been observed to partition readily into the gas-phase in the earth’s atmosphere.8 Despite the importance of BVOCs, the atmospheric behaviour of the higher molecular weight species is less well understood.9 Since the dominant pathway for their removal is through oxidation, in order to understand the atmospheric fate of these species it is important to know the rate with which they react with atmospheric oxidants such as the hydroxyl radical, the nitrate radical and ozone.

Sesquiterpenes (SQTs) are a class of high molecular weight, semi-volatile organic compounds (SVOCs) containing 3 isoprene units (C5H8). SQTs (C15H24) can vary in their molecular structure being acyclic, mono, bi or tri-cyclic. The sources of SQTs in the atmosphere are solely biogenic and research on SQTs as a defence mechanism.10 Furthermore, a recent study by Ormeno et al. (2006)11 suggests that plants also produce SQTs under environmental stresses such as drought or excessive heat. As a proportion of emissions from vegetation, SQTs are also a potential source of secondary organic aerosol (SOA). Studies by Griffin et al. (1999)15 and Bonn and Moortgat (2003)16 proposed that SQTs are the dominant source of SOA compared with monoterpenes because of their much larger (~100 times) reaction rate with O3. The overall estimate of SOA yield from all BVOCs is poorly constrained; recent modelling suggests a SOA yield between 12–70 Tg per year.17 According to Carlton et al. (2010)18 this large variability in SOA yields is related to the dearth of information on SQTs and other SOA precursors in models. However, recent developments in atmospheric chemical mechanism methodologies resolve some of the current issues.19–23

SQTs have low vapour pressures and their gas-phase reaction kinetics are not well characterised. Under standard laboratory conditions, low vapour pressure compounds can be difficult to handle in the gas phase. Here, surface : volume ratios of both reactors and trace gas introduction systems are high in comparison with the atmosphere, this may lead to significant wall losses.24 Furthermore, the condensed phase may participate in reaction systems.25 Recent laboratory studies of terminal alkenes with a high molecular weight at 395 K provided reaction rate constants that are in better agreement with model results than results obtained at 298 K. Recent work by McGillen et al. (2011)26 strongly suggests that low vapour pressure compounds should be studied at elevated temperatures, to avoid the formation of aerosol and to minimise wall losses. This work reports the first measurements of SQT ozonolysis at elevated temperatures. The reaction rate constants of four SQTs with ozone were measured using the relative rate method...
at 366 K. Experiments were conducted in the EXTRA chamber\textsuperscript{27} and reaction kinetics data were obtained using GC-FID.

**Experimental**

All experiments were conducted in the dark to eliminate photochemistry in the 123 litre, Teflon\textsuperscript{R}-coated EXTRA chamber. A detailed description of the chamber and its operation can be found in the earlier work of Leather \textit{et al.} (2010).\textsuperscript{27} The starting pressure for all experiments was \(~730 \pm 2\) Torr. On addition of \(O_3\) the final pressure stabilised at \(~780\) Torr. The temperature was held at 366 \(\pm 3\) K for the duration of each experiment.

The chamber was held at less than 1 Torr and 366 \(\pm 3\) K for a minimum of one hour prior to introduction of reactants in order to sufficiently eliminate remnants of the previous experimental cycle. The reference compound and the SQT of interest in an excess solution of cyclohexane were injected by micro syringe into the evacuated chamber. The cyclohexane had a multiple role: as a scavenger, a diluent and a thinning agent to ease injection. The reactant solution was introduced into a preheated round bottomed flask \textit{via} a septum. The flask temperature was maintained at \(~360 \pm 3\) K at all times with heavy duty heating tape (Omega Ltd.). Following injection, the flask contents were left for 10 minutes to ensure complete evaporation into the chamber, heated nitrogen was then flowed through the flask to fill the chamber to \(~730\) Torr and ensure that no reactants remained in the flask.

The composition of the chamber atmosphere was sampled at a rate of 13 sccm into a stainless steel loop (volumes of 100, 25 and 5 \(\mu\)l \textit{via} a heated 30 cm, 1/8\textsuperscript{\textit{\textdegree}} PFA Teflon\textsuperscript{R} line. The loop and sample line temperature were held at 360 \(\pm 3\) K. The sampling process was started 5 minutes prior to injection onto the GC column, in order to minimise memory effects from the previous injection. Following column injection, the loop and sample line were purged with a flow of heated nitrogen at 360 K for 5–10 minutes.

The concentrations of the sesquiterpene and the reference compound were measured using GC-FID by injection onto a 30 metre DB-1 capillary column with a diameter of 320 \(\mu\)m and 0.25 mm film thickness. The column was temperature programmed from 70–140 \(\textdegree\)C, with variations in the column flow between 0.5–1.6 ml min\textsuperscript{-1}.

An initial sample was taken before the addition of any ozone to establish the starting reactant concentrations. 4000 sccm of \(O_3/O_2\) is then injected prior to every subsequent sample and the relative decay of the reactant concentration is monitored. The \(O_3\) concentration in the chamber is in the ppm range. Ozone was generated using a discharge ozone generator (BMT 802N, BMT Messtechnik GmbH). Following \(O_3/O_2\) addition, \(O_2\) was flowed at 1 slm for 5 seconds to aid in mixing and to flush any remaining \(O_3\) into the chamber. Sesquiterpene concentrations within the EXTRA chamber varied between 8.4–14.2 ppm and the concentration of ozone was always at least an order of magnitude in excess.

Rate constants for the reaction of SQT with ozone were calculated using the relative rate technique where the decay of a sesquiterpene is measured relative to the decay of a reference compound with a well determined rate constant. Once the relative rate is calculated the absolute rate constant for the sesquiterpene can be calculated using the following expression:

\[
\ln \left( \frac{[\text{sesquiterpene}]}{[\text{reference}]_0} \right) = \frac{k_1}{k_2} \ln \left( \frac{[\text{reference}]}{[\text{reference}]_0} \right)
\]

where \([\text{sesquiterpene}]_0\) and \([\text{reference}]_0\) represent the starting concentrations of the sesquiterpene of interest and the reference compound (2,3-dimethyl-2-butene, respectively), and \([\text{sesquiterpene}]\) and \([\text{reference}]\), represent their concentrations after some reaction time has elapsed. Since these measurements were conducted in a rigid, leak-tight vessel with no volume change during ozone addition and since sampling volumes were negligibly small, the effects of dilution can be discounted in this case and are therefore not considered in expression (1).

The ozonolysis rate constant of the reference compound, 2,3-dimethyl-2-butene, was measured relative to 1-decene at 366 \(\pm 3\) K; the relative rate was found to be \(~6.3, k_{366}\) for 1-decene was measured directly in the EXTRA chamber under \textit{pseudo}\textendash first-order conditions by maintaining the concentration of 1-decene in excess of ozone at all times and using a Monitor Labs UV Ozone analyser to follow the decay of ozone. The ozonolysis rate coefficient for 1-decene at 366 K was found to be \(4.6 \times 10^{-18}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and from this the rate coefficient for 2,3-dimethyl-2-butene at 366 K was found to be \(2.89 \times 10^{-17}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. For a more detailed description of the \textit{pseudo}\textendash first-order technique see the recent paper by Leather \textit{et al.} (2010).\textsuperscript{27} The absolute rate coefficient of 1-decene could be influenced by the HO\textsubscript{2} formed by decomposition of the Criegee intermediate in the presence of HO\textsubscript{2} alongside OH radical formation from a 1,4-sigmatropic shift of the Criegee intermediate followed by bond fission.\textsuperscript{29,30} However, operating under excess alkene conditions and assuming 100% OH yield, using rate coefficients of \(4.61 \times 10^{-11}\) and \(4.6 \times 10^{-18}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} for OH reaction with alkenes and ozone, respectively, this would lead to \textless 10% error in the rate coefficient. As the rate coefficient for HO\textsubscript{2} + O\textsubscript{3} is an order of magnitude slower than that of OH + O\textsubscript{3}, the ozone concentration\textendash time profiles will not be affected. Furthermore, the self-reaction of HO\textsubscript{2} will dominate the loss of HO\textsubscript{2} under our experimental conditions as it is three orders of magnitude faster than the corresponding reaction with ozone, under our experimental concentration regime the HO\textsubscript{2} loss rate \textit{via} reaction with O\textsubscript{3} is at least a factor of 100 slower than the corresponding self-reaction. Therefore, secondary chemistry corrections are neglected since they exceed errors in the measurements of temperature, detector signal, pressure, and absolute alkene concentrations. For the relative rate measurements, the formation of OH would alter the concentration time profiles, however, cyclohexane is added in a large excess to act as an OH scavenger to eliminate secondary losses.

**Materials**

The sesquiterpenes studied and other compounds used were commercially available. The sources and purities are as follows: \(\beta\)-caryophyllene (99\%, Aldrich), \(\alpha\)-humulene (99\%, Aldrich), isolonfrofene (99.5\%, Aldrich), \(\alpha\)-cedrene (96\%, Aldrich), 2,3-dimethyl-2-butene (97\%, Aldrich), and cyclohexane (99\%, Aldrich).
**Results and discussion**

**Aerosol formation measurement**

Previous work\(^{26}\) strongly suggests that low vapour pressure compounds should be studied at elevated temperatures, to avoid the formation of aerosol and minimise mass losses. Aerosol formation from \(\alpha\)-humulene (as a case study) in the EXTRA chamber was measured before and after ozonolysis using a Portable Aerosol Spectrometer (GRIMM Standard Monitor #1.108) at 298 K and 366 K. Results showed that at 298 K a considerable amount of aerosol was produced, whereas at 366 K, within experimental error, no aerosol was produced. However, what Fig. 1 clearly demonstrates is that at 366 K the entire observed aerosol is volatilised, thus removing the potential heterogeneous loss of the SQTs to the aerosol surfaces. The rate of heterogeneous loss of SQT to the aerosol surface can be estimated by

\[
 k_{\text{loss}} = \gamma S \omega / 4
\]

where \(k_{\text{loss}}\) is the rate coefficient for heterogeneous loss, \(\gamma\) the reactive uptake coefficient, \(S\) is the specific surface area of aerosol particles (\(\text{cm}^2\ \text{cm}^{-3}\)) in the chamber, and \(\omega\) is the average molecular velocity of SQT. It should be noted that the GRIMM portable aerosol spectrometer has a cut off of 0.3 \(\mu\text{m}\), and thus will not account for aerosol below that size. Thus we are not observing a significant fraction of the small size aerosol being formed by oxidation of SQT, given that the loss is expected to increase for smaller sizes it is likely that the \(k_{\text{loss}}\) will be significant. Assuming an uptake coefficient of 0.1 the data shown in Fig. 1 would result in a loss rate of 7.6 \(\times\) \(10^{-2}\) \(\text{s}^{-1}\). This is a significant contribution to observed loss rate and could thus result in a significant bias of retrieved rate coefficients. This further supports the need to study sesquiterpene ozonolysis at an elevated temperature in order to obtain accurate rate coefficient measurements.

**Wall losses and thermal decomposition**

The concentration time profiles of \(\beta\)-caryophyllene in the absence of co-reactant (i.e. ozone) were monitored at 298 K, 366 K, 378 K and 400 K for several hours to ascertain the loss of reactant material to the chamber walls and to observe any thermal decomposition of the SQTs being studied. These experimental checks were conducted at the same pressure and on a comparable timescale to the standard ozonolysis. Table 4 shows that the loss of the reactant material is greatest at temperatures above 366 K. At the higher temperatures, this appears to be attributed to thermal decomposition of the \(\beta\)-caryophyllene. The calculated, combined wall loss and thermal decomposition rate at 366 K, \(k_{\text{wall}}\) is \((5.4 \pm 4.4) \times 10^{-7}\) \(\text{s}^{-1}\). The combination of aerosol loss and thermal decomposition limits the temperature range over which the ozonolysis of SQTs can be studied. Indeed, the temperature range is too small to enable an accurate determination of Arrhenius parameters.

**Relative rate determinations**

In all cases, relative rates were measured against the decay of 2,3-dimethyl-2-butene. The relative rate plots are displayed in Fig. 2 and the resulting rate coefficients are displayed in Fig. 3 and summarized in Table 1. Table 1 contains the experimentally obtained rate coefficients from this work at 366 K alongside previously reported ozonolysis rate coefficients and saturation vapour pressures. In order to compare the results of this study with literature measurements made at room temperature, the activation energy of 2-methyl-2-butene was used as the closest structural analogue of an SQT with known Arrhenius parameters. The \(E_a\) of 6.51 \(\text{kJ mol}^{-1}\) was calculated by the structure activity relationship (SAR) of Leather et al. (2010)\(^{27}\) and the pre-exponential factor \((A)\) for each SQT was calculated from the Arrhenius equation and the SQT rate coefficients measured in this work. In a recent study by Kim et al. (2011)\(^{31}\) an \(E_a\) of \((5.2 \pm 0.9)\) \(\text{kJ mol}^{-1}\) was measured for the ozonolysis of \(\beta\)-ocimene, which suggests that our estimation of activation energy is valid. This approximation serves merely to normalize the high temperature measurements to the 296 K dataset and render them comparable. Arrhenius parameters measured by Kim et al. (2011)\(^{31}\) support the use of this approximation (Fig. 4).

The limited number of determinations of ozonolysis rate coefficients for SQTs is a reflection of the difficulty of studying these compounds. Important early work was conducted by Shu and Atkinson (1994)\(^{10}\) using the relative rate technique for the SQTs in this study and more recently Pollmann et al. (2005)\(^{32}\) measured the ozonolysis rate constant for the SQTs in this study, in situ using an indirect technique. Fig. 3 is a comparison of the previously measured ozonolysis rate coefficients in the literature for the SQTs covered by our study, with room temperature data extrapolated to 366 K as outlined in a.

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**Fig. 1** A plot of aerosol formation during ozonolysis of \(\alpha\)-humulene at 298 and 366 K.
previous section. Studies that extend the temperature range above room temperature are even more limited, with, to the best of our knowledge, only one study by Kim et al. (2011).31

As the data in Table 1 and Fig. 3 show, the rate coefficients for β-caryophyllene and α-humulene reported in our work were found to be three orders of magnitude smaller than those previously measured by Shu and Atkinson (1994)10 and Pollmann et al. (2005)32 whereas the rate coefficients for α-cedrene and isolongifolene were in agreement with the values of Pollman et al. (2005)32 and Shu and Atkinson (1994).10 The lower rate coefficients reported in this work for α-humulene and β-caryophyllene in contrast to previous work10,32 can be attributed mainly to the difference in experimental conditions and the design of the EXTRA chamber which enables temperature control. The rate coefficients for α-humulene and β-caryophyllene determined by Shu and Atkinson (1994)10 were measured at 296 K whereas this study was carried out at 366 K, a temperature where we significantly reduce losses of reactant material to aerosol. Previous studies on SVOCs24,25,33,34 have acknowledged that when semi-volatile organic compounds are subjected to kinetic studies at ambient temperatures, the deposition of reaction materials on the walls and losses to aerosol particle formation result in inaccurate rate coefficient measurements, a fact shown by McGillen et al. (2011).26

Moreover our 298 K aerosol measurements show evidence of homogenous nucleation of α-humulene before ozonolysis.
and formation of large amounts of SOA after ozonolysis. The SOA formed from the products of ozonolysis would act as good surfaces for the condensation of SQTs and therefore cause a further undesirable loss. At room temperature, substances with a saturation vapour pressure between $1 \times 10^{-4}$ and 1 Pa have a significant chance of partitioning from gas to condensed phase. The likelihood is that gas to aerosol partitioning is particularly enhanced, given the concentrations used in atmospheric simulation chambers.

Furthermore our study of aerosol formation from SQTs in the EXTRA chamber shows a marked reduction in aerosol counts (pre ozonolysis) at 366 K. The evidence from McGillen et al. (2011) and from our further studies on aerosol and wall losses is in support of the newly measured rate coefficients for $\beta$-caryophyllene and $\alpha$-humulene. Furthermore, ozonolysis of SQTs is not expected to display a negative temperature dependence and thus it seems erroneous that the room temperature rate coefficient should be three orders of magnitude larger than those at 366 K. It should also be noted that oxidation of $\beta$-caryophyllene is used as a seed for Secondary Organic Aerosol formation studies. Indeed, Hoffmann et al. (1997) have estimated that aerosol products account for 100% of reacted $\beta$-caryophyllene upon ozonolysis. Also, Dekermenjian et al. (1999) have shown that aerosol formation occurs for all the systems studied, although did not quantify the aerosol yield. More recently, SOA yield studies of Beck et al. (2011) made estimations of the ozonolysis rate coefficients for the first and second generation products of $\alpha$-humulene and found $k_1$ and $k_2$ for $\alpha$-humulene to be $3.6 \times 10^{-16}$ and $3 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** Arrhenius plots for a selection of SQTs and alkenes from experiments and SAR.
The singling out of previous measurements of β-caryophyllene and α-humulene as erroneous while at the same time accepting the measurements of α-cedrene and isolongifolene from the same study of Shu and Atkinson (1994)\textsuperscript{40} might seem counter intuitive. However a juxtaposition of the limited Arrhenius parameters available for the SQTs studied here in comparison with other SQTs (Fig. 4) is further supporting evidence of the erroneous nature of the previous measurements of β-caryophyllene and α-humulene. Using $k_{366}$ from this work and $k_{286}$ from Shu and Atkinson (1994)\textsuperscript{10} an Arrhenius type analysis has been performed for β-caryophyllene and α-humulene. These points on the Arrhenius graph are in disagreement with all the other Arrhenius parameters in Fig. 4 from Kim et al. (2011)\textsuperscript{31} and from a limited temperature dependency for α-cedrene carried out in this study. These outlying points from an Arrhenius analysis cast further doubt on the previous measurements of α-humulene and β-caryophyllene. Indeed, Beck et al. (2011)\textsuperscript{49} also stated that the rate coefficient for α-humulene\textsuperscript{10} was seemingly too high. The rate coefficients for α-humulene and β-caryophyllene reported in this study are in line with the Structure Reactivity Relation (SRR) calculation for these two compounds used by Calvert et al. (2000).\textsuperscript{42} However, it must be noted that this SRR is limited in its accuracy as it neglects other factors impacting on rate coefficients (e.g. steric hindrance). McGillen et al. (2008)\textsuperscript{43} have shown that steric hindrance can have a major impact on the rate of ozonolysis. Whilst the approach was only applied to linear systems, it is clear that steric hindrance could also apply to the SQTs studied in this work. Thus it is likely that the rate coefficients predicted from the approach of Calvert et al. (2000)\textsuperscript{42} would be even slower than they are now (see Table 1). Whilst the saturation vapour pressures for β-caryophyllene and α-humulene are both slightly lower than α-cedrene, it is likely that aerosol formation, as shown in Fig. 1, could result in a bias in the experimentally retrieved rate coefficients.

**Atmospheric implications**

The extremely short lifetime of these compounds, typically minutes to hours (as shown in Table 2) will depend strongly on local oxidant levels. Table 3 summarises the concentration of ozone and NO$_3$ required for the oxidation by the species to be equivalent of that by the hydroxyl radical. The levels of NO$_3$ required (sub ppt in all cases except isolongifolene) to provide a loss rate equal to that produced by an OH level of 1.6 × 10$^6$ molecule cm$^{-3}$ suggest that NO$_3$ will dominate loss in urban areas. Even in daytime, the suggestion is that NO$_3$ levels of around 0.1–1 ppt may exist\textsuperscript{44,45} in polluted environments. In pristine environments (low NO$_x$s), oxidation by OH will dominate during the day. At night, only a modest contribution from O$_3$ oxidation will occur and here too, OH levels of around\textsuperscript{46,47} 1 × 10$^5$ molecule cm$^{-3}$ will compete with oxidation via O$_3$. Based on these kinetic data a global model estimate\textsuperscript{2,23} suggests that the percentage losses for each compound with respect to OH, NO$_3$ and O$_3$ are: 51%, 37%, 12% (α-cedrene); 58%, 33%, 9% (β-caryophyllene); 11%, 77%, 12% (α-humulene); 72%, 13%, 15% (isolongifolene). In addition the total lifetime for each compound is estimated to be ~2 hours (α-cedrene), ~50 min (β-caryophyllene); ~60 min (α-humulene), ~4 hours (isolongifolene). A dramatic reduction in the impact of ozonolysis as a loss process for these species is of course observed, using these new data. In addition, the role of the ozonolysis of SQT species in secondary aerosol formation is reduced significantly.

**Conclusion and future work**

Ozonolysis rate coefficients were determined for four sesquiterpenes β-caryophyllene, α-humulene, isolongifolene and α-cedrene in the gas phase at an elevated temperature of 366 ± 3 K and a pressure of ~780 Torr using the EXTreme RAnge chamber (EXTRA). The experimentally obtained rate coefficients agree with extrapolated room temperature rate coefficients for isolongifolene and α-cedrene but not for β-caryophyllene and α-humulene, which were found to be three orders of magnitude slower than this in the literature. These new measurements support the hypothesis that operating under ambient conditions, kinetic measurements of condensable species can be influenced adversely by heterogeneous processes and should therefore be treated with caution. The reduced rate coefficients would suggest that there is only a modest contribution from ozonolysis on the oxidation of sesquiterpenes within the troposphere.

**Acknowledgements**

We thank NERC under whose auspices this work was conducted.

**References**


6. Paper V

“Acid-yield measurements and product studies of gas-phase ozonolysis of isoprene as a function of humidity using chemical ionisation mass spectrometry (CIMS)”

by

Mohamed Ghalaieny, Asan Bacak, Kimberley Leather, Jennifer Muller, Thomas Bannan, Ping Xiao, Damien Martin, Dudley E. Shallcross and Carl J. Percival.

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Contributions: Mohamed Ghalaieny, Jennifer Muller and Thomas Bannan conducted the experiments. Asan Bacak and Kimberley Leather assisted with the experimental setup and the data analysis. Dudley Shallcross and Ping Xiao performed model integration of the data. Damien Martin provided gas calibration standards for organic acids. The work was conducted under the supervision of Carl Percival.
Acid-yield measurements and product studies of gas-phase ozonolysis of isoprene as a function of humidity using chemical ionisation mass spectrometry (CIMS)

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Abstract

Gas-phase isoprene ozonolysis experiments were conducted at room temperature to determine formic acid yields as a function of relative humidity (RH) using the integrated EXTreme RAnge chamber-Chemical Ionisation Mass Spectrometry technique, employing a CH\textsubscript{3}I ionisation scheme. RHs studied were < 1, 10, 20, 25, 30, 40\% \% and formic acid yields of (0.05 ± 0.004) and (0.18 ± 0.006) were determined at < 1 \% RH and 40 \% RH respectively, showing a strong water dependence. It has been possible to estimate the ratio of the rate coefficient for the reaction of the Criegee intermediate, CH\textsubscript{2}OO with water compared with decomposition. This analysis suggests that the rate of reaction with water ranges between $1 \times 10^{-12} – 1 \times 10^{-15}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and will therefore dominate its loss with respect to bimolecular processes in the atmosphere. Global model integrations suggest that ozonolysis of isoprene represents a source of 9.5 Tg yr\textsuperscript{-1} of HCOOH.
Introduction

Organic acids, specifically formic and acetic acid are known to be some of the most abundant and widespread trace gases in the atmosphere (Paulot et al., 2011). Past field studies show that the concentration of organic acids can, in some cases, exceed that of inorganic acids (Grosejean et al., 1990, D. Taraborrelli et al., 2009). There are many negative environmental effects caused by organic acids two issues of note are the contribution of organic acids to SOA formation (Zhang et al., 2004) and contribution to acid deposition (Finlayson-Pitts and Pitts, 2000). There is still a limited understanding of SOA formation which necessitates the continued study of contributing factors, such as the oxidation reactions of alkenes, e.g. isoprene, by O₃, OH and NO₃. Recent ground based observations by Rinsland et al. (2004) and airborne measurements by Le Breton et al. (2012) show that models underestimate formic acid formation. Whether this is an underestimate of emissions or an underestimate of in-situ production is not clear and warrants further determination of secondary sources of formic acid. Furthermore, comparisons between HCOOH measurements from the infrared atmospheric sounding interferometer (IASI) and modelled global formic acid concentrations show a discrepancy. The disagreement between models and measurements is discussed in further detail by Leather et al. (2012).

The oxidation of alkenes by Ozone is a key secondary source of formic acid proposed by Neeb et al. (1997). As BVOCs are known to be the largest pool of alkenes in the atmosphere and isoprene is the major single, non-methane VOC emitted by plants (Finlayson-Pitts and Pitts, 2000), quantifying the yield of formic acid from terpenoid (e.g. isoprene) ozonolysis provides a major insight into the discrepancy between modelled and measured formic acid emissions.

Isoprene has two double bonds and is subject to oxidation by radicals such as NO₃, OH, and O₃ that this study focused on. The generalised mechanism of ozonolysis through the addition of O₃ to an alkene’s double bond is well documented and is reviewed extensively in Calvert (2000) and more recently Johnston and Marston
Briefly: the ozone molecule breaks an alkene’s double bond through cycloaddition to form an energy rich primary ozonide (POZ). The exothermicity of the reaction (200-250 kJ.mol$^{-1}$) means the POZ retains a high amount of energy. This energy ‘richness’ results in rapid breakup or rearrangement of the POZ and the formation of a carbonyl compound and a carbonyl oxide (Criegee intermediate [CH$_2$OO]*). Depending on how much energy a CI has it will experience one of two fates: it can stabilise, which is key in the formation of formic acid, or it can go on to form other products through decomposition or rearrangement.

Scheme 1, taken from Le Bras (1997) shows the ozonolysis of isoprene and the three possible CIs that can be formed. Calculations of Zhang (2002) on the different reaction pathways from isoprene ozonolysis show that the stabilised SCI CH$_2$OO is a likely product of isoprene ozonolysis via any of the reaction pathways, although other more complex SCI can also form as shown in scheme 1. With the work of Zhang (2002) in mind, the focus of this paper is the fate of the CI CH$_2$OO.

Figure 1: Reaction scheme showing the different CI resulting from isoprene ozonolysis. Adapted from Le Bras (1997).
Ultimately, it is the fate of the Criegee intermediate that determines the end product yield and this has provoked much attention in the atmospheric chemistry community (Johnson and Marston, 2008; Welz et al., 2012, Taatjes et al., 2012, Taatjes et al., 2008, Donahue et al., 2011). Broadly, the two main fates with potential for HCOOH formation are isomerisation to form a dioxirane which can result in formic acid or other organic acids or stabilisation and further bimolecular reactions with atmospheric constituents. The fate of CI from any ozonolysis reaction is similar and a discussion of such a fate is omitted here for brevity, however the reader is referred to the recent and analogous work of Leather et al. (2012) on ethene for a more extensive overview.

In the case of SCI partaking in bimolecular reactions the formation of HMHP from the reaction of the stabilised Criegee intermediates with water and the subsequent decomposition of HMHP to HCOOH is the main pathway as described by the reactions (Neeb et al., 1997):

\[
[CH_2OO] + H_2O \rightarrow HOCH_2OOH \quad (2)
\]
\[
HOCH_2OOH \rightarrow HCOOH + H_2O \quad (3)
\]

This study is the first to utilise the highly selective and sensitive Chemical Ionisation Mass Spectrometry (CIMS) to measure HCOOH yields from Isoprene. The work extends the approach of Leather et al., (2012) on ethene with the aim of resolving the discrepancies reported on HCOOH yields as a function of RH (Neeb et al. 1997; Orzechowska and Paulson, 2005).

Experimental

Experiments were conducted in the dark in the 123 L Teflon®-coated EXTRA chamber, described in detail elsewhere (Leather et al., 2010; 2011 and McGillen et al., 2011), and shown in Figure 2. Briefly, the apparatus consists of the leak tight EXTRA chamber connected by sampling ports in the end flanges to the analytical equipment (CIMS, ozone analyser and pressure guage). The chamber’s temperature control allowed two day bake out cleaning procedures to be performed between experiments. The combination of 100% Teflon® surfaces, temperature and pressure

---

9 A highly unstable molecule comprised of two oxygen atoms and one carbon.
control results in a system of minimal wall losses with respect to oxidants and condensable hydrocarbons.

The first-order loss rate of ozone with respect to walls and thermal decomposition was found to be $6.94 \times 10^{-6}$ s\(^{-1}\) by monitoring the decay of the ozone signal using a Monitor Labs Ozone Analyser (Model 8810) through UV absorption at 254nm. The ozone loss rate was thus considered negligible with respect to the timescale of the experiments.

**Figure 2:** A schematic diagram of the EXTRA chamber.

Quantitative concentration-time profiles of HCOOH were determined using CIMS. The CIMS was coupled to the EXTRA chamber through a sample port via 70 cm of 1/8" o.d. PFA tubing. The CIMS sampled through a critical orifice at a flow rate of 0.8 SLM at 760 Torr and ~296 K with a residence time of 0.1 s in the sample line preceding the ion molecule region.

HCOOH was chemically ionised by $\Gamma$. $\Gamma$ was produced by passing a combined flow of $N_2 (1.5$ SLM) and 0.5% CH\(_3\)/H\(_2\)/O/N\(_2\) (1 sccm) through a Po\(^{210}\) Nuclecel radioactive
source (NRD Inc.). The following ion-adduct reaction describes the ionisation of HCOOH:

\[ \Gamma \cdot \text{H}_2\text{O}_n + \text{HCOOH} \rightarrow \text{HCOOH} \cdot \Gamma \cdot \text{H}_2\text{O}_n \]  

(1)

It allows formic acid to be detected selectively at m/z = 171.65 (Slusher et al., 2004). The CIMS system was set up in a manner similar to the work of Leather et al., (2012) and the reader is referred to that work for further detail in that regard.

The ozonolysis of isoprene was initiated by adding the reagents and N\(_2\) sequentially to the EXTRA chamber. Isoprene was diluted into a 2.5% solution in cyclohexane which acted as an OH radical scavenger and injection aid. The Isoprene solution was introduced into the chamber by a microsyringe (SGE, Australia). The injection was made through a septum into a 200 cm\(^3\) round bottom flask heated to 360K. The solution was left for 10 minutes to fully evaporate into the chamber. Nitrogen was then added to the chamber until the pressure reached 760 torr, and monitored using a MKS Baratron. Gaseous reagents were added to the chamber at a known flow rate and duration using calibrated 1179 MKS mass flow controllers. The relative humidity within the chamber was varied by injecting volumes of deionised water calculated to produce a known RH based on the volume of EXTRA and the experimental temperature. The initial reactant concentrations were varied as follows; [O\(_3\)] = 2.46 \times 10^{12} – 9.84 \times 10^{13} molecule cm\(^{-3}\), H\(_2\)O \(\leq\) 1– 30 % RH and isoprene = 4.92 \times 10^{13} – 2.23 \times 10^{15} molecule cm\(^{-3}\).

Materials

Isoprene (Sigma Aldrich, 99.54%), cyclohexane (99%, Aldrich) and Formic acid (Fisher Scientific UK, 98/100%) were used without further purification. Purified water (\(\geq\)15.0 M\(\Omega\) cm) was obtained from a PURELAB Option-S 7/15 (ELGA). N\(_2\), O\(_2\) (99.6%) were used as supplied by BOC. Ozone created using UVP ozone lamp and flowing lab grade O\(_2\).
Global Model Description

The Global Chemistry Transport model CRI-STOCHEM has been used to assess the mass of products formed in the atmosphere using data from this study. CRI-STOCHEM is described in detail in (Utembe et al., 2010 and Archibald et al., 2010). The model used is an updated version of the UK Meteorological Office tropospheric chemistry transport model (STOCHEM) described by Collins et al., (1997), with updates reported in detail in the recent paper of Utembe et al., (2010). STOCHEM is a global 3-dimensional CTM which uses a Lagrangian approach to advect 50,000 air parcels using a 4th-order Runge-Kutta scheme with advection time steps of 3 hours. The transport and radiation models are driven by archived meteorological data, generated by the Met office numerical weather prediction models as analysis fields with a resolution of 1.25° longitude and 0.83° latitude and on 12 vertical levels extending to 100 hPa. Full details of the model version employed are given in Derwent et al. (2008).

The common representative intermediates mechanism (CRIv2-R5) (Jenkin et al., 2008; Watson et al., 2008; Utembe et al., 2009), which represents the chemistry of methane and 22 emitted non-methane hydrocarbons was employed in the model. Each parcel contains the concentrations of 219 species involved in 618 photolytic, gas-phase and heterogeneous chemical reactions, with a 5 minute time step. The formation of secondary organic aerosol (SOA) is represented using 14 species, which are derived from the oxidation of aromatic hydrocarbons, monoterpenes, and isoprene (see Utembe et al., 2011).

The surface emissions (man-made, biomass burning, vegetation, oceans, soil and 'other' surface emissions) are distributed using two-dimensional source maps. Emissions totals for the base case run for CO, NOx and non-methane hydrocarbons are taken from the Precursor of Ozone and their Effects in the Troposphere (POET) inventory (Granier et al., 2005) for the year 1998. The emission of aromatic species ortho-xylene, benzene and toluene were taken from Henze et al. (2008). Biomass burning emission of ethyne, formaldehyde and acetic acid are produced using scaling factors from Andreae and Merlet (2001) per mole of CO emitted. NASA inventories are used for aircraft NOx emissions for 1992 taken from Penner et al. (1999).
lightning and aircraft NOx emissions are monthly averages and are 3-dimensional in distribution.

Results and Discussion

Assessment of instrument sensitivity.

Dilute mixtures of HCOOH in deionized water were injected into the Chamber with no other gases present and the HCOOH.I signal was monitored. From a linear plot of [HCOOH] vs. HCOOH.I signal it is estimated that the sensitivity for HCOOH was $8.83 \times 10^6$ molecule cm$^{-3}$ for a signal to noise ratio of one and a time constant of 1 s. Two distinct regimes of sensitivity were observed, low sensitivity at 2.5% RH and high sensitivity for all values of RH above 2.5%. The average value for low sensitivity was found to be $2.58 \times 10^7$ Hz molecule cm$^{-3}$ and the average value for high sensitivity was $8.83 \times 10^6$ Hz molecule cm$^{-3}$ for a signal to noise ratio of one and a time constant of 1 s. The sensitivity as a function of RH is shown in figure 3. Yield calculations took into account this variation in sensitivity by using the individual determination of sensitivity at each relative humidity to calculate the yield therein.
Figure 3: A plot of sensitivity of the CIMS instrument as a function of RH

Product yields

Product yields were determined with isoprene in excess typically by a factor of 10–100. Initial comparison of the HCOOH signal shows that [HCOOH] at RH 30 % exceeds that of RH < 1 % by more than a factor of 7, in the initial stages during isoprene ozonolysis. Figure 4 shows three temporal profiles of the formic acid produced at different values of relative humidity.
Figure 4: Formic acid concentrations in EXTRA as a function of reaction time at 0, 30 and 40 % RH

The yield of HCOOH was also calculated from its concentration at the end of the reaction (~ five hours) and the amount of O₃ consumed. [HCOOH] yields were quantified as a function of relative humidity (RH), as summarised in Table 1.

Table 1: A summary of the HCOOH yields from the ozonolysis of isoprene. From \(^a\)Neeb et al., 1997, \(^b\)Orzechowska and Paulson, 2005 and this work.

<table>
<thead>
<tr>
<th>RH (% )</th>
<th>Measured</th>
<th>Modelled</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.05 ± 0.0041</td>
<td>0.04</td>
</tr>
<tr>
<td>0</td>
<td>0.04(^a)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.52(^b)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.10 ± 0.005</td>
<td>0.09</td>
</tr>
<tr>
<td>20</td>
<td>0.16 ± 0.005</td>
<td>0.15</td>
</tr>
<tr>
<td>25</td>
<td>0.15 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.17 ± 0.006</td>
<td>0.20</td>
</tr>
<tr>
<td>40</td>
<td>0.18 ± 0.006</td>
<td>0.24</td>
</tr>
<tr>
<td>65</td>
<td>0.52(^b)</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.3(^a)</td>
<td></td>
</tr>
</tbody>
</table>
The products of the reaction were monitored repeatedly from the start of the reaction and the HCOOH concentration rose with time as figure 4 clearly shows. Figure 5 is a plot of the HCOOH yields from this study and others (Neeb et al. 1997; Orzechowska and Paulson, 2005) as a function of relative humidity and HCOOH yields from ethene ozonolysis (Leather et al., 2012). The yield of HCOOH is observed to increase as a function of relative humidity as expected in line with the postulation of Calvert et al. (1978) of water catalysis of Criegee intermediates.

Figure 5: Measured and modelled yields of formic acid from isoprene and ethene ozonolysis. Data from aLeather et al., 2012, bNeeb et al., 1997, cOrzechowska and Paulson 2005 and this work.

CIMS is the most sensitive technique to date used to probe the production of HCOOH in the isoprene /O3 system. While CIMS is selective to HCOOH, there remains the possibility that formic acid production is enhanced by heterogeneous processes during isoprene ozonolysis. Temperature and pressure control allow this system to be baked out during cleanout procedures, producing a small measured \( k_w \) (wall loss rate coefficient) with respect to ozone and HCOOH. and so one can expect little impact on HCOOH yields from heterogeneous losses. The first-order decay rate of ozone and HCOOH with respect to walls were determined to be \( 6.94 \times 10^{-6} \) s\(^{-1} \) and
5.46 × 10⁻⁷ s⁻¹ respectively. Our data, along with the data from Neeb et al. (1997), show the yield of HCOOH consistently rising with increasing relative humidity from 0-80%. The HCOOH yield of 0.52 from Orzechowska and Paulson (2005) at 65% RH is significantly above all other known yields from isoprene as shown in figure 5.

The HCOOH yields from other alkene systems reported by Orzechowska and Paulson (2005) are consistently higher than other work in the literature. This consistent discrepancy suggests that there may be an experimental bias in the indirect analytical technique used by Orzechowska and Paulson (2005) to quantify acid yields.

Previous studies of the ozonolysis of alkenes have chosen to refer to Criegee intermediates formed during ozonolysis as either stabilised or unstabilised (e.g. Kroll et al., 2001a; 2001b; Johnson and Marston, 2008). In the ozonolysis reaction, ozone reacts with the olefinic bond of an alkene through a 1,3-cycloaddition forming a primary ozonide, which decomposes to form a Criegee intermediate and a carbonyl co-product. The nascent Criegee intermediates may possess a range of (vibrational) energies and, depending on energy barriers, a certain fraction will be able to isomerise or decompose (unstabilised). The remainder will be below these energy barriers (stabilised), which affords them a long enough lifetime to be able to undergo bimolecular reactions (e.g. Welz et al., 2012; Taatjes et al., 2008; 2012). As pressure is increased, more Criegee intermediates will be ‘stabilised’ as a result of collisional quenching. The results of the HCOOH yield as a function of RH can be analysed using two possible scenarios, summarised here and presented in detail in Leather et al., (2012). The first kinetic analysis scenario assumes full stabilisation of all the Criegee intermediates in a given ozone-isoprene system and thus the CI fate proceeds via the following reactions to produce HCOOH:

\[
\text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{H}_2\text{O} \quad (3)
\]
\[
\text{CH}_2\text{OO} \rightarrow \text{products} \quad (4)
\]

The second scenario assumes that all the CIs are ‘hot’, i.e. above the energy barrier for decomposition and as such full decomposition occurs. In this case the fate of the ‘hot acid’ can be shown to proceed via reactions:
A simple model encapsulating these two reactions (3) and (4) is compared with measurement data in Figure 4. Here, the yield of HCOOH is defined as

\[ HCOOH_{\text{yield}} = \frac{k_3[H_2O]}{k_3[H_2O] + k_4} \]  

An analogous model of HCOOH yields can be constructed for reactions 6 and 7. By adjusting the ratio between \( k_6/k_3 \) or \( k_7/k_6 \) an excellent fit to the measurement data is obtained. A full discussion of the two scenarios can be found in Leather et al., (2012).

In the absence of any direct experimental evidence for the yield of stabilised Criegee intermediates from the ozone/isoprene system, it is not possible to differentiate between the first and second scenario of Criegee intermediate formation. However, it is natural to assume that the yield of HCOOH will be a combination of the two scenarios. An increasing contribution from scenario 1 with increasing RH as the abundance of \( \text{H}_2\text{O} \) molecules grows will contribute directly to collisional stabilisation and will therefore increase the yield through the SCI pathway. In a theoretical study Kroll et al., (2001b) state that much (~50%) of the Criegee intermediates from the ethene system are formed vibrationally “cold”. Indeed, Donahue et al. (2011) suggest that for C\(_2\)-C\(_{15}\) precursors all Criegee intermediates can be completely stabilised at 100 Torr. To date the yield of SCI from isoprene ozonolysis has only been determined experimentally in the work of Hasson et al. (2001) as 0.26. Here the \( Y_{\text{SCI}} \) was inferred from the yield of carbonyl products of the isoprene ozonolysis and assuming a different reactivity between the ‘Hot’ Criegee intermediates and SCI. However, it is also possible to infer an SCI yield from knowledge of the OH yield. The production of OH is believed to arise from the unstabilised CI therefore it has been suggested by Johnson and Marston (2008) that:

\[ Y_{\text{SCI}} = (1-Y_{\text{OH}}) \]
In the work of Hasson *et al.* (2001) the authors found an empirical relationship between $Y_{OH}$ and $Y_{SCI}$ by compiling their experimentally inferred $Y_{SCI}$ and $Y_{OH}$. They found that

$$Y_{SCI} = (1.325 - Y_{OH})/3.25$$

Table 2 summarises the inferred SCI yields for the ozonolysis of isoprene. There is a clear discrepancy between the 2 methods: Johnson and Marston suggest an average of 0.67 whereas the method of Hasson suggests a yield of 0.3. Indeed, there is a discrepancy between the work of Orzechowska and Paulson (2005) and co-workers Hasson *et al.* (2001), who report a HCOOH yield of 0.52, yet predict a SCI yield of 0.33.

**Table 2:** Yields of OH from Isoprene ozonolysis and yields of SCI. Unless otherwise stated the $Y_{SCI}$ is calculated from $Y_{OH}$ using the following equations $Y_{SCI} = 1 - Y_{OH}$ (Johnson and Marston, 2008) or $Y_{SCI} = (1.325 - Y_{OH})/3.25$ (Hasson *et al.*, 2001). Data from aNeeb *et al.*, (1997), bAtkinson *et al.*, (1992), cDonahue *et al.* (1998), dPaulson *et al.*, (1998), eGutbrod *et al.*, (1997), fMalkin *et al.*, (2010), gRickard *et al.*, (1999).

<table>
<thead>
<tr>
<th>$Y_{OH}$</th>
<th>$Y_{SCI}$ (Marston method)</th>
<th>$Y_{SCI}$ (Hasson method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26$^a$</td>
<td>0.74</td>
<td>0.32</td>
</tr>
<tr>
<td>0.27$^b$</td>
<td>0.73</td>
<td>0.32</td>
</tr>
<tr>
<td>0.65$^c$</td>
<td>0.35</td>
<td>0.20</td>
</tr>
<tr>
<td>0.25$^d$</td>
<td>0.75</td>
<td>0.33</td>
</tr>
<tr>
<td>0.19$^e$</td>
<td>0.81</td>
<td>0.34</td>
</tr>
<tr>
<td>0.26$^f$</td>
<td>0.74</td>
<td>0.32</td>
</tr>
<tr>
<td>0.44$^g$</td>
<td>0.56</td>
<td>0.27</td>
</tr>
</tbody>
</table>

In isoprene ozonolysis, methyl vinyl ketone (MVK) is produced from an attack on the 1,2-alkene and methacrolein (MACR) from an attack on the 3,4-alkene. Thus, the co-product of the Criegee radical, CH$_2$OO, is either MVK or MACR, depending on which double bond is attacked. Table 3 compiles literature yields of MVK and MACR, and the average yield of MACR is 0.38 and that of MVK is 0.17. A slightly
higher proportion of ozonolysis (59%) occurs at the 3,4-alkene thus explaining the higher MACR yield. The sum of the MACR and MVK yield sets an upper limit of 0.55 for the SCI from ozonolysis of isoprene, which is consistent with the HCOOH yields reported in this work.


<table>
<thead>
<tr>
<th>MVK</th>
<th>MACR</th>
<th>Total</th>
<th>RH</th>
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</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.35</td>
<td>0.5</td>
<td>Dry</td>
</tr>
<tr>
<td>0.18</td>
<td>0.41</td>
<td>0.59</td>
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</tr>
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<td>0.17</td>
<td>0.44</td>
<td>0.61</td>
<td>Dry</td>
</tr>
<tr>
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<td>0.38</td>
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<td>Dry</td>
</tr>
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<td>0.17</td>
<td>0.39</td>
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<td>Dry</td>
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<td>0.14</td>
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<td>Dry</td>
</tr>
<tr>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>9%</td>
</tr>
<tr>
<td>0.17</td>
<td>0.35</td>
<td>0.52</td>
<td>0%</td>
</tr>
<tr>
<td>0.24</td>
<td>0.42</td>
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<td>78%</td>
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</tbody>
</table>

In figure 3 the yield of HCOOH from the ozonolysis of ethene is shown for comparison. One would expect the HCOOH yield from the ozonolysis of isoprene to be approximately half that of the yield of HCOOH from the ozonolysis of ethene. In the isoprene system ozone will add to either of the terminal double bonds in both cases. As the molecule is not symmetrical it is assumed that there is only a 50% chance that the ozonide will yield CH$_2$OO. However, in the ethene system the molecule is symmetrical and thus CH$_2$OO will always be formed when the ozonide decomposes. This is consistent with both the yield reported in this work and those of Neeb et al. (1997). However, Orzechowska and Paulson (2005) report a higher yield for HCOOH from isoprene than in the ethene system, again pointing to a possible systematic bias in their work. It is clear that from indirect studies that it is not possible to define the SCI yield and work is needed to quantify the carbonyl oxide yield.
directly. However, work of Tatajes et al. (2008) and Welz et al. (2012) have been able to detect the carbonyl oxide directly for the first time and offers the exciting opportunity to quantify the carbonyl oxide yield directly for the first time.

**Model Results**

For the ozonolysis of isoprene, if it is assumed that the yield of CH₂OO is ~ 0.6, where the biradical is a product partner on formation of either methyl vinyl ketone or methacrolein and that these radicals exclusively form HCOOH, then the yield of HCOOH is approx. 19 Tg/yr. However, data from this work and previous work by Leather et al. (2012) suggest that of the CH₂OO formed about half (0.55) will yield HCOOH at the relative humidity levels encountered around isoprene emissions. Therefore, for isoprene, this then leads to an estimation of a total yield of HCOOH of 0.33 (0.6 x 0.55), consistent with the work of Neeb et al. (1997), amounting to an annual yield of about 9.5 Tg/yr. Ozonolysis of the major products of isoprene, methyl vinyl ketone and methacrolein are also potential sources of HCOOH. The yields of CH₂OO (Aschmann et al. 1996; Grosjean et al. 1993a) are reported to be between 0.85-0.95. Model estimates, using 0.55 as the fraction of CH₂OO produced that yields HCOOH, suggest a yield of HCOOH of around 4 Tg/yr.

**Monoterpene yields for HCOOH**

A number of monoterpene species contain a 1-alkene moiety and on ozonolysis will yield some CH₂OO and hence some HCOOH. Selections of these species have been added to the global model CRI-STOCHEM (e.g. Utembe et al. 2010). Integrations of this model have then permitted an estimation of the percentage loss of each monoterpene with respect to OH, NO₃ and O₃. These data, coupled with estimations of the branching ratio for ozonolysis of the 1-alkene moieties have been used to estimate the yield of HCOOH, relative to the total emission of that compound. This is not an attempt to provide an exhaustive list of HCOOH sources but to assess which monoterpenes are likely to be strong sources of HCOOH. The monoterpenes investigated include: acyclic 1-alkenes (myrcene and β-ocimene), monocyclic 1-alkenes (d-limonene and β-phellandrene) and bicyclic 1-alkenes (sabinene and β-pinene). The structures of these monoterpenes are summarised in figure 5 and their
rate coefficients for reaction with OH, NO₃ and O₃ and the fractional loss via reaction with these species derived from model integrations are shown in table 4.

**Table 4:** Rate coefficients (298 K) for the reaction of selected monoterpenes with OH, NO₃ and O₃ (all units are cm³ molecule⁻¹ s⁻¹) and percentage loss via reaction with each of these three reaction partners, derived from global model fields. Rate constant from aAtkinson *et al.*, (1986); bAtkinson (1991); cAtkinson *et al.*, (1990a); dShu and Atkinson (1994); eShorees *et al.*, (1991), fAtkinson (1986); gJohnson *et al.*, (2000) and hAtkinson *et al.*, (1990b)

<table>
<thead>
<tr>
<th>Monoterpene</th>
<th>k(OH)</th>
<th>k(NO₃)</th>
<th>k(O₃)</th>
<th>%OH</th>
<th>%NO₃</th>
<th>%O₃</th>
<th>Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acyclic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Myrcene</td>
<td>2.1 x 10⁻¹⁰a</td>
<td>1.1 x 10⁻¹¹b</td>
<td>4.9 x 10⁻¹⁶c</td>
<td>39.6</td>
<td>24.3</td>
<td>36.1</td>
<td>31 min</td>
</tr>
<tr>
<td>β-Ocimene</td>
<td>2.5 x 10⁻¹⁰a</td>
<td>2.2 x 10⁻¹¹b</td>
<td>5.6 x 10⁻¹⁶c</td>
<td>33.6</td>
<td>36.4</td>
<td>30.1</td>
<td>22 min</td>
</tr>
<tr>
<td>Monocyclic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-Limonene</td>
<td>1.7 x 10⁻¹⁰a</td>
<td>1.2 x 10⁻¹¹b</td>
<td>2.0 x 10⁻¹⁶d</td>
<td>42.3</td>
<td>37.6</td>
<td>20.1</td>
<td>42 min</td>
</tr>
<tr>
<td>β–Phellandrene</td>
<td>1.7 x 10⁻¹⁰e</td>
<td>8.0 x 10⁻¹²e</td>
<td>4.8 x 10⁻¹⁷e</td>
<td>58.9</td>
<td>34.4</td>
<td>6.7</td>
<td>59 min</td>
</tr>
<tr>
<td>Bicyclic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Pinene</td>
<td>7.8 x 10⁻¹¹f</td>
<td>2.5 x 10⁻¹²b</td>
<td>2.4 x 10⁻¹⁷g</td>
<td>66.0</td>
<td>26.0</td>
<td>8.0</td>
<td>2.4 hr</td>
</tr>
<tr>
<td>Sabinene</td>
<td>1.2 x 10⁻¹⁰b</td>
<td>1.0 x 10⁻¹¹b</td>
<td>8.8 x 10⁻¹⁷c</td>
<td>42.3</td>
<td>45.0</td>
<td>12.7</td>
<td>60 min</td>
</tr>
<tr>
<td>Camphene</td>
<td>5.3 x 10⁻¹¹b</td>
<td>6.6 x 10⁻¹³b</td>
<td>9.0 x 10⁻¹⁹g</td>
<td>86.3</td>
<td>13.1</td>
<td>0.6</td>
<td>4.5 hr</td>
</tr>
</tbody>
</table>

**Acyclic 1-alkenes**

**Myrcene**

Based on work by Lee *et al.* (2006) the ozonolysis of the non 1-alkene site is around 50% and assuming that both the remaining 1-alkene sites yield 50% CH₂OO this produces a yield for HCOOH (Y(HCOOH))

Y(HCOOH) = Emission total * 0.361 * 0.50 * 0.50 * 0.55 = Emission total * 0.050.
\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.301 \times 0.10 \times 0.50 \times 0.55 = \text{Emission total} \times 0.008. \]

**Cyclic 1-alkenes**

**d-Limonene**

Grosjean et al. (1993b) show that at least 10% of addition occurs at the 1-alkene (via HCHO yields). Jiang et al. (2010) have carried out theoretical studies that suggest that the 1-alkene addition has a branching ratio of about 0.24, but do not determine the decomposition products of the primary ozonide. So if we estimate that 50% of the addition leads to \( \text{CH}_2\text{OO} \) we then have

\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.201 \times 0.24 \times 0.5 \times 0.55 = \text{Emission total} \times 0.013. \]

**\( \beta \)-Phellandrene**

Hakola et al. (1993) estimate that addition to the 1-alkene is 0.35 at most, leading to

\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.067 \times 0.35 \times 0.5 \times 0.55 = \text{Emission total} \times 0.007. \]

**Bicyclic 1-alkenes**

**Sabinene**

The yield of Sabina ketone, from the reactions of \( \text{O}_3 \) with Sabinene yielding \( \text{CH}_2\text{OO} \) and the ketone, is about 50%, (Hakola et al., 1994; Yu et al., 1999). Therefore for Sabinene, we estimate the yield
\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.127 \times 0.5 \times 0.5 \times 0.55 = \text{Emission total} \times 0.023. \]

**Camphene**

Based on the product study of Jay and Stieglitz, (1989) it is assumed that formation of CH\(_2\)OO following ozonolysis accounts for about 50% of the products. Therefore

\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.006 \times 0.50 \times 0.55 = \text{Emission total} \times 0.002. \]

**β-Pinene**

The theoretical study of Nguyen et al. (2009) suggests that just 5.1% of ozone addition leads to CH\(_2\)OO formation. However, the yield of nopinone (the co-product to CH\(_2\)OO formation) from β-pinene ozonolysis is around 20% (Lee et al., 2006) and taking this value yields

\[ Y(\text{HCOOH}) = \text{Emission total} \times 0.08 \times 0.2 \times 0.55 = \text{Emission total} \times 0.009. \]

Based on such an analysis it emerges that myrcene and sabinene are potentially the biggest sources of HCOOH arising from ozonolysis of those studied. When estimating the yield of HCOOH it is clear that the fraction of loss that is via ozonolysis, the number of 1-alkene sites and the fraction of reaction occurring at these sites are all important factors. An estimation of the global emission for monoterpenes is often reported to be around 130 Tg/yr. Based on this figure and assuming all of this is one of the monoterpenes inspected here, the yield of HCOOH varies between 0.3 – 6.4 Tg/yr. Given recent work that shows that the ozonolysis of the sesquiterpene, β-caryophyllene (Ghalaieny et al., 2012) is much slower than previously reported and that only about 12% of oxidation is via reaction with ozone, it appears that ozonolysis of monoterpenes and possibly sesquiterpenes containing a 1-alkene moiety are not a huge source of HCOOH.

Recent work by Stavrakou et al. (2012) has suggested that terpenoids or a reactive and as yet unidentified biogenic VOC are a substantial source of HCOOH in order to reconcile satellite measurements and models, particularly in Boreal Forest areas. It
would seem that ozonolysis is not a mechanism capable of generating high levels of HCOOH from these terpenoids. Indeed, Stavrakou et al. (2012) concur with this assumption in their preliminary analysis. Whether oxidation of these terpenoids via OH, which has been suggested to yield HCOOH, or some other mechanism is responsible is unclear. However, the work of Stavrakou et al. (2012) suggests that current inventories underestimate HCOOH by a factor of 3-4.

Conclusions

This study has confirmed that the yield of HCOOH from the ozonolysis of isoprene has strong water dependence and rises rapidly with increasing relative humidity. Assuming a simple two channel model for the fate of the CH$_2$OO radical it has been possible to estimate the ratio of the rate coefficient for the reaction with water compared (k$_3$) with decomposition (k$_4$). Such an analysis suggests that k$_3$ probably ranges between 1×10$^{-12}$ – 1×10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and as such will indeed be the dominant loss process, other than decomposition, for this radical in the atmosphere. Global model integrations suggest that isoprene ozonolysis could contribute up to 9 Tg yr$^{-1}$ to the HCOOH budget. Further analysis would suggest that ozonolysis of monoterpenes could contribute between 0.3-6.4 Tg yr$^{-1}$. The fact remains that HCOOH is still underestimated, and it appears that ozonolysis of monoterpenes and possibly sesquiterpenes containing a 1-alkene moiety are not a significant source of HCOOH.
Figure 5: Structures of monoterpenes investigated using the global model.

Myrcene

β-Ocimene

d-Limonene

β-phellandrene

Sabinene

Camphene
References for paper V


7. Conclusions

There have been many kinetic measurements of the reaction rate of alkene ozonolysis at room temperature (e.g. Shu and Atkinson, 1994; Calvert et al., 2000; Mason et al., 2009). Room temperature data cannot be extrapolated for use at atmospherically relevant temperatures without calculating Arrhenius parameters, few of which exist for semi-volatile organic compounds (SVOCs) such as sesquiterpenes (Kim et al., 2011). The need to measure the reaction kinetics of SVOCs at elevated temperatures is apparent in order to eliminate losses to instrumentation surfaces and losses to any aerosol formed that can bias measurements (Kourtchev et al., 2009; Loza et al., 2010; Matsunaga and Ziemann, 2010). Indeed, the inexplicable increase in reactivity with ozone in the homologous series of terminal alkenes for compounds over nine carbon atoms is an example of this experimental bias, shown in figure 18.

![Graph showing measurements from this work and previous literature measurements and SAR estimates of terminal alkene ozonolysis rate coefficients plotted against carbon number (literature data have been extrapolated to 366K).](image-url)
The increase in terminal alkene reactivity could not be explained by several structure activity relationships or the existence of alternative reaction channels. In this work (Chapter five: McGillen et al., 2011), the reaction kinetics of C8-C14 terminal alkenes was studied at an elevated temperature and no increase in reactivity was observed throughout the series. The results of chapter four lead to the conclusion that the increased reactivity of higher carbon alkenes was most likely to be an experimental artefact caused by heterogeneous and surface losses of reactant material. A major atmospheric implication of this experimental bias in alkene reactivity is the overestimation of the importance of ozonolysis as a sink for semi-volatile NMHCs and subsequently as a source of secondary organic aerosol (SOA).

Similar to higher terminal alkenes, sesquiterpenes are semi-volatile NMHCs with low vapour pressures and have been considered a very important source of SOA. For example, the extremely fast room temperature ozonolysis reaction rate of β-caryophyllene, first measured by Shu and Atkinson (1994) as $1.5 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, is repeatedly cited as proof of this compound’s importance for SOA formation (e.g. Alfarra et al., 2012) even though the high reactivity of β-caryophyllene (and other SQTs) was in contradiction to basic SARs (Calvert et al., 2000). The elevated temperature relative rate protocol developed for terminal alkenes was applied to the ozonolysis of β-caryophyllene and three other sesquiterpenes (Chapter five: Ghalaieny et al., 2012) and found that β-caryophyllene and α-humulene were not as reactive with O$_3$ as previously thought and as table 10 shows.
Table 10 Absolute rate coefficients determined in this work along previous measurements in the literature and SAR predictions. Previous measurements were extrapolated from room temperature to 366 K using activation energy from 2-methyl-2-butene.

<table>
<thead>
<tr>
<th>Alkene</th>
<th>$k_{366} \times 10^{17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolongifolene</td>
<td>2.5 ± 1.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>4.2 ± 2.7</td>
<td>Pollmann et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>40 ± 27</td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>β-caryophyllene</td>
<td>5.9 ± 4.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1792 ± 794</td>
<td>Pollmann et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>1889 ± 657</td>
<td>Shu and Atkinson (1994)</td>
</tr>
<tr>
<td></td>
<td>18.90 ± 6.5</td>
<td>Winterhalter et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>41.4 ± 14.5</td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>α-humulene</td>
<td>6.4 ± 4.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>2281 ± 793</td>
<td>Pollmann et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>1906 ± 663</td>
<td>Shu and Atkinson (1994)</td>
</tr>
<tr>
<td></td>
<td>58.6 ± 24</td>
<td>Beck et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>100 ± 35</td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>α-cedrene</td>
<td>3.1 ± 1.9</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>5.5 ± 1.9</td>
<td>Pollmann et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>4.6 ± 1.6</td>
<td>Shu and Atkinson (1994)</td>
</tr>
<tr>
<td></td>
<td>40 ± 14</td>
<td>Calvert et al. (2000)</td>
</tr>
</tbody>
</table>

It was found that the reaction rate of β-caryophyllene with ozone was 3 orders of magnitude less than previously thought by Shu and Atkinson (1994). Similar revisions were made to the rate coefficient for α-humulene as a result of this work, leading to the conclusion that this fast reactivity of sesquiterpenes was also an experimental artefact. It is now thought that ozone only accounts for 12% of the atmospheric oxidation of sesquiterpenes, giving it less prominence than previously believed with important implications for the formation of SOA.

In addition to accurate determinations of reaction rate coefficients, an adequate assessment of the atmospheric importance of NMHCs also requires a quantification of the mass balance of key reactions such as ozonolysis through the laboratory measurements of important product yields.

Chemical ionisation mass spectrometry (CIMS) is known as a precise technique for the quantification of atmospheric trace gases. Chemical ionisation of analytes means that CIMS is extremely selective and highly sensitive resulting in sub ppt limits of
detection with a time response on the order of milliseconds (Huey et al., 1998; Slusher et al., 2004). Accurate quantification of certain trace gases requires attention to the choice of inlet material used. By conducting the first systematic study of the loss of trace gases to inlet walls (Chapter two: Ghalaieny et al., in prep), it was determined that PFA is indeed the preferable material for use in measuring ‘sticky’ trace gases in the atmosphere. Due to these findings, all inlets used in this study were constructed from lengths of PFA.

A field test of the Manchester CIMS with a custom made, heated PFA inlet, (Chapter three: von Bobrutzk et al., 2010) confirmed the instrument’s capability in measuring atmospheric trace gases. The Manchester CIMS was compared well with ten other instruments for NH$_3$ measurements in the most comprehensive intercomparison study in the UK. Indeed, the CIMS was one of the only instruments capable of tracking rapid variations in NH$_3$ concentrations which highly correlated with concentrations measured by other instruments of comparable time response, $R^2$ values of 0.89, 0.94 and 0.79 respectively are reported for the cQCLAS, Dual QCLAS and WaSul-Flux instruments. Amongst all the instruments in the intercomparison, CIMS was the instrument with the most accurate determination of the unified standard addition calibration of NH$_3$ used in the field experiment.

Taking into account the suitability and superiority of CIMS for accurate trace gas measurements and choosing the right inlet material and design (heating, length etc.), CIMS coupled with the EXTreme Range chamber (EXTRA) was used (Chapter six: Ghalaieny et al., in prep) to measure the yield of HCOOH from the ozonolysis of isoprene as a function of relative humidity. The measurement of HCOOH yield from isoprene was the first study of its kind using CIMS and only the second study utilising an online realtime measurement technique, FTIR (Neeb et al., 1997). The measured yield of HCOOH, a maximum of 0.18 at 40% RH was consistent with the previous FTIR measurements of Neeb et al. (1997). Additionally, the results were also consistent with the studies conducted using CIMS on HCOOH yields from ethene by Leather et al. (2012) and related measurements of radical yields from ethene by Alam et al. (2011). When integrated into a global model, The HCOOH yields measured in this work lead to the conclusion that the ozonolysis of isoprene accounts for 9.5 Tg yr$^{-1}$ of HCOOH production and that more work is needed to quantify
secondary sources and primary emissions of HCOOH to find agreement between models and measurements.

**Future work**

A key area of future research is the further quantification of HCOOH production from alkene ozonolysis. The research presented herein quantified the contribution of isoprene to the production of HCOOH in the atmosphere, but other sources have yet to be quantified. The ozonolysis of any terminal alkene is a source of carbonyl oxides (Criegee intermediates) that can react with water to yield HCOOH. Therefore further study of other atmospherically abundant ozone-alkene systems (e.g. propene, 1-butene, 2-methyl-2-butene, and 1,3-butadiene) is necessary in order to resolve discrepancies with models that continue to under-predict concentrations of HCOOH in the atmosphere (Paulot *et al.*, 2011; Stavarakou *et al.*, 2012). In a similar vein, studies of the formation of other organic acids (e.g. acetic, butyric and pyruvic acids) from the ozonolysis of asymmetric alkenes are important because field measurements indicate that these other organic acids also have photochemical sources rather than direct emissions (Veres *et al.*, 2011).

As has been demonstrated, the fate of Criegee intermediates (CI) is directly linked to the formation of HCOOH in the atmosphere. Therefore, simultaneous measurements of CI yields with HCOOH yields using techniques such as tunable synchrotron photoionization with multiplexed mass spectrometry (Taatjes *et al.*, 2008) or CI titration by HFA (Drozd and Donahue, 2011) would be fruitful future research. Also, direct measurements of CI yields from ozonolysis would yield important information (Welz *et al.*, 2012).

Finally, analogous field measurements of the NMHCs and organic acids mentioned above (Le Breton *et al.*, 2012) could be useful to complement laboratory measurements, and to test and validate the output of models.
8. Appendix: permeation tube calibration

The CIMS-F was calibrated continuously in the field using permeation tubes made by KIN-TEK (Lamarque, Texas). These devices were chosen because of the stability of their output during a certain stage in their lifecycle known as the saturation stage (Mitchell 2000) Permeation tube based calibration devices also benefit from being extremely compact in comparison with other gas standard delivery methods, such as gas cylinders.

Calibration source description

A permeation device is a hermetically sealed PTFE tube containing a concentrated solution of the analyte of interest (e.g. NH$_3$ or HNO$_3$). The permeability of the PTFE to the analyte inside is mainly driven by the difference in partial pressure between the inner and outer walls of the tube. It is also dependent on temperature and therefore the permeation rate varies depending on temperature (Mitchell 2000). Once the tube is heated the calibrant is emitted at a known rate measured in nanograms per minute (ng min$^{-1}$). The emission of calibrant is carried in a known flow of clean N$_2$ to the instrument to be calibrated. The concentration of the introduced calibrant is calculated from equation 2 below:

$$C = \frac{k \times E}{F}$$

Where E is the emission rate in ng min$^{-1}$ at a given temperature, k is a constant related to the molar mass of the emitted species supplied by the permeation tube manufacturer, and F is the flow of the carrier gas (N$_2$) measured in standard cubic centimetres per minute (sccm) and C is the concentration in ppm.

In order to accurately control the emission rate and hence the concentration a permeation oven with accurate temperature control is required. A field portable oven was designed and built that consisted of: a 14 cm long PTFE tube sleeved in aluminum sleeve to hold the permeation tube; a flexible Kapton Polyamide™ (Minco) heating element providing 6 W of power; a K type thermocouple to
provide temperature feedback to the PID temperature controller (Watlow series 935a heating controller). Figure 19 shows the completed permeation tube oven.

![Image](image.png)

**Figure 19:** The permeation tube oven used to calibrate the field CIMS.

Neumann *et al.* (Neuman, Ryerson *et al.* 2003) have shown that permeation tube emission rates require continuous calibration. This is to account for discrepancies in the nominal emission rate, to account for losses on the system walls and to quantify the emission rate at temperatures other than the certified one. In their work Neumann *et al.* (Neuman, Ryerson *et al.* 2003) developed a UV method for quantifying emission rates. They found emission rates varied by about 10% of that quoted by the manufacturer. The UV spectrometer analysis was also verified by trapping the gases in water and analysing the resultant solution using ion chromatography (ibid.). The quantification by ion chromatography was replicated to contribute to the calibration of the CIMS. The aim was to attain an effective emission rate that takes into account the factors mentioned above. The concept of the effective emission rate is illustrated in the figure 20, where $E_{\text{nom}}$ is the nominal emission rate quantified gravimetrically by the manufacturer, and $E_{\text{eff}}$ is the effective emission rate.
Figure 20: Schematic of the permeation tube system illustrating the concept of the effective emission rate.

When measured using ion chromatography, the average emission rates for ammonia and nitric acid were found to be 10% less than the predicted emission rate, a result in agreement with work carried out by Neuman et al. (2003).
9. References


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