DEPARTMENT OF BIOLOGICAL AND ENVIRONMENTAL SCIENCES

ANALYSING THE IMPACT CLIMATE HAS ON THE EMISSIONS OF BVOCs AND THE FORMATION OF TROPOSPHERIC OZONE

Collaboration with Skogaryd Research Catchment

Benedict De Grandis

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Abstract

Understanding the impact of a changing climate is becoming increasingly important especially when relating to air quality and the chemical processes associated. The formation of tropospheric ozone is a concern for the modern day due to the negative impacts it has on human health, animal health and vegetation. Understanding the complex links between biogenic volatile organic compounds, climate and the formation of ozone is becoming an increasingly more examined topic due to its importance. There is currently a good scientific understanding as to how climate will impact on the formation of ozone but there is significantly less understanding as to how stress will impact vegetation and the release of compounds which induce the formation of O₃.

This report is based on data collected from Skogaryd, a research catchment located approximately 100km north of Gothenburg. The detection of the biogenic compounds was done using a GC-FID where overall concentration could be detected and measured against climate data which was collected at the same site. The detection of the compounds was done using chromatograph analysis in Clarity computer software. Ozone zone data was also collected and supplemented with data provided by IVL from three other sites located in the vicinity of Gothenburg. Using this data, a relationship between compound concentration, climate and ozone has been formulated.

**Keywords:** Tropospheric Ozone, Climate, Gas Chromatograph, Skogaryd, Biogenic Volatile Organic Compounds.
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>BVOC</td>
<td>Biogenic Volatile Organic Compound</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionized Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>HONO</td>
<td>Nitrous Acid</td>
</tr>
<tr>
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<td>Infra-Red</td>
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<tr>
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<td>Nitrogen</td>
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<td>Ammonia</td>
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</tr>
<tr>
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<td>Ozone</td>
</tr>
<tr>
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<td>Hydroxyl</td>
</tr>
<tr>
<td>ppbv</td>
<td>Parts Per Billion by Volume</td>
</tr>
<tr>
<td>ppmv</td>
<td>Parts Per Million by Volume</td>
</tr>
<tr>
<td>SAO</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>SITES</td>
<td>Swedish Infrastructure for Ecosystem Science</td>
</tr>
<tr>
<td>SO₂</td>
<td>Sulphur Dioxide</td>
</tr>
<tr>
<td>SRC</td>
<td>Skogaryd Research Catchment</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>IVL</td>
<td>Swedish Environmental Institute</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<td>SR</td>
<td>Solar Radiation</td>
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1. Introduction

The Earth’s atmosphere essential for life as we know it, the combination of various gases make up the air we breathe, protection from the Sun as well as the nice insulating blanket which allows life to flourish. The cocktail of gases includes ingredients of nitrogen (N$_2$ 78.08%), oxygen (O$_2$ 20.94%), argon (0.93%). The remaining 0.05% is made up of various smaller quantities of trace gases; ozone (O$_3$), carbon dioxide (CO$_2$), water vapour (H$_2$O), nitrogen oxides (NO$_x$), sulphur dioxide (SO$_2$), ammonia (NH$_3$), methane (CH$_4$) and Volatile Organic Compounds (VOCs). Despite the low percentage quantities of trace gases, they still play a huge role in atmospheric properties.

The atmosphere consists of a relatively thin layer of gas surrounding the Earth, approximately 80km above the ground. The breakdown of the atmosphere consists of the troposphere which is approximately 12 km, followed by the stratosphere approximately 50 km then finally the mesosphere up to 80 km. Ground level pressure is about 1013 hPa, decreasing with height above the Earth. Currently the average temperature of the Earth is about 14.6 °C (287.6 K), which would be approximately -19 °C (254 K) without the insulating properties of ‘greenhouse gases’ and its impact on the radiative balance of the Earth system (Figure A1). The majority of atmospheric gas molecules do not interact with thermal radiation, however several of the trace gases do interact, predominately water vapour, CO$_2$, O$_3$, CH$_4$, N$_2$O and chlorofluorocarbons, these are classified as ‘greenhouse gases’. Essentially, these molecules absorb the outgoing radiation emitted from the Earth’s surface, and re-emit in all directions (Finlayson-Pitts et al., 1999).

A wide variety of Biogenic Volatile Organic Compounds (BVOCs) are emitted into the Earth’s atmosphere from different types of vegetation, marine and terrestrial environments (Atkinson et al., 2003; Guenther et al., 1995; Hoffmann et al., 1997). There is an ever extending list of BVOCs which is now estimated to be over 1000 different compounds, including; isoprenoids (isoprene and monoterpenes), alkenes, carbonyls and alcohols (Fall, 1999; Kesselmeier et al., 1999), it has been established that of these compounds isoprene and monoterpenes are the most prominent. The quantity and variety of BVOCs emitted is dependent on the type of vegetation species as well as the environmental conditions, including temperature and sunlight exposure (Atkinson et al., 2003; Calfapietra et al., 2013). VOCs can be classified as the entire set of gas phase atmospheric organics excluding CO (Carbon Monoxide) and CO$_2$ (Seinfeld et al., 2012).

It was suggested by Guenther et al. (1995) that the total global BVOC emissions is approximately 1150 Tg C year$^{-1}$. Worldwide biogenic sources of VOCs significantly outweigh the anthropogenic, contributing approximately 75-90% of the total emissions (Guenther et al., 1995; Lamarque et al., 2010). It has been estimated that approximately half of BVOC emissions comprise of isoprene, and where the combination of; Methanol, Ethanol, Acetaldehyde, Acetone, $\alpha$-Pinene, $\beta$-Pinene, Ocimene, Limonene, Ethene, and Propene contribute a further 30% (Calfapietra et al., 2013; Guenther et al., 2012), and most of these compounds are emitted from vegetative parts, flowers and roots (Dudareva et al., 2004). The combination of both the large emission quantity and the atmospheric reactivity of BVOCs play a significant role in global atmospheric chemistry (Cai et al., 2006; Chameides et al., 1988; McKeen et al., 1991). The impact of BVOC emissions are more determined by their reactiveness as opposed to their quantities, for example, a species which produced a large concentration of relatively unreactive
O3 precursors will be less important than a species which emits a lower concentration of highly reactive O3 precursors (Seinfeld et al., 2012). Although it can be argued that both play a significant role in altering the atmospheric balance.

BVOC emissions are extremely important precursors to the development of tropospheric ozone (Chameides et al., 1988). O3 is a gas which typically responsible for 5-16% of global temperature rise since pre-industrial times and also contributes to an increase in radiative forcing, see Figure 1.1, it both absorbs and emits terrestrial Infra-Red (IR) radiation in the 8-10µm region and absorbs Ultra-Violet (UV) and visible radiation, it is considered one of the most potent greenhouse gases (Ainsworth et al., 2012; Fishman et al., 1979; Wittig et al., 2009). At ground level the impact of O3 can be quite alarming, having significant impacts on human and biogenic health. Understanding the importance of this gas both in terms of future climate change and its long-term health implications makes this topic a priority.

The aim of this report is to analyse the impact BVOCs have on the formation of tropospheric O3 and what role changing climatic conditions play in this relationship. Correlating the changes in vegetation emissions with the climatic conditions particularly temperature and windspeed and understanding the relationship they have with the formation of O3.

1.1 Tropospheric Ozone (O3)

Tropospheric Ozone is produced predominately though complex atmospheric photooxidation of VOCs in the presence of NOx. One of the known reasons for the production of O3 is through

![Figure 1.1: This is the estimated impact of global average atmospheric radiative forcing (RF) from 1750-2011. The uncertainties are 5-95% confidence range, indicated by dotted lines for RF and solid lines for ERF. Illustration from the IPCC's Fifth Assessment Report. (IPCC, 2014b).](image-url)
the atmospheric photolysis of NO\textsubscript{x}. The formation occurs when NO\textsubscript{2} and NO are in the presence of sunlight at wavelengths < 424 nm (Finlayson-Pitts et al., 1999).

It is considered a harmful air pollutant causing adverse impacts on human health and ecosystem health, crop yield and health (Verstraeten et al., 2015). Comparatively, Stratospheric Ozone is an important greenhouse gas with an estimated globally-averaged radiative forcing of 0.40 ± 0.20 Wm\textsuperscript{-2} (Cooper et al., 2014), insulating the Earth and providing extremely important protection from the Sun’s UV rays. Stratospheric ozone is also the primary source hydroxyl (OH) radicals in the troposphere determining their lifetime of trace gases affected by oxidation. Guicherit (1988) suggests that the production of O\textsubscript{3} in the boundary layer comes from three distinct sources:

- “The transport of O\textsubscript{3} from the stratosphere across the troposphere into the boundary layer during meteorological events which sporadically occur around the jetstream;”
- Influx from the free troposphere;
- Production in the boundary layer itself, especially during periods of photochemical air pollution.”

The importance of the boreal boundary layer and its interaction with the formation of ozone through the oxidation of VOCs must not be overlooked. This area plays a very important role in the overall ozone flux due to the impact BVOCs have with the formation and removal of ozone. Kurpius et al. (2003) suggest that this the short lifetime of the reactive terpenes have a significant role in the deposition of ozone in the ecosystem as part of the boundary layer and thus influencing the overall ozone flux.

It is widely accepted that O\textsubscript{3} is the principal product of chemical reactions in the Earth’s troposphere (Fishman et al., 1979; Seinfeld et al., 2012). The huge variety of organics in the troposphere makes it extremely difficult to fully understand the dynamics of gas-phase chemistry and the formation of O\textsubscript{3} (Finlayson-Pitts et al., 1999). Understanding the formation of O\textsubscript{3} requires detailed information regarding the presence of NO\textsubscript{x}.

The global budget of O\textsubscript{3} can be calculated using various modelling techniques combined with detailed field data to determine the production and loss. Although there is a vertical exchange between the stratosphere and the troposphere, there is little doubt that chemical production and loss of O\textsubscript{3} even in clean air, is the dominant and the most important process determining tropospheric budget (Bojkov, 1988).

1.2 Volatile Organic Compounds (VOCs)

VOCs are emitted from a huge variety of different sources, both natural and anthropogenic (de Gouw et al., 2007; Fall, 1999). The largest source of global VOC emissions comes from tropical and extra tropical forests (Guenther et al., 1995). There is also a significant amount of anthropogenic emissions, predominately vehicle exhausts, fuel evaporation, industrial processes, household products and solvents (Guo et al., 2017). The life time in the atmosphere
of VOCs can vary from minutes to hours depending on conditions such as oxidant concentration.

According to Seinfeld et al. (2012), the best way to describe the relationship between VOCs and NOₓ in the formation of O₃ is to understand it as a competition for the OH radical. It has been well established that the reaction rate of VOCs in the troposphere will vary due to their reactions with OH radicals, NOₓ, radicals, O₃ already in the atmosphere and the photolysis rates (Biasioli et al., 2011; Seinfeld et al., 2012). The VOC-O₃ transition is a function of three factors; the type of species atmospheric concentration, the VOCs reaction rate with OH radicals, and the quantity of O₃ that is produced during oxidation (Atkinson et al., 2003; Carter, 1994; Seinfeld et al., 2012).

1.2.1 Biogenic Hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>Boiling Point (°C)</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Pinene</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>136.238</td>
<td>156-157</td>
<td>C₁₀H₁₆</td>
</tr>
<tr>
<td>β-Pinene</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>136.238</td>
<td>165-167</td>
<td>C₁₀H₁₆</td>
</tr>
<tr>
<td>d-Limonene</td>
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<td>136.238</td>
<td>176-177</td>
<td>C₁₀H₁₆</td>
</tr>
</tbody>
</table>

*This is a simplified molecular structure of the bonds between carbon atoms. Vertices represent the carbon bonds.

The woodland and agricultural field measurements and the emission studies conducted have demonstrated the ubiquitous nature of BVOCs and the huge variety of compounds (Seinfeld et al., 2012). These compounds play a significant role in both urban and regional air chemistry. Biogenic hydrocarbons contribute significantly to the formation of tropospheric O₃ especially where vegetation is particularly dense, they will also generate aerosols from relatively non-volatile secondary oxidation (Chameides et al., 1988; Griffin et al., 1999; Hoffmann et al., 1997).
One of the major difficulties in understanding the atmospheric impacts of biogenic hydrocarbons is understanding their ability to produce organic aerosols. Went (1960) was one of the first to suggest the interaction and formation of particles in the atmosphere, and although significant time has passed since this paper was published, the understanding of these interactions has undoubtedly improved but is not yet fully characterized (Hoffmann et al., 1997).

The three compounds that will be the focus of this report shown in Table 1.1 are characterised by their olefinic double bond, as a result of these bonds the molecules tend to be highly reactive in the atmosphere leading to relatively short lifetimes, hours or days (Seinfeld et al., 2012).

1.3 Nitrogen Oxides (NO\textsubscript{x})

The sources of NO\textsubscript{x} can be both anthropogenic and from natural occurrences. The primary sources of anthropogenic are from high temperature combustion process, fuel combustion vehicles, energy production and energy use. Natural sources include the burning of biomass, the photochemical processes in oceans, as well as the production from lightning strikes (Seinfeld et al., 2012). Photochemical theories have shown that there is an extremely close relationship between the cycle of tropospheric O\textsubscript{3} and those of nitrogen oxides (Marenco, 1988). Thus making the atmospheric chemistry involving NO\textsubscript{x} one of the most important molecules in the atmosphere (Seinfeld et al., 2012).

The formation of O\textsubscript{3} is dependent on the processes associated with NO and NO\textsubscript{2} in the presence of sunlight at wavelengths < 424 nm,

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \] \hspace{1cm} (1)

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] \hspace{1cm} (2)

The M in the reactions represents any other molecule that will absorb the excess vibrational energy, stabilizing the formation of the O\textsubscript{3}. In the presence of NO there is also the opportunity for the O\textsubscript{3} to revert to its previous stage,

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \] \hspace{1cm} (3)

1.4 Hydroxyl Radicals (OH)

For many years the role of OH radicals and the contribution it plays in the formation of photochemical oxidants has been well understood (Harris et al., 1982). According to Finlayson-Pitts et al. (1999) a major source of OH radicals in remote environments is the production through photolysis of O\textsubscript{3}, followed by OH reaction with water vapour. If it were not for the regenerating properties of OH and its high reactivity with trace species, then the concentration in the troposphere would be far too low to have any significant impact (Seinfeld et al., 2012):
\[ O_3 + h\nu(\lambda \lesssim 336 \text{ nm}) \rightarrow O( ^1\text{D}) + O_2, \quad (4) \]

\[ O( ^1\text{D}) + H_2O \rightarrow 2\text{OH}, \quad (5) \]

\[ O( ^1\text{D}) \xrightarrow{\text{M}} O( ^3\text{P}). \quad (6) \]

The formation of nitrous acid (HONO), HONO concentrations peak during the night-time especially in urban environments. During daytime when sunlight is present, the HONO undergoes photodecomposition, leading to the formation of OH (Calvert et al., 1994):

\[ \text{HONO} + h\nu(\lambda < 400 \text{ nm}) \rightarrow \text{OH} + \text{NO}. \quad (7) \]

If HONO builds up overnight, then early morning sunshine will cause photodissociation leading to significant formation of OH, this happens before other sources become more dominant (O\(_3\) and CH\(_2\)O photolysis). This early morning interaction can potentially cause an increase in O\(_3\) formation (Calvert et al., 1994; Harris et al., 1982). Due to the photolytic nature of OH formation, it is a major oxidant primary during daylight hours (Finlayson-Pitts et al., 1999).

The concentration of oxidizing free radicals and their impact on O\(_3\) formation will vary depending on the concentration of NO\(_x\). The solar UV intensity, water vapor, location, season and time of day will all play impacts on NO\(_x\) concentration. If OH radicals are present with NO\(_x\) then it will lead to the production of O\(_3\) the absence of NO\(_x\) can lead to the destruction of O\(_3\) (Fehsenfeld et al., 1988).

### 1.5 Secondary Organic Aerosols (SOA)

It has been widely acknowledged that the study of SOAs and the associated particulate matter formation and chemical transformations are some of the most uncertain topics in atmospheric chemistry, this is due to the complexity associated with the oxidation processes and the huge variety of chemical mechanisms in the atmosphere. Hallquist et al. (2009) suggest that between 10,000 and 100,000 different organic compounds have been measured in the atmosphere. Better understandings have come from recent developments in chemical modelling and the underlying SOA formations (Kroll et al., 2008). Estimating global SOA production has been assessed using two different approaches. There is the more traditional bottom-up approach as well as the alternative top-down approach. The traditional approach is an estimate where inferred or biogenic and/or anthropogenic VOC precursor fluxes are combined into the global model (Hallquist et al., 2009). Within the laboratory the data from oxidation leading to SOA formation will be used to obtain a total global organic aerosol field (Chung et al., 2002). Goldstein et al. (2007) suggest that the alternative top-down inverse approach estimate, inferring the total SOA production rate through constraining the eventual fate of the known precursor emissions. And it is suggested that these two approaches will give different results. Bottom up estimates give SOA fluxes of 12-70 Tg/yr corresponding to the fluxes of biogenic secondary organic carbon (BSOC) of 9-50 Tg/yr which gives a ratio of 1.4 which is assumed in many different modelling studies (Kanakidou et al., 2005). Comparatively, the top-down estimates are a few orders of magnitude larger than the bottom up, between 140-910 TgC/yr.
The formation of SOAs comes from the condensation of low vapor pressure products of the oxidation of organic gases (Kroll et al., 2008; Pandis et al., 1992). Turpin et al. (2000) define SOAs “Low-volatility products from the gas-phase oxidation of reactive organic gases condense or absorb onto particle surfaces or absorb into pre-existing particulate matter resulting in the addition of material to atmospheric particles. On top of this, the less-volatile organics may also contribute to the formation of particulate matter due to the chemical reactions of VOC emitted in the ‘condensed phase’ (Robinson et al., 2007), these reactions are initiated by the reactions with various radicals and O3.
2. Experimental Procedure and Equipment

2.1 Location

Skogaryd Research Catchment (SRC) is a controlled rural environment established in 2013 by University of Gothenburg and the Swedish Research Council. The catchment itself is located 58°23’N, 12°09’E, hemiboreal, approximately 100km north of Gothenburg, Sweden (Figure A5 and A6). The site is affiliated with the Swedish Infrastructure for Ecosystem Science (SITES). SITES is a national coordinated infrastructure for terrestrial and limnological field research, consisting of nine research stations covering the different landscapes and climatic regions in Sweden. The experiments will be conducted at site ‘F’, which is identified as ‘Forest on Mineral Soil’ where the primary vegetation type is Norwegian Spruce (Figure A6).

2.2 Sampling Methods – Set Up and Procedure

The ozone sampling has been split into three distinct climate zones; late autumn (period 1), late winter (period 2) and mid spring (period 3). Initial sampling began on the 15th November 2018, this continued up until the 7th December 2018. Instrument complications meant that sampling was paused up until the 27th February 2019. From this point onwards, ozone data has continued to be sampled through periods 2 and 3 until the 26th April 2019.

The GC sampling did not follow the same period as the ozone sampling. Subsequently period 2 and 3 have been combined to improve data analysis and addressing trends. Initially GC data sampling began on the 15th November 2018 until the 20th November 2018. After difficulties with machinery the data collection was paused and recommenced on the 15th April 2019 until the 26th April 2019.

<table>
<thead>
<tr>
<th>Period</th>
<th>Dates</th>
<th>Avg. Temp. (°C)</th>
<th>Avg. Windspeed (m/s)</th>
<th>Avg. Net Solar Radiation (W/m²)</th>
</tr>
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<td>2.19</td>
<td>(-14.77)</td>
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<tr>
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<td>27/02/19 – 29/03/19</td>
<td>3.11</td>
<td>2.58</td>
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<tr>
<td>3</td>
<td>30/03/19 – 26/04/19</td>
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<table>
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<td>15/11/18 – 20/11/18</td>
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<td>2.35</td>
<td>-8.26</td>
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<td>2</td>
<td>15/04/19 – 26/04/19</td>
<td>10.98</td>
<td>2.40</td>
<td>111.16</td>
</tr>
</tbody>
</table>

These dates were selected partly due to the limitations with the instruments but also because there are distinct climatic variations. The variations are predominately differences in temperature, average solar radiation linked to seasonal changes. Table 2.1 shows the differences in climatic averages through periods 1, 2 and 3. There are three clearly defined periods, with an
increase of approximately 2°C between P1 and P2 and almost 4°C increase between P2 and P3. There is also a notable increase in the amount of net SR from P1 to P3. Using these three periods it will be possible to assess easier the impact climate has on the production of ozone.

The sample inlet is situated within the Norwegian Spruce canopy, at a height of 16m above the ground. The sampling line is attached to the measurement tower next to the cabin (Figure A8 and A9). The line runs for 33m made from Teflon tubing, which has a diameter of ¾ inch. To accommodate the fittings for the instruments the ¾ inch tubing was converted down to ¼ inch. All tubing within the experiment has been decontaminated using a nitrogen flow before the circuit was constructed.

To ensure that there was minimal sample contamination the tubing was back-flushed with nitrogen for 48 hours prior to full experiment commencement. The inlet and tower tubing are heated meaning moisture doesn’t collect within the sample inlet preventing sample contamination. A continuous flowrate within the system generated by a pump is between 10-20 L/min. The layout of the experiment (see Figure A2) ensures even distribution of the air samples between the ozone monitor and the autosampler.

It should however be mentioned that the climate measurements although in the same location were taken at different heights, ozone and VOCs were collected at 16m whereas the windspeed, net radiation and temperature were measured above the tree canopy at 33m where consistent measurements can be taken. Due to icing and undesirable conditions the windspeed data experienced times where sampling could not take place thus data is missing.

2.3 Gas Chromatography Flame Ionization Detector (GC FID)

During the sampling phases compound were detected using a DANI Master GC, with an FID and a split/splitless detector. The GC oven provides the housing and the heating for the analytical columns, this is where the compounds will be separated through incremental heating. This is achieved though air circulation and oven insulation which guarantees a homogenous, stable and accurate heating, providing precise analytical performance. The GC has the capability to cool and heat the oven extremely quickly which allows almost real time analysis. The temperature range for the oven operates from below ambient and up to a maximum temperature of 500°C, allowing a wide variety of compound separation. The maximum temperature used during sampling was 215°C, well within the GC’s capability. Selecting the correct temperatures, and the time increments is essential to separate the desired compounds and will help to establish their retention times, this will be discussed further in section 2.3.1. Before sampling commenced, the GC oven was heated to 300°C for a period of 30 minutes, this ensured that any unwanted residue has been removed and results are not impacted. Typically using established measurement techniques for BVOCs there must be a trade-off between frequency and speciation. Using conventional GC-FID methods has a semi limited sample capacity, only offering on average a sample every 10-30 minutes (Jones et al., 2014).

The GC used a SL/IN 86/2 split/splitless injector. To obtain optimal results, the sample must be volatized as quickly as possible, this was done through setting the injector temperature 20-30°C above the maximum oven temperature set for analysis. The ideal temperature is the minimum temperature at which complete vaporization of the sample is obtained without giving
signs of thermal compound degradation. To allow the GC to work correctly the correct carrier gas and column dimensions must be input. The use of a split injection allows analysis of the main components where the sample is injected into a hot injector. The vapours are then divided into two different parts: is carried into the column using the carrier gas while the other is discharged out the GC through the split line. As recommended, this experiment used an automatic sampler which increased the sample repeatability compared with that of a manual injection.

The Purge Vent and the Split Vent flow rates are maintained though The Injector Pressure Regulator and the Injector Pressure Sensor. To ensure they are working correctly before commencing sampling the exhaust gases were measured, correct operating flow rates should be stable at 5 and 10ml/min depending on the vents at the rear of the GC, this is crucial to ensure that the injected sample does not pass through the column before data collection has taken place. Before sampling began the seal around the injector was checked to ensure it had been correctly maintained, because after extend use as there may be the occurrence of cracks leading to leakage which will impact the sample. To ensure the sample had free progress from the injector to the column it was checked to make sure there were no blockages present.

The FID 86.10 is a micro flame produced at the nozzle outlet when the Hydrogen flow contacts the air flow. The detector works using a normal condition base line where the pure carrier gas will ironize molecules once in contact with the flame, this then produced an electric charge, this charge generated a weak and constant current, the base line. When the organic compounds entered the flame from the column through combustion, the number of charges produced increased and subsequently the ionizing current increased. The signal was observed as an output which was observed and measured through fluctuations in mV, the change is mV is proportional to the number of charges produced. The variation of the signal in time, caused by the passage of an organic compound though the flame, determined the registration of a peak. The auto ignition had been set to ‘on, so that when the detector temperature reached 200°C then the system will start the auto ignition sequence.

To avoid condensation of compound in the line the temperature of the detector was set at a value which was higher than the maximum oven temperature. Also, to avoid any water condensation the temperature was set to over 100°C ensuring water vaporisation.

2.3.1 GC FID Method Adaptation

Before the equipment was taken into the field, methods were set within laboratory conditions to determine the GC’s optimal initial temperature, the ramping speed and the final temperature within the method to measure α-Pinene, β-Pinene and Limonene. During this process it is also important to set the flow rates for the gases within the detector. This was predominately developed using a few different testing conditions whilst running the GC, with guidance from the DANI Master GC Operating Manual rev. 3.2 to determine the best conditions.

Table 2.3 shows the method applied to the field data sampling. The GC will be held at the initial temperature of 40°C until the auto sampler has collected the sample. The autosampler will then run its method before injection to the GC. Once the sample was ready it was automatically injected into the GC and the oven methodology commenced. Once injected the temperature increased from 40°C up to 80°C over a period of 2 minutes. Once reaching 80°C the temperature
was held for 1 minute from which the temperature then be increased up to 170°C at a rate of 20°C/min. The temperature was then held at 170°C for 1 minute, then increased up to 215°C at a rate of 30°C/min where the temperature was again held for another 2.5 minutes in order to remove any lingering compounds preventing contamination of future samples. After the method was complete, the GC rapidly cooled back down to its initial temperature of 40°C where it sat dormant until the autosampler injection from which the process repeated.

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Upper Temperature (°C)</th>
<th>Hold Time (min)</th>
<th>Temperature Ramp Rate (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>40</td>
<td>0.00</td>
<td>20.0</td>
</tr>
<tr>
<td>Ramp 1</td>
<td>80</td>
<td>1.00</td>
<td>20.0</td>
</tr>
<tr>
<td>Ramp 2</td>
<td>170</td>
<td>1.00</td>
<td>30.0</td>
</tr>
<tr>
<td>Ramp 3</td>
<td>215</td>
<td>2.50</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2.3 GC Oven Methodology for in Field Data Collection

This method was developed within laboratory conditions to be a successful at separating the desired compounds. This contains a sustained period of high temperature at the end of the cycle to limit the contamination of lingering compounds in preparation for the purusing sample cycle.

Table 2.3 shows the flow rates and gases being used for the detector within the GC. Helium with a purity of >99.9996% has been selected as the carrier/auxiliary gas and set at a rate of 25ml/min. It has been suggested that the higher the purity the better the signal. All gases were supplied from a gas cylinder through a regulator which allowed constant pressure application. The only exception was the N₂ which was supplied from a nitrogen generator.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow Rates (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aux (He)</td>
<td>25</td>
</tr>
<tr>
<td>H₂</td>
<td>40</td>
</tr>
<tr>
<td>Air</td>
<td>280</td>
</tr>
<tr>
<td>N₂</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2.4 Detector Flow Rates for in Field Data Collection

2.3.2 GC FID Calibration

Initially it was important to establish a baseline voltage for the detector, this was done by running the GC for a few hours at varying temperatures, predominately 200°C or greater. This process eliminated noise from the detector through heating out any lingering samples within the column. Figure A3 shows one of the initial chromatographs produced whilst testing the GC. The figure suggests that the GC was partially contaminated, containing dirt, dust and other alien compounds. The small increase in gradient within the chromatograph might suggest column bleeding, which, if there is no improvement may need to be replaced for future analysis. During testing the baseline was established to be approximately 4.6mV which is within the expected limits.

Once the baseline was established calibration of compounds began. This was done through exposing the sampling inlet of the GC to the desired compounds for 10 minutes individually before running a cycle, then once individual values were established all compounds were
exposed simultaneously (Figure A4). Figure A4 shows the chromatograph of all three compounds; α-Pinene, β-Pinene and Limonene. There was a clear separation between the peaks, indicating that the compounds varying retention time and the temperatures they are reactive was suitable as part of the GC method. Having established the retention times of the compounds this was used after infield sampling as a guide to whether the desired compounds are present within the sample. It is important to note that the GC method was not altered between lab testing and field measurements.

2.4 CDS ACEM 9350 Autosampler

Sampling and sample preparation were instigated automatically using the autosampler functions. The capacity to sample near real time was possible due to the duel tube. Selecting the continuous sampling setting allowed continuous sampling onto one of the tubes, while the other tube was being injected and analysed. It was important to observe that the optimum time and temperature settings varied according to the sample being analysed, the collection tubes and focusing trap materials, and the GC column. Temperatures in the Valve Compartment, sampling line and the Transfer Line were set high enough to prevent any sample condensation onto the transport tubing or fittings. It is important to note that after a period of testing, sample tubes may need to be renewed in the future order to avoid sample contamination.

2.4.1 CDS ACEM 9350 Autosampler Method Adaptation

Collection of sample matter was at a flow rate of between 10-20L/min. The sample was collected in the autosampler tubes, where it was dried for 2 minutes at a temperature of 80°C. In preparation for injection the sample was then be heated to 300°C in the trap and then sent through the transfer line which was preheated to 300°C and finally injected into the GC. The ‘GC time’ was set to 18 minutes, which allowed the GC to run its sampling method and cool in preparation for the next sample injection.

Table 2.5 Autosampler Methodology for in Field Data Collection

<table>
<thead>
<tr>
<th>Sampling Stage</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Tube Dry</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>Tube Heat</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>Focusing Trap</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Trap Heat</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>Valve Oven</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>Transfer Line</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>GC Time</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*This methodology has been determined in reference with the GC oven temperatures as well as the CDS Analytical Operation Manual.*
2.5 Ambient Ozone Monitor

Collecting ozone data was done using the 2B Technologies Ozone Monitor Model 202. Data collection was provided using the associated 2B Technologies Data computer software. The machine has a built-in air pump which will provide air to either the absorption cell or through the ozone scrubber and then onto the absorption cell at a flow rate of approximately 1 L/min. The monitor is capable of measuring between 3 parts-per-billion by volume (ppbv), up to 250 parts-per-million (ppmv). Sampling rates were recorded in ppb with a sample resolution of one recording every 10 seconds. The ozone monitor continued sampling until the experiment was finished.

2.6 Clarity Software

The Data Apex Clarity software was set up to work in conjunction with the GC-FID. All data collection, data reports, method adaption, calibration, chromatograph analysis and GC-FID temperatures and flowrates, were set using the Clarity software. This also allowed remote access through Team Viewer were any problems with the method could be adapted without physically visiting the sampling site.

2.7 Literature Review

To develop a more comprehensive and scientific understanding of the processes associated with the formation of O₃ in the troposphere, BVOCs and the impacting climactic forces, various sources were utilised, predominately online scientific papers, articles and journals from databases including; Google Scholar¹, Web of Science², Gothenburg University Library³ (Appendix B). There was also extensive use of Finlayson-Pitts et al. (1999) and Seinfeld et al. (2012) books, due to the volume of in depth information relating to atmospheric chemistry and the chemical processes associated.

2.8 Data Analysis

2.8.1 Data Pre-Processing

Due to the large amount of data which has been collected over a large time period the data first had to be organised to correctly process before any statistical analysis could be performed. In efforts make the data available, and to meet the requirements for statistical analysis and graph formation a form of pre-processing took place, this stage removed some of the problems which could have been faced (Famili et al., 1997).

The organisation initially involved transferring all data into an excel format where it can be easily manipulated into appropriate manageable results. When comparing the data, it was essential that the sampling time matched. E.g. the sampling resolution for ozone collection was one sample every 10 seconds, however comparing this to the climate data, the sampling
resolution was taken every 30 minutes. To combat this divergent set of results an average ozone value every 30 minutes, corresponding with the climate data was calculated.

Comparing the ozone and climate data against the GC data was more complicated. As the sampling resolution for all three sets of data (ozone, GC compounds and climate) was different, methods had to be employed to make the data comparable. GC sampling takes place every 37th minutes, so to satisfy the ozone data which has a sample every 10 seconds the data was collected and averaged every 222nd value. Climate data was a little different since the sampling was taken every 30 minutes. In this instance the closest value would be taken to whichever time corresponded to the 37th minute of the GC cycle which due to the sampling of the climate data would give a maximum error of ±14 minutes.

Primary ozone data collection was taken in ppb, however the data provided by IVL was measured in µg/m³. To keep the data comparable, it was important to convert ppb into µg/m³. Although the collection was taken outside the cabin, the ozone monitor was taking measurements within a cabin where the temperature was constant at approximately 25°C with at a pressure of 1 atmosphere, the following equation was used:

\[
\text{Concentration (µg/m³)} = 0.0409 \times \text{concentration (ppb)} \times \text{molecular weight}
\]

The molecular weight of O₃ is 48g/mol. Subsequently all corresponding ozone data was converted into µg/m³ (Boguski, 2006).

2.8.2 Statistical Analysis

To make a comparison between two sets of values, in this case the various compound concentrations a statistical t-test and a R² has been employed. This test will allow a comparison of the mean values of the two data sets (Limentani et al., 2005). The value of the R² analysis will show how close two data sets are to the fitted regression line, the values will be between 0 and 1 where 1 shows that the model explains all variability, and 0 the model explains none of the variability. The t-test will determine the statistical significance of the two data sets. This report will examine a two tailed paired t test to compare the data sets.

2.8.3 Chromatograph Interpretation

At the end of every GC method cycle a two-dimensional chromatograph was produced (Figure A4) and can be analysed to assess the compound retention times and the compound concentrations. Compound concentrations are measured using the y-axis, whereas the x-axis depicts time elapsed from the injection point. Using Clarity software, the compound peaks were automatically detected noting the retention time and the concentration measured in mV. Using this information, it is possible to extrapolate the data to determine the most frequent peaks and whether there was any connection between the peaks and the retention time. Although retention times varied marginally, anything within ±0.002s of corresponding peaks were considered to be the same compound.
2.9 Collaborating Ozone Data

Supplementary ozone data has been provided by the Swedish Environmental Research Institute (IVL) with funding from the Swedish Environmental Protection Agency (EPA) from the locations: Råö, Ytterby and Östad. It is important to note that the data provided has not been verified. The data has been provided in μg/m³ at averaged hourly intervals.
3. Results

This section will discuss and analyse the results of both GC data sampling and ozone sampling. Initially the results will examine the changes in ozone in relation to; temperature, windspeed and average solar radiation. The results concerning ozone will be split into three periods, as discussed in Table 2.1. The second part of the results will discuss data provided by IVL, using their data a comparison can be made to reassure the data collected is accurate and can be verified. Lastly an analysis between ozone data and GC compound data, this will allow investigation into the varying types of compound and their relationship with ozone formation as well as climatic influences, it will also include an assessment to analyse the source of the compounds.

3.1 Climatic Conditions

Each period is made up of approximately the same number of data points which will allow a solid comparative analysis. Table 3.1 shows the average temperature, net Solar Radiation SR and the changes in windspeed as well as the standard deviation for ozone. Period 1 is averaged as the coldest period with the lowest average net SR, lowest ozone concentrations and the lowest wind speed. However, the variation in windspeed is not particularly high, only fluctuating by 0.4m/s from the averages between the three periods. Period 1 (P1) also contains the lowest maximum and minimum ozone values, with a standard deviation of 18. P1 was selected to represent late autumnal or early winter climates, pre-winter solstice, where in the northern hemisphere daylight hours were decreasing.

<table>
<thead>
<tr>
<th>Period</th>
<th>Avg. Ozone (µg/m³)</th>
<th>S/D Ozone</th>
<th>Avg. Temp. (°C)</th>
<th>Avg. Net SR (W/m²)</th>
<th>Avg. Windspeed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41</td>
<td>18</td>
<td>1.3</td>
<td>(-15)</td>
<td>2.2</td>
</tr>
<tr>
<td>Max</td>
<td>79</td>
<td></td>
<td></td>
<td>73</td>
<td>5.6</td>
</tr>
<tr>
<td>Min</td>
<td>2</td>
<td></td>
<td>-10.5</td>
<td>-90</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>58</td>
<td>15</td>
<td>3.1</td>
<td>38</td>
<td>2.6</td>
</tr>
<tr>
<td>Max</td>
<td>87</td>
<td></td>
<td>14.1</td>
<td>466</td>
<td>7</td>
</tr>
<tr>
<td>Min</td>
<td>14</td>
<td></td>
<td>-7.2</td>
<td>-98</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>87</td>
<td>24</td>
<td>7.0</td>
<td>98</td>
<td>2.5</td>
</tr>
<tr>
<td>Max</td>
<td>155</td>
<td></td>
<td>22</td>
<td>553</td>
<td>6.5</td>
</tr>
<tr>
<td>Min</td>
<td>21</td>
<td></td>
<td>-5</td>
<td>-106</td>
<td></td>
</tr>
</tbody>
</table>

Period 2 (P2) showed an increase in the average ozone compared with P1, increasing by 17 µg/m³, average temperature also increases but only by 2.8°C with the maximum and minimum temperatures not changing significantly from P1. The increase in SR was the most notable change from P1 to P2, with an average increase of 53 W/m² and a maximum increase of 393.2 W/m². P2 was selected to represent late winter or early spring conditions, post winter solstice, where in the northern hemisphere daylight hours are increasing.

Period 3 (P3) has the highest values for all climatic conditions except windspeed. The average ozone levels have increase by 29 µg/m³ compared with that of P2, also maximum ozone is
almost double both P1 and P2. The ozone standard deviation has increased to 23.8 compared with 18 and 15 for P1 and P2 respectively. Although the temperature on occasions has dropped below 0°C the average temperature has increased to 7°C with a maximum for the period of 22°C. Although average temperature has increased by 3.9°C compared with P2, the solar radiation has increased more than it compared with P1 and P2. P3 showed an increase of 86.4 W/m². P3 was selected to represent mid spring conditions, generally warming with longer daylight hours.

3.2 Ozone Concentration

Figure 3.1 shows the concentration of ozone with relation to fluctuations in temperatures for all Periods 1-3. The data suggests that there is a positive strong correlation for P3, the warmest of the periods. P3 has an $R^2$ value of 0.6781, which would suggest that an increase in temperature has a direct impact on the formation of ozone, especially for warmer periods. This is supported by the lower $R^2$ values for both P1 and P2, 0.0171 and 0.1485 respectively. The higher the temperature the higher the concentration of ozone, within the temperature range of approximately -12 to 23°C. The low $R^2$ values in P1 and P2 suggest that during winter time there are more important factors determining the concentration of ozone than temperature.

Figure 3.1 also suggests that at warmer temperatures smaller increases in temperature will have a bigger impact on the concentration of ozone compared to that of the same increases in temperature at lower temperatures. This can be shown through the gradients of the lines of best fit, where the shallow P1 best fit line only has a gradient of 0.62 compared with P3 gradient of 3.32 which is significantly higher. P2 has a gradient of 1.72 which is predictably approximately half way between P1 and P3.

Figure 3.2 shows the correlation between windspeed and the concentration of ozone. Like Figure 3.1, it shows a distinct difference between all three periods. The figure suggests that overall an increase in windspeed will lead to a slight increase in ozone concentration. However, P1, P2 and P3 have a relatively low $R^2$ value (0.21, 0.32 and 0.18 respectively), this could suggest that the relationship between windspeed and ozone concentration is limited, it plays a
role but not a significant one. It is likely that ozone concentration and windspeed are influenced by other factors, including diurnal changes in temperature and SR.

![Figure 3.2](image)

**Figure 3.2:** The collective ozone data from Periods 1-3 as a function against windspeed variations.

Figure 3.3 shows the relationship between net SR and ozone concentration. The plot initially looks as though there is little structure to the scatter, the pattern suggests that there is little correlation. There is some uncertainty with the net SR given that the data has negative values which may influence the result of the statistical testing. This is reflected in the low $R^2$ values for P1, P2 and P3 which are 0.05, 0.17 and 0.13 respectively. It also seems that the incline of the best fit lines are relatively low, this suggests that changes in net SR will not impact the ozone concentration. However, it has been well scientifically established that SR does play a significant role in ozone formation, these large scatter points which appear to become more scattered from P1 – P3 could be a resulting impact of nocturnal values skewing the data.

![Figure 3.3](image)

**Figure 3.3:** The collective data for Periods 1-3 as a function against net SR variations.

The formation of scatter in Figure 3.3 could suggest that the distribution could be influenced by other climatic variables. The obvious distinction between P1 which has a low distribution of values, and P2 and P3 which is significantly more scattered. However, scientific research would suggest that SR does play a large role in the formation of ozone, but it is not reflected in the data.
Figure 3.4 shows the diurnal variation of ozone concentration for all period. The graph shows a clear distinction between P1, P2 and P3, where each progressive period has a consistently higher level of ozone concentration. All periods appear to follow a similar trend, gradually building at approximately 7:00 and peaking toward the early afternoon. P1 has a relatively stable concentration throughout the day beginning and ending at approximately 40µg/m³. During the middle period of the day the ozone concentration increases to approximately 47µg/m³.

P2 shows a very similar pattern to P1, however, the beginning value is 54µg/m³ and initially the concentration decreases marginally to 49µg/m³ at 6:00, from there the concentration increases until peaking at 15:00 with a value of 67µg/m³. At 15:00 there is a gradual decrease slow reducing in concentration until 23:00 where the value is 57µg/m³.

P3 shows the most dramatic fluctuations in ozone concentration, it also claims the highest values. Initially the concentration is 83µg/m³ and similarly to P2 the concentration initially decreases down to a value of 68µg/m³. From the 6:00 minimum the concentration sharply increases up to 102µg/m³ from which the concentration plateau’s until approximately 19:00 after which the values begin to gradually decrease toward 23:00.

Figure 3.5 is an example of the fluctuation of climate and ozone concentration through time. It compares the two different variables against one another on separate axis making it easier to see directly the influence of one variable has on the other. The figure compares temperature, windspeed and net SR. It is evident from the figure that there is a clear relationship with all climactic elements. This is consistent throughout P1 (Figure A12) and P2 (Figure A13), although the relationship is not as strong as it is in P3. Figure 3.5 shows that there is a very strong relationship between temperature and ozone concentration, showing that with an almost instantaneous increase in temperature will cause an increase in ozone concentration. It should also be noted that the variation in temperature can most likely be attributed to diurnal variations, where peak temperature and ozone concentration can be attributed to early afternoon. Figures A12 and A13 do follow a similar pattern although this is less evident in P1, where the
temperatures are colder and overall concentrations of ozone are much lower than P3. These figures would suggest that an increase in temperature will cause an increase in overall ozone concentration.

Windspeed follows a very similar pattern to temperature, Figure 3.5 suggests that an increase in windspeed will increase the levels of ozone concentration. The fluctuations in windspeed are very similar to those of the diurnal variation changes of temperature. It can be observed that the peak in windspeed do not directly correspond with the peaks in ozone concentration, there is a small delay between peaks. This suggests that it takes a small period for the ozone concentration to react to an increase or decrease in windspeed. Although ozone concentrations are lower, a similar pattern can be observed in Figures A12 and A13. It is important to consider the overall average windspeed throughout the sampling periods was relatively low, it could potentially be the case with increasing windspeed ozone concentration may decrease. I can be observed that the peaks in windspeed have caused a decline in the concentration of ozone. Unfortunately, the data does not provide a period of high windspeed, so it is difficult to establish the correlation high windspeed over an extended period would have on the concentration of ozone.

The net SR shown in Figure 3.5 shows a very strong correlation between peaking values and the concentration of ozone. The SR peaks are a result of an increase in daylight hours, this can be compared to P1 and P2 (Figure A12 and A13) where the daylight hours were fewer thus the net SR was lower. However, a similar resultant can be seen in the case of ozone concentrations. There is a small delay between peaking SR and maximum ozone concentration, suggesting that the impact SR has on ozone concentration is time dependant. As expected the net SR is increasing as the date moves further from the winter solstice and toward the summer solstice, the overall peak height is increasing. It can be argued that the same trend is followed with ozone concentration, as daylight hours increase, so does the concentration. This suggests that an increase in SR will lead to higher concentrations of ozone due to the associated photochemical effects. Although not evaluated in this report, wind direction can also play a large role in ozone concentrations due to upwind influences.

3.3 IVL Ozone Data

The data provided by IVL has been used as supplement to the primary data collected from Skogaryd. It was important to understand the overall patterns of ozone concentrations for areas near to Skogaryd. Having more than one source of data from different locations will allow a comparison between the data. In this instance it is provided using three routinely monitored sites. It is important to note that the IVL data has not been verified.

Figure 3.6 is a scatter plot representing P3 ozone concentration in all three IVL sites as well as the primary data from Skogaryd. The plot suggests a strong positive correlation between all data, which is represented by a high R² value. The lowest R² value relates to the relationship between Råö and Skogaryd (0.38) which can be explained due to the distance between the two locations.
Figure 3.5: Ozone concentration compared with climatic variations over time for Period 3. The graphs represent temperature (top, orange), windspeed (middle, orange) and net SR (bottom, orange) compared with ozone concentration. Ozone concentration is represented in blue for all graphs.
The highest $R^2$ value is between Ytterby and Östad (0.83), which is understandable given both sites are in relatively close proximity to one another and are managed by IVL and financed by the Swedish EPA. Figures A10 and A11 both have very similar $R^2$ values suggesting support to the data collected at Skogaryd.

Figure 3.7 highlights the important relationship diurnal temperature changes have on the formation of ozone. Not only in Skogaryd but also the other sites. The behaviour of the ozone concentration is similar to the patterns displayed in Figure 3.4. At the beginning of the day there is an initial decrease in ozone concentration from 00:00 until approximately 06:00. This is progressively more exaggerated from P1 to P3 as the impact of temperature becomes more prominent.

![Figure 3.6: The comparison of Period 3 ozone concentration data from Skogaryd and the three Swedish EPA data sites (Ytterby, Östad and Råä). Data provided by IVL.](image)

![Figure 3.7: Diurnal variation of Period 3 ozone concentration from Skogaryd, the three Swedish EPA data sites (Ytterby, Östad and Råä) and temperature measured at Skogaryd. Data provided by IVL.](image)
From 00:00 the temperature decreased from approximately 5°C down to 2°C until the minimum temperature reached at approximately 7:00. The minimum ozone concentration for all four sites is approximately the same time. From 7:00 the temperature begins to rise in an almost linear fashion until the maximum of approximately 12°C is reached at 17:00.

However, it appears that the maximum ozone concentration peaks at approximately 14:00 where there is a small plateau and then begins to drop consistently with the drop-in temperature. Periods 1 and 2 (Figure A14 and A15) show a similar pattern although not as exaggerated as Figure 3.7. Temperatures and ozone concentrations are consistently lower during these periods however peak ozone concentration correlates with the peak temperature. P1 and P2 also suggest a smaller variation in diurnal activity, increases in temperature and ozone concentration are proportionally lower than values in Figure 3.7.

3.4 GC and Compound Data

3.4.1 Period 1

Figure A17 shows a typical example of the formation of various compounds found in a gas chromatograph. There is a clear distinction between peaks and the retention time is easily available at the top of the peaks. Figure A17 shows the variety of compounds detected during sampling.

An analysis has been performed on compound relationship with ozone concentration, temperature and the interactions between compounds. From this information it is possible to determine if the compounds were from anthropogenic or biogenic emissions and the impact the compound has on the formation of ozone. To establish correlations between compounds a $R^2$ and a two-tailed paired t-test were performed in a matrix as shown in Tables 3.2 and 3.3. It is also important to remember that the collection periods have changed compared with ozone collection data (see Table 2.2).

Alterations had to be made to the data due to sampling failures. It became evident that one of the autosampler sampling tubes was not working properly therefore all data presented from that tube were omitted meaning that the sampling resolution has been doubled.

Table 3.2 shows the comparison between the main 6 detected compounds found consistently during sampling Period 1. Initially the $R^2$ and T tests were performed to establish the strength of the correlation between the two compounds and the capacity they have influencing one another. The highlighted numbers represent values which are greater than 0.6 and less than 0.01 for the $R^2$ and P values respectively.

The highlighted values suggest that there is a strong correlation between the peaks. Table 3.2 shows that there is an $R^2$ value higher than 0.6 between; Peak 1 and Peak 5, Peak 2 and Peak 4, Peak 4 and Peak 5 and Peak 5 and Peak 6. There is also a clear detachment from Peak 3 and all other compounds, the $R^2$ results show there is almost no correlation, the values are less than 0.1 for; Peak 3 and 4, Peak 3 and 5 and only just over 0.2 for Peak 3 and 6. These high $R^2$ values suggest that there is a correlation between the processes and compound sources associated with the formation of each peak.
Table 3.2 also shows P values for a comparison of the same compound peaks. To establish whether the p value passes the null hypothesis, which is that there is a relationship between peaks, the significance level was set at 0.01, values less than the significance level are highlighted in red. These values show that there is a significance between the two peaks and the null hypothesis is true. Two values (Peak 3 and 4 and Peak 4 and 5) show that the null hypothesis is not true and that the relationships between the two compounds is not significant.

Table 3.2 A correlation matrix of all 6 major detected peaks found when analysing the gas chromatographs showing both the R² and p values for Period 1. Highlighted and coloured numbers are those with a correlation above 0.6 for R² value and less than 0.01 when comparing P values from the T-Test.

<table>
<thead>
<tr>
<th>R-Squared</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Peak 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.17</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.14</td>
<td>0.09</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 4</td>
<td>0.24</td>
<td>0.80</td>
<td>0.09</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>0.71</td>
<td>0.48</td>
<td>0.09</td>
<td>0.64</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Peak 6</td>
<td>0.46</td>
<td>0.35</td>
<td>0.21</td>
<td>0.40</td>
<td>0.66</td>
<td>X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T-Test</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Peak 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 2</td>
<td>4.3E-13</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 3</td>
<td>3.6E-18</td>
<td>4.0E-07</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 4</td>
<td>1.9E-17</td>
<td>1.3E-18</td>
<td>0.76</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>1.9E-10</td>
<td>1.0E-09</td>
<td>0.009</td>
<td>0.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Peak 6</td>
<td>5.2E-27</td>
<td>2.8E-33</td>
<td>6.0E-11</td>
<td>1.4E-20</td>
<td>6.4E-08</td>
<td>X</td>
</tr>
</tbody>
</table>

Figure 3.8 is a visual representation of the relationship between Peak 3, temperature and ozone concentrations over P1. Peak 3 has been highlighted as it does not appear to follow ozone formation at all over time. As Table 3.2 suggests, there is a detachment in trend between the concentration of Peak 3’s compound and the concentration of ozone. Temperature has been included in the figure to establish if it impacts the concentration of either ozone or the compound being measured. In this case temperature does not appear to play any significant role in compound or ozone concentration.
Figure 3.9 shows a collection of 3 different compounds with varying retention times, ozone concentration and temperature through P1 sampling dates. The figure clearly shows that all three compounds follow a similar trend to the ozone concentration suggesting that the compounds are related to ozone formation. Figure 3.9 does suggest that increases in ozone concentration precede the increases in compound concentration, however when values are decreasing both ozone and compound concentration follow a similar trend.

Figure 3.9: Compound measurements from Period 1, ozone concentration and temperature changes. Peaks 4, 5 and 6 have been highlighted due to the similarity of the trend when compared with ozone concentration. The respective retention times are approximately 6.35, 10.00 and 12.24 minutes after injection. Temperature is assigned to the secondary axis.

3.4.2 Period 2

Retention time analysis suggests that there are no overlapping compounds between P1 and P2 of the GC data sampling. There were limitations whilst sampling that not all peaks appeared in the analysed chromatographs, therefore Figures 3.10 and 3.11 only contain data from Peaks 8 and 10. There was not enough data to establish any a correlation between ozone concentration and temperature. This uncertainty in data quantity is reflected in Table 3.3 which is a correlation matrix between the 5 peaks detected in P2.

Table 3.3 A correlation matrix of all 5 major detected peaks found when analysing the gas chromatographs showing both the R² and p values for Period 2. Highlighted and coloured numbers are those with a correlation above 0.6 for R² value and less than 0.01 when comparing P values from the T-Test.

<table>
<thead>
<tr>
<th>R-Squared</th>
<th>Peak 7</th>
<th>Peak 8</th>
<th>Peak 9</th>
<th>Peak 10</th>
<th>Peak 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.79</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.93</td>
<td>0.86</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 4</td>
<td>0.44</td>
<td>0.20</td>
<td>0.60</td>
<td>0.55</td>
<td>X</td>
</tr>
<tr>
<td>Peak 5</td>
<td>0.76</td>
<td>0.82</td>
<td>0.69</td>
<td>0.55</td>
<td>X</td>
</tr>
</tbody>
</table>

T-Test

<table>
<thead>
<tr>
<th></th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 2</td>
<td>2.7E-10</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.6</td>
<td>0.008</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 4</td>
<td>2.7E-13</td>
<td>0.2</td>
<td>0.5</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>0.1</td>
<td>0.005</td>
<td>0.8</td>
<td>4.7E-05</td>
<td>X</td>
</tr>
</tbody>
</table>
The numbers highlighted reflect $R^2$ values greater than 0.6 and p values less than 0.01. Correlations between Peak 8 and 10 are very low, with an $R^2$ value less than 0.2 and a relatively high P value of 0.21. These suggest that there is no statistical significance between the two compounds and the null hypothesis is false.

Figures 3.10 and 3.11 show the variations of compounds over time with a comparison between ozone concentrations and temperature fluctuations. Figure 3.10 does not appear to show any correlation between Peak 8 and ozone concentration. It also appears that temperature variations do not impact compound concentration but impact ozone concentration which supports results made in Section 3.2, peaks in temperature coincide with peaks in ozone concentration. However, the diurnal variation shown in Figure 3.12 show that Peak 8 does follow the predicted temperature changes in diurnal variation. This could also be attributed to impact of SR and its increase toward the middle of the day when the SR is at its highest as opposed to the corresponding temperature increases over the same period. The trend of Peak 8 in Figure 3.12 follows a similar pattern to those ozone concentrations observed in Figures 3.4 and 3.7, there is an initial decrease in compound concentration during the morning when approaching 08:00 from which point the compound concentration increases peaking between 15:00 and 16:00.
Figure 3.11 shows fluctuations in Peak 10 concentrations compared with temperature and ozone fluctuations. There is a very pronounced correlation between Peak 10 and ozone concentration which seem to comply with diurnal temperature changes. Figure 3.12 shows Peak 10’s diurnal variations. Peak 10 shows a similar trend to Peak 8, where concentration reduces in the early morning until between 08:00 and 09:00 where concentrations begin to increase peaking at between 15:00 and 16:00.

![Figure 3.12: Period 2 compound concentration diurnal variation](image)

Unfortunately, after data analysis the field measurements were unable to detect the pre-desired compounds (α-pinene, β-pinene and Limonene). This could be due to a number of reasons, including: values could have been too small for the GC to detect, the season may not be suited to the release of these compounds, equipment malfunctions among other.
4. Discussion

The results suggest that future climate change and changes in meteorology will have an impact on the concentration of tropospheric ozone. According to Sekiya et al. (2012) the changes to ozone in the future will not be limited to a regional scale but will also strongly affect interannual variation globally. This can be attributed to the changes associated with ozone concentration relationships between SR, temperature, relative humidity, windspeed and direction (Santurtún et al., 2015).

4.1 Temperature and Ozone Concentration

Results show that there is an extremely prevalent relationship between the formation of ozone and variations in temperature, however this could be a ‘proxy parameter’ representing SR diurnal variation (Stathopoulou et al., 2008). It is widely accepted that any increase in temperature will cause an increase in ozone concentration because heat accelerates the chemical reactions taking place in the lower atmosphere (Stathopoulou et al., 2008; Walcek et al., 1995). This can be explained due to the intensity of the collisions among the reacting molecules, in this instance precursors to ozone formation (NOX, VOCs, BVOCs). The reaction rates within the lower atmosphere can be represented by Arrhenius’ equation:

\[ k = A e^{\left(\frac{-E_d}{RT}\right)} \]  

(10)

Where \( A \) is the collision frequency, \( E_d \) is reaction energy constants representing laboratory constraints dependent on each reaction. \( T \) is absolute temperature and \( R \) is the gas constant (Chang et al., 2011). This equation suggests that for most chemical reactions, the interaction between molecules increases exponentially as temperature increases (Walcek et al., 1995), however this is a generalisation. All chemical reactions will have a different dependency on temperature, some will have a higher sensitivity and thus temperature will become a dominant factor. However Walcek et al. (1995) also suggests that the formation rate is dependent on the temperatures precursor reactions.

Diurnal variation will have an impact on the formation, it is suggested by Dueñas et al. (2002) that nocturnal hours should be considered differently from diurnal hours, this is prominently due to the fact that ozone concentration is reduced/destroyed during the night due to higher NO concentration (equation 3) and that temperature plays a more important role in ozone formation during diurnal hours. The changes in the boundary layer mean that there is also no new ozone formed during the night. The nocturnal and diurnal variability is evident in Figures 3.4 and 3.7, where if we consider the time of year and the extent of diurnal hours, P3 has a significantly higher impact on ozone concentration than P1 where nocturnal hours are longer. This can also be attributed to the photochemical effect of ozone formation which will be discussed in Section 4.3.

In the likely event that global temperature increases then it is likely that the formation of ozone will also increase. This is likely to be more prevalent in cities where the concentration of ozone
precursors such as NO\textsubscript{X} is more readily available due to the presence of combustion engines and the exhaust gases they produce.

4.2 Windspeed and Ozone Concentration

There are several reasons why windspeed will have a significant impact on the concentration of ozone, depending on conditions variations in windspeed can have a positive or negative impact on ozone. It is suggested that a major impact of windspeed on ozone concentration is the contribution of downward transport of ozone from above the canopy. In the case of Figure 3.5 it appears that windspeed is having a positive impact on ozone formation. The influence of wind in this case may not be as significant as more open collection positions due to the protection of the canopy where ozone sampling took place. Conventionally, an increase in windspeed will cause a reduction in overall concentration due to the wind dispersal of the pollutants. However, this impact is significantly more complicated in relation to secondary pollutants (Dueñas et al., 2002).

High wind velocity, there is likely to be an increase in ozone concentration and a lower concentration of NO, whereas lower wind velocities will decrease the level of ozone and increase the concentration of NO\textsubscript{X} (Dueñas et al., 2002; Rodríguez et al., 2001). This is due to the destructive nature of NO which will cause the breakdown of O\textsubscript{3} demonstrated in equation 3.

Although wind direction measurements have not been made in this complain it has been suggested that it could also have a significant impact on the concentration and transport of ozone from other places. This is because areas which are downwind from any major industrial activity or traffic congestion could experience and increase in anthropogenic volatiles levels which are transported through the movement of air masses.

The impact climate change may have on the global patterns of wind speeds is yet to be fully understood my scientists. But climate change may change the geographical distribution of wind as well as altering the inter/intra-annual variability (Pryor et al., 2010).

4.3 Solar Radiation and Ozone Concentration

The impact SR has on the formation is significant, not just because of the photochemical effects but also the increase in temperature associated with increases in SR. Santurtún et al. (2015) suggest that ozone follows very clear seasonal fluctuations presenting higher values in the summer and daytime compared to winter and night time due to the photochemical properties which is exactly what the results suggest. It can be argued that photochemical interactions are the most important for the formation and destruction of ozone. The formation of ozone is produced from the photolysis of NO. However effective ozone increase is due to a complex chain of chemical reactions predominately the oxidation of VOCs. This process will inevitably take time to occur which could potentially explain the small lag between peak SR and peak O\textsubscript{3} concentration shown in Figure 3.5. Increases in SR can be observed in Figure 3.5 as the days become longer and the Northern Hemisphere approaches its summer solstice. Thus, in can be
expected that the relationship between SR and ozone formation will continue to increase as daylight hours grow longer.

Figures 3.4 and 3.7 also show the diurnal importance SR has in the formation of ozone, due to the natural peak coinciding during maximum SR exposure in the early afternoon. There are instances where the fast-photochemical reactions cause a decrease in ozone formation, usually in the afternoon where NO$_X$ becomes limited, and the impact of these photochemical reactions is reduced. During the morning there is an opposite effect where levels of NO$_X$ an VOC are high, coupled with the increase in SR can influence fast increases in ozone concentration (Derwent et al., 1998). This could be contributing factor when considering the changes to ozone concentration during the day. There is however a notable difference between spring/summer conditions compared with autumn/winter conditions.

According to Lelieveld et al. (1990) it is important to consider cloud formation and its reduction in radiation when discussing the photochemical effect. Models which do not consider it are likely to overestimate ozone concentrations. The formation of clouds will have a scattering effect of SR reducing the overall potency in photochemical reactions, thus reducing the potential for ozone formation at ground level. IPCC (2014a) suggest that cloud cover since the 1970’s overall has increase with a few exceptions in central Europe and China, but there is an overall low confidence in the variability and trends of global cloud cover.

4.4 Compound Climactic Variation and Ozone Concentration

It has been well established that certain BVOCs emissions are a product of changes in SR intensity and temperature, which is highlighted in the results section. However, it is not clear to the extent this has on the formation of ozone. Unfortunately, it has not been possible to identify the compounds which were detected by the GC, although the data did reveal a distinction between two different types of VOCs, potential emitted from either anthropogenic or biogenic sources and the impact they have on the formation of ozone. Comparing the chromatographs collected in the field and calibration chromatographs suggest that α-Pinene, β-Pinene and limonene was not present during the two sampling periods. In addition (Atkinson et al., 2003) suggest that due to the extreme reactivity of certain BVOCs it may be difficult to detect them even in ‘clean’ conditions, monoterpenes typical have a lifetime of between 5 minutes and 3 hours during the daytime and approximately half at night, whereas isoprene has up to 3 hours (Kesselmeier et al., 1999). Future analysis should include the evaluation of detected compounds to determine their chemical structure, for example using Mass Spectrometry.

The correlations between temperature and the concentration of ozone detected in P1 seems to not be particularly strong, this is evident in Figure 3.9. This suggests that even in the presence of low winter temperature the formation of ozone is still partially BVOC dependent. One possible explication of this is the increase in the growing season due to slight increases in winter average temperature raising it above 0°C for extended periods. Even a small increase in winter temperatures has the potential to increase growth by 7-20% (Niinemets et al., 2008; Peñuelas et al., 2010) increasing the overall emissions of BVOCs as well as leaf litter and the possibility of higher fertilization levels. Although the growth of trees is slow, the activity during winter periods will enable a continual release of BVOCs. The decoupling in P1, between Peak 3 and
ozone concentration shown in Figure 3.8 suggests the presence of a non-biogenic compound that does not have any interaction with ozone formation or the other detected compounds.

Figure 3.11 show a very clear coupling between temperature, ozone formation and the BVOC detected during P2, Peak 10. These fluctuations suggest that the BVOC is temperature and light dependent which would suggest the presence of isoprene which plays a role in the formation of ozone. Ozone formation is determined partly by the relationship between VOCs and NOx concentrations, high concentrations of reactive BVOCs in the presence of NOx with favourable climatic conditions will lead to higher concentrations of O3. Given that reactive BVOC emissions are triggered by warmer temperatures and stressed conditions it can be concluded that a changing climate warming will induce an increase in reactive BVOCs leading to a potential increase in the formation of O3 (Calfapietra et al., 2013; Chameides et al., 1988). There is also the potential that the increase in O3 may be the cause of the increase in BVOC emissions, this could be due to the stomatal intake of vegetation causing a defence response thus increase compound intensity especially when coupled with high temperatures and stressed conditions during summer months (Peñuelas et al., 2010). This process can reduce the concentration of O3 due to the reactions that occur within the leaf, specifically the interaction with cell walls. This can be particularly evident at night when the antioxidant impacts of BVOC emissions is reduced and stomatal uptake is more damaging (Calfapietra et al., 2013) and has a large impact on the total ozone flux which could explain the ozone reduction during nocturnal hours. The impact of BVOCs will be dependant on the type of vegetation that is present when sampling, vegetation will behave different under a variety of climatic variables. To better understand the impact of BVOC emissions and their impact on ozone formation sampling should be taken during the summer when vegetation is more active and ozone levels are higher.
5. Conclusion

As part of this project it has involved the installation of a GC-FID in Skogaryd a remote location in the middle of a forest environment. This system will remain at Skogaryd and will be available for further future use. This may be important when considering follow up campaigns. The project detected 10 different compounds throughout the sampling periods, and although the compounds were not identified the temporal variations of the compounds revealed two types of compounds. One of the types of compounds did correlate to ozone concentration, whereas one type of compound did not correlate to ozone concentration.

The entire campaign shows that climate parameters are co-varying with tropospheric ozone, directly and indirectly through the emissions of BVOCs. Although there was no direct identification of compounds a strong argument can be made that the net BVOC emissions will have an overall increasing effect on O$_3$ concentration. This is evident in both winter and spring conditions. From this we can conclude that changes in climactic conditions will have a positive effect on ozone formation, predominately due to increases in temperature and BVOC emissions. It is likely that an increase in temperature will cause an overall annual increase in O$_3$. Increasing environmental stresses such as periods of high temperature will likely cause peaks in ozone formation, this will be particularly evident when in the presence of NO$_X$ and when confined to urban environments. However, it may be more complex when in the presence of a NO$_X$ limited environment. It is difficult to conclude fully the impact climate change will have on windspeed, and in turn what impact that might have on future ozone concentrations. Should the average windspeed increase globally then from this report it can be concluded that ozone formation is likely to increase, especially in areas downwind of major pollutant sources. Windspeed may also influence the transport horizontally and vertically of pre-formed ozone as well as ozone precursors.

Due to the importance of this topic and the increasing long-term meteorological changes and the impact they will have on the concentration of tropospheric ozone it is paramount that this research is continue. In the future to continue this work it may be important to consider the impact of precipitation, land use changes, or the potential impact pest may have on vegetation and the emissions of BVOCs. They may also benefit from the measurements of NO$_X$ emissions to coincide with ozone and compound detection. It may also be important to include detections in varying forest, rural and urban environments to compare results.
6. Acknowledgements

Mattias Hallquist, thank you for your support and feedback throughout this project. Your initial ideas helped me to formulate this project and build ideas on how to tackle the problems faced.

David Allbrand, without your help I don’t think I would have been able to collect any of the data at Skogaryd. You have helped me to set everything up and get things running for which I am very thankful.

Leif Klemedtsson, thank you for letting me have access to Skogaryd and Per Weslein for helping me with the climate data.

Mikael Alfresson, thank you for you help with fixing the GC the autosampler as well as all the other problems I faced along the way. I think you went above and beyond your call of duty to help me.

Thank you all at the Atmospheric Chemistry Department, you have made it a very welcoming place and a great learning environment.
7. References


Figure A1: This is a diagram showing the global mean energy balance of the Earth. The numbers indicate estimates for the averaged energy balance components as well as their uncertainty ranges. This is a representation of conditions at the beginning of the 21st Century. Units Wm\(^{-2}\). Adapted from: Wild et al. (2013).
Figure A2: This is a simplistic representation of the experimental layout. The arrows indicate the direction of airflow within the tubes. Insulated tubes are shown as a larger line with an arrow, between the autosampler and the GC as well as the sample gas inlet.
Figure A3: A Gas Chromatograph from initial testing of the GC FID, this is a sample of the output before the baseline had been established. The peaks represent compound or noise within the column and the detector.
Figure A4: A Gas Chromatograph from the calibration stage of testing. The three prominent peaks represent (from left to right): α-Pinene, β-Pinene and Limonene.
**Figure A5:** This is a map of the areas surrounding the north of Gothenburg with the Skogaryd Research Catchment highlighted within the red circle.
**Figure A6:** This is a more detailed map of the Skogaryd Research Catchment. Different land types are marked with different letters. The subsites include: A. Mycklemossen, B. Erssjön, C. Följesjön, D. Clear Cut, E. “Forest on drained organic soil”, F. “Forest on mineral soil”, G. Stream Waters.
**Figure A7:** This is a map showing the IVL ozone sampling sites positioning as well as the positioning of Skogaryd as comparison. All locations are marked, Skogaryd (far North), Ytterby (middle West), Östad (middle East) and Råö (far South). The map was generated using google maps ([https://www.google.com/maps](https://www.google.com/maps)).
Figure A8: This is a photo of the meteorological tower where the sampling has taken place. The total height of the tower is 38m (Thelin, 2019).

Figure A9: This is a photo of the cabin where the experimental equipment is kept. Tubing from the tower runs into the cabin where it is connected to the equipment (Thelin, 2019).
Figure A10: A scatter plot representing the comparison of Period 2 ozone concentration data from Skogaryd and the three Swedish EPA data sites (Ytterby, Östad and Rää). Data provided by IVL.

Figure A11: A scatter plot representing the comparison of Period 1 ozone concentration data from Skogaryd and the three Swedish EPA data sites (Ytterby, Östad and Rää). Data provided by IVL.
Figure A12: A collection of graphs showing ozone concentration compared with climactic variations over time for Period 1. The graphs represent temperature, windspeed and net SR compared with ozone concentration.
Figure A13: A collection of graphs showing ozone concentration compared with climactic variations over time for Period 2. The graphs represent temperature, windspeed and net SR compared with ozone concentration.
Figure A14: This plot shows the diurnal variation of Period 1 ozone concentration from Skogaryd, the three Swedish EPA data sides (Ytterby, Östad and Rää) and temperature measured at Skogaryd. Data provided by IVL.

Figure A15: This plot shows the diurnal variation of Period 2 ozone concentration from Skogaryd, the three Swedish EPA data sides (Ytterby, Östad and Rää) and temperature measured at Skogaryd. Data provided by IVL.
Figure A16: Period 1 compound diurnal variation.
Figure A17: A chromatograph taken from field sampling during P2. Varying compounds are evident with changing retention times.
Appendix B

1Google Scholar - https://scholar.google.com/
2Web of Science - https://webofknowledge.com/
3Gotheburg University Library - http://www.ub.gu.se/