

## Report

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Schafers, Richard. 2014. **Volatile organic compounds: ambient flux measurements**. Edinburgh, NERC/Centre for Ecology & Hydrology, 76pp. (CEH Project no. C04845, C04486)

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**Volatile Organic Compounds: Ambient flux measurements**

**Placement Report**

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**27/05/2014**

## Abstract:

Biogenic volatile organic compounds (BVOC) are gases emitted and deposited at the Earth's surface. These gases are important because of their roles in atmospheric chemistry. One of the major challenges in atmospheric science is measuring fluxes of these trace atmospheric species, both at the individual plant level, ecosystem scale and regionally. In this work different techniques for measuring fluxes were explored and applied in the field and the laboratory, using micrometeorological and leaf-level techniques respectively. Emissions to the atmosphere may be quantified by means of an emission factor  $\epsilon$ , which is defined as the emission rate of a BVOC from an ecosystem or plant species, normalised to specific environmental conditions. Flux measurements at the ecosystem scale were made at the remote field site south of Edinburgh: Auchencorth Moss. Measurements were made using a proton transfer reaction mass spectrometer coupled with micrometeorological measurements. An emission factor of  $1.83 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  was calculated for isoprene emission but was also found to be a function of time. An emission factor of  $4.0 - 9.0 \text{ mg m}^{-2} \text{ h}^{-1}$  for isoprene was extracted from historical data for Alice Holt research forest, which is primarily an oak forest from 2005. The emission factor from Alice Holt is within the range reported for similar sites but the Auchencorth measurements are larger than the most comparable results available. Moss measurements of isoprene made in the laboratory suggest the presence of isoprene emitting biomass other than *Sphagnum* moss at Auchencorth due to the difference in emission factors. A database of published above-canopy BVOC fluxes was created and includes most data published between 1985 and 2013. From this an overview of the development of the measurement techniques has been obtained from which it appears that employing various methods to capture BVOC fluxes would be the ideal approach to determine a more complete understanding of BVOC emissions and their contributions to atmospheric chemistry and climate.

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## 1. Introduction:

The emission of biogenic volatile organic compounds (BVOC) has been studied since the early nineteen eighties but interest in the subject increased greatly in the nineteen nineties with the development of analytical techniques, instrumentation capable of measuring ambient concentrations and fluxes, and greater scientific awareness of their atmospheric chemistry. The importance of BVOC and techniques commonly employed to measure their fluxes was reviewed (Schafers 2013) as part of this work (attached in appendix) and references other literature reviews (Kesselmeier and Staudt 1999; Fuentes, Lerdaun et al. 2000; Laothawornkitkul, Taylor et al. 2009).

Due to the large numbers of different organic chemicals present in the atmosphere, and the wide variety of biological release mechanisms, a study of the full atmospheric cycling of all the chemical species is not feasible. Research has more pragmatically mostly focussed on some of the more atmospherically abundant chemicals. Isoprene in particular plays a key role in atmospheric chemistry and climate regulation because it is emitted globally in large quantities (Lathiere, Hauglustaine et al. 2006; Stavrakou, Muller et al. 2009). The ability to measure and calculate or model isoprene emission accurately across a range of scales is therefore beneficial for predicting air composition in fast-changing environments and atmospheres. It is necessary to initialise atmospheric chemical models with isoprene emission rates from specific surfaces, however the surface consists of many plant species, ecosystems and countries, for most of which research is scarce or non-existent. This is problematic because isoprene emission rates are highly plant-species specific, and extrapolation across plant genus and families is often inaccurate (Guenther, Hewitt et al. 1995; Simpson, Guenther et al. 1995). Therefore, to make progress many BVOC flux measurements across a wide range of ecosystems and environments need to be made. Emissions to the atmosphere may be quantified by means of an emission factor  $\epsilon$ , which is dependent on plant species, climate and ecological factors.

### 1.1 Peatland emissions

Peatlands account for 3% of the land cover of the terrestrial Earth's surface (Joosten 2002) and exist on all continents across many different climates including boreal, arctic and even tropical areas and are a considerable source of carbon due to their ability to sequester it. The species composition of peatlands tends to be dominated by mosses and grasses which are often waterlogged. BVOC exchange from peatland sites has not been studied widely and therefore emission fluxes for these ecosystems are not currently well defined. In fact, there are only a handful of measurements from Sweden for such ecosystems (Janson and De Serves 1998; Janson, De Serves et al. 1999; Haapanala, Rinne et al. 2006; Holst, Arneth et al. 2010) and only one set of direct BVOC flux measurements from Holst et al. (Holst, Arneth et al. 2010) These studies found that isoprene emissions were low compared to higher emitters, such as forests, but concluded that low emissions were most likely due to the cold temperatures rather than low emission potential. Measurement of fluxes of any gas from any individual plant species is challenging due to many BVOC emissions being under the limit of detection. Moss species are particularly difficult due to the small size of individuals, so a small canopy chamber deployed in the field to enclose a clump of moss will also include other small plant species. Enclosure measurements mitigate these issues by allowing specimen isolation and the ability to detect lower emissions but they also introduce complications of their own. For instance, trying to estimate the surface area of the moss being sampled is especially error-prone and the wetness of moss samples mandates the use of specially modified equipment and drying pumps to cope with these additional demands. The result is that these few studies have not captured the full understanding therefore this clearly demonstrates the need for more data. Auchencorth moss was selected for study because it is a peatland ecosystem for which the majority of infrastructure required for BVOC flux measurements is already in place. Within 1 km of Auchencorth, the peatland site, Whim bog, was selected as a source of moss material for laboratory investigation because of ease of access.



Figure 1.1 Site photograph of Auchencorth Moss

### 1.2 Oak forest emissions

Deciduous forests cover large areas of the Earth's surface and are a high emitter of BVOC including isoprene and monoterpenes. There have been lots of studies (Isebrands, Guenther et al. 1999; Cojocariu, Escher et al. 2005; Fowler, Nemitz et al. 2011; Kaser, Karl et al. 2013; Miyama, Okumura et al. 2013) despite the challenges of working with such large plant species but the majority of research has been on pine and coniferous forests (see chapter 3). To contrast the data collected at Auchencorth Moss, data that had previously been acquired in 2005 at an English oak forest, Alice Holt, was analysed to give insight into the proportionate significance of BVOC emissions from British peatland sites by comparison with emissions from a contrasting habitat with a high emission potential. Despite the known emission potentials of the *Quercus* genus, there remains a relatively small amount of BVOC flux data for these forest ecosystems, of which these are the first measurements from a British region.



Figure 1.2 Aerial photograph of Alice Holt forest (Forestry-Commision 2007-2011)

### 1.3 Field experimental approaches to calculating $\epsilon$

Fluxes of BVOCs can be measured directly using a proton transfer reaction mass spectrometer (PTR-MS) coupled with the disjunct eddy covariance technique (DEC). This approach will mostly work only when there are

sufficiently high concentrations of the BVOC to measure changes at frequencies of the order of 1Hz. There is a requirement to have a uniform fetch in the footprint of the measurements and a good knowledge of the species composition. The CEH instrument has previously been deployed to forests where the requirement to have a forest footprint means that the measurements have to be carried out on a tall tower significantly above the canopy height. To monitor BVOC exchange at an ombrotrophic peat bog in temperate Scotland could potentially be a challenge because of the low temperatures, low BVOC emitting plant species and the remote location.

#### 1.4 Laboratory experimental approaches to calculating $\epsilon$

Species level understanding of BVOC emissions, how and when they occur and what drives the magnitude of the emissions, is relevant both for understanding the fundamental bio-physical-chemistry of plants and how that can change with environment, and for deriving a deeper understanding of full ecosystem measurements. Though this type of experiment is possible in the field, enclosure measurements of *Sphagnum capillifolium* were performed in the laboratory, on samples harvested from Whim bog to investigate the isoprene emitting potential of this species because it is commonly one of the dominant vegetation types found in these ecosystems.



Figure 1.3 Photograph of Whim bog (ExpeER-Ecosystem-Research 2014)

#### 1.5 Exploiting existing datasets for synergistic metadata analyses as physical chemistry and biological understanding improves

Examining the movement and interactions of BVOC in the atmosphere is important to develop our knowledge and understanding of complex atmospheric chemistry and to ascertain the roles these compounds play in physical processes and climate change. BVOC flux data is regularly used to develop and improve atmospheric climate and emission models. It is therefore important that high quality BVOC flux data obtained at the canopy scale is readily available to facilitate this process. The availability of a freely accessible and comprehensive database of BVOC flux data could greatly assist in this endeavour by providing a unified resource which gives the BVOC modelling community access to valuable input data but also allows researchers to use the data or for comparison with other work. While BVOC flux databases do exist, they tend to only include data for specific regions or projects i.e. a flux database for data collected within Europe (Various 2014).

#### 1.6 Aims of this work

The primary aims of this project were to (i) further the understanding of BVOC emission fluxes from UK ecosystems by generating isoprene emission factors (ii) assess the different approaches from “leaf-level” to “canopy-scale” measurements (iii) contribute to a major project which aims to make all BVOC flux datasets available in a database for future research. The main contribution to (iii) was to read and assess the BVOC flux literature and identify suitable studies for inclusion, developing a practical approach to potentially enabling future ensemble studies exploiting the data archive of BVOC field studies.

Chapters 2 and 3 describe the work carried out during the placement:

Chapter 2 details the research carried out with the practical methods for measuring BVOC emissions and was assessed at both ecosystem and leaf-level to gain a variety of data for comparison. It describes the acquisition of new experimental data and the analysis of pre-existing data sets to produce isoprene emission factors for use in models of atmospheric chemistry and climate. The work carried out can be broken down into three distinct “projects”, the objectives of which were:

1. Field flux measurements: Collect and analyse BVOC flux data for an ecosystem that had previously not been studied.
2. Method development: Develop and refine methods to analyse an existing set of BVOC data to generate an isoprene emission factor for use in modelling studies.
3. Laboratory approaches: Measure BVOC emissions from sphagnum moss in the laboratory and derive an emission flux dataset using an enclosure system.

Chapter 3 covers the beginnings of the development of a BVOC flux database system, VOCsNET, which entailed:

1. Searching for studies in the scientific literature which may contain BVOC flux measurements.
2. Reading the papers to determine whether the results were appropriate for inclusion in VOCsNET.
3. Preliminary analysis of the results that have been identified thus far.

The construction of the VOCsNET database is ongoing and requires substantial amounts of further work.

The overarching observations and conclusions are drawn together in the final concluding chapter, where recommendations for future approaches to BVOC research are made.

## Chapter 2: Experimental Measurements

### 2.1 Experiment overviews

BVOC concentration and flux measurements were made at Auchencorth Moss with a proton transfer reaction-mass spectrometer (PTR-MS). The disjunct eddy covariance (DEC) method, described below was applied to calculate BVOC fluxes. A back-calculated isoprene emission factor,  $\epsilon$ , for the field site is computed using the MEGAN emission algorithm (Guenther, Karl et al. 2006) from the measured flux, and the results analysed for temporal variation and uncertainties. Theoretical emissions of isoprene from Auchencorth for 2011-2013 were determined using this emission factor and the results compared with CO<sub>2</sub> flux measurements to determine the fraction of reactive carbon lost from Auchencorth Moss in the form of isoprene.

Analysis of an existing data set for an oak forest in England, Alice Holt, was performed using processes similar to those used on the Auchencorth data to extract isoprene emission factors using the G95 (Guenther, Hewitt et al. 1995) and MEGAN emission algorithms proposed by Guenther et al, in 1995 and 2006 respectively. Oak is the largest isoprene emitter in Europe however there are only a handful of direct flux measurements above European oak, all of which are concentrated around France (see Chapter 3).

Laboratory measurements of BVOC from red and green sphagnum moss samples, gathered from Whim, were carried out at the Centre for Ecology and Hydrology (CEH) laboratories using an enclosure system coupled with an automated thermal desorption gas chromatography mass spectrometry analysis system. Net normalised isoprene emission factors are calculated for the moss samples.

The data compared from these experiments are used to assess the variability in measurements at the different scales with the different techniques and to compare the values derived.

### 2.2 Methods

#### 2.2.1 Site Descriptions:

1. Auchencorth Moss is an ombrotrophic peat bog located South of Edinburgh nearby Penicuik, Scotland (55.792° N, 3.243° W) at an altitude of 260m above sea level. CEH has used this site to intensively monitor fluxes and concentrations of trace gases and aerosols for many years and it has a flux footprint mainly towards the South-West. The dominant vegetation is moss, mostly *Sphagnum*, but *Pleurozium schreberi*, *Polytrichum commune*, *Eriophorum vaginatum* and *Molinia caerulea* are also present in large quantities. These are all known isoprene emitters with the exception of *Eriophorum vaginatum* and other species which are not as common. While most of these species have been detected to emit isoprene using enclosure systems, it was not known whether the sensitivity of the PTR-MS would be sufficient to detect canopy scale fluxes of isoprene at this study site. The field site is relatively isolated from anthropogenic disturbances although parts of the ground are damaged from off-road vehicles used to transport equipment to and from the site. The terrain is typically wet, with patches of vegetation often completely submerged, and average temperatures range from approximately 1° C in winter up to 19° C in the summer months.
2. Alice Holt forest is located in South-East England, south of Surrey (51.168° N; 0.850° W) at an altitude of 80m above sea level. The dominant vegetation over the entire forest is oak, *Quercus robur* and *petraea*, with a scattering of about 10% ash, *Fraxinus excelsior*. The understory comprises woody shrubs and herbs of which hazel, *Corylus avelanna*, and hawthorn, *Crataegus monogyna*, are the most abundant. (Wilkinson 2013)

- Whim bog is another ombrotrophic peat bog located near Lamancha, Scottish Borders (55.765° N; 3.271° W). The dominant vegetation is *Sphagnum* moss species, as is typical for peatland ecosystems. The site is mainly used to investigate the effects of nitrogen exposure on local flora and how this influences nitrogen and carbon cycles in these ecosystems. Different experimental plots receive different doses of wet NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> treatments. In addition, there is a dry NH<sub>3</sub> deposition transect. The site is reasonably isolated from anthropogenic disturbances although construction work and personnel were in close proximity to the site when moss samples were collected on 07/02/2014. *Sphagnum capillifolium* samples were collected from control plots, from non-treated off-plot sites, and from the dry NH<sub>3</sub> deposition transect. In addition, samples of both red and green forms were taken from control and NH<sub>3</sub> deposition treatment plots.

### 2.2.2 Disjunct eddy covariance

The DEC method is regularly used because it allows multiple compounds to be measured directly but also because it allows the use of slower sensors than those required for eddy covariance (EC). Principally it is very similar to EC, described in further detail elsewhere (Schafers 2013), but differs in a few key areas: Samples are captured repeatedly over short times (typically 500ms or less) and separated by a fixed time interval. Multiple compounds may be measured discretely in a cycle, rather than continuously in EC, which allows multiple compounds to be observed virtually simultaneously.

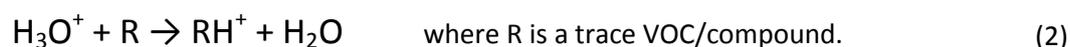
The flux of a BVOC,  $F$ , is given by the mean covariance of the vertical wind velocity,  $w'$ , and concentration,  $c'$ , over the total number of samples,  $n$ , taken during an averaging period of typically 30 minutes:

$$F = \frac{1}{n} \sum_{i=1}^n (w'c')_i \quad (1)$$

where the time spent sampling and analysing a compound is referred to as the “dwell time” with the total time elapsed for each cycle called the “duty cycle”. Excellent agreement between results obtained using both methods was demonstrated in 2013 (Park, Goldstein et al. 2013).

### 2.2.3 DEC Instrumentation:

Fluxes of BVOC were measured at Auchencorth moss and Alice Holt forest using a PTR-MS. Additional details regarding the application of PTR-MS for measuring BVOC are provided by (Hayward, Hewitt et al. 2002; de Gouw and Warneke 2007). BVOC emissions have been quantified using these instruments since just before the year 2000. Trace gases are ionised inside the drift tube of the PTR-MS by primary ions (hydronium H<sub>3</sub>O<sup>+</sup>), and the product is detected with a quadrupole mass spectrometer. However, the proton transfer reaction is only favourable if the compound has a proton affinity,  $E_{pa}$ , greater than water (691 kJ mol<sup>-1</sup>) (Blake, Monks et al. 2009). Proton affinity is often used to describe the ability of a gas phase molecule to accept a proton and is defined as the negative of the enthalpy change at standard conditions. The proton transfer reaction which occurs in the PTR-MS drift tube is given in Equation 2.



This reaction is exothermic and quick if proton affinity of R ≥ H<sub>2</sub>O

Ambient air therefore functions as a buffer gas and can be directly introduced without sample preparation by cause of the major components of air having proton affinities lower than water. These factors make the instrument suited to online operation, with minimal user input required once in measurement mode. Typical PTR-MS instruments have a response time of less than a second and sensitivities in the ppt range which makes them

effective at measuring trace BVOC but it should be noted that detection of all BVOC—mainly alkanes smaller than C<sub>5</sub>— and greenhouse gases, such as methane and carbon dioxide, is not viable due to the proton affinity constraints. This is demonstrated in table 2.1 where everything below and above water is detectable or not using PTR-MS respectively (with hydronium ions as the primary ions). The proton affinities and chemical formula of some common BVOC and the main constituents of air are also provided for reference.

Compound	Chemical Formula	Proton affinity (kJ mol <sup>-1</sup> )(NIST 2014)
Argon	Ar	369.2
Oxygen	O <sub>2</sub>	421.0
Nitrogen	N <sub>2</sub>	493.8
Carbon dioxide	CO <sub>2</sub>	540.5
Methane	CH <sub>4</sub>	543.5
Carbon monoxide	CO	594.0
Propane	C <sub>3</sub> H <sub>8</sub>	625.7
Water	H <sub>2</sub> O	<b>691.0</b>
Acetone	C <sub>3</sub> H <sub>6</sub> O	812.0
Isoprene	C <sub>5</sub> H <sub>8</sub>	826.4

Table 2.1 Proton affinities and chemical formula of common BVOC and the main components of air

## 2.2.4 BVOC sampling:

### 2.2.4.1 Auchencorth:

BVOC sampling was carried out using a PTR-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria), in conjunction with the DEC technique. The PTR-MS was operated at a drift tube temperature, pressure and voltage of 303 K, 2 mbar and 550-600 V respectively. Maintaining these conditions resulted in an  $E/N$  ratio of approximately 125 Townsend ( $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ) where  $E$  is an electric field applied over the drift tube and  $N$  is the number density of the gas in the drift tube. The electric field helps to restrict the formation of unwanted cluster ions, by augmenting the kinetic energy of the reagent ions, because their existence impedes the interpretation of the mass spectra. Various compounds were measured continuously, for periods of 30 minutes, during 3 days in July 2013. BVOC were sampled continuously from ambient air through ~20m of PTFE tubing (I.D. 6mm, O.D. ¼”) that ran from the sampling inlet directly below the sonic anemometer into a tow-a-van where the PTR-MS and air-conditioning units were housed. The tow-a-van was strategically positioned so as to avoid disrupting the typical flux footprint of the tower by placing it away from the prevailing wind direction. The sonic anemometer continuously monitored the three wind components,  $u$ ,  $v$ , and  $w$  at a sampling frequency of 20 Hz. The sampling inlet and anemometer were mounted close together on a pole at an elevation of 3 m. All of the tubing was insulated and buried underground in an effort to minimise exposure to the weather and animals. Furthermore a heating cable was placed alongside the sampling line to reduce water condensation and limit adsorption/desorption effects of the measured compounds onto tube walls. The dwell time for the selected suite of protonated masses was set to 500 ms per mass with the exception of the primary ions and first water cluster (H<sub>2</sub>O)<sub>2</sub>, which were set to 100 ms. The mass to charge ratios,  $m/z$ , that were measured along with likely compounds that can be detected at those values is displayed in Table 2.2.

<i>m/z</i>	Date range of measurements	Possible compounds (GmbH 2008)
33	08/07/2013 – 29/07/2013	<b>methanol</b> , hydrazine, fluoromethylene
41	08/07/2013 – 12/07/2013	cyclopropene, propyne, 1,2-propadiene
47	15/07/2013 – 18/07/2013	ethanol, formic acid, dimethyl ether, methanol cluster
59	08/07/2013 – 12/07/2013	<b>acetone</b> , propanal, acetylacetone, methyl vinyl ether
60	08/07/2013 – 12/07/2013	acetamide, 1 & 2 propanamine, trimethylamine
61	15/07/2013 – 18/07/2013	<b>acetic acid</b> , methyl formate, 1-propanol
69	08/07/2013 – 29/07/2013	<b>isoprene</b> , furan, pentanal, octanal, nonanal
71	15/07/2013 – 18/07/2013	<b>methyl vinyl ketone (MVK) &amp; methacrolein (MACR)</b>
73	15/07/2013 – 18/07/2013	butanal, butanone, <b>methyl ethyl ketone (MEK)</b>
75	19/07/2013 - 29/07/2013	<b>hydroxyacetone</b> , methyl acetate, propanoic acid, 1 & 2 butanol
87	19/07/2013 - 29/07/2013	hexanol, pentanal, 2 & 3 methylbutanal
93	19/07/2013 - 29/07/2013	<b>toluene</b> , p-cymene
137	19/07/2013 - 29/07/2013	<b>monoterpenes (MT)</b> , methyl benzoate, adamantane

Table 2.2 dates that *m/z* ratios were measured using PTR-MS and possible contributing compounds at each *m/z* with the most likely compounds in bold.

#### 2.2.4.2 Alice Holt:

Various BVOCs were measured sequentially in a cyclic manner using DEC between the 15<sup>th</sup> of June and the 16<sup>th</sup> of August in 2005 at the Alice Holt forest site in projects carried out by Emily House as part of her PhD. A PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was used to detect the emission of VOCs. The mean canopy height was 20.5m with measurements taken above canopy at 28.5m. The dwell times that the protonated compounds were measured for ranged between 10-50 ms.

#### 2.2.4.3 Whim bog:

After harvesting from Whim, a total of 23 moss samples were transferred into moist peat pots and set in a large horticultural tray of damp moss vegetation that was collected alongside the samples at Whim. The tray of samples was first kept in a glasshouse but was later moved into the lab where the temperature was warmer (~ 25 ° C), to activate isoprene emissions. Moss samples were weighed using a balance and then placed into a specially modified LICOR LI6400 moss chamber. Modifications include a T-piece which was inserted into the gas flow tubing at the exit of the chamber and a charcoal filter to scrub inflowing air of ambient BVOC. The sample was allowed to equilibrate for 30 minutes before sampling for 60 minutes. The moss was kept at a temperature of 20 ° C and light levels were maintained at 1000  $\mu$  mol during the sampling and equilibration periods. BVOC samples were collected in March and April of 2014 using adsorbent tubes filled with Tenax. Air was drawn through the tubes using a "Pocketpump 210-1002MTX air sampling pump" at a flow rate of 200 ml min<sup>-1</sup> yielding samples of 12 l. Samples were stored in a cold room until analysis with GC-MS was performed. Samples were analysed using a Perkin Elmer GC-MS fitted with a Turbomatrix ATD. Sample tubes were desorbed at 280 ° C for 6 minutes onto a cold trap held at -30 ° C. The cold trap was then flash-heated to 300 ° C and held for 5 minutes causing injection of the sampled BVOCs onto the GC column. The GC column was held at 35 ° C for two minutes, then heated to 160 ° C at four ° C min<sup>-1</sup>, followed by a final heating to 300 ° C at 45 ° C min<sup>-1</sup>. The temperature was held at 300 ° C for 10 minutes.

Isoprene identification was achieved by injecting and analysing an isoprene gas standard (30 ml, 700 ppb) which allowed the relative quantification of isoprene from moss samples.

### 2.2.5 Data Analysis and the G95 and MEGAN models

In order to convert raw PTR-MS and wind velocity data into a flux it is first necessary to process the data. Once processed, the measured fluxes are normalised to a set of standard conditions (e.g. to a reference temperature and PAR value) using an emission algorithm to produce an emission factor suitable for use in models of

atmospheric chemistry and climate. The processing of raw data and use of emission algorithms are outlined briefly below, but the reader is referred to the literature (Guenther, Hewitt et al. 1995; Guenther, Karl et al. 2006; Taipale, Ruuskanen et al. 2010) for detailed explanations and mathematical processing.

### 2.2.5.1 Data Analysis

Raw data from the PTR-MS and sonic anemometer were processed using the “Flux analysis” software version 5.4. The analysis software calculated the VOC fluxes based on the DEC method which included the following basic steps:

- (i) Rotation of the coordinate frame to correct for misalignment of the sonic anemometer.
- (ii) Application of calibration factors, zero air subtraction and conversion of raw counts to  $\mu\text{g m}^{-3}$ .
- (iii) Determination of the lag time between sonic anemometer and PTR-MS through the use of a cross correlation function.
- (iv) Calculation of the flux based on equation (1). The fluxes for each averaging period were then plotted against the calculated dimensionless emission activity factor,  $\gamma$  from which an emission factor was obtained by calculating the gradient.

All Auchencorth BVOC flux data were filtered to exclude data where PAR levels dropped below  $300 \mu\text{mol m}^{-2} \text{s}^{-1}$  as the MEGAN model performed very poorly under low light levels, regularly generating implausible negative fluxes (e.g.  $-200 \text{ mg isoprene m}^{-2}\text{h}^{-1}$ ). The filtered results occurred almost exclusively at night time when emissions were expected to be either close to zero or perhaps slightly negative indicating deposition. Alice Holt BVOC flux data has only had the filter applied when using the MEGAN model because G95 was able to estimate emissions under low light levels with more success. This was achieved by using logic functions in excel to filter out any results that fell below this threshold.

### 2.2.5.2 G95 Emission Algorithm

To facilitate comparison of BVOC flux results from different ecosystems, an emission factor, normalised to standard conditions, can be estimated at the canopy/ecosystem-scale. The standard approach is to apply an emission algorithm to the BVOC flux data, resulting in an emission factor that is representative of the ecosystem from which measurements were made. This process is described for the G95 model and was developed by Guenther et al. (Guenther, Hewitt et al. 1995) Once an emission factor has been calculated, it is possible to model BVOC emissions,  $F$ , by calculating the emission activity factor,  $\gamma$ . This scales emissions relative to environmental conditions – specifically temperature and photosynthetically active radiation (PAR), or incidence of light. The light and temperature dependence of  $\gamma$  is split into two components,  $C_L$  and  $C_T$  respectively and their product,  $C_L \cdot C_T = \gamma$ . The specific form of  $C_L$  and  $C_T$  is shown in Equation 4.

$$\gamma = C_L \cdot C_T = \frac{\alpha C_P Q}{\sqrt{1 + \alpha^2 Q^2}} \cdot \frac{e^{\frac{C_{T1}(T-T_S)}{RT_S T}}}{1 + e^{\frac{C_{T2}(T-T_M)}{RT_S T}}} \quad (3)$$

$$C_L = \frac{\alpha C_P Q}{\sqrt{1 + \alpha^2 Q^2}} \quad \& \quad C_T = \frac{e^{\frac{C_{T1}(T-T_S)}{RT_S T}}}{1 + e^{\frac{C_{T2}(T-T_M)}{RT_S T}}} \quad (4)$$

where  $Q$  is PAR flux ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ),  $T$  is leaf temperature (K),  $T_S$  is leaf temperature at  $30^\circ \text{C}$ ,  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $\alpha$ ,  $C_{T1}$ ,  $C_{T2}$  and  $T_M$  are empirical coefficients.

This enables BVOC emission fluxes,  $F$ , to be estimated using Equation 5.

$$F = \epsilon \gamma \rho \quad (5)$$

where  $F$  is the estimated BVOC emission flux,  $\varepsilon$  is an ecosystem specific emission factor and  $\rho$  is a factor which accounts for production and loss with plant canopies.

A constant value of 0.96 was used for  $\rho$  as suggested by Guenther et al (Guenther, Karl et al. 2006).

### 2.2.5.3 MEGAN Emission Algorithm

The MEGAN algorithm is an updated version of the G95 algorithm (Guenther, Karl et al. 2006). The main difference being that MEGAN factors previous days light and temperature data into its calculations rather than only current conditions. The standard amount of previous days of data that MEGAN considers is one and 10 days although these numbers were chosen for modelling purposes (Guenther, Karl et al. 2006). In this work we used the Alice Holt data for a sensitivity analysis to ascertain the optimal number of days previous light and temperature data to include within the emission algorithm.

## 2.3 Results & Discussion

### 2.3.1 Auchencorth:

#### 2.3.1.1 Normalised emission factor, $\varepsilon$

The PTR-MS was run for 19 days in July 2013. However, the majority of these data failed quality tests. This was due to a failing secondary electron multiplier, which resulted in a very low primary ion count and therefore poor sensitivity, but was exacerbated by technical difficulties such as the instrument overheating due to the air conditioning system failing. Two and a half days of high quality data were extracted from this period. Despite the plethora of  $m/z$  ratios that were sampled over the measuring campaign, only  $m/z$  69 exhibited fluxes above the limit of detection. The signal from  $m/z$  69 was attributed to isoprene emission because the remote location of Auchencorth and isolation from anthropogenic disturbances made contributions from furan highly improbable. Minor contributions from aldehydes, however, such as those given in Table 2.2 cannot be ruled out but it was thought unlikely. This could be confirmed in future work by sampling with PTR-MS in conjunction with GC-MS measurements or perhaps by using a newer and more sophisticated PTR-ToF-MS instrument which would enable distinction between compounds with very similar  $m/z$  ratios.

The isoprene concentrations observed at Auchencorth Moss with the PTR-MS are shown in Figure 2.1. These concentrations were up to a factor of three times smaller during the day, but were greater during the nights, than hourly on line GC-MS isoprene measurements performed concurrently at Auchencorth Moss. The difference in concentrations during the day could be due to the lower measuring height of the GC-MS, which is about one to two m in comparison to three m for the PTR-MS. As we observe an emission flux of isoprene, there must have been a vertical gradient in isoprene concentrations, which would result in larger concentrations at ground level and would explain why the GC-MS concentrations are higher for this period due to its lower elevation. The higher isoprene concentrations seen during the nights with the PTR-MS however are most likely inaccurate, and suggest that a more suitable background subtraction needs to be applied, which can be roughly estimated using the GC-MS measurements for future work. There was unfortunately not enough time to do this for this report as the existence of the GC-MS measurements was discovered too late. The GC-MS is calibrated regularly, whereas the PTR-MS was not calibrated in the field due to technical difficulties and a typical sensitivity was therefore used for these calculations. This sensitivity may no longer be suitable because modifications to the PTR-MS to increase its primary ion count, and therefore sensitivity, were made prior to deployment. Further work will need to fully calibrate the modified PTR-MS and then apply a simple correction factor to the numbers reported here. Further, the GC-MS samples from a different location at the field site compared to the PTR-MS inlet which could further contribute to this inequality although the effect this has is thought to be minor in comparison to the points discussed earlier.

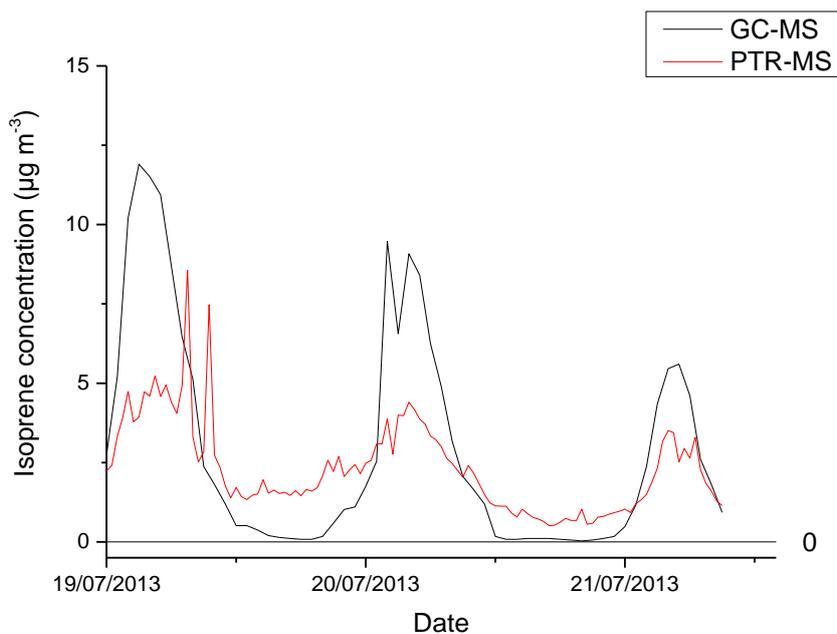


Figure 2.1 Isoprene concentration measurements at Auchencorth Moss in July 2013. The red line indicates data from the PTR-MS and the black line shows data from the GC-MS.

The isoprene flux detected at Auchencorth Moss in July 2013 is presented in Figure 2.2 where there is a clear diurnal cycle in view.

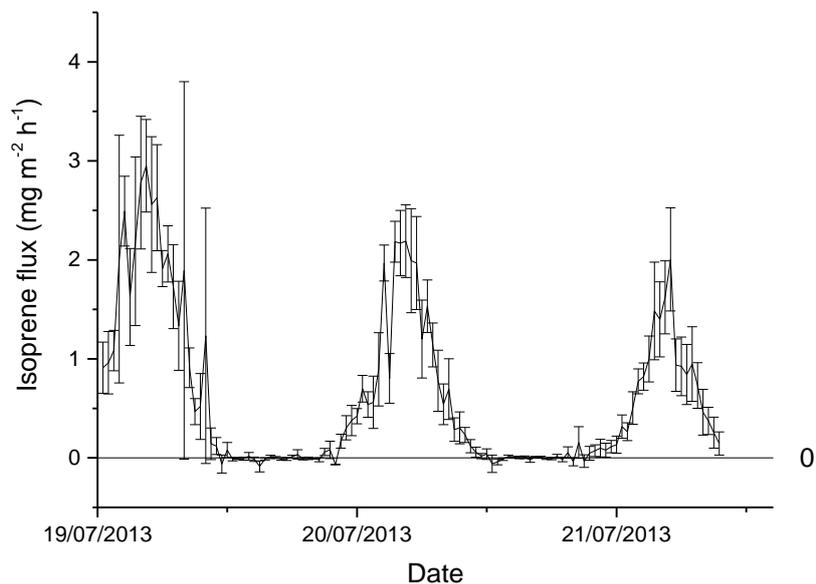


Figure 2.2 Isoprene flux data with error bars calculated by characterising the background noise of the cross-correlation function for data acquired during the measuring campaign.

A normalised isoprene emission factor of  $1.83 \pm 0.07 \text{ mg isoprene m}^{-2} \text{h}^{-1}$  was obtained for the Auchencorth field

site from the July 2013 measurements using the MEGAN model. The emission factor was normalised to a PAR of  $1000 \mu \text{ mol m}^{-2} \text{ s}^{-1}$  and a temperature of  $30^\circ \text{ C}$ . The graph from which this result was extracted is shown in Figure 2.3.

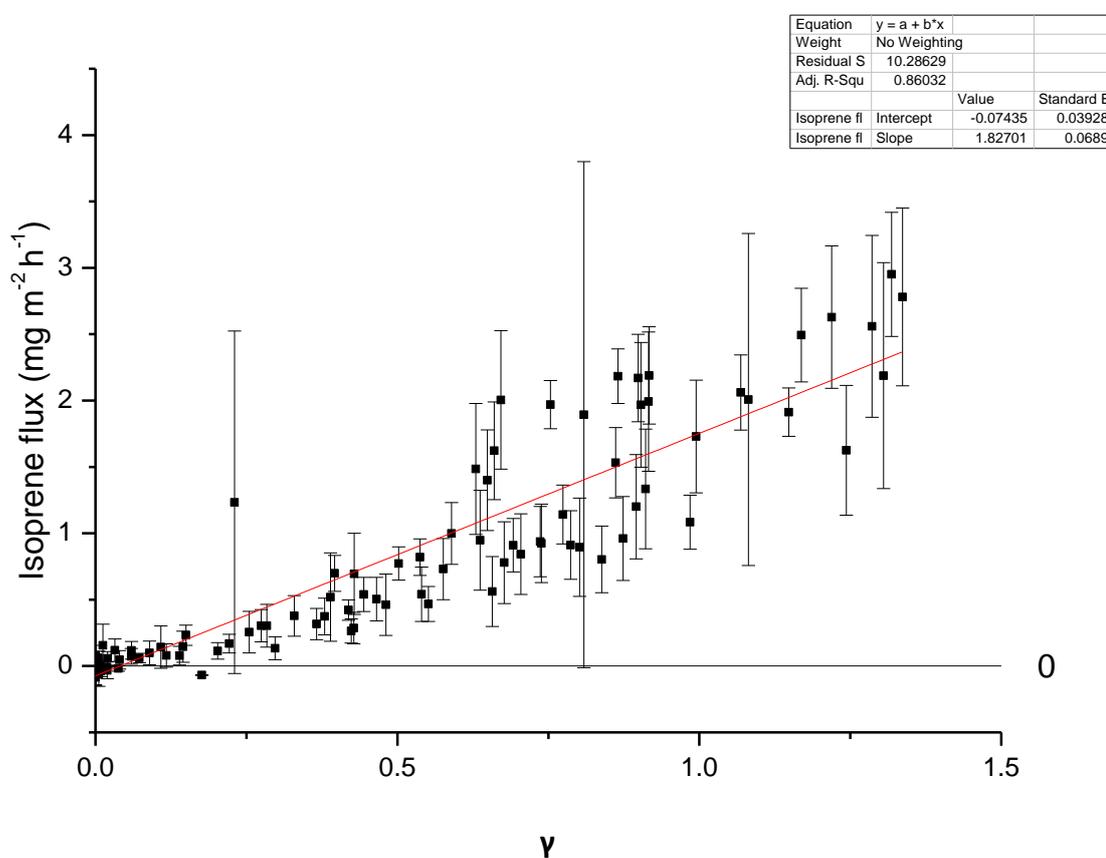


Figure 2.3. Emission flux of isoprene (Auchencorth) plotted against the activity factor,  $\gamma$ . The gradient gives the emission factor,  $\epsilon$ .

To our knowledge, this is the first measurement of this nature from a British peatland ecosystem. This makes comparison with other results in the literature challenging. The most comparable results available are for sub-arctic wetland sites in Sweden where mean normalised isoprene emission rates of  $0.373 \text{ mg m}^{-2} \text{ h}^{-1}$  and  $0.707 \pm 0.405 \text{ mg m}^{-2} \text{ h}^{-1}$  were reported by Holst et al. in 2010 (Holst, Arneth et al. 2010) and Janson and De Serves in 1998 (Janson and De Serves 1998) respectively. The isoprene flux reported by Holst et al. was obtained using DEC and is just over 20% of the respective flux found at Auchencorth but was standardised to  $20^\circ \text{ C}$  which helps to explain the difference as the Auchencorth measurement was scaled to  $30^\circ \text{ C}$ . However, Janson's emission factor which was acquired using a Teflon chamber was normalised to the same parameters that were used in our analysis, but was still significantly lower than what was observed at Auchencorth. A potential reason for this may be due to lower temperatures during measurements at the Swedish site but this should theoretically be accounted for by the normalisation of the emission algorithm, although it is unknown how well the algorithm achieves this in practice. The variation in emission rates is more likely due to the different environments and geographical locations that measurements were acquired from. The dominant vegetation at the Swedish sites is mostly sphagnum moss, which while present at Auchencorth is accompanied by large quantities of many other species, several of which their potential to emit isoprene is currently unknown and could therefore be responsible for the higher emission factor observed.

It should be noted that the weather at Auchencorth during the measuring period was significantly brighter and warmer than previous years- temperatures regularly reached 30 ° C. This was helpful because it means that environmental conditions were closer to the standard model conditions 30 ° C and 1000  $\mu\text{mol m}^{-2}\text{s}^{-1}$  used in the MEGAN emission model and consequently the results obtained were less dependent on the emission algorithm to normalise to these conditions than they would have been with more typical weather. The emission factor for a peatland ecosystem presented here should assist in optimising European air quality models as there is a distinct lack of data for similar ecosystems and land types.

### 2.3.1.2 Diurnal variation in basal emission factor

The base emission factor for isoprene derived from the MEGAN model appeared to vary greatly depending on the time of day. Generally, it increased gradually in the morning until it peaked around midday before tailing off in the evening. This trend can be observed for a few days of data in Figure 2.4.

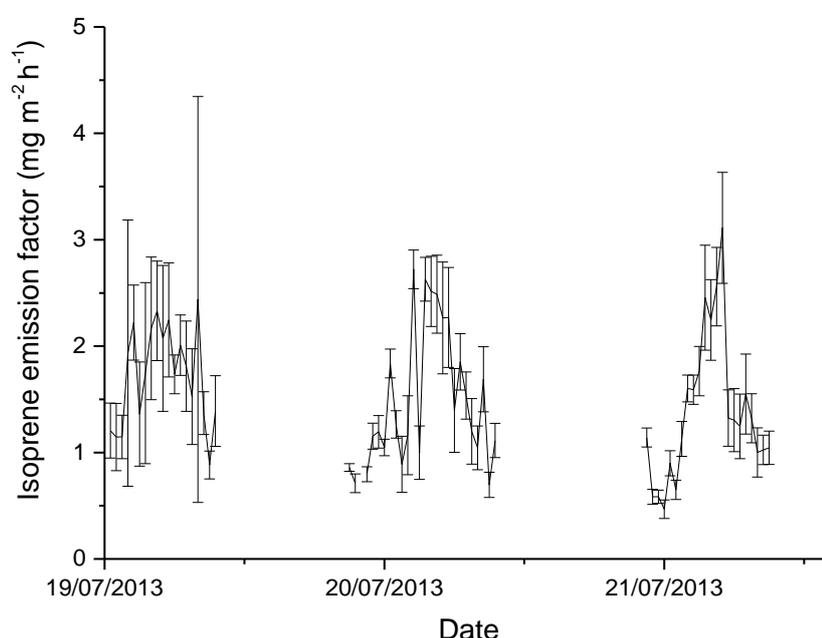


Figure 2.4. Diurnal variation in the isoprene emission factor observed at Auchencorth.

Basal emission factors are by their nature constant values used to initialise models although this is clearly not the case for these results. It appears to follow a diurnal pattern, with the maximum value occurring around midday when the temperature and sunlight is most intense. This deviation implies that the algorithm fails to perfectly capture or account for all of the physical processes involved in emission, which could lead to gross misrepresentation of BVOC emissions because static emission rates are used in most models. (Hewitt, Ashworth et al. 2011) Furthermore, many of the emission factors used in models are from leaf-level observations made at a specific time of day- and therefore unable to account for the temporal change.

Clearly, further work is needed to establish the biophysical processes controlling this diurnal variation, which (Hewitt, Ashworth et al. 2011), who observed a similar trend above tropical forests and oil palm plantations, have attributed to circadian control of emission factors. Until this process can be represented within the emission algorithm, emission factors should perhaps be expressed as a diurnally dependant function to replicate this behaviour more accurately in modelling activities. Furthermore, field studies should state the range of values observed.

### 2.3.1.3 Estimation of net carbon exchange at Auchencorth

The isoprene emission factor presented in section 2.3.1.1 was combined with micrometeorological data for years 2011 through 2013 to estimate isoprene emissions from Auchencorth moss using the MEGAN emission model. This was achieved by scaling the predicted emissions to reflect the area of the field site, which was estimated using satellite images (Google Earth). The amount of reactive carbon in the form of isoprene which was released into the atmosphere, according to the MEGAN model, from the Auchencorth field site from 2011 to 2013 is shown in Figure 2.5.

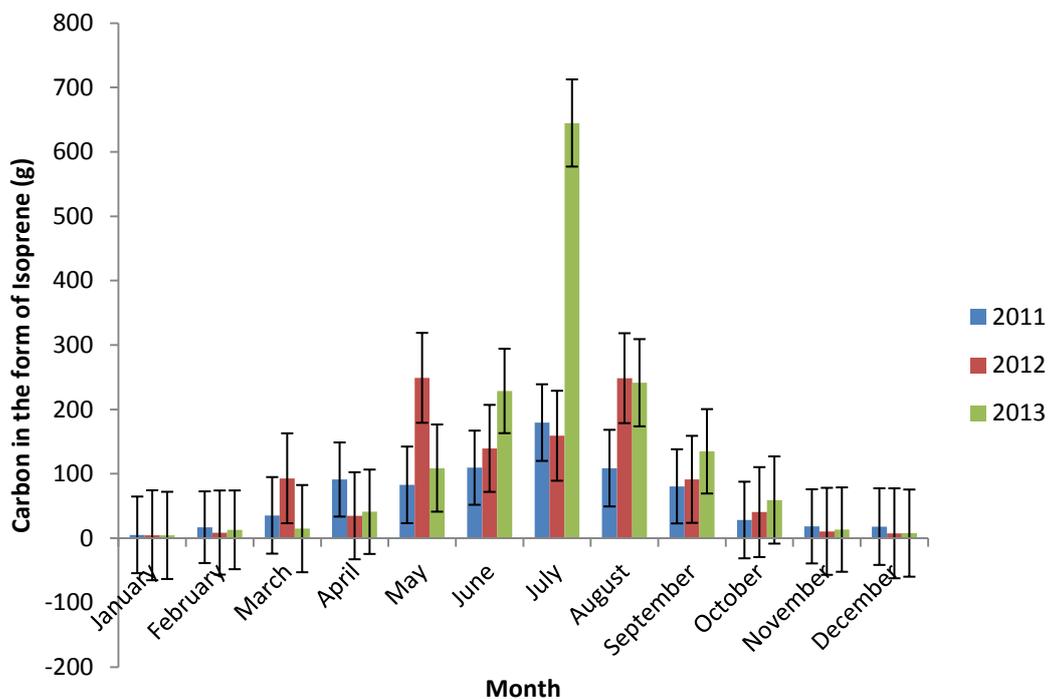


Figure 2.5 Estimated isoprene carbon emissions from Auchencorth by year (MEGAN)

Isoprene is expected to be the dominant BVOC emitted and therefore emissions were estimated using MEGAN for the years 2011-2013 as shown in Figure 2.5. The emission data were obtained by inputting the back calculated emission factor and appropriate PAR and temperature data into the MEGAN emission algorithm. These resulting modelled fluxes were then compared to onsite measurements of CO<sub>2</sub> exchange at Auchencorth from which it is probable that “Auchencorth moss” acts as a substantial net carbon sink. This analysis shows that isoprene fluxes represent less than a 1% loss of reactive carbon from the total that is sequestered by Auchencorth Moss. Perhaps try to find out typical values for say tropical forests.

### 2.3.1.4 Flux footprint & direction

The flux footprint for the Auchencorth field site was calculated according to the footprint model from Kormann and Meixner (Kormann and Meixner 2001). Flux data was sorted into different groups based on the spatial direction which it came from by looking at the data from the sonic anemometer. This allowed wind roses for the mean flux and concentration at Auchencorth to be produced, which are shown in Figure 2.6.

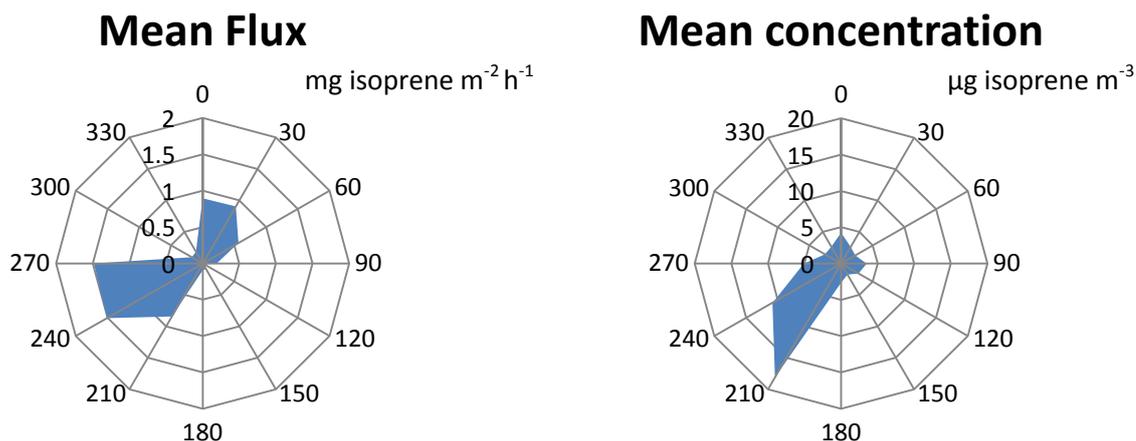


Figure 2.6 Wind roses of mean flux and concentration for the measuring campaign at Auchencorth

The wind roses verify that the flux footprint is largely from the Southwest but there also appears to be a smaller contribution from the Northeast. Investigating the main species of vegetation present in these directions could help to identify the plant species that are the most prolific isoprene emitters at Auchencorth. The results could then be validated by screening the targeted species using enclosures.

#### 2.3.1.5 Other details

BVOC field measurements were performed in July and August 2013 however the quantity of data acquired was limited due to various technical difficulties. Nevertheless, the two and a half days of high quality data obtained in July demonstrated that Auchencorth Moss can become a significant source of isoprene to the atmosphere during the hotter periods of the year. The detection of isoprene from a peatland ecosystem using a canopy-scale DEC system is an important result because it establishes that our system is sufficiently sensitive to measure fluxes from low emitting ecosystems of this nature, although the warmer weather and increased emission rates somewhat relaxed the demands for measurement sensitivity. The acquisition of more data would have strengthened the statistical significance of the results but this will be addressed in future work where greater volumes of data and coverage will be targeted. This, in conjunction with individual screening of more individual plant species to ascertain the dominant isoprene emitters, will assist with developing our knowledge of BVOC emissions from peat bogs and similar ecosystems. Furthermore, extending this work to include other important BVOC, such as monoterpenes, could further deepen our understanding of BVOC emissions in atmospheric chemistry and climate.

The PTR-MS failed shortly after this data set was acquired and was still not operational as of May 2014 due to electrical malfunction and technical difficulties. The current flux calculations were performed using an old calibration factor which needs to be updated to better represent modifications that were subsequently made to the instrument. The inlet system was upgraded and a new ion source installed which yielded a sensitivity boost up to a factor of four with the peak primary ion count rate reaching over 40 million counts  $\text{s}^{-1}$ . Updated zero-air calibrations should be retrospectively applied to the original PTR-MS data when this becomes available. The lack of a recent zero air correction will not impact the outcome of the flux analysis which is based on deviations from the mean although it will alter the concentrations of BVOC observed.

## 2.3.2 Alice Holt:

### 2.3.2.1 Normalised emission factors

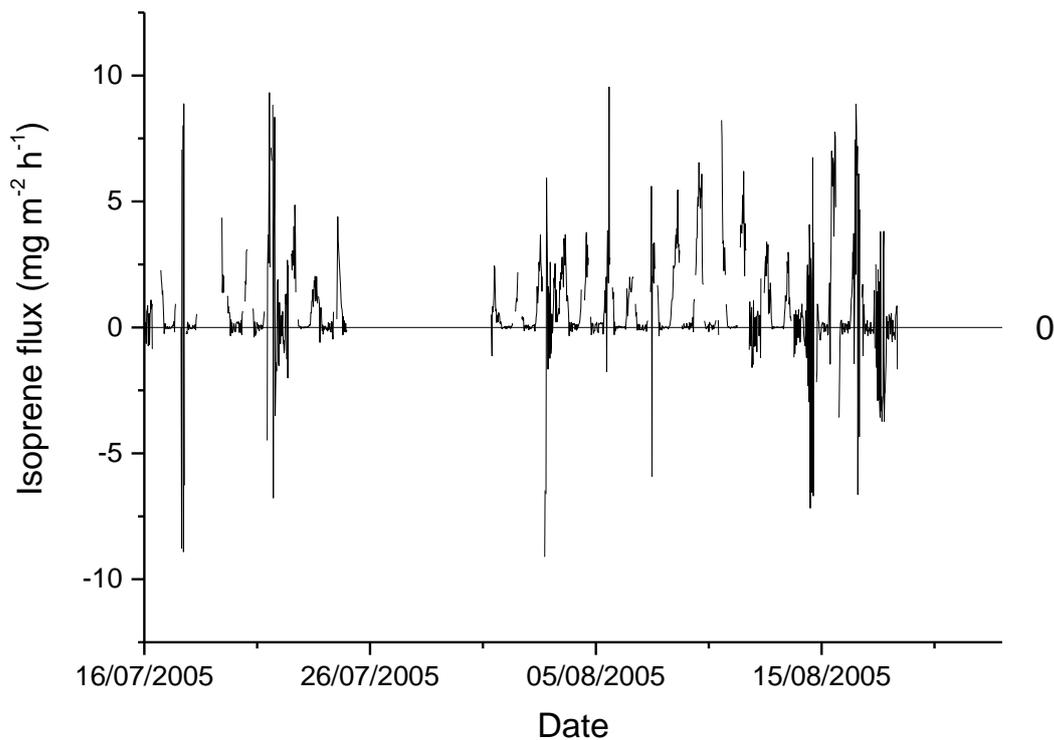


Figure 2.7 Isoprene flux for the Alice Holt measuring campaign, errors were obtained by characterising the background noise of the cross-correlation function but have been omitted from this figure as they severely hinder visual interpretation.

The first isoprene emission flux observed over British oak is shown in Figure 2.7. This should therefore be a useful resource for the modelling community as there are currently very few published emissions for European oak forests. There were technical difficulties during the measuring campaign which resulted in a lapse of PTR-MS measurements which can be seen in Figure 2.7.

The emission factors obtained from the isoprene emission data for the Alice Holt forest site were  $9.0 \pm 0.4$  mg isoprene  $m^{-2} h^{-1}$  and  $4.0 \pm 0.2$  mg isoprene  $m^{-2} h^{-1}$  using the G95 and MEGAN algorithms respectively. The plots of measured flux against the emission activity factor,  $\gamma$ , from which these emission factors were derived are shown in Figure 2.8 and Figure 2.9 for the G95 and MEGAN algorithms respectively. The plot of isoprene emission flux against the activity factor,  $\gamma$ , is not particularly linear when using the G95 algorithm as can be seen in Figure 2.8. It was initially thought that this may be due to the fact that this algorithm does not account for previous days light and temperature data but this was found not to be the case when the same behaviour was observed using an updated algorithm, MEGAN, which considers this. It looks like a function, such as a polynomial, could improve the fit of the data although it is possible that a systematic error could explain the patterns observed. Another explanation is that there are as of yet unknown factors or mechanisms at play which are presently unaccounted for by these models. This could potentially help to explain the diurnal cycle that was also observed in the emission factor for this site, which should be constant if the algorithms exactly replicated emissions.

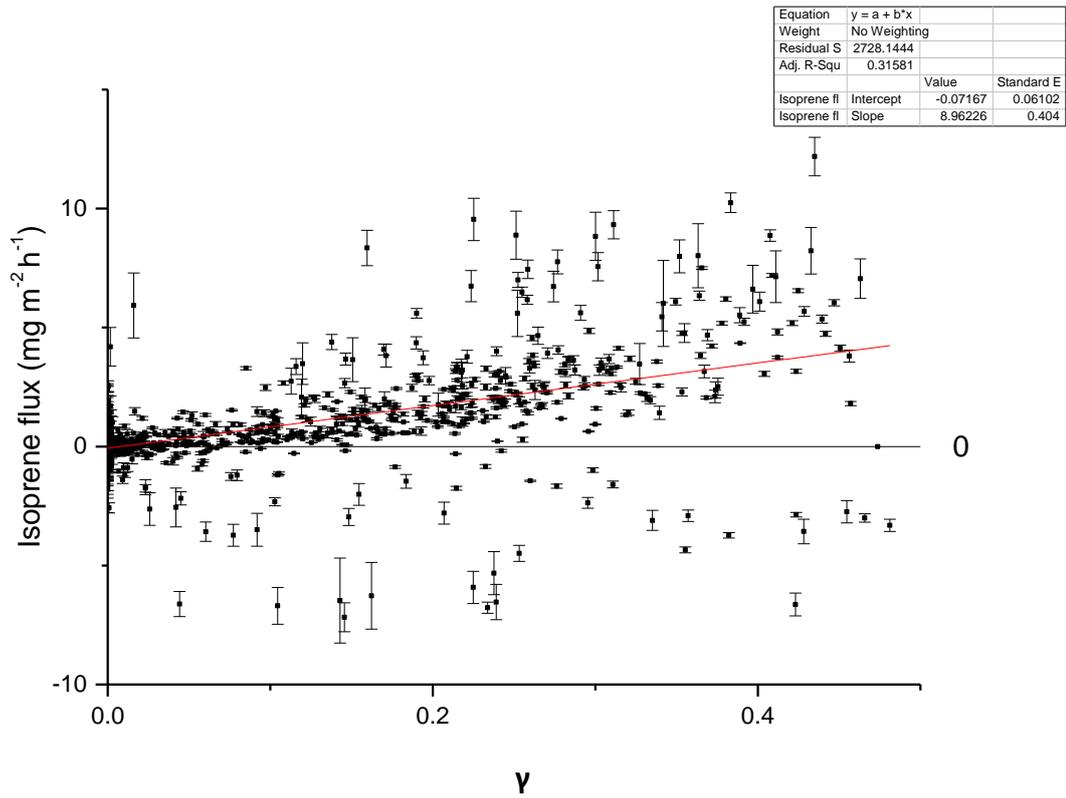


Figure 2.8 Emission flux of isoprene plotted against the activity factor,  $\gamma$  for the G95 emission algorithm.

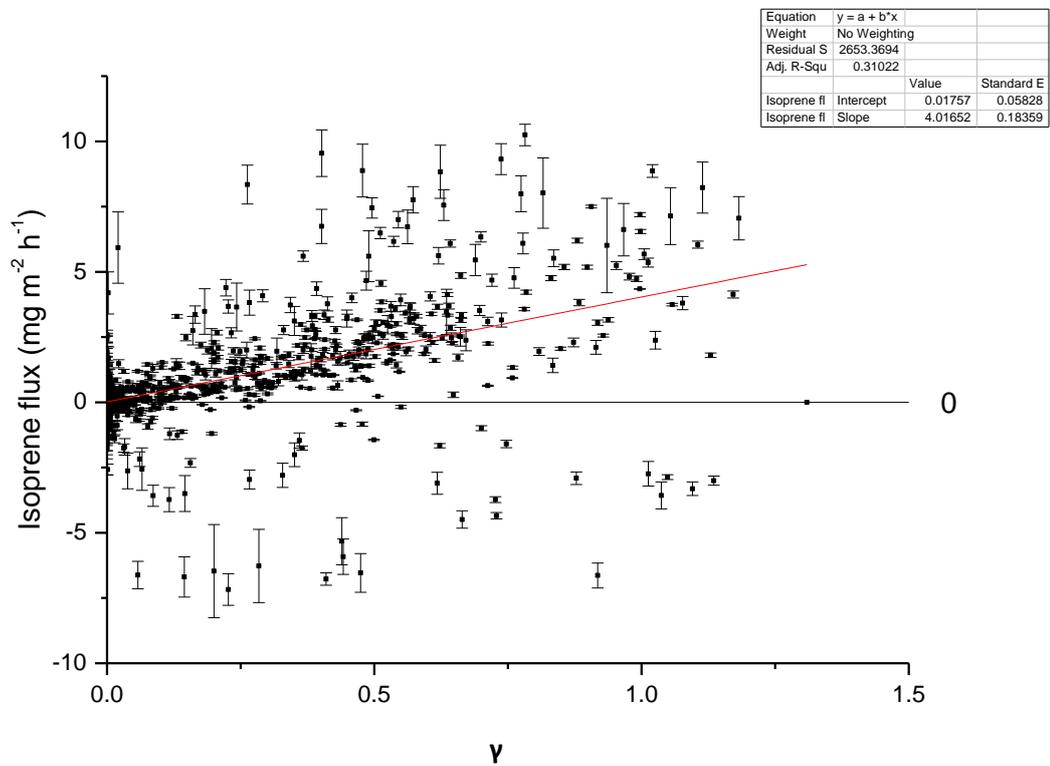


Figure 2.9 Emission flux of isoprene plotted against the activity factor,  $\gamma$  for the MEGAN emission algorithm.

The isoprene emission factors obtained for the Alice Holt data set using the G95 and MEGAN algorithms were not in agreement, even when considering their errors. The emission factor using G95 was over double that obtained for MEGAN. However, the results from the MEGAN model are probably more realistic because it is a much newer model, by more than 10 years, which is still employed today. (Stavrakou, Muller et al. 2014) The discrepancy in the uncertainty of the emission factor between the two algorithms is mainly due to the data filtering that was performed when using MEGAN. This was because the low light flux results, which were removed from the MEGAN data set, incur a much larger random error because the signal from the PTR-MS is usually accompanied with more noise due to lower concentrations of BVOC.

### 2.3.2.2 Diurnal variation in emission rates

There appeared to be diurnal variation in the emission rate, as was seen in the Auchencorth data, when using both the G95 and MEGAN algorithms as shown in Figures 2.10 and 2.11 respectively.

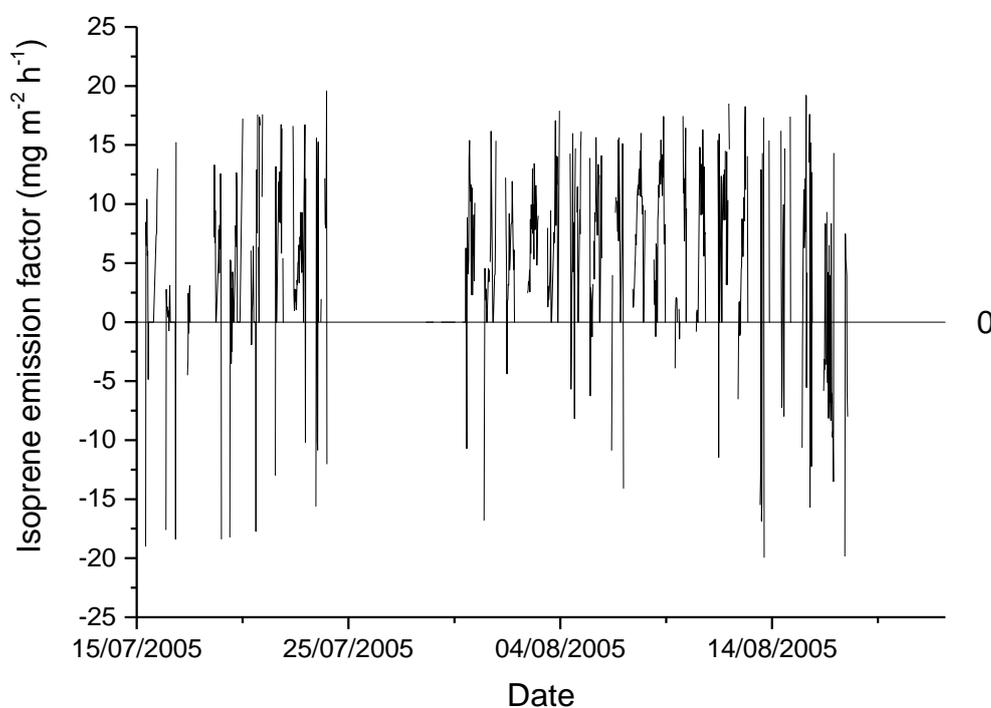


Figure 2.10 Variation of the emission factor observed during the measuring campaign at Alice Holt forest using the G95 algorithm.

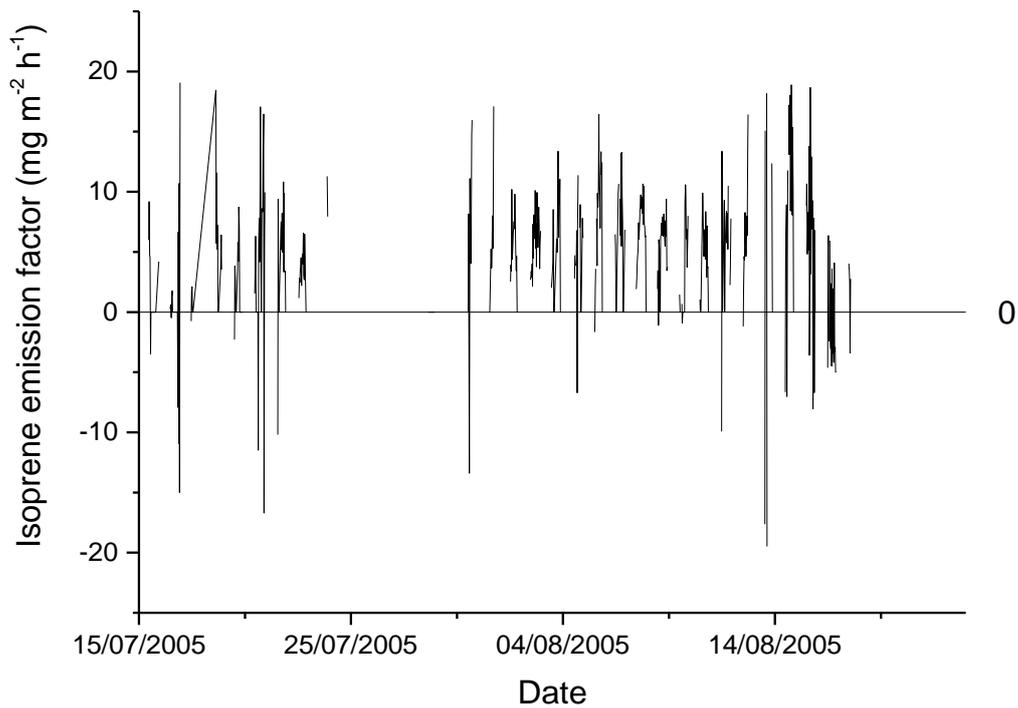


Figure 2.11 Variation of the emission factor observed during the measuring campaign at Alice Holt forest using the MEGAN algorithm.

The diurnal variation in the emission factor observed in these data may be due to the simplistic way in which the canopy has been treated using the G95 and MEGAN models, effectively as one large leaf that covers the entire canopy. The manner in which light is attenuated as it travels through different layers of the canopy, and the resultant changes to the emission rate at different tiers was thought to be a possible reason for this divergence because the models that were used for analysis neglect to consider this. However, as this behaviour was also encountered for the Auchencorth data, this is thought unlikely, as canopy depth at Auchencorth is much smaller. This not only makes separating the canopy into discrete levels much more difficult but also means that changes to the emission rate for different layers would likely be small, and probably negligible, as the canopy layers at Auchencorth are all very similar. Therefore, this suggests that there may be another process responsible, perhaps circadian control (Hewitt, Ashworth et al. 2011) given the observed diurnal variation.

### 2.3.2.3 Optimisation of emission factors

The effect of changing the number of previous days light and temperature data included within the MEGAN model algorithm was investigated using the Alice Holt data to see if an optimum value could be found. The standard parameters are one and 10 days, termed  $Days_x$  and  $Days_{yz}$  respectively, but this was extended up to three and 20 days by adding functionality into the excel spreadsheet which allowed these numbers to be changed. For example, this allowed one and 11 days, two and 15 days or any other combination to be used. The linearity of the flux vs  $\gamma$  plots using the modified parameters was investigated by checking the  $R^2$  and “M-Score” values. The “M-score”,  $M$ , is the normalised mean square error between the observed and modelled data and is given by equation 3:

$$M = \frac{(\overline{E_o - E_p})^2}{\overline{E_o} \cdot \overline{E_p}} \quad (3)$$

Where  $E_0$  is the observed emission,  $E_p$  is the predicted emission and over bars indicate mean values.

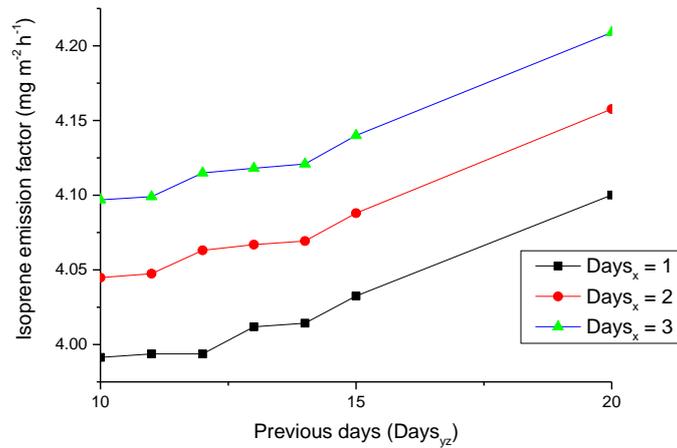


Figure 2.13 Isoprene emission factor variation with changing previous days light and temperature data.

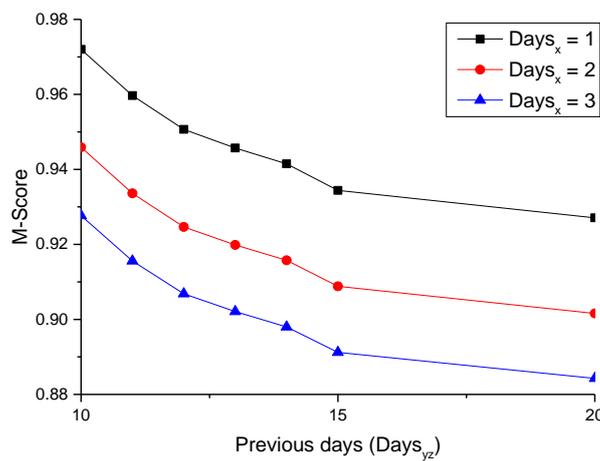


Figure 2.14 M-Score variation with changing previous days light and temperature data.

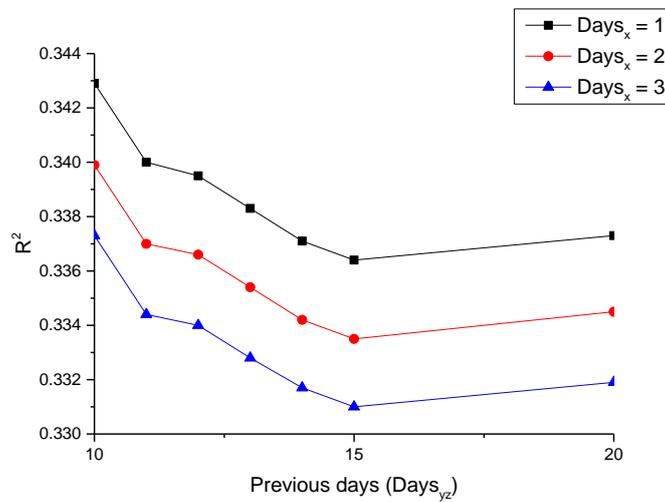


Figure 2.15 R<sup>2</sup> value variation with changing previous days light and temperature data.

Increasing the number of previous days light and temperature data that MEGAN considers from the standard values slightly increases emission factors but also results in a poorer fit to the data. M-scores and  $R^2$  values decrease as the time parameters are increased from the defaults used in the MEGAN model as shown in Figures 2.14 and 2.15 respectively. It was therefore decided to leave the days previous data that MEGAN includes unchanged from the standards in order to estimate emissions with more accuracy.

### 2.3.2.4 Other details

The Alice Holt data set represents one of the very first collected by the DEC method. Consequently, the dwell times that were used to sample BVOC compounds were very short in comparison to what is more conventionally used nowadays (Langford, Misztal et al. 2010; Hortnagl, Bamberger et al. 2011; Laffineur, Aubinet et al. 2012). Dwell times as short as those used in this dataset, 50ms or less, result in measurements with very large random errors which severely obfuscate the determination of genuine fluxes within cross correlation functions. Consequently, many of the calculated fluxes are negative due to the random error being greater than the magnitude of the measurement. This is in stark contrast to the Auchencorth data set where none of the flux data are negative, although some may be when considering their errors. This results in a much poorer linear fit for the flux vs  $\gamma$  plots for the Alice Holt data when compared to the Auchencorth data, with  $R^2$  values of  $\sim 0.3$  and  $0.86$  respectively which subsequently results in larger uncertainties in the emission factors obtained for the Alice Holt data due to increased uncertainty in the gradient.

### 2.3.3 Whim bog:

Mean isoprene emission factors from *Sphagnum* moss samples were found to be  $0.20 \pm 0.02 \mu\text{g g}^{-1}\text{h}^{-1}$  based on total dry mass of moss samples. The mean emission rates for the different moss treatments that were sampled are displayed in Figure 2.16.

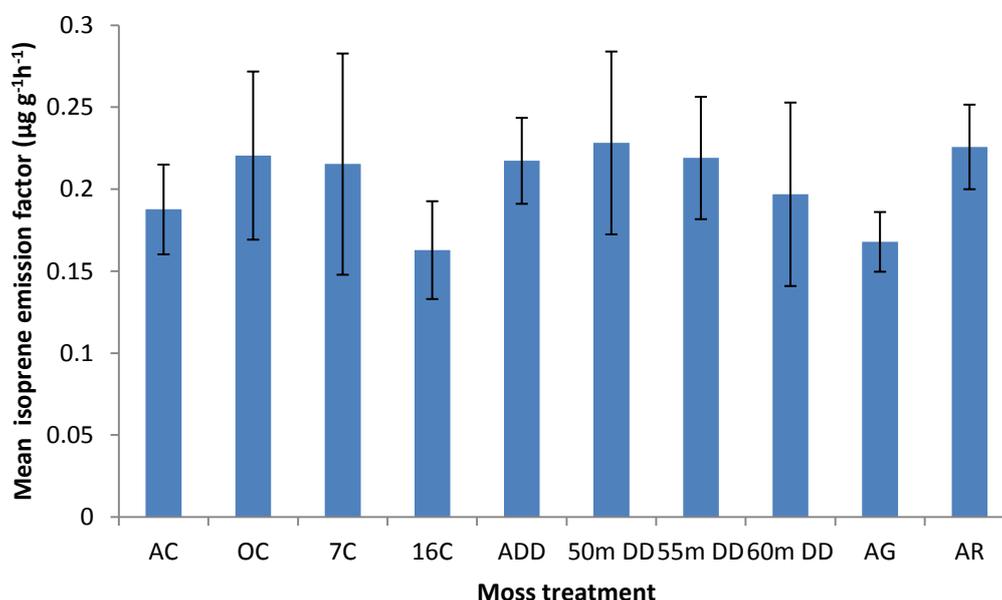


Figure 2.16. Mean isoprene emission factor for different moss treatments ( $\pm$  SE) for total dry mass of moss samples. (AC- All control samples,  $n=11$ ; OC-Off-plot control samples,  $n=2$ ; 7C-Control samples from plot 7,  $n=3$ ; 16C-Control samples from plot 16,  $n=6$ ; ADD-All samples that were treated with dry nitrogen deposition,  $n=12$ ; 50m DD-Dry deposition at 50m from source (green and red samples),  $n=5$ ; 55m DD-Dry deposition at 55m from source (green and red samples),  $n=4$ ; 60m DD-Dry deposition at 60m from source (green and red samples),  $n=3$ ; AG-All green samples,  $n=9$ ; AR-All red samples,  $n=14$ )

The isoprene emission factor was then calculated assuming that it is only the capitulum (head) of the moss samples that emit isoprene and these results are shown in Figure 2.17 although this will have increased the uncertainty of these measurements compared to the whole mass emission factors due to the additional process of removing the capitulum heads that was required.

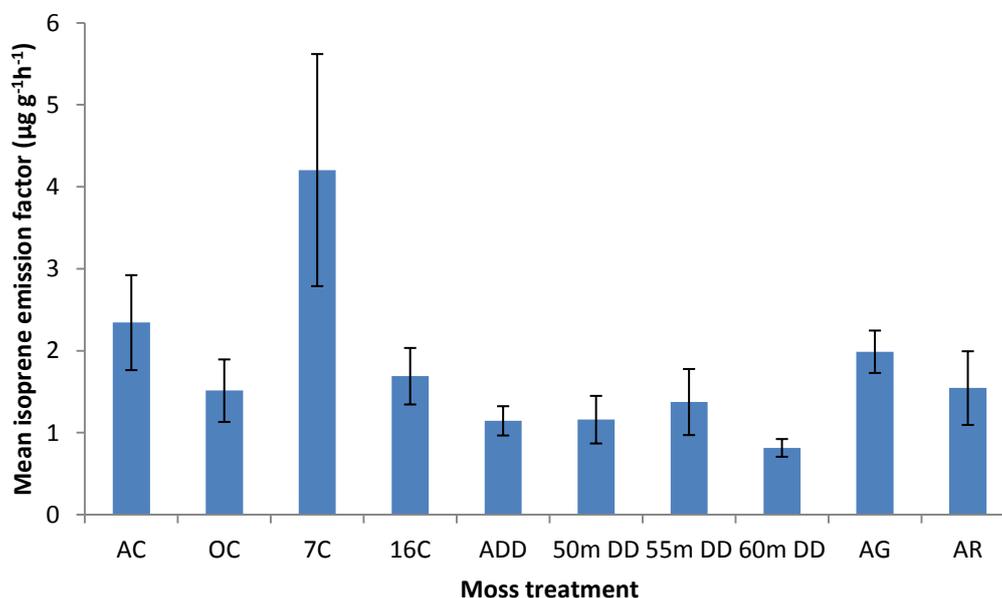


Figure 2.17. Mean isoprene emission factors ( $\pm$  SE) for different moss treatments for the capitulum mass of moss samples, (AC- All control samples, n=11; OC-Off-plot control samples, n=2; 7C-Control samples from plot 7, n=3; 16C-Control samples from plot 16, n=6; ADD-All samples that were treated with dry nitrogen deposition, n=12; 50m DD-Dry deposition at 50m from source (green and red samples), n=5; 55m DD-Dry deposition at 55m from source (green and red samples), n=4; 60m DD-Dry deposition at 60m from source (green and red samples), n=3; AG-All green samples, n=9; AR-All red samples, n=14)

These emission factors were extrapolated to give an area-based measurement relative to the mean sphagnum moss biomass ( $\text{g dry mass m}^{-2}$ ) at comparable sites in Finland. (Laiho, Ojanen et al. 2011) The mean extrapolated isoprene emission factor over all samples was  $0.074 \pm 0.07 \text{ mg m}^{-2}\text{h}^{-1}$ . The upscaled emission factors for different moss treatments are shown in Figure 2.18 for the total dry mass of moss samples.

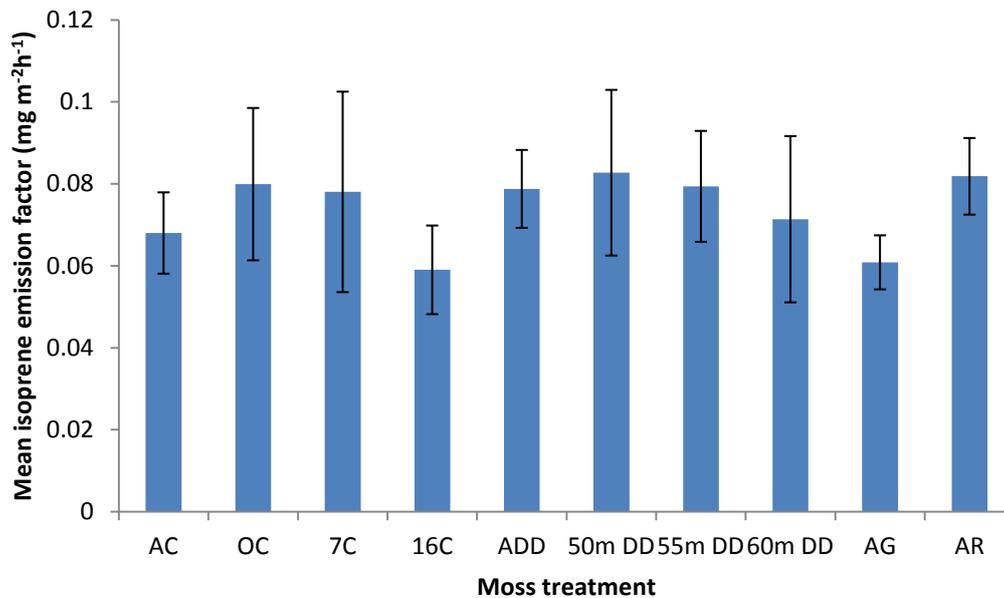


Figure 2.18 Extrapolated mean isoprene emission factors for different moss treatments ( $\pm$  SE) for total dry mass of moss samples, (AC- All control samples, n=11; OC-Off-plot control samples, n=2; 7C-Control samples from plot 7, n=3; 16C-Control samples from plot 16, n=6; ADD-All samples that were treated with dry nitrogen deposition, n=12; 50m DD-Dry deposition at 50m from source (green and red samples), n=5; 55m DD-Dry deposition at 55m from source (green and red samples), n=4; 60m DD-Dry deposition at 60m from source (green and red samples), n=3; AG-All green samples, n=9; AR-All red samples, n=14)

Comparison of the extrapolated emission factor of  $0.074 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  with the isoprene emission factor of  $1.83 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  from Auchencorth (section 2.3.1.1) suggests that approximately just 4% of the isoprene observed at Auchencorth can be attributed to *Sphagnum* moss. The moss laboratory measurements are normalised to 20 ° C whereas the Auchencorth measurements were normalised to 30 ° C which accounts for a portion of this difference because isoprene emissions are generally temperature dependent. For example, the Alice Holt isoprene emissions drop by about 75% when normalising to 20 ° C from 30 ° C using the G95 algorithm. Assuming emissions decrease similarly for the MEGAN model, it would result in an emission factor of  $\sim 0.45 \text{ mg m}^{-2} \text{ h}^{-1}$  for the Auchencorth field site when normalised to 20 ° C which would bring the moss emissions up to about 16% of this figure. However, it is unfortunately not a trivial matter to change the normalisation temperature of the MEGAN model. Unlike G95, there isn't a single variable,  $T_s$ , which can be changed to alter the normalisation temperature which is probably a consequence of the additional complexity of the MEGAN emission algorithm.

Therefore, either there are other sources of isoprene emitting biomass at Auchencorth that have not yet been identified, environmental conditions cause the *Sphagnum* moss to emit more in the ecosystem compared to the laboratory or the DEC measurements have larger uncertainties than thought. *Molinia caerulea* is suspected to be a likely emitter and has been selected for further study this summer. (Owen 2014)

However, it should be noted that the uncertainties associated with scaling up emissions in this way are very large, probably at least a factor of two (Owen, Boissard et al. 2001) and very possibly much higher. The fact that the area based emission factors were obtained using mean moss biomasses from a different site will also increase the uncertainty of these results. Dried moss biomass data, collected at Auchencorth in 2003 & 2004 for the Carboment project was examined to determine whether a mean mass per square metre more characteristic of this field site could be calculated but it was decided that the variation in these masses was too large to be used. The mass of moss ranged from 1.44 to 652.3 g dry weight moss m<sup>-2</sup> for 17 collections spread over the course of 18

months. (Anderson 2014) It is also unclear whether removing *Sphagnum* moss from its natural environment affected the emissions that were subsequently measured in a laboratory. Whilst every effort was made to try and keep conditions similar to the site from which the moss samples were taken, the environment still differed in many ways. At Whim, the moss was exposed to the elements and surrounded by other vegetation but at CEH the moss was stored in a warm laboratory where the air was still and was watered using a spray bottle instead of receiving rainwater naturally. This may have had an effect on the isoprene emissions observed due to the unfamiliar environment. Furthermore, the actual sampling process was very stressful for the moss and certainly not representative of its natural environment. Each moss sample spent at least 90 minutes within the adapted LICOR enclosure and was therefore severely dehydrated after sampling due to the use of a drying system which was necessary to safely operate the LICOR and avoid damage to its components. It is therefore entirely plausible that the emission potential of the moss observed under these circumstances is not typical of moss in its' natural habitat. This could also contribute to the difference in isoprene emission factors seen between the enclosure moss measurements and DEC canopy-scale measurements.

In spite of all uncertainties associated with the chamber measurements, each moss sample was subject to the same conditions, and comparisons can be made between different moss treatments and colour types. In this experiment, red sphagnum moss emits ~ 25% more isoprene than equivalent green samples (P=0.02). Further, isoprene emissions from mosses growing on the dry deposition treatment transect were ~50% lower than controls (P=0.01). No other statistically significant trends could be found between the moss samples but this is not to say that they do not exist. Increasing the number of sample sizes for different treatment types could potentially reveal additional relationships which were not apparent for the moss samples that were studied.

A summary table of all isoprene emission factors that were obtained during measurements or analysis during the placement is displayed in Table 2.3

Measurement	Emission factor	Method	Comment	Factors
<b>Auchencorth Moss</b>	$1.83 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$	DEC	Short measurement period	Full ecosystem (peatland), summer conditions
<b>Alice Holt</b>	4.0 to 9.0 $\text{mg m}^{-2} \text{ h}^{-1}$	DEC	Short "dwell times"	Full ecosystem (oak forest), summer conditions
<b>Whim bog</b>	$0.074 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$	Enclosure	Relatively small sample pool and extrapolation	Single species, artificial conditions

Table 2.3 Summary table of isoprene emission factors and accompanying measurement details.

It can be seen from Table 2.3 that emission factors from multiple environments, some of which are highly contrasting in terms of emission potential, have been successfully obtained. Moreover, the discrepancy between the emission factors from Auchencorth Moss and the *Sphagnum* moss from Whim bog effectively illustrates the potential for misrepresenting emissions when extrapolation of enclosure measurements is applied.

## 2.4 Conclusions

The first British canopy-scale isoprene emission factors for peatland and oak forest ecosystems were successfully determined which will help to develop our understanding of BVOC emissions from these ecosystems, especially for similar sites within Britain. Furthermore, these emission factors can be used as input data for atmospheric models which could improve the accuracy of regional emissions. Enclosure measurements of moss samples performed in the laboratory yielded an isoprene emission factor which was extrapolated in order to allow comparison with the canopy-scale peatland emission factor. It was found that the magnitude of the moss emission factor was  $0.074 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  which was much smaller than the peatland emission factor,  $1.83 \pm$

0.07 mg m<sup>-2</sup> h<sup>-1</sup>, approximately a factor of 0.04 although this rises to 0.16 when crudely normalising the peatland emission factor to 20 ° C. The enormous difference between the enclosure and field measurement clearly conveys the huge potential in variability of measurements obtained at differing scales. Considering the disparity in emission factors that was found using leaf-level and canopy-scale techniques, it is perhaps best to utilise a wide selection of approaches in the future to help determine the real emissions and the factors and mechanisms which drive them.

## Chapter 3: VOCsNET

### 3.1 Introduction

This chapter describes the beginning of work undertaken to construct a global BVOC flux database (VOCsNET) and the trends in BVOC flux measurements that have been identified from this information. All dates mentioned refer to when the measurements were actually taken, rather than the date they were published, unless otherwise stated.

### 3.2 Methods

There are potentially a large number of research papers which may be suitable for inclusion into VOCsNET, however the process of searching the literature to find all the studies which have the right type of measurement data and information is not a trivial task. Figure 3.1 shows a flow chart of the sorting process and logic used to identify and screen papers for suitability and to record the metadata.

Papers presenting above canopy fluxes of BVOCs were located using Thomson Reuters' "Web of Knowledge" citation indexing service in August 2013. The service has since been rebranded "Web of Science" (WoS). In order to assemble a comprehensive representation of BVOC research to date, the following compounds and criteria were searched for on "Web of Science" in the "Topic" field:

*((isoprene or monoterpen\* or sesquiterpen\* or ((biogenic or natural) and oxygen\* and (volatile or VOC\*))) and flux\* and (measure\* or field\*))*

The research papers which were available with Natural Environment Research Council (NERC) CEH and University of Edinburgh licences were downloaded, wherever possible. The paper was then read to determine whether it contained flux data that would be suitable for insertion into the VOCsNET database.

Any BVOC fluxes that were reported in terms of ground area, rather than per gram dry biomass, were deemed to be suitable and enclosure measurements were excluded unless the enclosure used was a large ground surface chamber with area based measurements. While it is possible to upscale the enclosure measurements expressed in terms of gram dry mass, the results obtained in this manner would not be representative of an ecosystem or land area. Furthermore, the uncertainties of these measurements would be very high (see Introduction and chapter 2). It was therefore decided that these measurements would not be as helpful to modellers and that the focus should be on true canopy-scale flux measurements. However, as this study included recording very basic metadata from the papers with enclosure measurements (authors, year of publication), and as the papers have been archived, where available, extrapolation of these results could contribute to an extension of VOCsNET which could provide useful comparisons.

If papers were found to contain canopy/ecosystem scale BVOC flux measurements, detailed metadata were entered into a Microsoft Excel spreadsheet. Data fields in the spreadsheet are summarised in Table 3.1. The data fields were kept deliberately simple to allow easy identification of patterns in the dataset. The data fields included the authors, date of study and measurement dates, vegetation present, ecosystem type, sampling technique(s) used, any notes of interest and coordinates of study site(s). Missing information was obtained, wherever possible, from other

papers that shared a common study site otherwise it was searched for online but could not always be located. This occurred relatively rarely and was noted in the relevant field whenever it did. It was almost always the coordinates of the site that were not provided and it was sometimes necessary to estimate the coordinates using Google maps. Metadata fields in the excel spreadsheet for papers that were thought to be suitable for inclusion into the VOCsNET database are over 95% complete. If a paper was deemed to be unsuitable, the reason for this was recorded.

<b>Data fields</b>
Paper #
File path
Author(s)
Year of publication
Vegetation
Location/ecosystem type
Coordinates
Date(s) of measurements
Notes (technique(s) used, BVOC measured)
Journal
Gap-filling, uncertainties, issues encountered

Table 3.1 Data fields for VOCsNET database as part of the VOCsNET-suitability identification process

A flow chart of the process used to identify and screen papers for suitability is provided in Figure 3.1 for clarity.

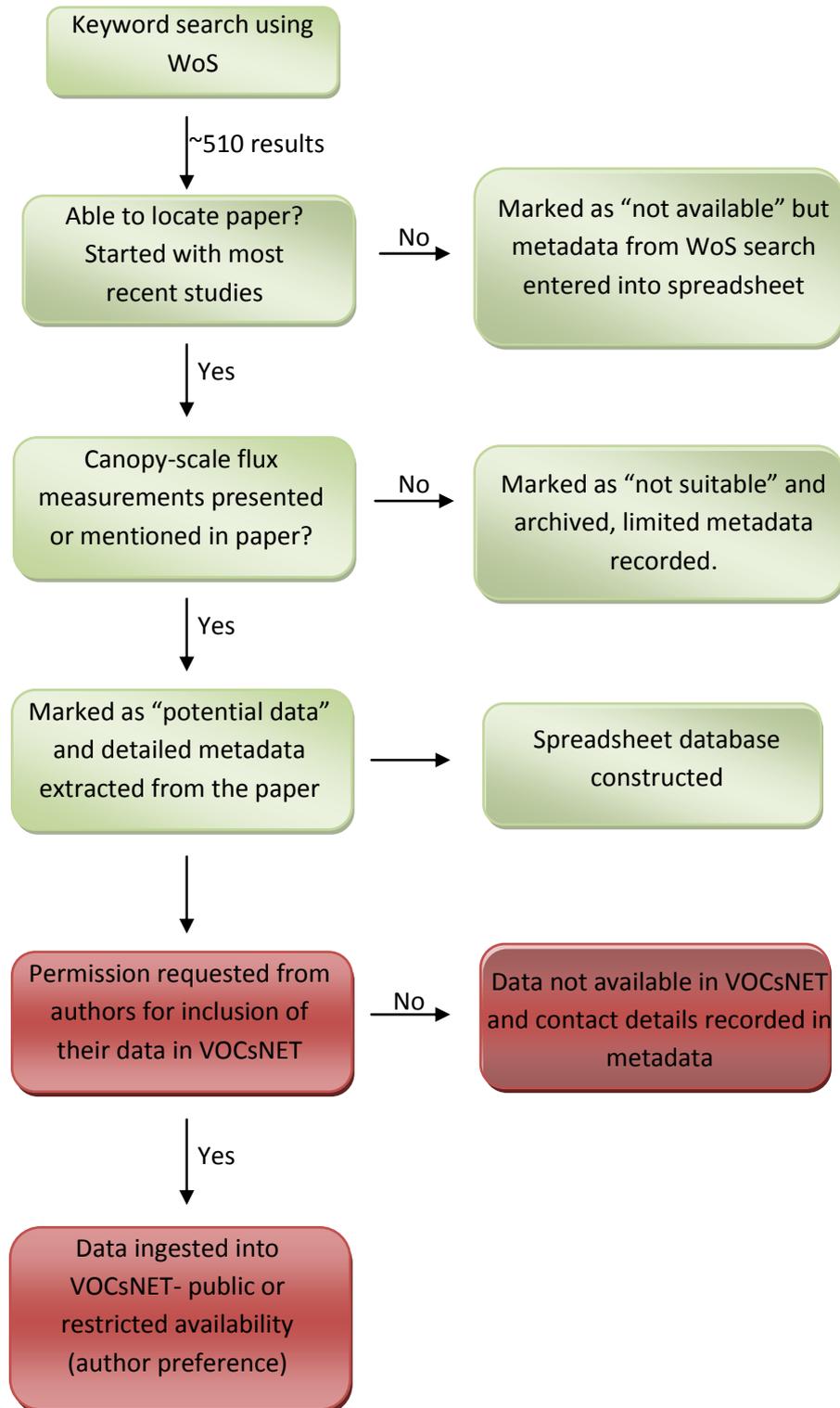


Figure 3.1 Flow chart of the process used to establish a BVOC flux database, green shading indicates completed tasks and red shading represents tasks to be completed (future work).

### 3.3 Results & Discussion

#### 3.3.1 Papers published

Using the search terms described in the methods section, Web of Knowledge returned 510 papers that potentially reported canopy scale BVOC fluxes. 181 of these were deemed to be suitable while the remainder consisted primarily of enclosure and laboratory measurements. From these papers it was determined that there were 282 data sets that could be entered into the VOCsNET database due to many papers presenting results for multiple study sites or applying more than one BVOC sampling technique.

The temporal distribution of suitable data sets is presented in Figure 3.2 according to the total number of canopy scale flux measurements that were made per annum.

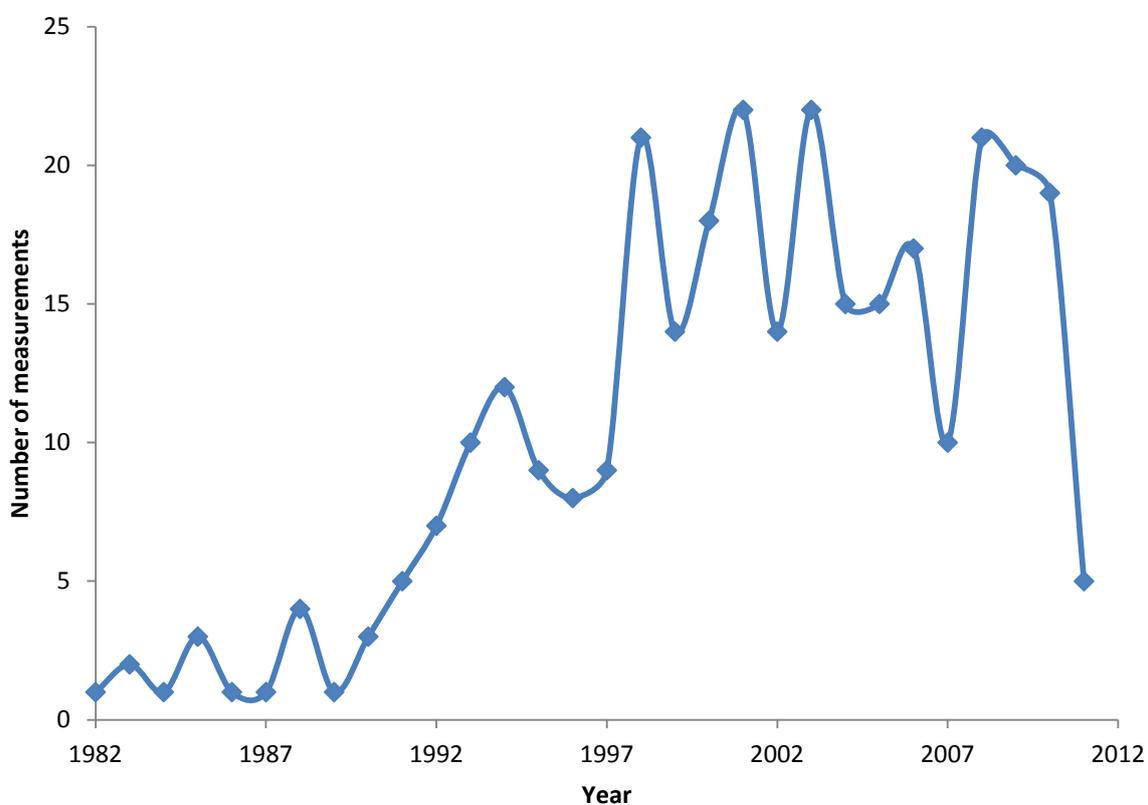


Figure 3.2 Total number of canopy scale BVOC flux measurements per annum

### 3.3.2 Research by measurement technique

The annual distribution of suitable data sets obtained using different BVOC sampling techniques is shown in Table 3.1.

Number of Site Study Measurements by technique								
Year	Container	EC	DEC	REA	Gradient	AT	Unknown	Other
2011	1	2	0	0	0	<b>2</b>	0	1
2010	1	6	5	1	1	0	3	1
2009	3	3	<b>7</b>	0	0	<b>2</b>	<b>4</b>	1
2008	2	7	5	1	2	0	1	3
2007	1	1	3	1	2	1	0	0
2006	6	2	5	0	0	0	0	1
2005	2	3	3	1	1	0	0	3
2004	7	1	4	1	0	0	0	0
2003	3	<b>10</b>	3	0	0	0	2	2
2002	3	5	1	2	0	0	1	2
2001	5	6	0	<b>5</b>	1	0	0	3
2000	4	7	1	1	0	0	0	1
1999	2	2	0	3	1	0	0	2
1998	<b>10</b>	1	0	2	3	0	0	2
1997	0	0	0	3	2	0	0	1
1996	0	2	0	4	2	0	0	0
1995	1	0	0	0	<b>6</b>	0	0	1
1994	1	1	0	2	5	0	1	2
1993	0	0	0	0	<b>6</b>	0	0	<b>4</b>
1992	0	0	0	2	3	0	0	2
1991	0	0	0	0	3	0	0	2
1980-1990	0	0	0	0	6	2	0	8
1980-2011	52	59	37	29	44	7	12	42

Table 3.1 (Method Key: Container – Cartridges/containers, EC – Eddy covariance, DEC – Disjunct eddy covariance, REA – Relaxed eddy accumulation, Gradient – Gradient methods, AT – Atmospheric tracer(s), Unknown – sampling technique unknown, Other – Simulation/estimations/uncommon techniques) Bold indicates peak number of measurement

The same information for years 1991-2011 is displayed graphically in Figure 3.3.

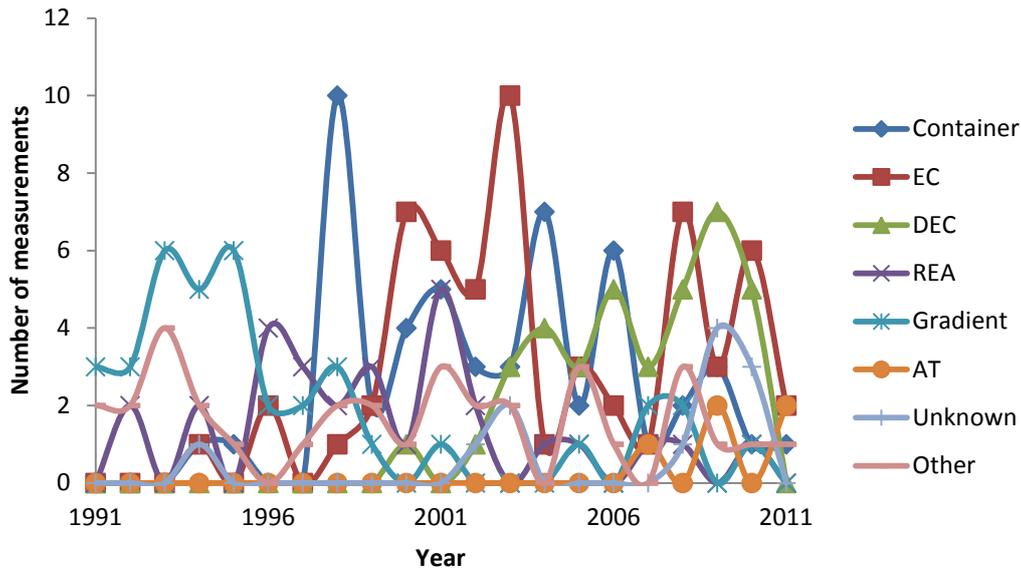


Figure 3.3. Number of annual BVOC measurements taken using different sampling techniques (Container – Cartridges/containers, EC – Eddy covariance, DEC – Disjunct eddy covariance, REA – Relaxed eddy accumulation, Gradient – Gradient methods, AT – Atmospheric tracer(s), Unknown – sampling technique unknown, Other – Simulation/estimations/uncommon techniques)

The number of site study measurements increases over time with spikes occurring around 1990 and 1998. This can be observed in Figure 3.2 where it is apparent that the number of measurements per year increases gradually but is generally relatively stable outside these periods. The number of measurements for 2011 is almost certainly highly incomplete as many results will not have been published when work for this report was carried out.

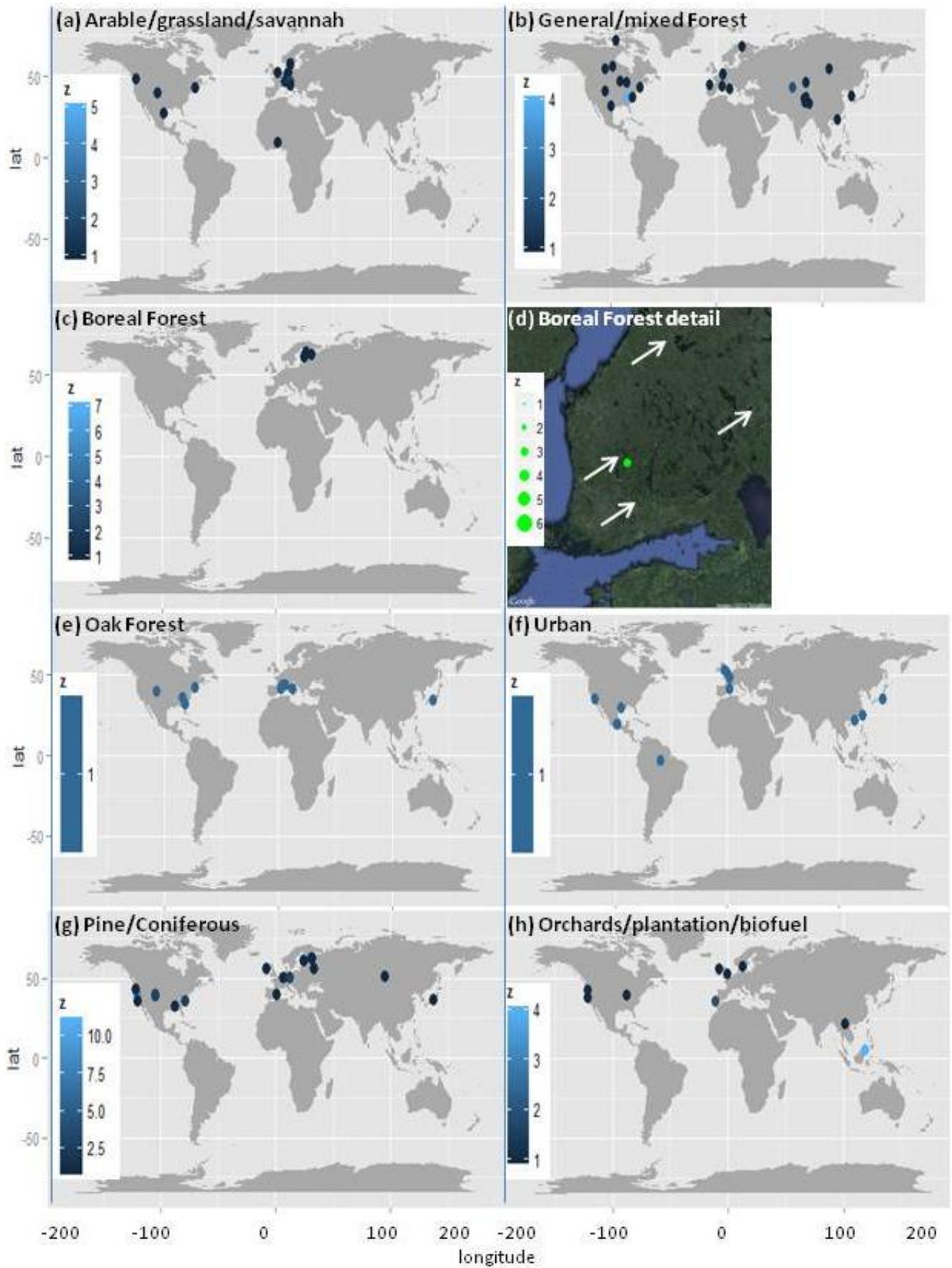
Looking at Figure 3.1 and Table 3.1, it can be seen that the first considerable increase in the total number of annual measurements occurs roughly concurrently when relaxed eddy accumulation (REA) data appears for the first time in 1992. Prior to this the most common technique used to acquire BVOC fluxes were gradient methods. Similarly, the second sizeable rise in the number of annual measurements, around 1998, follows the emergence of eddy covariance (EC) as a viable micrometeorological technique for BVOC sampling in conjunction with increased use of REA by the scientific community. Although REA and EC are first implemented in 1992 and 1994 respectively, it seemed to take several years for both techniques to gain widespread adoption. The application of REA started to increase greatly in 1996 and eventually peaked in 2001 but greatly declined in frequency thereafter. This can probably be attributed to the adoption of EC as these measurements begin to increase from 1996 and peak in 2003 a couple of years after REA was most utilised. It is possible that many researchers who used REA in the past may have migrated to EC because it is a direct sampling technique which does not rely on empirical parameterisations. Annual EC measurements, at their peak, are a factor of two higher than those for REA and it continues to be extensively employed today. EC's enduring popularity suggests that this method is greatly preferred by the scientific community. The gradient method relies on the average concentration difference, taken over a suitably long timescale, between at least two different heights above the canopy. Furthermore, both the gradient and relaxed eddy accumulation methods rely upon empirical parameterisations and are therefore indirect measurement techniques. Drawbacks to using the

gradient method include additional uncertainties due to the differing flux footprints that arise from measuring at different heights and the possibility of reactive compounds either decaying, or interacting, between measurements taken at different elevations.

The REA method avoids the issues encountered by measuring at different heights but suffers from sample losses due to reactions of BVOC with the container walls. However the fact that samples may be stored for analysis at a later date, and that fast response sensors are not required when using the REA, and gradient, techniques is highly advantageous and consequently these techniques were widely used when fast sensors for many BVOCs were not yet available. REA and the gradient method are used sparingly today now, most likely due to the fact that EC and DEC are both feasible and preferable for the reasons outlined earlier.

### **3.3.3 Site study locations by vegetation/ecosystem for all available data**

Because modellers are often interested in specific ecosystems or vegetation, the site study measurement locations were categorised based on the dominant vegetation present at each site or the ecosystem type that was most appropriate for all available data. The positions of the sites are colour coded to indicate the number of measurements at each location.



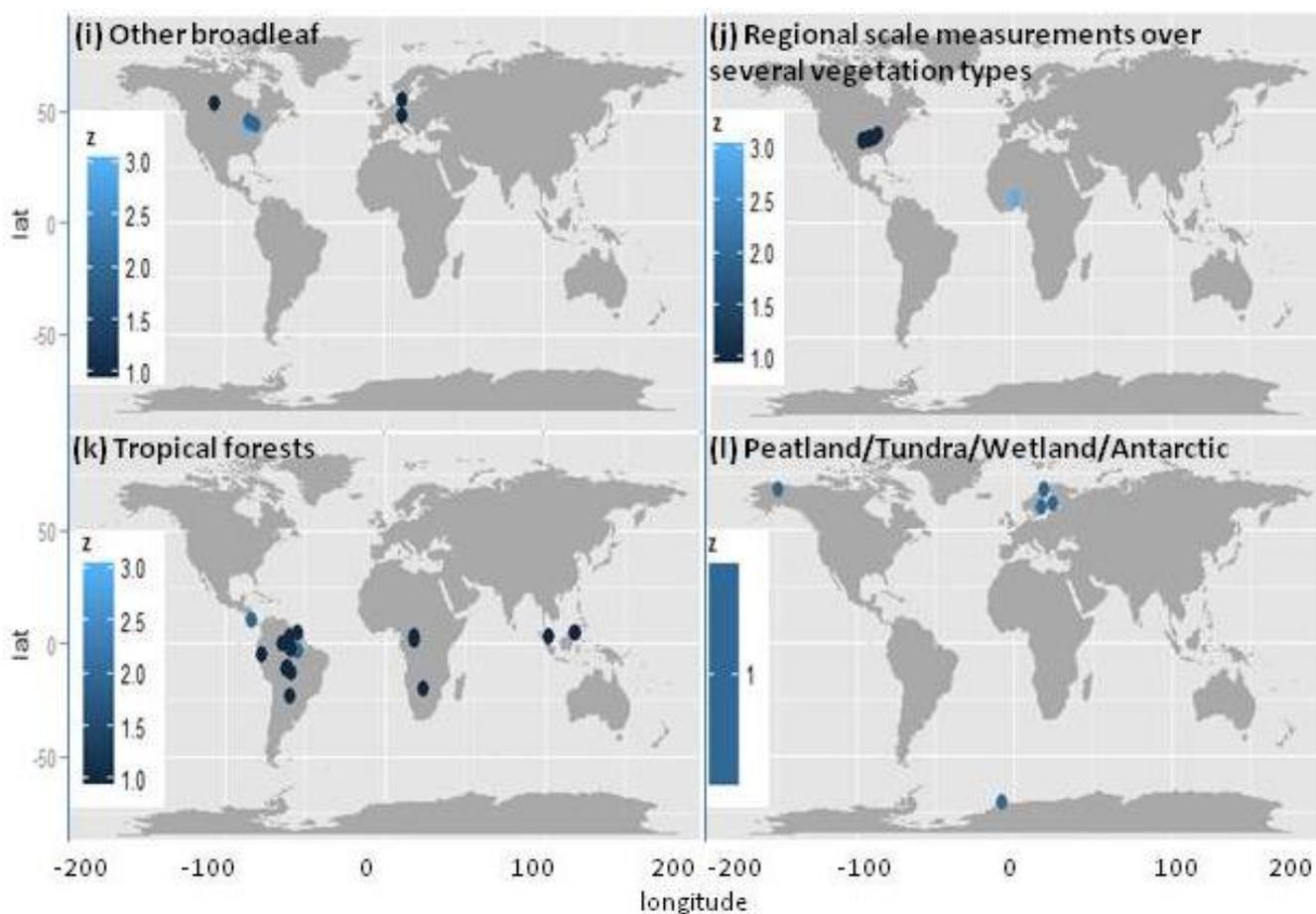


Figure 3.4 Geographical location of canopy-scale flux measurements sorted based on ecosystem of site or dominant vegetation. (d) is a higher spatially resolved map of (c) , z is a scale to indicate the number of measurements at each location.

For “arable/grassland/savannah type” ecosystems, there were 22 measurements as shown in Figure 3.4 (a), although the coordinates of three measurements were unknown. Figure 3.4 (a) suggests that there has been a relatively large quantity of BVOC flux data taken over “arable/grassland/savannah” type ecosystems, with a total of 22 data sets available. However, this data is distributed very unevenly. As can be seen from the map, there are a handful of measurements taken in North America and one in Africa but the majority of the available data were obtained in mainland Europe. This results in a conglomerate of data concentrated in a similar vicinity but overall global coverage is poor with no data available for eastern Europe, Australia, South America and Greenland.

Any measurements that originated from sites with diverse forest vegetation were designated as a “general/mixed forest” ecosystem, of which there were 31 measurements at 27 unique locations. The global distribution of measurements for this ecosystem type is displayed in Figure 3.4 (b).

Boreal forests are primarily composed of coniferous trees and are found at latitudes  $>50^\circ$  N. There were 10 measurements, all from Finland, that were specifically described to be from a “boreal forest”, of which six measurements came from the same site. This can be seen in Figure 3.4 (c) and a higher spatially resolved map of these measurements is shown in Figure 3.4 (d) to provide detail of sites occurring closely together.

Forests that were almost homogenous in composition for *Quercus* species vegetation were termed oak forests and are shown in Figure 3.4 (e). Ten unique measurements that met these criteria were found.

Urban measurements were labelled as any measurements that occurred within cities or places where people live. 12 unique measurements of this class were identified and their locations are given in Figure 3.4 (f).

Forty four measurements at 20 unique locations were found for site studies that stated the dominant vegetation was pine or coniferous trees which can be seen in Figure 3.4 (g). “General/mixed” and “pine/coniferous” forests seem to be well represented as there have been 31 and 41 measurements respectively which are spread out globally. There are no measurements for these ecosystem types in South America and Africa although this is to be expected due to their locations where forests are usually tropical.

Figure 3.4 (h) shows 13 measurements spread over nine sites for orchards, plantations or biofuel sites.

Ten measurements from six different sites were found for any data where the vegetation was primarily other broadleaf species and is shown in Figure 3.4 (i). There are fewer data available for “oak” and “other broadleaf” forests in comparison to the other forest categories with only 10 measurements available for both. The most obvious omission for both forest types is data from Eastern Europe. This, in combination with the high emission potential of oak in particular highlights a requirement for wider representation of this ecosystem type.

Fifteen measurements at nine individual sites were found to be over a regional scale or several vegetation types although coordinates were not available for two measurements. This information is displayed in Figure 3.4 (j)

Twenty six measurements were recognised to be from tropical forests, from 23 distinct sites and can be found in Figure 3.4 (k). The coordinates for one measurement were not available.

Measurements from six separate peatland, tundra, wetland and Antarctic sites made up the remaining results. These vegetation/ecosystem types have been studied the least. The locations of the measurements that have been taken for all of these ecosystems have been plotted graphically on a world map in Section 3.3.3 and Figure 3.4 (l). The countries where these measurements are located, such as Alaska and Antarctica, tend to be very cold with temperatures regularly below 0 ° C. This makes detecting BVOC fluxes extremely difficult because emissions increase with temperature and therefore emissions from these locations are likely to be low. These sites also tend to be remote due to the harsh conditions which can make travelling very difficult, especially the transportation of instruments that are often sensitive, heavy and delicate. These factors could help to explain the lack of measurements for these ecosystems.

The BVOC flux data gathered so far cover a fairly wide range of ecosystems and vegetation types globally. However, it is forests that have been studied most extensively with just under 70% of the data found being for ecosystems of this variety. This figure is comprised of data from different forest types, including pine/coniferous, general/mixed, tropical, other broadleaf, oak and boreal forests in descending order of number of BVOC flux measurements. Forests have been greatly studied for a number of reasons but their extensive global coverage and abundance of high BVOC emitting vegetation are likely the main causes. BVOC fluxes are therefore obtained relatively easily for these ecosystems due to high emissions which are above the limits of detection of the instruments used for measurements. Over the years advances in instrumentation has lowered limits of detection, thereby allowing the study of vegetation and ecosystems that are lower emitters of BVOC although the larger emissions from forests potentially allows for greater capture of high quality data which reduces the extent of gap-filling which would otherwise be required from lower emitting ecosystems. The global percentage of land area occupied by forests is approximately 30% (Nix 2014) and their distribution is shown in Figure 3.5 which was created from data from the Food and Agriculture Organization of the United Nations (FAO 2014). It can be seen in Figure 3.4 that most of the measurements have been made in North America, Europe and Brazil. Average isoprene fluxes are on the order of approximately 2 - 10 mg m<sup>-2</sup> h<sup>-1</sup> for a typical tropical rainforest. (Karl, Guenther et al. 2007; Kuhn, Andreae et al. 2007) An isoprene emission factor of 54 µg C g<sup>-1</sup> h<sup>-1</sup> for oak trees in Germany was measured using EC which is comparable to leaf-level measurements of oak species (Spirig, Neftel et al. 2005).

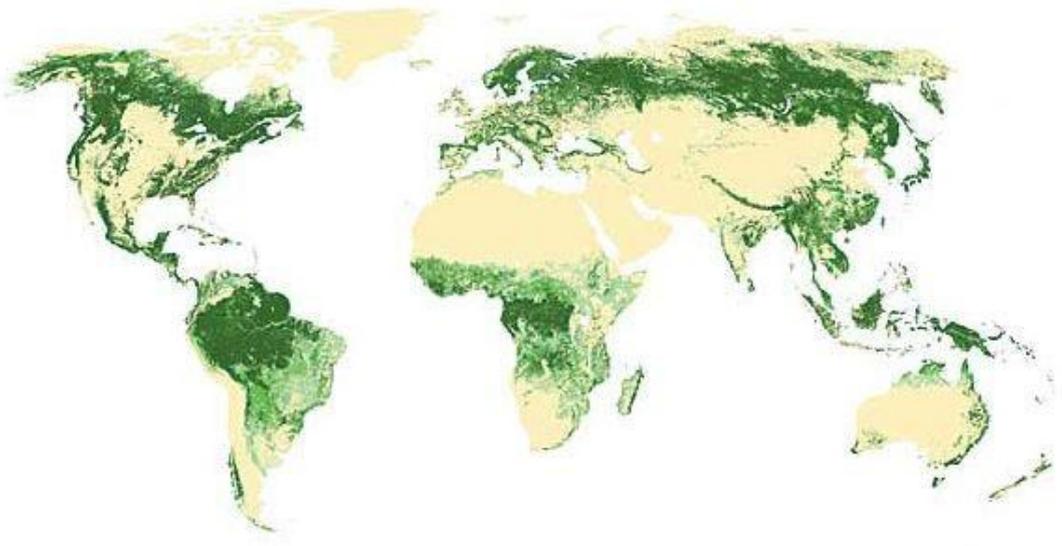
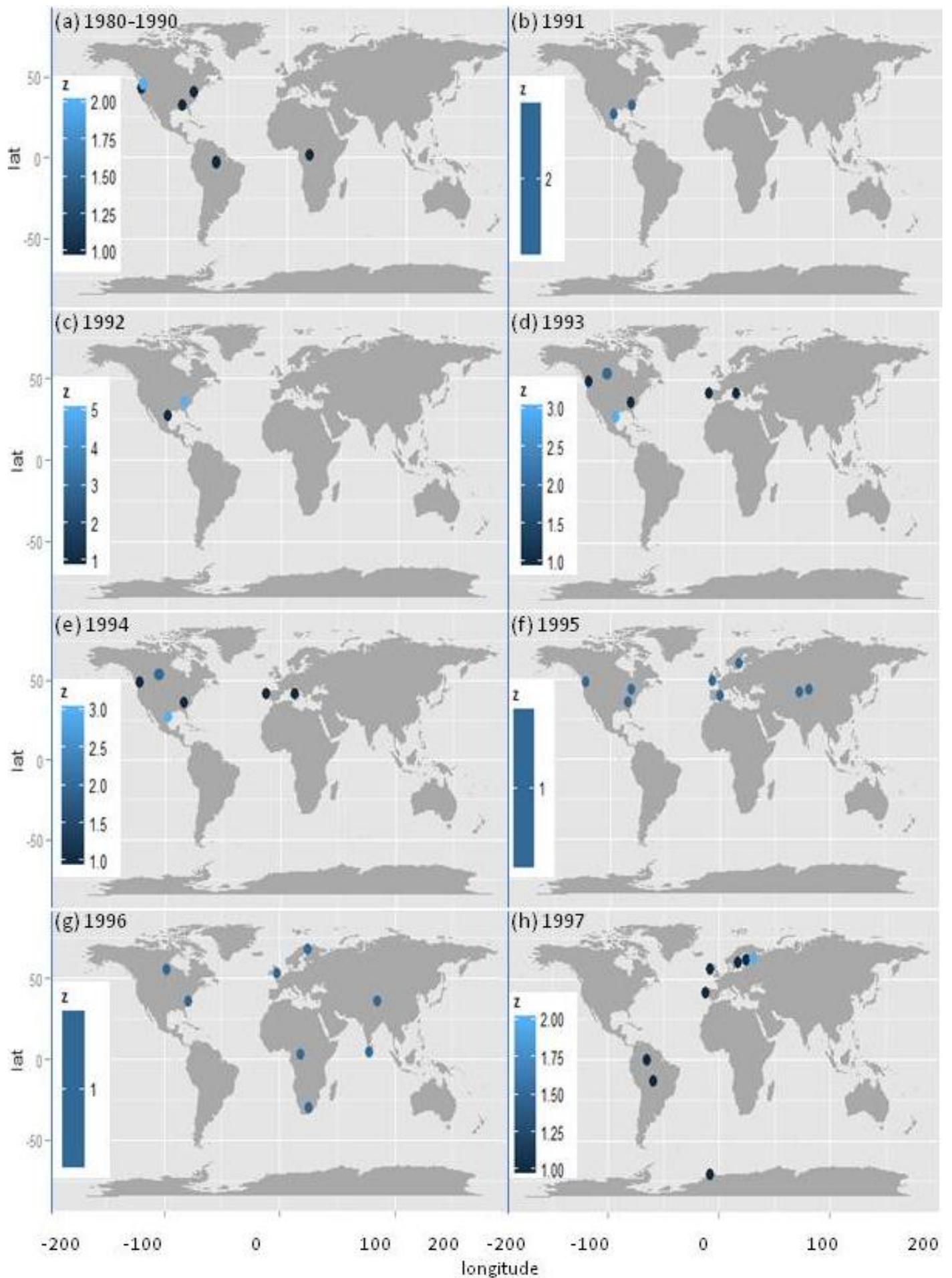
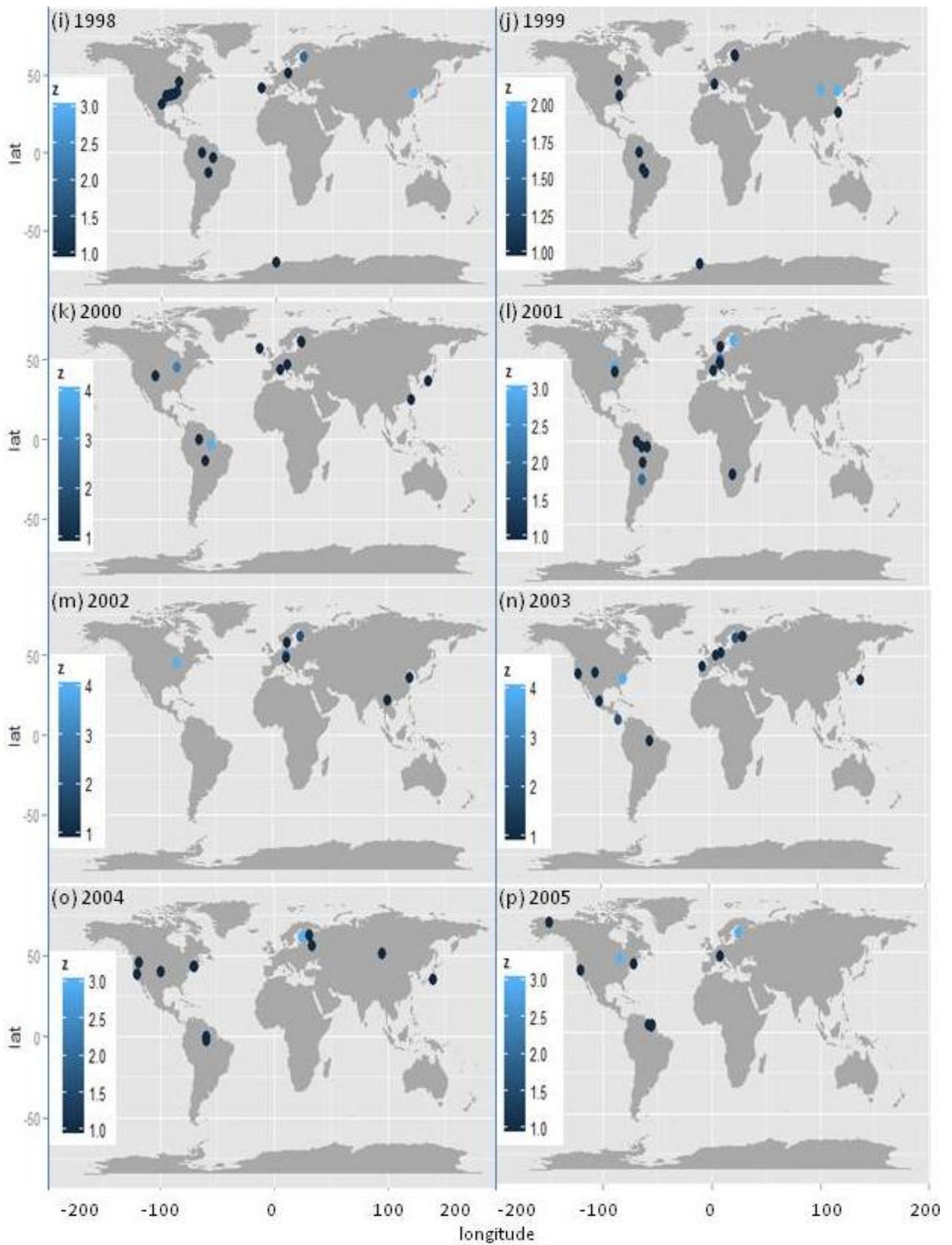


Figure 3.5 Global Forest coverage (dark green represents closed forests, mid-green represents open and fragmented forests and light green represents some trees in shrubs and bushland) (Nix 2014)

#### 3.3.4 Site study locations by year

The site study locations of measurements was categorised according to the year that they were taken and the results displayed geographically. This data is presented beginning with the oldest results but years 1980-1990 are grouped into one map (Figure 3.5 (a)), due to the low number of data procured during this time. Yearly maps were produced for all subsequent years (Figure 3.5 (b) – (v)).





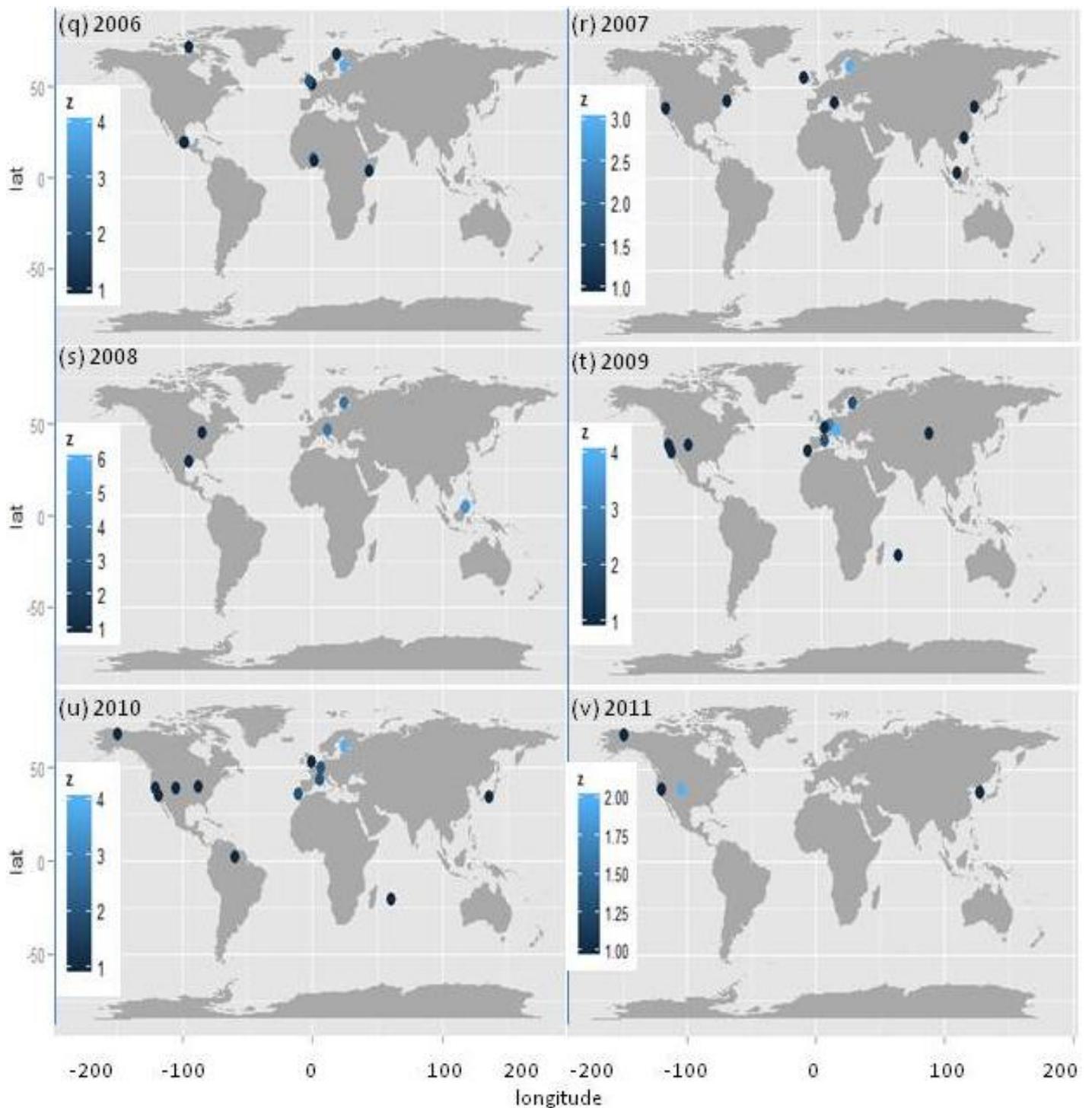


Figure 3.6 Geographical positions of canopy-scale flux measurements by time, (map (a) covers a period of 10 years, and all other maps are yearly)

From 1980 to 1994 (Figure 3.5 (a) – (e)), most BVOC flux data were obtained in North America with just a few other measurements spread across South America, Africa and Europe. This was probably due to the fact that key scientists located in America, such as Alex Guenther, were among the first to take interest in BVOC emissions. Guenther is a named author for 7 papers during this period which is by far greater than from any other researcher from any other country. Gradient methods were the sampling technique of choice in this time period and almost exclusively used, although there were a couple of instances where atmospheric tracers were used before the emergence of REA and EC measurements in the early 90s which would eventually supersede the gradient method.

Surprisingly, there appears to be no canopy scale BVOC flux measurements at all for Australia and Greenland based on the criteria of this literature search. This is a problem because it means that there is little to no data available for these countries and any emissions will have to be estimated using data from other regions, which is not ideal considering BVOC emissions are highly species specific. Furthermore, both of these countries are very large: Australia and Greenland have land areas of approximately eight and two million square kilometres respectively which makes them the 7<sup>th</sup> and 13<sup>th</sup> largest countries by land area (Brinkhoff 2014). Consequently the implications they could have to global emissions may be profound and is an area which requires attention from the scientific community although considering Greenland is largely covered in ice and snow priority should be given to Australia due to its greater emission potential. Overall, there appear to be site studies of BVOC flux measurements for only a handful of countries so far, with the majority of measurements coming from the same countries. This leaves significant portions of the world without appropriate representation which should be targeted by future studies.

It should be noted that many of the measurements for different years and also vegetation/ecosystem types occur at the same sites. For instance, 10 out of the 41 measurements for pine/coniferous forests were performed at the Station for Measuring forest Ecosystem-Atmosphere Relations (SMEAR 2) in Hyytiala, Finland. Other sites that are heavily reused for multiple measurements include the University of Michigan Biological Station (UMBS) in USA and Bukit Atir Global Atmospheric Watch (GAW) station in Malaysia to name a few. This occurs because it is easier and more economical to setup measurements where infrastructure already exists and therefore increases the amount of data that is and will probably continue to be produced from such sites. It could be argued that the availability of such facilities may deter researchers from investigating new study sites although the importance of additional data, across all ecosystems and covering all areas of the globe, cannot be overstated. It is possible, for example, that a forest in Eastern Europe might have a different emission pattern to a forest in Western Europe. Until there is better global coverage of emission fluxes, important BVOC flux variations will be missed.

### 3.3.5 Future work

The results presented here are representative of the vast majority of BVOC research until August 2013. It is in no way an exhaustive list of BVOC research conducted so far for a number of reasons: The nature of the “Web of Science” service is responsible for most of the omitted work because it is operated using a subscription model. Consequently it may not be possible to find select papers if access to all of the databases is not available. This problem became apparent when the number of hits returned using identical search terms changed depending on the institution from which the search was performed. This problem was further exacerbated as the number of hits returned from the same institution decreased when an identical search was performed at a later date because there had been trial subscriptions to databases which had expired between the search dates. Unfortunately, these potential papers were lost because these circumstances were not anticipated although a copy of the search results was subsequently created to avoid future occurrences. In addition, papers should be searched for using other bibliographic databases such as SCOPUS, Google Scholar and potentially PubMed in order to locate suitable papers which are not found on Web of Science. This was not attempted in this work due to time constraints. Furthermore there were occasional issues with downloading the papers from certain academic journals which means there will inevitably be gaps in the data presented although these should be minor.

New measurements will have to be added to the database when they are published and therefore many of the site studies geographical maps will also need to be created or updated in the future when measurements for the relevant years are published. This is particularly true for the most recent years but also applies to older measurements which are occasionally published up to and in excess of ten years after the measurement date(s).

It would also perhaps be sensible to change to using a bespoke database programme that is designed for this task because using Microsoft Excel to analyse the metadata is rather clumsy as it is very difficult to represent the complex details of the measurements numerically. It was therefore necessary to input text which described the details of the measurements for many metadata fields because they were highly specific. However, this made using logic commands in Excel to quickly filter out this data impossible for many circumstances due to the difficulty of broadly categorising much of the metadata. Consequently, manual counting by eye was required for much of the analysis which not only introduces uncertainty in the data presented due to human error but is also incredibly time-consuming. The use of a database programme which could accommodate for the variation in measurement details would substantially increase the efficiency of this process and allow additional trends in the data to be identified by enabling more comparisons to be performed.

### **3.4 Conclusions**

It appears that there has been a relatively large amount of canopy-scale BVOC flux research conducted thus far. VOCsNET currently accounts for just under 300 suitable data sets, the majority of which are for forest ecosystems at just under 70% out of the total data although the authors' have yet to be contacted to request their permission for inclusion in the database. It was also apparent that BVOC flux measurements tend to be available for the same countries or regions and that there are many places for which no data has been published. However, the lack of such measurements available for Australia is probably the country for which this causes the most concern due to its large land area and climate which both have potential to be significant contributors to BVOC emissions on a global scale.

The work presented here establishes a foundation for setting up the VOCsNET flux database however it is clear that a lot more work is required, to update the literature search, extract the actual emission measurements, and to populate an on-line database. The completion of these steps in the future should allow the successful deployment of a comprehensive and freely accessible canopy-scale BVOC flux database which should be a valuable resource for the scientific modelling community and may therefore facilitate the development of models of atmospheric chemistry. This could help to determine the roles that BVOC play in atmospheric chemistry and climate which would greatly further our understanding of these processes.

## 4 Overall summary and conclusions

### 4.1 Experimental assessments

Isoprene emission factors for different ecosystems and plant species, some of which are the first of their kind, were successfully determined as follows:

- An isoprene emission factor of  $1.83 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  was calculated for a peat bog in Scotland, Auchencorth Moss using PTR-MS and the DEC technique for measurements taken in July 2013.
- An isoprene emission factor of 4.0 to  $9.0 \text{ mg m}^{-2} \text{ h}^{-1}$  was computed for a British oak forest, Alice Holt, using a PTR-MS and the DEC technique from a pre-existing data set from 2005.
- A mean extrapolated isoprene emission factor of  $0.074 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$  for *Sphagnum* moss harvested from Whim bog in Scotland was acquired using enclosure techniques in March and April of 2014.

These emission factors will enable models to be initialised more appropriately for British regions than was previously possible.

### 4.2 Database development

A database of canopy-scale BVOC fluxes, VOCsNET, was created from information contained within scientific papers that were published between 1985 and August 2013. Preliminary work towards the launch of this database in the future is described below:

- Scientific papers which potentially present suitable BVOC flux measurements were searched for in the literature using a keyword search on Web of Science.
- The papers from the Web of Science search were read to verify whether they contained suitable data.
- A database containing detailed metadata for the suitable papers was created and updated as necessary.

This work forms an essential foundation for the VOCsNET database and provides insight into the current global state of canopy-scale BVOC flux research.

### 4.3 Overall Conclusions

The variability of the experimental results obtained during this placement provides evidence of the need for more high quality BVOC flux measurements to be obtained across a wide range of ecosystems and countries. The importance of appropriately initialising models of atmospheric chemistry using emission factors derived from canopy-scale flux measurements could suggest that eddy covariance type measurements should be employed rather than other techniques in these scenarios. However, as there are issues with all BVOC sampling techniques, from eddy covariance to enclosure measurements, key information and details will be missed if a combination of techniques is not applied. Diurnal variation was observed in the emission factors obtained for both the Auchencorth and Alice Holt data sets. Quantification of this behaviour, due to its potential to influence emission estimates, could therefore be of great importance for modelling purposes.

### 4.4 Recommendations for future work

The acquisition of more high quality BVOC flux data from as many countries and ecosystems as possible should be an immediate aim for the BVOC scientific community. This in conjunction with the development of new models and the refinement of ones which already exist should help to improve our understanding of the implications that BVOC emissions have to atmospheric chemistry and climate. The availability of a flux database, such as VOCsNET, could help immensely to realise this goal and should therefore be a focus for future work. However, if resources were limited, work should perhaps be focused on acquiring more measurements because the availability of a flux

database such as VOCsNET should only increase the rate at which developments are made rather than halt progress altogether as may happen if measurements ceased to be made.

## Acknowledgements

*The author wishes to thank Christine Braban, Mat Heal, Ben Langford and Sue Owen for their help and advice in writing this report. I would also like to thank Pete Levy for advice with using R and for providing sample code as well as the Auchencorth Moss field team and Eiko Nemitz for helping to set up the experiments. My gratitude also extends to the ECLAIRE project and CEH project NEC04845 for funding and to Emily House for permission to work with her Alice Holt data set.*

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## Appendices

### Literature review of BVOC measurement techniques

Atmospheric Chem.

# BVOC Measurement Techniques

Richard Schafers

BVOC fluxes · remote sensing · eddy covariance ·  
relaxed eddy accumulation · enclosure chambers

*The Earth's climate is derived from the interaction of solar radiation with the physical and chemical properties of the Earth's surface and atmosphere. Volatile organic compounds (VOC) are released into the atmosphere ubiquitously from both biogenic and anthropogenic sources; however emissions from biogenic sources (BVOC) dominate. BVOC are important as they not only contribute to the formation of ozone through atmospheric chemistry- they are also strongly involved in aerosol formation and growth. Yet, emission factors for BVOC for many plant species are not quantified and net emissions from most ecosystems are unknown. Consequently, improving our understanding of the emission factors for plants (and the parameters which control this) and the emission fluxes of BVOC from various ecosystems would greatly improve our ability to perceive and predict changes in atmospheric composition and radiative forcing. This minireview provides an overview of the most widely adopted techniques used to measure the emission of BVOC.*

## 1. Introduction

**What are biogenic volatile organic compounds (BVOC)?** BVOC are carbon containing substances which may evaporate readily under ambient conditions and are produced by biological processes in living organisms such as plants and animals<sup>(Kesselmeier and Staudt 1999; Fuentes, Lerdau et al. 2000; Carpenter 2007)</sup>. BVOC encompass a vast number of organic compounds such as alcohols, ketones and esters but do not include the major greenhouse gases carbon dioxide or methane. It is common for BVOC to be further categorised according to their structure and/or properties. For example, BVOC which contain an oxygen atom are referred to as oxygenated volatile organic compounds (oxVOC) while those which are very short lived (lifetimes on the order of minutes or less) because they are highly reactive, are known

as very reactive BVOC (VR-BVOC). Additionally, the family of compounds derived from the compound isoprene/hemiterpene are known as terpenes, which are structural isomers of isoprene unit combinations. The huge number of possible permutations gives rise to a truly enormous quantity of discrete compounds in this category. Consequently, terpenes terminology is assigned to the number of isoprene units – 1: hemiterpene, 2: monoterpene, 3 sesquiterpene etc. Examples of various BVOC are shown in Table 1.

**Why are BVOC emitted from plants and animals?** The biological purpose of BVOC emissions appears to be varied. Some have been shown to function as a means of communication media within and between plants<sup>(Baldwin, Halitschke et al. 2006)</sup> and insects but also contribute to biochemical defence and protective strategies in plant tissue; however, some may be just biochemical by-products. It was proposed by Sharkey and Singaas<sup>(Sharkey and Singaas 1995)</sup> that isoprene production may help to provide thermal protection within plant leaves with subsequent research supporting this theory<sup>(Sharkey, Singaas et al. 1996; Sharkey, Wiberley et al. 2008)</sup>. The Gaia

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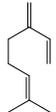
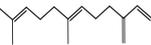
hypothesis<sup>(Lovelock 1972)</sup>, or variants thereof, assume that the BVOC production which leads to aerosol formation is a form of biological climate regulation although there is little evidence for this.

**What happens when BVOC are emitted?** Owing to their high vapour pressures, many BVOC are emitted in significant quantities to the troposphere. BVOC are involved enormously different extents. Several species of BVOC including isoprene are oxidised quickly in the atmosphere, which in the presence of NO<sub>x</sub> and sunlight may lead to ground level ozone formation. Photolysis of oxVOC such as acetone and acetaldehyde are a considerable source of hydroxyl radicals (OH). Higher molecular weight BVOC including monoterpenes are thought to be key precursors to secondary organic aerosol (SOA) formation. It is clear then

in processes such as the formation of secondary organic aerosol (SOA) and production of ground level ozone<sup>(Liu, Trainer et al. 1987)</sup>. The potential of BVOC emissions to affect atmospheric chemistry<sup>(Trainer, Williams et al. 1987; Thompson 1992)</sup> and the global climate needs to be understood to contextualise anthropogenic climate perturbations. Different BVOC affect atmospheric chemistry and climate to

that BVOC are an extremely important class of compounds with far reaching consequences which should be well understood, however the current state of knowledge is probably in its early stages and developing the best measurement techniques to understand emissions of BVOC is a key challenge for atmospheric science in the twenty-first century. This review outlines the state of the art methods and assesses some potential of developing techniques and whether these can address the current knowledge gaps.

**Table 1.** Examples of BVOC & their chemical properties<sup>(Dayah 1997; NIST 2014)</sup>

Compound	Category	Chemical Formula	Molecular Structure	Properties <sup>[a]</sup>	Typical Source(s)	Typical Tropospheric Concentration <sup>[b]</sup>	References
<b>Isoprene</b>	Hemiterpene	C <sub>5</sub> H <sub>8</sub>		68.12 g mol <sup>-1</sup> 34.07 °C 0.681 g cm <sup>-3</sup>	Commonly emitted from vegetation- trees, shrubs & mosses	1- >5 ppb	(Guenther, Baugh et al. 1996; Kuhn, Ganzeveld et al. 2010; Jones, Hopkins et al. 2011)
<b>Limonene</b>	Monoterpene	C <sub>10</sub> H <sub>16</sub>		136.24 g mol <sup>-1</sup> 176 °C 0.841 g cm <sup>-3</sup>	Trees (Oak,Pine)	71 ppt	(Jones, Hopkins et al. 2011)
<b>Myrcene</b>	Monoterpene	C <sub>10</sub> H <sub>16</sub>		136.23 g mol <sup>-1</sup> 166-168 °C 0.794 g cm <sup>-3</sup>	Trees	10 ppt	(Bouvier-Brown, Goldstein et al. 2009)
<b>Acetone</b>	oxVOC	C <sub>3</sub> H <sub>6</sub> O		58.08 g mol <sup>-1</sup> 56 °C 0.791 g cm <sup>-3</sup>	Commonly emitted from vegetation	4 ppb	(Park, Goldstein et al. 2013)
<b>(E)-B-Farnesene</b>	Sesquiterpene / VR-BVOC	C <sub>15</sub> H <sub>24</sub>		204.35 g mol <sup>-1</sup> 124 °C 0.813 g cm <sup>-3</sup>	Plants (upon wounding) and aphids (upon death)	3-6ppt	(Bouvier-Brown, Goldstein et al. 2009; Kikuta, Ueda et al. 2011)



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**[a] Molar mass , boiling point and density, respectively.**  
**[b] Highly variable between locations- given as a guide**

## 2. Enclosure measurements (leaf level)

Enclosure measurements involve surrounding all or part of a plant and then, either, sampling air in the enclosure into an instrument attached to the enclosure, or, taking samples which are analysed off-line. Enclosures such as leaf cuvettes and branch enclosures (see, for example, Figure 1) are regularly used to measure BVOC emissions from plant and tree parts (e.g. a leaf or a branch) as this technique enables BVOC exchange and environmental control to be studied at a fine scale.



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fluxes are calculated by sampling both the incoming and outgoing air flows and air residence time in the enclosure to derive the net rate at which the BVOC are emitted from the individual leaf or the branch by difference. After the experiment, the biomass which emits the BVOC is measured. For isoprene studies, it is only the leaves which are weighed so that the net flux can be expressed per mass of enclosed leaves- it is only leaves which emit isoprene. Typical mean daytime fluxes for oak<sup>(Guenther, Baugh et al. 1996)</sup> species are in the range  $14.1 - 49.0 \mu\text{g C g}^{-1} \text{h}^{-1}$ . Fluxes can also be expressed per surface area or as a function of leaf area index (LAI). Many enclosure chambers are designed to allow temperature and light control which allows a parameterised emission function to be constructed. For example, the measured isoprene emission capacities<sup>(Guenther, Baugh et al. 1996)</sup> for the oak species mentioned earlier were  $75-114 \mu\text{g C g}^{-1} \text{h}^{-1}$ . These emission capacities are larger than the mean fluxes because they are normalised to standardised PAR and leaf temperature levels. This allows comparison with results from other sites/species where environmental conditions differ.

Other BVOC are known to be emitted from bark<sup>(Amin, Atkins et al. 2012)</sup> and roots<sup>(Crespo, Hordijk et al. 2012)</sup>, although this is usually a response to infestation. Leaf enclosure measurements report higher BVOC fluxes than branch enclosures<sup>(Guenther, Zimmerman et al. 1996)</sup>, attributed to differing light levels from the surrounding canopy.

Enclosure measurements are perhaps the simplest approach to measure BVOC. They are especially suited to situations where it is desirable to study species specific emission rates or BVOC exchange at the leaf level.

However, the enclosure method has several drawbacks. It is labour intensive<sup>(Baldochi 1997)</sup> and the process of placing an enclosure over a leaf or branch is invasive and alters the natural environment, introducing changes to environmental factors such as temperature and incident photosynthetically active radiation (PAR) as well as disruptions to diffusion and gas concentration gradients<sup>(Bowling, Turnipseed et al. 1998)</sup>. Behaviour observed under these conditions may not be representative of the unperturbed state. Moreover it has been shown that plants

release BVOC when subjected to physical damage<sup>(Fall, Karl et al. 1999; Farag and Pare 2002)</sup> and hence great care must be taken when installing enclosures in order to minimise this contribution.

### 2.1 Micrometeorological techniques (canopy)

It is not possible to enclose a forest or diverse ecosystem to assess the flux of BVOC with enclosure techniques; therefore, canopy-scale techniques using micrometeorological techniques were developed in the past decade. These techniques are dependent on having an analytical method with a response time of the order of 1 second, allowing the variation of the chemical concentration as a function of wind eddy direction. These turbulent BVOC fluxes, transported by vertical eddies within the atmospheric boundary layer (ABL), are determined from the covariance of the BVOC mixing ratio and the vertical component of the wind speed according to equation (1):

$$F = (w - \bar{w})(c - \bar{c})$$

$$F = \overline{w'c'} \quad (1)$$

where:

$F$  = Flux

$w$  = instantaneous vertical component of wind speed

$c$  = instantaneous mixing ratio of BVOC



**Figure 2.** Horizontal air flow to the right composed of several eddies.

An eddy is a portion of air which is rotating in space with examples depicted in Figure 2 by the circular arrows. The smallest eddies with the shortest periods and highest frequencies are usually found near the surface of the canopy. As an eddy increases in size, its angular velocity decreases and its period increases due to the slower speed at which the eddy is revolving- it takes a longer time for a point on a larger eddy to rotate all the way back round to its original position.

All eddies regardless of size can transport BVOC and therefore it is important that all contributions to flux measurements are considered. Measuring at a high rate (typically 10-20Hz) allows the fluctuations of high frequency eddies to be accounted for, but due to the longer periods of the lower frequency eddies, measurements must be averaged over a suitably long time period to account also for these contributions.

Environmental conditions may change over time, especially as the measuring period is increased- referred to as non-stationarity- and thus a balance between measuring length and maintaining "stationarity" must be found. A measuring period of 20-30 minutes is regularly used<sup>(Bowling, Turnipseed et al. 1998; Langford, Misztal et al. 2010)</sup> because it usually allows sufficient data to be obtained and includes the contributions from larger

eddies while also being short enough that the environmental conditions do not change significantly.

The sampling area over which micrometeorological measurements apply, known as the “flux footprint” is substantially larger than leaf level measurements but is susceptible to change. The main variables which affect the flux footprint are horizontal wind velocity<sup>(Baldochi 1997)</sup>, the standard deviations of horizontal and vertical velocity fluctuations and the measurement height of the instrument tower. Consequently the “flux footprint” must be calculated at least as regularly as the chosen measuring period for best results. It is noted that the information derived at the canopy scale is now only species specific in a plant monoculture.

### 2.1.1 Eddy Covariance

Eddy covariance (EC) depends upon the availability of high frequency analytical techniques because the mixing ratio of BVOC must be measured at least as quickly as the velocity of the eddies i.e. the mixing ratios are measured at a rate equal to or greater than the movement of the air. This is the main reason that eddy covariance has only been adopted by the scientific community fairly recently as suitable technology was not previously available<sup>(Guenther and Hills 1998)</sup>.

EC assumes that only the vertical wind component needs to be considered. i.e only the “w” component contributes to flux measurements. During a sufficiently long averaging period over level terrain, the average fluctuations of “w” should approach zero. This is not always achieved due to sonic anemometer misalignment or uneven topography, and thus the horizontal wind components may contribute slightly to the vertical component. Instead of manually adjusting the anemometer, this can be corrected for mathematically by applying rotations to the original coordinate frame so that the fluctuations of “w” are set to zero. However this is only possible assuming a 3 dimensional sonic anemometer is used (1D sonic anemometers may be used for REA).

This approximation assumes that vegetation to be monitored is of uniform height and the terrain is level.

As the period of turbulent air near the surface is shorter than eddies higher up, measurements taken at lower heights require higher frequencies to effectively detect fluxes.

Further up, larger eddies dominate and transfer the majority of flux allowing lower frequencies to be used due to the longer periods of larger eddies. Measurements must be taken over a suitably long timescale to ensure that sufficient data is obtained and to reduce the effects of random uncertainties due to fluctuations in weather conditions. This improves the quality of the data by helping to minimise the effect which random fluctuations would otherwise have. An emission factor of  $54 \mu\text{g C g}^{-1} \text{h}^{-1}$  for an oak forest in Germany was measured using EC<sup>(Spirig, Nefel et al. 2005)</sup> which is comparable to leaf scale measurements of oak species.

### 2.1.2 Relaxed Eddy Accumulation

Relaxed eddy accumulation (REA) is an approach which is suited to ascertain bidirectional BVOC fluxes. Bidirectional fluxes can occur when wind passes close to the

ground. As the net mean movement of the vertical component of air “ $\bar{w}$ ” over a sufficiently long time period over level terrain is equal to zero, fluxes can only arise if a vertical gradient in BVOC concentration exists. Negative concentration gradients, where concentrations are higher near the surface, are the result of emission fluxes, whereas positive concentration gradients result from deposition fluxes. Fluxes are obtained by collecting samples of air within adsorbent cartridges or canisters and evaluating the mixing ratios of the BVOC being monitored with respect to vertical updrafts and downdrafts of air. A vertical wind component with a positive magnitude indicates an updraft of air while a negative value corresponds to a downdraft. A sonic anemometer is used to measure the vertical movement of turbulent air. Samples from up and down drafts are channelled into separate containers which are analysed automatically -using techniques like gas chromatography- or can be transported to a laboratory for offline analysis.

Fluxes ( $F$ ) are calculated according to the equation:

$$F = b\sigma_w(c_{up} - c_{down}) \quad (2)$$

Where:

$c_{up}$  &  $c_{down}$  are the mixing ratios of a BVOC in an updraft and downdraft respectively. (Dimensionless quantity)

$\sigma_w$  is the standard deviation of the vertical wind speed &

$b$  is an empirically determined coefficient of proportionality

Midday isoprene canopy fluxes at a forest site<sup>(Guenther, Baugh et al. 1996)</sup> of between  $3\text{-}5 \text{ mg C m}^{-1} \text{ h}^{-1}$  have been observed using this technique.

REA is especially useful when measuring BVOC in the absence of high frequency sensors or for investigating compounds like formaldehyde which do not respond well to rapid response ( $\geq 1 \text{ Hz}$ ) techniques such as eddy covariance. Fluxes for almost any compound which can be stored in a stable state may be obtained<sup>(Bowling, Turnipseed et al. 1998)</sup> and the ability to use slower sensors makes REA a highly versatile technique.

### 2.1.3 Airborne Measurements

Airborne micrometeorological measurements have become much more common recently and involves placing the instrumentation onto aircraft<sup>(Karl, Apel et al. 2009; Murphy, Oram et al. 2010; Baghi, Durand et al. 2012)</sup> but balloon systems are also used<sup>(Greenberg, Guenther et al. 1999; Roscoe, Colwell et al. 2005)</sup>.

This introduces significant difficulties in comparison to ground based methods. For instance the instruments often have to be modified<sup>(Borbon, Gilman et al. 2013)</sup> to meet airline regulations which make maintaining operating temperatures/conditions very challenging with the limited space and control available<sup>(Eerdeken, Ganzeveld et al. 2009)</sup>.

Furthermore, the instrument must be powered down for take-off which is problematic as it can take a long time for the instrument to return to normal operation from a cold start, particularly as flight time is limited and costly, placing limits on the quantity and continuity of the data which can be obtained practically. However, as the measurement height is significantly greater than that of ground-based measurements, the fluxes observed are more representative of larger areas/ecosystems. Although the increased elevation greatly

increases the flux footprint, this occasionally means BVOC are below the limit of detection of the instrument<sup>(Haapanala, Rinne et al. 2007)</sup>. This can be alleviated by lowering the measuring altitude but is not always possible due to air traffic control. Flight times and paths are bound by the same restrictions and may not be ideal for VOC measurements. Mean daytime fluxes of  $2.1 \text{ mg C m}^{-2} \text{ h}^{-1}$  for isoprene were measured using REA<sup>(Kuhn, Andreae et al. 2007)</sup> in the Amazon rainforest and was verified using ground based in-situ measurements. While airborne REA flux measurements have become commonplace it is only recently that the viability of airborne EC flux measurements have been demonstrated<sup>(Karl, Misztal et al. 2013)</sup>.

## 2.2 Remote Sensing

Remote sensing involves analysing satellite image data to compute BVOC emissions. This makes it the least direct technique; however this enables the emissions from vast areas or remote/inaccessible locations to be determined and is occasionally the only practical option. Consequently, remote sensing is a particularly useful approach when attempting to quantify emissions from places with highly heterogeneous topography and/or vegetation cover but can also be used if the location to be studied features different ecosystem types as remote sensing is not particularly suited to studying individual species. Remote sensing of formaldehyde columns from various satellites has been used extensively to estimate isoprene emissions around the world since just before the year 2000<sup>(Palmer, Abbot et al. 2006; Palmer, Barkley et al. 2007; Barkley, Palmer et al. 2008; Millet, Jacob et al. 2008; Stavrou, Muller et al. 2009; Stavrou, Muller et al. 2009)</sup>.

Mean monthly isoprene emissions<sup>(Barkley, Palmer et al. 2008)</sup> from the Amazon rainforest of  $15.1 \text{ Tg C}$  have been inferred in this manner although it should be noted that these measurements carry additional uncertainty in comparison with more traditional techniques because the measurements are derived from the breakdown product formaldehyde. This is an inherent disadvantage to remote sensing because the lifetimes of many BVOC are too short to allow them to be measured directly without serious underestimation. However most BVOC estimates obtained using remote sensing have been shown to be comparable with field measured data<sup>(Nichol and Wong 2011)</sup> which highlights the promise of this technique for future applications.

## 3. Calculation of Fluxes

It has long been known that the emission of most BVOC is highly dependent on temperature<sup>(Fehsenfeld, Calvert et al. 1992)</sup>. The emission of many BVOC peaks at  $\sim 35\text{-}45^\circ \text{C}$ <sup>(Guenther, Zimmerman et al. 1993)</sup> and declines with further increases in temperature. The dependency of incident light exposure to BVOC emissions is more complicated. Emissions of several species, such as isoprene, are strongly influenced by exposure to sunlight- or PAR. In isoprene's case, emissions rise with PAR levels, but plateau once a saturation point is reached. This suggests that isoprene is produced directly in response to light exposure as isoprene emissions reach a maximum and are stable as PAR continues to increase<sup>(Tarvainen, Hakola et al. 2005)</sup>. Emissions of monoterpenes and sesquiterpenes have been shown to depend only on temperature<sup>(Dement, Tyson et al. 1975; Guenther, Zimmerman et al. 1993)</sup> due to these compounds being produced and stored within the plant. This is perhaps due to

the role which these compounds play in enticing pollinators towards the plant and their ability to ward off herbivores<sup>(Schilmüller, Schauvinhold et al. 2009)</sup> which consequently makes it advantageous for the plant to possess a stockpile.

Additionally the emissions obtained from branch or leaf measurements can be extrapolated<sup>(Rasmussen and Went 1965)</sup> to estimate the emissions from an entire tree, forest or ecosystem. This introduces a considerable source of error and results obtained in this manner should ideally be validated using another technique-preferably a method which does not alter natural environmental conditions.

The data obtained from BVOC field campaigns is normally put into emission algorithms which have been developed by the scientific community. The earliest emission algorithms only accounted for temperature but some also included light dependence<sup>(Guenther, Zimmerman et al. 1993; Guenther, Hewitt et al. 1995)</sup>. Over the years many of these algorithms have been revised<sup>(Guenther, Karl et al. 2006; Guenther, Jiang et al. 2012)</sup> to incorporate other environmental factors important to BVOC emissions including the effect of previous PAR levels and temperatures. A basic outline of a commonly used algorithm for isoprene emission<sup>(Guenther, Hewitt et al. 1995)</sup> (G95) proposed by Guenther et al. in 1995 is described here:

The emission flux of isoprene,  $F$ , from leaves is given by:

$$F = \varepsilon D \gamma \quad (3)$$

where  $D$  is foliar density ( $\text{kg dry matter/m}^2$ ),  $\varepsilon$  is an ecosystem dependant emission factor ( $\mu\text{g C m}^{-2} \text{ h}^{-1}$ ) standardised to  $30^\circ \text{C}$  and a PAR flux of  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , and  $\gamma$  is a dimensionless factor which adjusts for light and temperature dependence.

The light dependence for isoprene emission is labelled  $C_L$  and the temperature dependence  $C_T$ . Their product,  $C_L C_T = \gamma$ .

$$C_L = \frac{\alpha C_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \quad \& \quad C_T = \frac{e^{\frac{C_{T1}(T-T_S)}{RT_S T}}}{1 + e^{\frac{C_{T2}(T-T_M)}{RT_S T}}}$$

where  $Q$  is PAR flux ( $\mu\text{mol m}^{-2} \text{ s}^{-1}$ ),  $T$  is leaf temperature (K),  $T_S$  is leaf temperature at  $30^\circ \text{C}$ ,  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $\alpha$ ,  $C_{L1}$ ,  $C_{T1}$ ,  $C_{T2}$  and  $T_M$  are empirical coefficients.

Sometimes the empirical coefficients of the emission algorithm are optimised until there is good agreement with the observed data because they are ecosystem specific<sup>(Langford, Misztal et al. 2010)</sup> and the originals may not be appropriate.

$\gamma$  can be calculated using temperature and PAR data, from which the ecosystem specific emission factor,  $\varepsilon$ , can be calculated (providing the foliar density has been calculated or estimated) using flux data from the measurements. Alternatively, if an emission factor is known, one can predict fluxes for an ecosystem using temperature and PAR data using equation 3.

## 4. Discussion

To better understand emissions of BVOC it is necessary to devote time and resources towards researching emissions from as many ecosystems as possible, rather than just the most prolific emitters, to gain a more complete understanding. Measurements to date tend to come from the same locations and research stations, probably due easily accessible pre-existing infrastructure and facilities. This has resulted in a relatively small selection of highly studied sites but has left considerable gaps in our knowledge when considering BVOC research on a global scale. This has been ameliorated in recent years with remote sensing helping to fill the gaps, but the importance of direct measurements cannot be understated as the uncertainty is up to an order of 2 greater than for in-situ methods<sup>(Barkley, Palmer et al. 2008)</sup>. While it is often too expensive and unpractical to take measurements at these unstudied locations, the situation could change rapidly as the portability of analytical instrumentation improves. Currently instruments are not designed for use in the field and safe transportation is often a major hurdle. This is slowly changing and portable instruments<sup>(Angloscientific 2013)</sup> are emerging, but they are currently less sensitive than the laboratory based instruments which are typically used (and often modified for field use). As the ease of taking measurements instrument sensitivity improves, the quantity of data for less studied ecosystems should increase.

The vast majority of studies have mainly focused on a select handful of compounds, isoprene and monoterpenes in particular, because of their importance to atmospheric chemistry and high emissions which usually allow detection. The huge number of variables and environmental conditions which affect BVOC emissions can make comparing measurements from different studies very challenging. This is apparent looking at the isoprene emission factors for oak species given in the leaf scale and EC sections. The difference in the values- EC being  $\sim 20\text{-}60 \mu\text{g C g}^{-1} \text{h}^{-1}$  lower than the enclosure values- is probably due to the presence of species other than oak in the flux footprint. More importantly, the measurements from both studies were in agreement with other methods that were performed simultaneously at each site.

As instrument sensitivity and limits of detection improve, important compounds that are emitted in lower quantities will be detected more easily allowing further study. Aside from improved sensitivity, modification of existing instruments can also increase the number of compounds that can be studied. For instance, the proton transfer reaction mass spectrometer, (PTR-MS) can be used with different reagent ions to identify more compounds. A variation using time of flight technology (PTR-TOF-MS<sup>(Ruuskanen, Mueller et al. 2011)</sup>) can also be used to allow identification of compounds with very similar molar masses that is not possible using conventional PTR-MS (allows identification of specific monoterpenes rather than the total sum thereby providing more information).

Out of all the techniques discussed, eddy covariance has probably provided the most gains in information because it has allowed the most direct and continuous measurements to be made. This is important because the accumulation of more data not only reduces its' uncertainty but also allows identifications of trends or behaviour which may otherwise have been missed. However, this can still be improved substantially as many studies still use small data sets<sup>(Kaser, Karl et al. 2013; Miyama, Okumura et al. 2013)</sup>. Alternative novel forms of analysis may allow the use of more data than was previously possible by using wavelet analysis and fast Fourier transform to examine turbulent fluxes because stationarity is not a requirement.

A significant improvement for many airborne flux measurements is possible if ensuring that measuring takes place in the constant flux layer<sup>(Karl 2013)</sup>- approximately the lowest 10% of the ABL where fluxes are nearly identical to those on the surface. The constant flux layer is on the order of 50-100 m<sup>(Danard 1981; Geernaert 2003)</sup>, which could be challenging, or impossible, to safely maintain such a low altitude depending on topography.

Finally, along with more measurements from various ecosystems, a unified database of all available flux measurements would help to facilitate the improvement of new and existing models, by providing access to the latest measurements. Making flux data more accessible could help researchers to see what work has already been done and encourage peer review, helping identify areas which require further study.

*The author wishes to thank Christine Braban, Mat Heal, Ben Langford and Sue Owen for their help and advice in writing this review.*

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1992	MONSON, RK; JAEGER, CH; ADAMS, WW; et al.	PLANT PHYSIOLOGY Volume: <b>98</b> Issue: <b>3</b> Pages: <b>1175-1180</b>
1992	SIMPSON, D	ATMOSPHERIC ENVIRONMENT PART A-GENERAL TOPICS Volume: <b>26</b> Issue: <b>9</b> Pages: <b>1609-1634</b>
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2009	Turnipseed, A. A.; Pressley, S. N.; Karl, T.; et al.	Atmospheric Chemistry and Physics 9 (981-994) uncertainty in single DEA measurements very large (~40%)
2009	Velasco, E.; Pressley, S.; Grivicke, R.; et al.	Atmospheric Chemistry and Physics 9 (7325-7342) Empirical approach used to determine plausibility of fluxes due to inability of classical data analysis and error propagation to account for all sources of error.
2010	Bamberger, I.; Hoernagl, L.; Schnitzhofer, R.; et al.	Biogeosciences 7 (1413-1424) ~6000 half hourly fluxes were obtained for each VOC species measured. 76% (m/z 33), 67% (m/z 45), 64% (m/z 99) and 70% (m/z 137) passed all quality tests and were used in the subsequent analysis
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2010	Ferreira, J.; Reeves, C. E.; Murphy, J. G.; et al.	Atmospheric Chemistry and Physics 10 (8453-8467) PTR-MS used had a 10-15 second frequency and 15% accuracy.
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2011	Laffineur, Q.; Aubinet, M.; Schoon, N.; et al.	Atmospheric Environment 45 (3157-3168) Wood panel Factory 3km from field site 230-270 degrees influenced results. 17% of MT data was rejected
2011	McKinney, K. A.; Lee, B. H.; Vasta, A.; et al.	Atmospheric Chemistry and Physics 11 (4807-4831)

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2011	Nichol, Janet; Wong, Man Sing	Atmospheric Environment 45 (2937-2943)
2011	Park, Changhyoun; Schade, Gunnar W.; Boedeker, Ian	JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES 116
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2012	Brilli, Federico; Hoertnagl, Lukas; Bamberger, Ines; et al.	Environmental Science & Technology 46 (3859-3865) <b>On Average 25% of data is missing due to quality or regular zero-air calibrations. The data gaps do not exceed 2 hours and were filled by linear interpolation to calculate VOC fluxes over 24 hour periods.</b>
2012	Copeland, Nichola; Cape, J. Neil; Heal, Mathew R.	Atmospheric Environment 60 (327-335)
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2012	Laffineur, Q.; Aubinet, M.; Schoon, N.; et al.	Atmospheric Chemistry and Physics 12 (577-590) Backgrounds were taken at the bottom of the tower rather than the top which could be significant as measurements were taken ~50m, could have an effect on background as air tends to be more humid nearer the ground and therefore O <sub>2</sub> <sup>+</sup> ion counts tend to be greater than they are higher up. Data was filtered from 230-270 degrees as a wood panel factory was located in this direction about 3km away from site. These factories are known to be emitters of MT and Methanol.
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2012	Rinne, J.; Markkanen, T.; Ruuskanen, T. M.; et al.	Atmospheric Chemistry and Physics 12 (4843-4854)
2012	Zhang, Haofei; Worton, David R.; Lewandowski, Michael; et al.	Environmental Science & Technology 46 (9437-9446)
2013	Kim, So-Young; Jiang, Xiaoyan; Lee, Meehye; et al.	Atmospheric Environment
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2013	Kaser, L.; Karl, T.; Schnitzhofer, R.; et al.	Atmospheric Chemistry and Physics 13 (2893-2906)
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