Atmospheric Measurements of Biogenic and Anthropogenic Emissions by Broadband Cavity Enhanced Absorption Spectroscopy

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Abstract:

This thesis describes the quantification of biogenic and anthropogenic trace gases using the highly sensitive spectroscopic technique of broadband cavity enhanced absorption spectroscopy (BBCEAS). This technique uses a high finesse optical cavity to make absorption measurements over extended path lengths within a compact instrument and over wavelength ranges that are sufficiently broad to enable several overlapping absorbers to be quantified simultaneously. Here, BBCEAS was applied to measure I₂ emissions in coastal regions, NO₂ in urban ambient air, and VOC oxidation products during experiments in an atmospheric simulation chamber. Much of the work used a novel, mobile, battery-powered BBCEAS system to measure gas concentrations in very close proximity to their emission sources.

The dominant emission source of iodine into the atmosphere in coastal regions comes from intertidal macroalgal beds. Gas-phase iodine chemistry perturbs the HO_x and NO_x radical cycles, provides additional sink reactions for tropospheric ozone, and initiates nucleation of new aerosol particles. Results are presented from an extensive laboratory study of I₂ emissions from five species of temperate seaweeds. Time- and speciesdependent I₂ emission rates were quantified in studies mimicking the progressive exposure of seaweeds to air around low tide. Seasonal differences in I₂ emission rates were investigated. By deploying the BBCEAS instrument from a boat, I₂ concentrations were also measured directly above *Laminaria digitata* and *Ascophyllum nodosum* seaweeds growing in their natural habitat.

 NO_x emissions affect urban air quality directly and indirectly (the latter via formation of tropospheric ozone and secondary aerosol). BBCEAS was applied to measure NO_2 and the optical extinction from aerosol particles at locations around the Leicester University campus. BBCEAS results were compared with commercial NO_x (chemiluminescence) and aerosol instrumentation. The mobile BBCEAS instrument was also deployed to investigate the dispersion of NO_2 from the roadside.

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1 Introduction

The atmosphere is the thin gaseous layer that separates the surface of the Earth from space and is essential for maintaining life on the surface.(1) The atmosphere consists mainly of nitrogen (78.08%), oxygen (20.95%) and argon (0.93%) – here the values are for dry air.(2) In addition the atmosphere also contains water vapour (0 - 4%), carbon dioxide (400 parts per million by volume, ppmv),(3) hydrogen (0.5 ppmv), methane (1.8 ppmv),(4) the remaining noble gases and other short-lived trace gas species. These trace gases are typically found at concentrations of the order of one part per billion (ppbv; i.e. one molecule in a billion air molecules), and despite their low concentrations they have a significant impact on the atmosphere.(5) The composition of the atmosphere is controlled by the chemical and physical transformation of natural and anthropogenic trace gases, which in turn have significant effects on key issues including air quality and climate change. Another important atmospheric constituent in terms of air quality and climate is aerosol, which describes particles of liquid or solid matter suspended in a carrier gas.

The primary focus of this thesis is the detection and quantification of biogenic and anthropogenic trace gas emissions into the troposphere using highly sensitive spectroscopic instrumentation. Broadband cavity enhanced absorption spectroscopy (BBCEAS) was applied to measure I₂ emissions in marine environments, NO₂ in urban ambient air, and the oxidation products of volatile organic compounds (VOCs) during an atmospheric simulation chamber study. The BBCEAS technique is an advanced form of optical spectroscopy, which was applied to make highly sensitive measurements of multiple atmospheric absorbers across the instrument's broad wavelength range (typically 50 nm). The technique uses a high finesse optical cavity to enable absorption measurements to be made over extended path lengths within a compact instrument. This chapter provides an introduction to the chemistry of the troposphere in order to explain the motivation for the work in this thesis and to put the applications of the BBCEAS technique into context. Particular focus is paid to the key tropospheric species including NO₂, which influence tropospheric chemistry and urban air quality. A significant proportion of this thesis also focuses on biogenic halogen emissions into the marine boundary layer (MBL) and specifically those of molecular iodine (I2) from macroalgae released into the troposphere at coastal regions. This chapter therefore also provides an introduction to the atmospheric chemistry of reactive iodine species (RIS) and their previous measurements in the field.

1.1 Structure of the Atmosphere

The vertical structure of the atmosphere can be divided into distinct regions at different altitudes (Figure 1.1). The notional dividing lines between regions (tropopause, stratopause etc.) occur where the temperature gradient changes sign – indeed whether the temperature increases or decreases with altitude determines the vertical stability within the layer and hence many of its other properties.(5, 6)



Figure 1.1 The layers of the atmosphere, subdivided based on temperature, mixing mechanism and degree of ionisation (from Brasseur and Solomon)(7)

The troposphere describes the lowest region of the atmosphere that extends from the ground to a height of 8 - 18 km dependent on latitude. The absorption of solar radiation by the Earth's surface results in a region of warmer air forming below a region of cooler air. This unstable temperature distribution causes high levels of vertical mixing and turbulence within the lower troposphere. The presence of the tropopause restricts the

levels of vertical mixing between the troposphere and the stratosphere and therefore most reactive trace gases, which are emitted from the surface, will remain within the relatively well-mixed and turbulent troposphere. Consequently, the troposphere contains a substantial amount of chemical processes. The stratosphere describes the poorly vertically mixed region that extends from the tropopause to a height of around 50 km. The stratosphere contains the stratospheric ozone layer, which consists of 90% of the total atmospheric ozone budget. Ozone absorbs harmful ultraviolet (UV) light from the Sun and limits the solar radiation reaching the troposphere to wavelengths longer than 290 nm. The temperature of the stratosphere increases with height owing to the absorbance of UV light by ozone being more prevalent at higher altitudes. The upper atmosphere above the stratopause consists of two further temperature inversions resulting from a decrease in ozone concentration (and hence *in situ* heating) in the mesosphere and the absorption of short wavelength radiation by nitrogen and oxygen species in the thermosphere.

1.2 Chemistry of the Troposphere

Trace gases and aerosol particles control the chemistry of the troposphere. They may either be directly emitted (primary) or formed through chemical reactions (secondary) within the troposphere itself. The majority of chemical transformations within the troposphere are initiated and propagated by radical species, primarily the hydroxyl radical (OH) during the day and the nitrate radical (NO₃) at night. The high reactivity of these two species means that they are short-lived and found in very low abundance. Nevertheless they are responsible for initiating the oxidation and removal of the majority of trace gas emissions that enter the troposphere. Such oxidation reactions typically yield products that have lower saturated vapour pressures and/or are more water-soluble than their precursors. Thus the oxidation products often condense onto existing aerosol particles to form, for example, secondary organic aerosol - Chapter 3 includes BBCEAS measurements of glyoxal and methyl glyoxal formed during VOC oxidation experiments in the EUPHORE atmospheric simulation chamber to study partitioning of these di-carbonyl species onto seed aerosol. In rare cases, such as iodine oxides formed from the atmospheric processing of iodine-containing emissions (Chapter 4 & 5), the products can condense to form new aerosol via homogeneous or "gas-to-particle" nucleation.

1.2.1 Hydroxyl Radical Chemistry

The hydroxyl radical is a highly reactive molecule with an unpaired valence electron. It is primarily produced through the photolysis of ozone in the presence of water vapour (R1.1 + R1.2). Only some 10% of electronically excited oxygen atoms generated from ozone photolysis react in this way; the remainder are quenched to the ground state and recombine with an oxygen molecule to reform ozone (R1.3 + R1.4). Other sources of OH include the photolysis of HONO in polluted air (HONO + $hv \rightarrow$ OH + NO) and the photolysis of hydrogen peroxide in clean, low NO_x conditions (H₂O₂ + $hv \rightarrow$ 2 OH).(8-10)

$O_3 + hv \ (\lambda > 340 \text{ nm}) \rightarrow O_2 + O(^1D)$	R1.1
$O(^{1}D) + H_{2}O \rightarrow 2 OH$	R1.2
$O(^{1}D) + M \rightarrow O(^{3}P) + M$	R1.3
$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$	R1.4

Hydroxyl radicals react with the majority of oxidisable trace gases in the troposphere including carbon monoxide (CO) and hydrocarbons (HC) (Figure 1.2). Such reactions generally involve the regeneration of OH radicals through the production of peroxy radicals such as HO₂ and their reaction with nitric oxide (HO₂ + NO \rightarrow OH + NO₂). This reaction is also important for linking HO_x recycling to the chemistry of NO_x. Not all reactions recycle OH: an important exception is the removal of OH through its reaction with NO₂ to form nitric acid (OH + NO₂ + M \rightarrow HNO₃ + M), which may be removed from the gas phase through deposition. The net outcome of the chemistry shown in Figure 1.2 is the production of tropospheric ozone (O₃). Ozone is a harmful air pollutant in urban areas and a greenhouse gas. The chemistry of O₃ production is discussed further in Section 1.2.3.



Figure 1.2 Daytime cycling of HO_x and NO_x species in the troposphere (adapted from Monks et al.)(9)

1.2.2 Nitrate Radical Chemistry

The nitrate radical is the major atmospheric oxidant at night, when levels of OH are (essentially) zero owing to a lack of photolysis. NO_3 is formed through the reaction of NO_2 with ozone (R1.5) or the thermal decomposition of its reservoir compound N_2O_5 (R1.6).

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
 R1.5

$$N_2O_5 \rightarrow NO_3 + NO_2$$
 R1.6

During the day, NO₃ is lost through photolysis (R1.7) and its rapid reaction with NO (R1.8). At night when levels of NO are generally low, the main NO₃ sinks are conversion to its reservoir compound N₂O₅ and subsequent heterogeneous loss on aerosol particles (R1.9 – 1.10) and the reaction of NO₃ with volatile organic compounds (VOCs), especially with the C=C double bonds of unsaturated (often biogenic) hydrocarbons (R1.11).

$NO_3 + hv \rightarrow NO + O_2 \text{ or } NO_2 + O$	R1.7
---	------

 $NO_3 + NO \rightarrow NO_2 + NO_2$ R1.8

 $NO_2 + NO_3 + M \rightarrow N_2O_5$ R1.9

 $N_2O_5 + H_2O \rightarrow 2 \text{ HNO}_3$ R1.10

 $NO_3 + VOC \rightarrow organic nitrates$ R1.11

1.2.3 Nitrogen Oxides

The fast transitioning nitrogen oxide species NO and NO₂ (NO_x) are pollutant gas species that come mainly from anthropogenic sources (although there are a few natural sources, e.g. lightning). The primary NO_x source in urban areas is high temperature combustion, which includes the burning of fossil fuels in vehicle engines and home heating.(11) Typical NO_x concentrations range from approximately 10 - 1000 parts per billion by volume (ppbv) in urban areas, compared to approximately 0.2 - 10 ppbv for rural regions.(1) The NO and NO₂ species are generally considered together as NO_x as they rapidly intercycle via reactions 1.12 to 1.14. These reactions combine to form the NO_x photochemical steady-state, which is a null cycle with no net formation or loss of tropospheric O₃.(12)

$$\begin{split} \text{NO}_2 + h\nu \ (\lambda < 420 \text{ nm}) \rightarrow \text{NO} + \text{O}(^3\text{P}) & \text{R1.12} \\ \text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} & \text{R1.13} \end{split}$$

$$NO + O_3 \rightarrow NO_2 + O_2$$
 R1.14

However, net formation of O_3 does occur if the conversion of NO to NO₂ takes place without the consumption of a molecule of O_3 . As previously discussed in Section 1.2.1, the reaction of OH with VOCs forms peroxy radicals (HO₂ or RO₂), which will be recycled back to OH through their reaction with NO (R1.15).

$$NO + HO_2 \rightarrow NO_2 + OH$$
 R1.15

Crucially, R1.15 generates a molecule of NO₂; but unlike R1.14 in the NO_x photochemical steady-state, R1.15 does so without consuming ozone. The photolysis of this NO₂ again forms NO and O(³P) (R1.12) with the latter reacting with O₂ (R1.13) leading to a net production of O₃. R1.15 is also important in linking the recycling reactions of the HO_x and NO_x families. NO_x is removed from the atmosphere via the reaction of OH and NO₂ to form HNO₃ (daytime) or via NO₃ and N₂O₅ sinks at night (Section 1.2.2).

A high percentage of NO_x emissions, especially in urban areas, are produced by road vehicles (38.3%).(13) The other sources of NO_x emissions in European environment agency (EEA) member countries include energy production and distribution (22.1%),

commercial, institutional and household emissions (14.8%), energy use in industry (13.4%) and non-road transport (7.1%), with the remaining contributions from industrial processes, agriculture and waste (4.3%). The majority of ambient NO_x emanating from vehicle exhausts is primarily emitted as NO (typically 90 to 95%). NO_x emissions from petrol vehicles have decreased considerably since the introduction of catalytic emission control systems to control vehicle emissions in 1992. However, the situation for diesel vehicles is very different with vehicles registered in the late twothousands observed to emit similar or higher NO_x levels compared to those from the early nineteen-nineties.(14) Figure 1.3 shows the NO_x/CO₂ emission ratio versus year of manufacture for the major classes of vehicle based on the analysis of remote sensing data by Carslaw et al.(15) This failure of modern vehicle emission standards to decrease NO_x emissions from diesel vehicles results from significant levels of primary NO₂ being emitted directly from their exhausts,(16-18) which in some cases contributes up to 70% of their total NO_x emissions.(19) These direct emissions are linked to the types of catalyst systems used on diesel vehicles, such as oxidation catalysts and particulate filters, which were fitted to control emissions of other pollutants but indirectly enable the increased oxidation of NO to NO₂.



Figure 1.3 NO_x/CO₂ emission ratio for major classes of vehicle based on the analysis of remote sensing data (from Carslaw et al.)(15) The error bars show the 95% confidence interval in the mean

NO_x emissions close to the ground in highly populated areas are detrimental to human health. Emissions of NO₂ have a negative effect on human health through inflammation of the airways and have been observed to increase symptoms of bronchitis and reduce lung function growth through long-term exposure to the concentrations currently measured in many urban areas. NO₂ also has substantial indirect health effects including the formation of nitrate aerosols, which form an important fraction of hazardous particulate matter (PM), and tropospheric O₃.(20) NO₂ also contributes to eutrophication and acid rain through the aqueous deposition of its main sink, HNO₃. European legislation places an upper limit on the annual mean NO₂ concentration of 40 μ g m⁻³; there is also a hourly limit of 200 μ g m⁻³ not to be exceeded for more than 18 hours a year.(21) The implementation of both hourly and yearly limit values aimed to reduce the harmful effects of both short- and long-term pollutant exposures on human health. Despite this, European inhabitants still regularly breathe air that does not meet the required standard, with exceedances of limit values generally most prevalent at roadside locations in highly populated urban environments.(22)

1.2.4 Aerosol

An aerosol consists of solid or liquid particles suspended in air (as distinct from "particulate matter" (PM) which refers specifically to the particles). The particles may either be directly emitted or produced by secondary chemical reactions within the atmosphere.(23) Typical constituents of urban aerosols include sulphate (SO₄²⁻), nitrate (NO₃⁻), organic compounds (VOCs), black carbon (BC), and metals and other species found in vehicle fuels and from the degradation of mechanical components. Figure 1.4 shows a typical ambient particle distribution as a function of particle size expressed by particle number, ΔN , surface area, ΔS , and volume, ΔV . The plot of particle number versus particle diameter (top panel) shows that the atmosphere typically contains a greater number of small particles (< $\approx 0.1 \ \mu$ m) relative to large particles.(5) However, the majority of surface area (middle panel) and particle volume (and hence mass), ΔV , (bottom panel) is found in particles with larger diameters (> 0.1 μ m). Therefore, in terms of air quality, particles of size 0.1 μ m or less are quantified by their number concentration and larger particle size distributions are generally characterized by their mass concentration.(24)



Figure 1.4 A typical ambient particle distribution as a function of particle size expressed by particle number (top panel), surface area (middle panel) and volume (bottom panel).
Vertical scaling is individual to each panel. Figure from Heal et al.,(24) and adapted to indicate the size ranges of PM_{2.5} and PM₁₀

Particles in the lower troposphere are observed in three size distributions or modes, termed nucleation mode (< 0.1 µm diameter), accumulation mode ($\approx 0.1 µm - 2 µm$) and coarse mode (> 2 µm). The nucleation mode contains secondary particles that are formed *in situ* through source condensation processes and chemical reactions in the atmosphere. These particles grow into the accumulation mode through coagulation and condensation. The coarse mode consists of the larger, directly emitted, primary particles, which are typically generated by mechanical processes (e.g. abrasion, wind erosion/suspension). Air quality legislation limits mass concentrations of particles below set aerodynamic diameter size limits, where PM₁₀ refers to particles of 10 µm diameter or less, and its subset PM_{2.5} refers to particles of 2.5 µm diameter or less. PM_{2.5} is of most concern in terms of human health because smaller particles can penetrate further into the human body and cause more harm to the peripheral alveolar regions of the lungs.(25) There is also growing evidence that very small particles (PM_{0.1}; diameters below 100 nm) are especially harmful because they can enter the blood stream by crossing the air-blood boundary inside alveoli.(24)

1.2.5 Glyoxal and methyl glyoxal

Glyoxal (GLY, CH(O)CHO) and methyl glyoxal (MGLY, CH₃C(O)CHO) are the smallest and most prevalent α -dicarbonyls in the troposphere.(26) They are oxygenated VOC (OVOC) intermediates and are produced by the OH and O₃ initiated oxidation of VOCs in the atmosphere.(27-30) OVOC compounds are formed from the reactions of peroxy radicals, RO₂, which are produced through the chemistry previously outlined in Figure 1.2. Reactions R1.16 to R1.19 demonstrate the formation of OVOCs using formaldehyde, HCHO, as an example. Here, CH₄ reacts with OH to form the peroxy radical, CH₃O₂. The CH₃O₂ radical then reacts with NO through R1.18 (analogous to R1.15) to produce HCHO and HO₂. HO₂ will subsequently be recycled back to OH via R1.15.

$CH_4 + OH \rightarrow CH_3 + H_2O$	R1.16
$CH_3 + O_2 \rightarrow CH_3O_2$	R1.17
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	R1.18
$CH_3O + O_2 \rightarrow HCHO + HO_2$	R1.19

The primary source of GLY and MGLY in the atmosphere is the oxidation of biogenic isoprene, C_5H_8 , emitted when vegetation is exposed to sunlight.(31) Other significant sources include anthropogenic acetylene for GLY and the oxidation of biogenic acetone for MGLY. Figure 1.5 shows the formation of GLY through several reaction pathways initiated by the oxidation of isoprene. MacDonald et al.,(32) showed the extent of the biogenic GLY source through *in situ* DOAS measurements above the tropical rainforest canopy in Borneo. Concentrations of GLY up to 1.6 ppbv were observed along with formaldehyde at maximum levels of 4.5 ppbv. The high levels of OVOCs were accounted for by the large measured amounts of forest isoprene emissions and the high concentrations of OH radicals observed within the region.



Figure 1.5 Isoprene oxidation scheme to show the formation of glyoxal and methyl glyoxal (by Galloway et al.)(33)

GLY is formed from the atmospheric oxidation a number of VOC sources and has therefore been applied as a tracer for oxidation chemistry in urban areas.(34) Its short atmospheric lifetime (≈ 2 h) is also advantageous because it cannot be transported far away from its emission source. The atmospheric lifetimes of GLY and MGLY are mostly determined by their photolysis and reactions with OH, however a significant amount of scientific interest relates to their contribution to the formation of secondary organic aerosol (SOA).(35, 36) SOA contributes a significant fraction of the organic component of atmospheric aerosols (30 - 60% in urban air and > 70\% in rural air),(37) and subsequently has a significant effect on air quality, visibility and climate. GLY and MGLY are highly soluble in water, which enables their uptake by aqueous aerosol particles and cloud droplets.(38) The atmospheric significance of the reactive uptake of GLY onto SOA was investigated by Liggio et al., (39) through comparison of calculated heterogeneous GLY reaction rate constants and associated lifetimes with known gaseous loss processes (photolysis and reaction with OH). Reactive uptake coefficients, γ , were calculated for gaseous GLY onto ammonium sulphate seed aerosols. Heterogeneous reaction rate constants, k, and associated lifetimes were calculated for GLY using Equation 1.1 and applying model surface area distributions, a, adapted from
Seinfeld and Pandis.(40) Here, the parameter, ω , represents the gas kinetic mean molecular speed of the GLY species.

Equation 1.1

$$k = \frac{\omega a \gamma}{4}$$

Liggio et al.,(39) estimated GLY lifetimes due to heterogeneous reactions under typical ambient conditions ranged between 5 min (urban environment) to 287 min (free troposphere). These values were compared with the estimated lifetimes for the reaction of GLY with OH radicals (300 min) and GLY photolysis (221 min). The heterogeneous loss of GLY from the gas phase was therefore estimated to be at least as important as its other known gaseous loss processes.

1.3 Atmospheric Chemistry of Iodine

1.3.1 Iodine Gas Phase Chemistry

The emissions, reactions and sinks of gaseous reactive iodine species (RIS) have received considerable scientific interest in recent years. RIS have a significant influence on the oxidising capacity of the marine boundary layer (MBL) and account for a major proportion of surface ozone removal.(41) The atmospheric chemistry of iodine is initiated by the photolysis of molecular iodine (I₂) and iodocarbons (RI) to produce iodine atoms (I) – the sources of these iodine precursors will be discussed in Section 1.3.3. Iodine atoms are less reactive than chlorine and bromine, and primarily react with tropospheric ozone and not with any organic molecules. The rapid reaction of I atoms and ozone produces the iodine monoxide radical (IO), which is central to the majority of iodine chemistry in the troposphere. IO may be rapidly photolysed back to I atoms and $O(^{3}P)$ atoms, with the latter reforming O₃. Hence reactions R1.21 – R1.23 are a photostationary steady-state with no net effect on the concentration or reactivity of iodine species or O₃.

 I_2 , CH_3I , CH_2I_2 , etc. + $hv \rightarrow I$ + products R1.20

$$I + O_3 \rightarrow IO + O_2$$
 R1.21

$$IO + hv \rightarrow I + O(^{3}P)$$
 R1.22

 $O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$ R1.23

Early interest in the atmospheric chemistry of iodine was piqued by its ability to catalyse the destruction of tropospheric ozone. Chameides and Davies realised the potential atmospheric significance of iodine chemistry over thirty years ago,(42) and assigned the catalytic removal of tropospheric ozone along with the conversion of NO to NO₂ and HO₂ to OH to iodine atoms produced through the photolysis of methyl iodide (CH₃I) observed in the MBL. More recently, Davis et al.,(43) assigned 6% of total column tropospheric ozone destruction in marine environments to iodine chemistry, which could rise to as high as 30% in regions of high biological activity. This modelling also showed shifts in the ratios of HO₂ to OH and NO₂ to NO of -9% and +3% respectively due to RIS chemistry arising from a 10 pptv increase in CH₃I.

A net destruction of tropospheric ozone can occur when IO radicals formed in R1.21 react with themselves or with other species, rather than being photolysed to form $O(^{3}P)$. The self-reaction of IO, shown in Cycle 1, regenerates I atoms through the formation and subsequent photolysis of iodine dioxide (OIO) without the production of an oxygen atom. The net result of the cycle is therefore the transformation of two molecules of O_{3} into three molecules of O_{2} .

Cycle 1:	
$(I + O_3 \rightarrow IO + O_2) \times 2$	R1.21 (×2)
$IO + IO \rightarrow OIO + I$	R1.24
$OIO + hv \rightarrow I + O_2$	R1.25
Overall: $2 O_3 \rightarrow 3 O_2$	

The efficiency of Cycle 1 depends heavily on whether the photolysis of OIO produces $I + O_2$ rather than IO + O (the latter channel is neutral in O₃). Cycle 1 is thought to dominate the destruction of tropospheric ozone when concentrations of IO are high (> 2 pptv).(44) At lower IO concentrations, the reaction of IO and HO₂ becomes more

significant, leading to the formation HOI (R1.26). The photolysis of HOI (R1.27) regenerates an I atom without also producing $O({}^{3}P)$; hence ozone is lost. The photolysis co-product is an OH radical, and so Cycle 2 also creates an additional pathway for the conversion of HO₂ to OH, thereby perturbing partitioning in the HO_x family.

Cycle 2:	
$I + O_3 \rightarrow IO + O_2$	R1.21
$IO + HO_2 \rightarrow HOI + O_2$	R1.26
$HOI + hv \rightarrow OH + I$	R1.27
Overall: $HO_2 + O_3 \rightarrow OH + 2O_2$	

Cycle 2 was assigned by Stutz et al., (45) as the dominant mechanism for tropospheric ozone loss in environments containing low NOx concentrations (i.e. [NOx] below 500 pptv). This is because in higher NO_x conditions, HO₂ will be converted back to OH through its reaction with NO (R1.15) in preference to reacting with IO to produce HOI (R1.26). In semi-polluted environments, IO radicals will react with both NO (Cycle 3) and NO₂ (Cycle 4). Cycle 3 is a null cycle, which regenerates I atoms and (indirectly) recycles O₃ via NO₂ produced in the reaction of IO and NO. The reaction R1.28 also shifts the partitioning of NO_x species further towards NO_2 . Cycle 3 becomes competitive with the other cycles at NO concentrations above 40 pptv.(46) O₃ depletion can occur through Cycle 4 but only if $IONO_2$ is photolysed to $I + NO_3$ and not $IO + NO_2$. The ozone depletion efficiency of RIS will also be limited by the irreversible uptake of OIO and higher iodine oxides onto aerosol particles (section 1.3.2).

Cycle 3:	
$I + O_3 \rightarrow IO + O_2$	R1.21
$IO + NO \rightarrow I + NO_2$	R1.28
$NO_2 + hv \rightarrow NO + O(^3P)$	R1.29
$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$	R1.30
Overall: null cycle	

Cycle 4:	
$I + O_3 \rightarrow IO + O_2$	R1.21
$IO + NO_2 + M \rightarrow IONO_2$	R1.31
$IONO_2 + hv \rightarrow I + NO_3$	R1.32
$NO_3 + hv \rightarrow NO + O_2$	R1.33
$NO + O_3 \rightarrow NO_2 + O_2$	R1.34
Overall: $2 O_3 \rightarrow 3 O_2$	

1.3.2 Iodine Aerosol Chemistry

Iodine dioxide (OIO) radicals formed through the recombination of IO radicals (R1.24) may either undergo rapid photolysis and return to Cycle 1 or react with themselves or with IO to form higher iodine oxides (R1.35 and 1.36). The higher iodine oxides have low vapour pressures and have been directly linked to the nucleation of new particles under ambient conditions. Loss of iodine oxides to particles is also a sink of iodine from the gas phase.(47, 48)

$$IO + OIO + M \rightarrow I_2O_3 + M$$
 R1.35

$$OIO + OIO + M \rightarrow I_2O_4 + M$$
 R1.36

The chemistry leading to the formation of higher iodine oxides (I_xO_y) and subsequent iodine oxide particle (IOP) formation is uncertain. Various particle compositions and formation mechanisms have been proposed through both theoretical and experimental methods. A laboratory study by Jimenez et al.,(49) proposed that the iodine tetraoxide (I_2O_4) structure was the key initiator of IOP formation, after a lack of hygroscopic growth was observed from IOPs generated following CH₂I₂ photolysis (whereas the alternative I₂O₅ structure is very hygroscopic). In contrast, Saunders and Plane,(50) observed that particles consisting mainly of I₂O₅ were formed through the dry reaction of I₂ and O₃. These authors proposed the formation of the stable iodine oxide, I₂O₅, through the oxidation of I₂O₄ by O₃ (R1.37), followed by polymerization to form IOPs (R1.38).

$$I_2O_2 \xrightarrow{O_3} I_2O_3 \xrightarrow{O_3} I_2O_4 \xrightarrow{O_3} I_2O_5$$
 R1.37

$$I_2O_5 + (I_2O_5)_n \rightarrow (I_2O_5)_{n+1} + M$$
 R1.38

A further study by Saunders et al.,(51) demonstrated the formation of IOPs without the presence of O_3 , and hence suggested that IOP formation was initiated through the polymerization of I_2O_3 and I_2O_4 formed through R1.35 and R1.36. A soft ionization mass spectrometry study by Gomez Martin et al.,(52) of clusters formed in $I_2 + O_3$ gas mixtures concluded that I_2O_4 is the most likely iodine oxide to initiate aerosol nucleation and that the dimerisation of I_2O_4 (I_2O_4 – I_2O_4) is the key step in IOP nucleation.

The growth of IOPs in the MBL may impact the local climate directly through scattering and/or absorption of solar radiation or indirectly through the enhancement cloud cover attributable to a higher concentration of cloud condensation nuclei (CCN).(53, 54) The supply of RIS and iodine oxides is limited by the tidal cycle, for reasons discussed below in Section 1.3.3. It has therefore been proposed that, once nucleated, IOPs can grow to CCN active sizes (> 50 nm diameter) through the condensation of other species that are present in the coastal environment, including water vapour, ammonia and both mineral and organic acids.

1.3.3 Iodine Emission Sources

The oceans are overwhelmingly the dominant source of atmospheric iodine species. Gas exchange between the ocean and the atmosphere is controlled by both biotic and abiotic processes. Seawater contains iodine as a mixture of dissolved iodide (Γ) and iodate (IO₃⁻) ions at combined average concentrations between 450 and 500 nmol dm⁻³,(55); concentrations are higher in tropical and subtropical waters and temperate coastal regions.(56) Γ and IO₃⁻ were measured in the English Channel at approximate concentrations of 350 and 250 nmol dm⁻³ respectively with no significant seasonal variation.(57) The volatilisation of iodocarbons of biogenic origin (including CH₃I and CH₂I₂) was originally thought to be the major source of iodine in the MBL.(58) However, measured concentrations of iodocarbons in the MBL were insufficient to account for the concentrations of IO radicals (up to \approx 10 pptv) observed in long-path DOAS experiments (Section 1.3.4). An additional I_2 source resulting from the deposition of O_3 onto the ocean surface in the presence of sunlight was proposed. Garland and Curtis,(59) first demonstrated that the release of I_2 from the sea surface was inversely proportional to O_3 in the surrounding atmosphere. More recent lab studies by Sakamoto et al.,(60) observed significant gaseous emissions of I_2 and much lower IO concentrations from the heterogeneous reaction of gaseous ozone and a potassium iodide (KI) solution (albeit it at 2 orders of magnitude higher iodide concentrations than present in seawater). The reaction of tropospheric ozone with Γ on the sea surface to volatilise I_2 is shown by reactions R1.39 to R1.41.

$\Gamma + O_3 + H^+ \longrightarrow HOI + O_2$	R1.39
$HOI + I + H^+ \rightarrow I_{2 (aq)} + H_2O$	R1.40
$I_{2(aq)} \leftrightarrow I_{2(q)}$	R1.41

The deposition of ozone on the sea surface is a significant ozone sink and was assigned by Ganzeveld et al.,(61) to account for one third of the total global ozone deposition flux. As previously discussed, the photolysis of I_2 and HOI released into the atmosphere will yield I atoms that will subsequently form reactive IO radicals through their rapid reaction with tropospheric ozone. The atmospheric significance of reactions 1.39 and 1.40 was recently emphasized by Carpenter et al.,(62) who showed that they could account for 75% of total IO production observed over Cape Verde in the tropical Atlantic ocean.

It is well established that biogenic emissions make substantial contributions to reactive iodine species in the atmosphere. Microalgae (phytoplankton) and macroalgae (seaweed) produce RIS over the open ocean and at temperate coastal regions respectively. One of the primary focuses of this thesis is the emission of iodine compounds by macroalgae in to the MBL at coastal locations, and these are generally significantly larger RIS fluxes than those observed over the open ocean. However, the contribution of phytoplankton to the emission of iodocarbons and iodine from seawater is also significant in relation to their potentially ocean wide distribution. As previously discussed, the formation of I_2 from seawater is directly linked to the aqueous concentration of Γ , which is found in seawater along with IO_3^- . Phytoplankton have been observed to reduce IO_3^- to I^- in seawater,(63) and may therefore increase the formation and emission of I₂.(64)

Emissions of I₂ by intertidal brown macroalgae were recently established as the major source of atmospheric RIS in temperate coastal regions. Küpper et al.,(65, 66) demonstrated that seaweed plants accumulate and store iodide from surrounding seawater as an antioxidant reservoir when they are submerged and not under stress. Thermodynamic and kinetic calculations have shown the accumulation of Γ to be more favourable in terms of its reaction with reactive oxygen species (ROS) than the other halides (Cl⁻ and Br⁻) available in the ocean.(67) Brown algal kelp species, specifically *Laminaria digitata*, have been shown to accumulate significant quantities of iodine: up to 0.4% and 5% of their dry weight in adult and young plants respectively. Küpper et al.,(65) reported an average iodide accumulation of 1% dry weight, which represents a 10⁴ fold enhancement of iodide over its concentration in seawater. The majority of iodine is stored as Γ in the peripheral tissue of *L. digitata* plants (Figure 1.6), specifically the meristoderm and the first cell layers of the outer cortex.



Figure 1.6 Rutherford backscattering spectrometry (RBS) and particle-induced X-ray emission (PIXE) elemental maps of the meristoderm and the outer cortex in a *L. digitata* stipe (from Verhaeghe et al.)(68)

When seaweed plants are exposed to air by the outgoing tide, they experience oxidative stress caused by tropospheric ozone, dessication and higher solar irradiance. Significant quantities of Γ are subsequently sourced to the thallus surface of the seaweed plant, which acts as a defence mechanism and detoxifies both gaseous and aqueous oxidants. The reaction of aqueous Γ and gaseous O₃ (R1.39 to 1.41) is responsible for significant

I₂ emissions into the MBL, with the surface of the plants providing a much more abundant source of iodide than the ocean's surface. Dangeard, (69) and Kylin, (70) first showed that the oxygen dependent volatilisation of RIS occurs in the cell apoplast (cell wall). More recently, specific peroxidase enzymes called the vanadium dependent haloperoxidases (VHPO) have been shown to play the major role in the chemical defence mechanisms of macroalgae against oxidative stress.(57) Figure 1.7 shows the mechanism for the VHPO catalyzed oxidation of Γ in the presence of hydrogen peroxide (a ROS species) which enables the uptake and distribution of iodine by macroalgae.(71) The enzyme first coordinates one molecule of H₂O₂ to form a stable peroxovanadate intermediate. This intermediate subsequently reacts with Γ to form HOI, which produces I₂ externally to the plant through its (inorganic) disproportionation reaction with Γ and H⁺. It is important to note that volatile iodocarbons may also be produced through the reaction of HOI with organic molecules and the direct emission of I₂ is therefore dependent on the volatilization of iodine species before they can react with any organic compounds. The reaction of HOI with iodide also depends on $[H^{+}(aq)]$, with I₂ being the favoured product at the slightly alkaline pH of seawater (pH 7.4).



Figure 1.7 Enzyme catalytic cycle of vanadium dependent haloperoxidases, enabling the uptake and release of iodine species by macroalgae (adapted from Leblanc et al.)(71)

1.3.4 Field Observations of Reactive Iodine Species

Atmospheric measurements of iodine in the MBL are generally performed in two distinct environments, the coastal MBL and the open ocean. Open ocean observations of reactive iodine species are generally characterized by small IO radical fluxes and are not likely to be influenced by emissions from coastal macroalgae. Allan et al.,(72) and Read et al.,(41) reported DOAS measurements IO over the remote marine boundary layer off the north coast of Tenerife and at Cape Verde respectively. Allan et al.,(72) observed IO, at levels up to 3 pptv that that correlated strongly with solar irradiation, but not the cycling of the tides. Measurements by Read et al.,(41) were the first to detect IO radicals (concentrations between 1 - 3 pptv) at an open ocean site that was not influenced by local biological sources such as macroalgae. The concentrations of reactive iodine and bromine species were directly linked to an observed depletion in tropospheric ozone, and indicated the presence of iodine chemistry occurring over the open ocean. Mahajan et al.,(73) later established that measured concentrations of iodocarbons at Cape Verde were insufficient to account for the observed levels of IO and proposed an open ocean source of I atoms, which involved the production of I₂ resulting from the deposition of O_3 in the presence of sunlight. Carpenter et al.,(62) proposed that seawater emissions of HOI were potentially much larger than those of I₂, however direct proof for this mechanism operating in the atmosphere has not yet been possible because existing analytical techniques are unable to detect HOI at its ambient concentrations. Lawler et al.,(74) recently reported the first measurement of I₂ by chemical ionization tandem mass spectrometry over an open ocean location at Cape Verde that was not impacted by coastal macroalgal emissions. Mixing ratios of I₂ were highest at night and ranged between < 0.2 - 1.67 pmol mol⁻¹. The previously proposed sea-air flux of HOI produced by the ozonolysis of seawater was assigned as the potential I₂ source.

Rather than the open ocean, this thesis focuses on emissions of iodine into the coastal MBL in areas of high biological activity. Here reactive iodine chemistry is typically characterized by large fluxes of iodine released into the atmosphere at times of low tide from macroalgae (seaweeds) growing locally. Such emissions lead to higher concentrations of RIS than observed at open ocean sites (e.g. Cape Verde) and to nucleation bursts of iodine oxide particles (which are generally not observed at open ocean sites).

Interest in the atmospheric chemistry of iodine in the coastal MBL was initiated through observations of reactive iodine species, initially IO but subsequently I2 and OIO, at Mace Head, Ireland, and Cape Grimm, Tasmania.(75-77) Alicke et al.,(75) performed the first measurements of RIS in the MBL through the detection of IO during the day at mixing ratios up to 6.6 pptv using long-path differential optical absorption spectroscopy (LP-DOAS). DOAS has since been applied to further measurements of IO at Mace Head, (72, 77, 78) and in other coastal locations including Cape Verde, (41) Brittany, France, (79, 80) the North Sea, Germany, (80) the Gulf of Maine, USA, (81) and Alcântara, Brazil.(82) An extensive table of IO measurements is available in Saiz-Lopez et al.(44) DOAS instruments average concentrations over long light paths and therefore generally measure IO at lower levels (< 30 pptv) than single point measurements. For example, DOAS measurements made by Mahajan et al., (79) as part of the RHaMBLe (Reactive Halogens in the Marine Boundary Layer) campaign in Roscoff, France observed IO concentrations (peak = 10.1 pptv) that were significantly lower than those observed through single point measurements. Here, the peak concentrations of IO reported through cavity ring-down spectroscopy (CRDS) (27.6 pptv maximum),(83) and laser induced fluorescence spectroscopy (FAGE-LIF) (54 pptv maximum),(84) were observed in the daytime and coincided with times of low tide (Figure 1.8).



Figure 1.8 Time series of reactive iodine species measured throughout the RHaMBLe campaign in Brittany, France. The red symbols are path integrated LP-DOAS measurements and the yellow triangles correspond to in situ I₂ measurements by BBCRDS and IO measurements by FAGE LIF (from McFiggans et al.)(85)

Measurements of the iodine dioxide radical (OIO) are much less frequent and have been generally limited to the night time. OIO was first detected in the marine boundary layer at Cape Grimm, Tasmania during sunset (3 pptv peak).(75) Subsequent observations of OIO have been made during night time at Mace Head, Ireland, through DOAS (3.0 and 9.2 pptv maximum during the NAMBLEX (North Atlantic Marine Boundary Layer Experiment),(77) and PARFORCE campaign (New Particle Formation and Fate in the Coastal Environment),(80) respectively) and CRDS (13 pptv maximum) during the NAMBLEX campaign.(86) Measurements of OIO are not as common as those of IO, for example OIO (3 pptv detection limit) was not detected in Lilia, France, despite observations of IO made through DOAS.(80) The first daytime measurement of OIO (30 pptv max) was observed by DOAS in a polluted environment in the Gulf of Maine, USA.(81) The only previous measurement of OIO in Roscoff, France was made at night time, with a maximum concentration of 8.7 pptv observed through DOAS.(79). Again the review of Saiz-Lopez et al.,(44) provides a summary table of OIO observations up to 2011.

Iodocarbon emissions from seaweeds had previously been assigned as the major source of RIS in coastal regions, (87, 88). The relatively short-lived compound CH₂I₂ was identified as the iodocarbon that provided the largest I atom flux through photolysis. Chamber experiments by O'Dowd et al., (89) and Jimenez et al., (49) demonstrated the formation of new particles from the photolysis of CH₂I₂ in the presence of O₃. McFiggans et al.,(47) subsequently demonstrated the formation of aerosol particles from macroalgal emissions, specifically those from Laminaria species when exposed to ambient concentrations of O_3 . The particles formed were shown to be a similar composition to those formed by previous chamber photolysis experiments. DOAS measurements of I2 and GC-MS measurements of CH2I2 at Mace Head were used to determine the comparative contribution of both species to the total I atom flux in the region (Figure 1.9). The contribution from I_2 to the I atom flux was at least 3 orders of magnitude greater than that from CH₂I₂ and the formation of IOPs were therefore shown to be most likely derived from emissions of I₂ and not organic iodine. The dominance of I₂ emissions over iodocarbons was confirmed by the previously discussed field observations of large I2 concentrations measured in close proximity to seaweed beds during the RHaMBLe campaign (Figure 1.8). Concentrations were significantly higher than those of the measured iodocarbons (Figure 1.10) despite the shorter photolysis time of I_2 .



Figure 1.9 Iodine atom flux from the photolysis of I₂ and CH₂I₂ at Mace Head (from McFiggans et al.)(47) Measurements show a significantly greater I atom flux from the photolysis of available I₂ than CH₂I₂



Figure 1.10 Time series of a selection of GC/MS-measured short-lived halocarbons (CH₂IBr and CH₂I₂) with superimposed tidal height measured during the RHaMBLe campaign (from Jones et al.)(90)

Saiz-Lopez et al.,(77) used long-path DOAS to make the first direct spectroscopic measurements of I_2 in the MBL at Mace Head during the NAMBLEX campaign (Figure 1.11). Peak I_2 mixing ratios (93 pptv max) were observed corresponding with low tide. Bitter et al.,(86) also observed a maximum of 94 pptv of I_2 around a tidal minimum at NAMBLEX using broadband cavity ring-down spectroscopy (BBCRDS). Subsequent measurements of I_2 at Mace Head have been performed through LP-DOAS (61 pptv max),(80) and *in situ* Denuder,(91) techniques (140 pptv max). The detection and quantification of I_2 has also been performed at Mweenish Bay, Ireland (Denuder,

547 pptv max),(91, 92) Roscoff, France (LP-DOAS, 52 pptv max),(79) and (BBCRDS, 50 pptv max),(93), Ria de Arousa, Spain (Fluorescence, 300 pptv max),(73) and California, USA (APCI/MS/MS, 4.0 pptv max).(94) These measurements were all made in regions of high biological activity with concentrations of I_2 generally showing a high dependency on tide height.



Figure 1.11 Concentrations of I₂, OIO and IO observed at Mace Head, Ireland, during August 2002 by Saiz-Lopez et al.(77)

The production of coastal aerosol and CCN was originally attributed to the oxidation of dimethyl sulphide (produced by planktonic algae growing in sea water) to yield highly condensable gas phase sulphuric acid.(95) However, this was shown to be unlikely owing to measurements of insufficient concentrations of H₂SO₄ and the observed production of marine aerosol not coinciding with peak H₂SO₄ concentrations.(96) The first evidence for iodine initiated new particle formation was provided by the previously discussed observations of RIS at Mace Head, Ireland, specifically iodine oxides, the peak concentrations of which did coincide with bursts of ultrafine particulates. O'Dowd et al.,(97) observed the nucleation of ultra-fine aerosol particles in the clean MBL around the times of daytime low tides. It was concluded that the exposed inter-tidal

zone provided the source of new particles' precursor gases,(98) which were speculated to be either VOCs and/or alkyl halide derivatives.

The PARFORCE project, conducted from 1998 to 1999 at Mace Head, observed a significant increase in particles with diameters between 3 and 10 nm that correlated with low tides on 90% of days monitored.(99) O'Dowd et al.,(89) demonstrated new particle formation from condensable iodine-containing vapours formed through the photolysis of CH₂I₂ in the presence of O₃ in atmospheric smog chamber experiments – these experiments showed CH₂I₂, O₃ and UV radiation were essential in new particle formation. The substantial concentrations of RIS observed at low tide during the NAMBLEX campaign indicated that I₂ was the most likely precursor for IOP formation. The I₂ emissions and the subsequent formation of new particles from localized pockets of iodine oxides were later attributed to occur in the narrow inter-tidal zone where seaweeds were uncovered by the tides.(48) This led to a "hot spot" theory being proposed by Pechtl et al.,(100) and Burkholder et al.,(101) which was subsequently confirmed by the previously discussed in situ measurements of I₂ and IO in both Mace Head and Roscoff, France. Figure 1.12 shows measurements made in Roscoff, France as part of the RHaMBLe campaign, in which significant particle bursts were observed to correlate with low tide along with the previously discussed measurements of IO.(79, 83-85) Particles of diameters between 3 - 10 nm were observed at concentrations up to 3×10^5 cm⁻³ and had the potential to go on to form CCN.



Figure 1.12 Particle number concentrations and size distribution evolution during the RHaMBLe campaign (from McFiggans et al.)(44, 85)

Since the major source gas for iodine oxide particles is I_2 emitted by seaweeds in response to their exposure to air (including ozone), it is reasonable to expect there to be a correlation between enhanced ozone deposition and particles. Whitehead et al.,(102, 103) made the first direct measurements of coastal O₃ deposition at the RHaMBLe campaign in Roscoff. They observed a faster deposition velocity for ozone over an exposed seaweed bed (*Fucus serratus* and *Fucus vesiculosus*) than over seawater once the tide returned. The same authors also reported increases in UFP concentrations around low tides (when O₃ deposition rates were fastest) and a growth in particles to sizes where they can become active as CCN. Very recently, an aerosol mass spectrometry study by Allan et al.,(104) showed iodine to be a component of small diameter, newly nucleated particles observed over the sea ice at Hudson Bay during the Aerosol-Cloud Coupling And Climate Interactions in the Arctic (ACCACIA) campaign. In that case, the iodine is likely to have an inorganic source rather than from seaweeds.

1.4 Motivation for this Thesis

This thesis applies BBCEAS instrumentation to the detection and quantification of biogenic and anthropogenic emissions in contrasting coastal and urban environments. The target trace gas species (I₂, NO₂, glyoxal) and aerosol optical extinctions measured here play important roles in the chemistry of the atmosphere and their quantification is essential to improving knowledge of atmospheric processes and reaction pathways. The BBCEAS instrumentation provided highly sensitive (ppbv to pptv, depending on the target species), highly selective (unambiguous spectroscopic detection) measurements at high time resolution (1 s to 20 s). Moreover the BBCEAS instrument used in 3 out of 4 results chapters in this thesis was mobile and battery-powered, enabling the concentrations of the target trace species to be quantified accurately and rapidly very close (≈ 1 metre) to their emission sources.

2 Cavity Based Spectroscopic Techniques for Atmospheric Measurements

Measurements of atmospheric parameters are essential to understanding the chemical and physical processes in the atmosphere. This thesis presents measurements of tropospheric trace gas species, which are typically found at low concentrations in ambient air. The measurement techniques applied to atmospheric trace gases must therefore have a high sensitivity to detect species at typically observed ambient pptv to ppbv levels. Measurement techniques must also provide selective measurements that are not influenced by any other species present in the analysed air sample. This is particularly important owing to the complex and rapidly varying mixture of trace gas species present in ambient air. This chapter provides an introduction to the broadband cavity enhanced absorption spectroscopy (BBCEAS) technique applied to the highly sensitive and selective measurements of trace gas species in this thesis.

2.1 Absorption Spectroscopy

The absorption of radiation across the electromagnetic spectrum has been extensively used to determine the chemical composition of the Earth's atmosphere.(5, 11, 105) Electromagnetic radiation is characterised by its frequency, v, wavelength, λ , and velocity, c, $(2.99 \times 10^8 \text{ ms}^{-1}$ in a vacuum), which are connected by the equation: $c = v\lambda$ (Figure 2.1). The way in which radiation interacts with matter depends on the energy of a photon, E, which is directly proportional to its frequency and is defined by the equation: $E = hv = hc/\lambda$, where h is Plank's constant (6.63 $\cdot 10^{-34}$ Js).



Figure 2.1 The electromagnetic spectrum and atomic and molecular transitions which occur through interaction with radiation of different wavelength ranges (from Platt and Stutz)(11)

The interaction of atoms or molecules with radiation (light) in the ultra-violet (UV) and visible region of the electromagnetic spectrum will result in the reconfiguration of the outer electron shell of the interacting species (electronic excitation). When light passes through a species, energy from the light is used to promote an electron from the ground state to an electronically excited state. Electronic excitation can occur when the energy required for transitions between the ground state and electronically excited state of a species correspond to the energy of the interacting UV or visible photons. The application of absorption spectroscopy enables the identification of target molecules based on their characteristic interactions with electromagnetic radiation at specific wavelengths. Lambert-Beer's law (Equation 2.1) can be applied to the analysis of gaseous (or liquid) absorbers in a sample.

Equation 2.1

$$transmittance(\lambda) = \frac{I(\lambda)}{I_0(\lambda)} = exp(-\alpha(\lambda)L) = exp[-\sum_i \sigma_i(\lambda)c_iL]$$

Here $I_0(\lambda)$ represents the initial intensity emitted by a source of radiation, and $I(\lambda)$ is the radiation intensity after passing through a layer of thickness, *L*. The parameter, $\alpha(\lambda)$, represents the summation performed over all absorbing and scattering species and is composed of the combined absorption cross-sections, $\sigma_i(\lambda)$, of the measured species, *i*, and their concentrations, c_i . The concentration of a given species can therefore be determined from the measured ratio $I_0(\lambda)/I(\lambda)$ using knowledge of the relevant absorption cross-sections and light path length (Figure 2.2), where the optical depth (*OD*) of a layer of absorber is expressed by Equation 2.2.



Figure 2.2 The basic principle of absorption spectroscopic trace gas detection (adapted from Platt and Stutz)(11)

Equation 2.2

$$OD = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \alpha(\lambda)L = \sum_i \sigma_i(\lambda)c_iL$$

As previously discussed, atmospherically relevant trace gas species are often short lived and found at low concentrations. Measurement techniques with a high sensitivity and selectivity are therefore desirable for measurements in ambient air. The differential optical absorption spectroscopy (DOAS) technique applies Lambert-Beer's law over long light path lengths and a broad spectral bandwidth to detect trace gas species that are weak absorbers and/or are found at low concentrations.

2.2 The DOAS Principle

First pioneered by Platt and Perner,(106, 107) the DOAS technique, applies long, typically multi-kilometre path lengths to the high sensitivity measurement of a wide variety of absorbing trace gas species in the atmosphere. A broad spectral bandwidth is deployed which enables the identification and quantification of multiple overlapping atmospheric absorbing species through the fitting of their specific absorption cross-sections over a wide wavelength range. The fitted spectra of structured absorbers can also be distinguished from Rayleigh and Mie light scattering caused by molecules and particles in the air.

Rayleigh scattering describes the scattering of light by a molecule or particle with a radius much smaller than the incident radiation wavelength. Rayleigh scattering exhibits a strong wavelength dependence (to a first approximation varies as λ^{-4}),(108) and is symmetric in the forward and backward directions of the incident light beam. Mie scattering describes the scattering of light by a particle with a radius that is comparable to or larger than the wavelength of the incident light. Mie scattering has a weaker wavelength dependence (proportional to $\lambda^{-1...3}$) than Rayleigh scattering and exhibits a strong preferential scattering in the forward direction of the incident light.

Equation 2.3 shows the expansion of Lambert-Beer's law that enables the concentrations of trace gas absorbing species to be determined through consideration of the other factors that influence the light intensity during atmospheric measurements

(Figure 2.3). The concentrations, c_i , and absorption cross sections, σ_i , of various trace gases species, *i*, are consider along with light extinction by both Rayleigh, $\varepsilon_R(\lambda)$, and Mie, $\varepsilon_M(\lambda)$, scattering and the parameter $A(\lambda)$, which includes turbulence and all instrumental effects.

Equation 2.3

$$trans(\lambda) = \frac{I(\lambda)}{I_0(\lambda)} = -L\left(\sum_i (\sigma_i(\lambda)c_i) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)\right) A(\lambda)$$



Figure 2.3 Sketch of absorption spectroscopy measurements in ambient air (adapted from Platt and Stutz)(11)

Figure 2.4 shows an example of the DOAS fitting procedure similar to that applied to atmospheric measurements made in this thesis. The spectral fitting procedure shown is for an example measurement of two hypothetical atmospheric absorbers (A and B), which possess overlapping absorption cross-sections in the spectral region of interest (a).(109) The first step of the fitting process is to record an observed, $I(\lambda)$, and a reference, $I_0(\lambda)$, spectrum. The $I_0(\lambda)$ spectrum is typically obtained from a direct measurement of the instrument light source using the same detection system as for the $I(\lambda)$ measurements. The contribution of both absorbers to the $I(\lambda)$ spectrum is shown in panel (b) on top of the background absorption caused by the Raleigh and Mie scattering of non-absorbing species.



Figure 2.4 DOAS fitting procedure for two hypothetical atmospheric absorbers (A and B) with overlapping absorption spectra (from Ball and Jones)(109)

Next, the $I(\lambda)$ and $I_0(\lambda)$ spectra are used to calculate the optical depth (*OD*) of the measured absorption path using Equation 2.2. The *OD* includes contributions from all structured absorbers and light scattering non-absorbers present in the operating spectral region of the instrument. The smoothly varying light extinction which results from Rayleigh and Mie scattering may then be removed through application of a high pass filter and typically a polynomial function, $P(\lambda,n)$, of order *n* (Equation 2.4). Panel (c) shows the resulting differential optical depth, ΔOD , after subtraction of a fitted second order polynomial, $P(\lambda,2)$. The application of a high pass filter enables measurements of structured absorbers to be made free from contributions of unknown or uncharacterised light extinction by non-absorbers.

Equation 2.4

$$\Delta OD = \sum_{i} \sigma_{i}(\lambda) c_{i}L - P(\lambda, n)$$

Atmospheric absorber concentrations are subsequently quantified using reference absorption cross sections, $\sigma_i(\lambda)$, which are obtained through previous laboratory measurements and typically available from online spectral databases. Here the parameter, *i*, represents an individual absorbing or scattering species (in Figure 2.4 i = A or B). Differential absorption cross sections, $\Delta \sigma_i$, are calculated through subtraction of the polynomial, $P_i(\lambda, n)$, (previously applied to the calculation of ΔOD) from the individual absorption cross sections (Equation 2.5). Fitted absorber concentrations may then be obtained through the simultaneous fitting of the calculated differential absorption cross sections to the measured differential optical depth using an appropriate minimization method. The combined fitted spectrum is represented by the solid curve overlaying the measured spectrum in panel (c) and contains contributions from the individual differential absorption cross sections shown in panel (d).

Equation 2.5

$$\Delta \sigma_i(\lambda) = \sigma_i(\lambda) - P_i(\lambda, n)$$

Knowledge of the concentrations of all fitted absorbers present in a sample therefore enables the subsequent retrieval of the underlying extinction/absorption through subtraction of the combined fitted spectrum from the measured spectrum in absolute absorption units.

2.3 Cavity Based Spectroscopy Techniques

The investigation of atmospheric processes in the field often requires the measurement of multiple variables and hence the deployment of multiple instruments to the same location. It is therefore advantageous for instruments to operate on a significantly reduced spatial scale to that of the long path DOAS technique whilst retaining a high sensitivity and selectivity. Cavity ring-down and cavity enhanced spectroscopy techniques quantify atmospheric absorbers through application of a passive optical resonator (cavity) to achieve long light path lengths across a small sample volume.

2.3.1 Cavity Ring-Down Techniques

Cavity ring-down spectroscopy (CRDS) instruments typically achieve multiple kilometre light path lengths through application of a high finesse optical cavity contained within a physical path length of generally around one metre.(110) The measurement of weakly absorbing and/or highly dilute atmospheric absorbers can therefore be achieved with a similar sensitivity to DOAS but on a significantly reduced

physical scale. The first CRDS measurements were performed by O'Keefe and Deacon in 1988 who observed the CRDS spectrum of O_2 in air.(111) Since then CRDS has become a widely deployed technique for the high sensitivity measurement of weakly absorbing or highly dilute gaseous species in the atmosphere as documented in comprehensive review articles by Berden et al.,(112) Brown,(113) and more recently by Hancock and Orr-Ewing.(114)

The CRDS technique operates by measuring the rate at which light is absorbed while circulating in an optical cavity. Narrowband CRDS techniques operate using a light source that has a spectral width narrower than the absorption feature of the target species. A monochromatic pulsed laser light source is used to provide light to an optically stable cavity constructed by two high reflectivity concave mirrors (> 99.99% reflectivity) that are separated by a known path length, *d*. The mirrors are generally contained within two adjustable mirror mounts to enable their realignment if necessary to maximise reflectivity across the cavity. Light is directed into the cavity through one of the cavity mirrors, often called the input mirror, and undergoes multiple reflections to generate a significantly enhanced effective optical path length. During each reflection, light is lost from the cavity through interactions between light and the cavity mirrors. The light leaking out of the cavity through the output mirror is measured as a function of time by a suitable detector such as a photomultiplier tube or an avalanche photodiode. The laser is then switched off and the decay of the light exiting the cavity is recorded as the cavity ring-down time, $\tau(\lambda)$ (Figure 2.5).



Figure 2.5 Schematic of the cavity ring-down principle (adapted from Berden and Engeln)(110)

The measured ring-down time is inversely proportional to all losses within the cavity and is determined by time it takes for the light exiting the cavity to reach 1/e of the initial light intensity that entered the cavity. Equation 2.6 describes the ring-down time for an empty cavity, $\tau(\lambda)$, in terms of mirror separation, *d*, speed of light, *c*, and the geometric mean reflectivity of the cavity mirrors, $R(\lambda)$. In this case, all losses will be determined by the reflectivity of the cavity mirrors. Ring-down times are measured in absolute units of time and are subsequently fitted with exponential curves. A typical CRDS instrument operating over a physical path length of less than one metre will produce empty cavity ring-down times of many tens of microseconds, which is equivalent to effective optical path lengths of ten kilometres or more.(110)

Equation 2.6

$$\tau(\lambda) = \left(\frac{d}{c|lnR(\lambda)|}\right)$$

The addition of absorbing gases into the cavity will reduce the ring-down time because additional light will be lost on every reflection owing to its interactions with species contained within the cavity. The intensity of light leaking out of the cavity, $\tau'(\lambda)$, is now directly related to the ring-down time of the empty cavity and the attenuation of light by the absorbing sample (Equation 2.7), using quantities previously defined by Lambert-Beer's Law (Equation 2.1).

Equation 2.7

$$\frac{1}{\tau'(\lambda)} = \frac{1}{\tau(\lambda)} + c\alpha(\lambda) = \frac{1}{\tau(\lambda)} + c\sum_{i} \sigma_i(\lambda) x_i$$

Through application of Equation 2.7, the absorption cross-section of a sample may therefore be determined through comparison of the ring-down times obtained both with and without an absorbing sample in the cavity. Cross-sections can be constructed by scanning the wavelength of the laser light across the spectral region of interest and hence enables the CRDS determination of absolute absorber concentrations. However, the sequential scanning of individual wavelengths is time consuming and may prolong acquisition times. The major disadvantage of the CRDS technique when applied to atmospheric measurements is that the absolute concentrations of absorbers can only be obtained if the wavelength dependent losses from scattering by aerosol particles and other overlapping absorbers are known. CRDS is therefore unlikely to be applied to the measurement of broad absorption features across extended spectral ranges, similar to those achieved through the DOAS technique. Atmospheric target species are therefore typically measured at selected wavelengths where their absorption is particularly strong, while avoiding wavelengths where other common atmospheric species exhibit significant absorption features. Interfering species may also be prevented from entering the cavity (e.g. through application of an aerosol filter on the cavity inlet). The application of a broadband light source to measure the components of Equation 2.7 enables the application of a DOAS type fitting procedure to quantify the contribution of multiple absorbers to an absorption spectrum and separate any continuum absorbance from non-absorbers.

2.3.2 Broadband Cavity Enhanced Absorption Spectroscopy

Broadband variants of CRDS operate using a light source with a spectral width generally much wider than the absorption features of a sample contained within the cavity.(115) The light that leaks out of the output mirror of the cavity therefore contains a mixture of different wavelengths with varying ring-down times and enables an extended portion of a sample's absorption spectrum to be captured in one scan. The identification and quantification of absorbing species can therefore be attained without the need for scanning the wavelength of the light source and is therefore advantageous in regards to the capture of fast transitioning atmospheric species. The use of a single, fixed broadband light source also simplifies the experimental approach but at the same time reduces the spectral resolution compared to that achieved with a narrowband laser.

Cavity enhanced absorption spectroscopy (CEAS), is a variant of BBCRDS, which uses a continuous wave (CW) light source to provide light to the cavity. The CW light source maintains the light circulating in the cavity at a steady-state by continuously replenishing photons lost through absorption and scattering within the cavity and through interactions of light with the cavity mirrors. Engeln et al.,(116) showed that light transmitted through the cavity at a steady state is directly proportional to the ringdown time of the cavity. The steady state is therefore determined by the intensity of the broadband light source, the wavelength dependent reflectivity of the cavity mirrors and the absorption and scattering of light by species contained within the cavity. The absorption spectrum of a sample, $\alpha(\lambda)$, can therefore be obtained from light transmitted through an empty cavity, $I_0(\lambda)$, and a cavity containing the sample, $I(\lambda)$, using **Equation 2.8** when the mirror reflectivity, $R(\lambda)$, and geometric separation, *d*, are known.

Equation 2.8

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right) \cdot \left(\frac{1 - R(\lambda)}{d}\right)$$

Commonly used CW light sources include arc lamps and high intensity light emitting diodes (LEDs). A simplified BBCEAS instrument schematic using an LED light source is shown in Figure 2.6. Light is typically collimated before entering the cavity to produce a well-defined beam for injection into the optical cavity and to minimise the straying and scattering of light around the instrument optics. Light exiting the cavity is typically dispersed in wavelength using a grating spectrograph and recorded using a multi-element detector, such as a charge-coupled device (CCD) camera or linear diode array. The spectral region in which a BBCEAS instrument operates is determined through the combination of the outputted wavelength range of the LED light source, the wavelength dependent reflectivity of the cavity mirrors and the operating bandwidth of the detector.



Figure 2.6 Simplified schematic of broadband cavity enhanced absorption spectroscopy using a blue high intensity LED light source (adapted from Ball and Jones)(115)

BBCEAS instrumentation has been widely deployed to provide measurements of multiple atmospheric absorbing species across the full range of near-UV and visible wavelengths. Instruments operating at blue wavelengths have been previously deployed to measure NO_2 ,(117-120) and the oxidation products of VOCs, glyoxal,(118, 121) and

methyl glyoxal.(121) BBCEAS instruments have also been widely applied to measure reactive iodine species including IO at blue wavelengths,(122) and I₂,(122-126) and OIO,(122) at green wavelengths. BBCEAS measurements have also been performed in the red wavelength region to measure NO₃ and N₂O₅,(120, 127-129) and at near-UV wavelengths to measure HONO,(130, 131) often with the simultaneous detection of NO₂. Recent studies have also applied BBCEAS to measure aerosol optical extinction as a function of wavelength in both the near-UV,(132) and blue,(133) spectral regions.

In BBCEAS, the wavelength dependent reflectivity of the cavity mirrors must be independently determined from the measurement of $I(\lambda)$. A commonly used method involves measuring the absorption spectrum of a reference sample of known composition through **Equation 2.9**. Previously used reference absorbers include measurements of NO₂,(117, 128) oxygen's collision complex, O₂–O₂,(117, 127) and the Rayleigh scattering by different non-absorbing gases.(118, 129)

Equation 2.9

$$R(\lambda) = 1 - (\alpha_{ref}(\lambda) \cdot d) \cdot \left(\frac{I_0(\lambda)}{I_{ref}(\lambda)} - 1\right)^{-1}$$

The DOAS fitting procedure, outlined in Section 2.2, can be applied to BBCEAS measurements to obtain the concentrations of individual structured absorbers present across the wide spectral region of the instrument (**Equation 2.10**). The DOAS procedure decomposes the spectrum into contributions from structured absorbers, $\alpha_i(\lambda)$, and the underlying light extinction by other species, $\alpha_{cont}(\lambda)$. Concentrations are retrieved through fitting the reference absorption cross sections of overlapping absorbers, $\sigma_{1,2...}(\lambda)$, to the calculated differential absorption spectrum of a sample.

Equation 2.10

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right) \cdot \left(\frac{1 - R(\lambda)}{d}\right) = \sigma_1(\lambda)c_1 + \sigma_2(\lambda)c_2 + \dots + \alpha_{cont}(\lambda)$$

The BBCEAS $\alpha_{cont}(\lambda)$ measurement may contain contributions from variations in the reference, $I_0(\lambda)$, spectra and/or light scattering by non-absorbing species (e.g. aerosol particles) contained within the cavity. Thus if contributions from variations in the $I_0(\lambda)$

spectra can be ruled out through instrument calibration, the variations in $\alpha_{cont}(\lambda)$ can be assigned to light extinction by non-structured absorbers and most likely Mie scattering by aerosol particles contained within the cavity. The $\alpha_{cont}(\lambda)$ measurement is therefore dependent on the number of particles contained within a sample (concentration) and their size (radius) and composition (the ability to absorb or scatter light = refractive index). Thus, even for particles of the same composition, a large number of small particles can produce a larger $\alpha_{cont}(\lambda)$ measurement than a smaller number of larger particles amounting to the same total mass/concentration.

Information on particle size may be obtained through calculation of the wavelength dependence of the $\alpha_{cont}(\lambda)$ measurement. Equation 2.11 describes the extinction of a particle (assumed spherical), σ_{ext} , in terms of its extinction efficiency, Q_{ext} , and geometric cross-sectional area, πr^2 .(110)

Equation 2.11

$$\sigma_{ext} = Q_{ext}\pi r^2$$

Figure 2.7 shows the calculated Q_{ext} of water droplets as a function of the size parameter $(x = \frac{2\pi r}{\lambda}).(110, 134)$ It is important to note that different particle compositions will have different refractive indices and will therefore generate different Q_{ext} parameter curves. For a typical ambient particle (e.g. r = 50 nm) analysed at the wavelength of light used for BBCEAS $\alpha_{cont}(\lambda)$ measurements in Chapter 3 and 6 of this thesis ($\lambda = 450$ nm), the calculated size parameter would be equal to 0.7.



Figure 2.7 Calculated extinction efficiencies of water droplets as a function of the size parameter from Berden and Engeln,(110) (reprinted from Rudic et al.)(134) The top axis shows corresponding droplet diameters for a wavelength of 560 nm. The two insets show expanded regions for small (top inset) and relatively large particles (bottom inset)

For BBCEAS measurements of ambient aerosol, it would be theoretically possible to reconstruct $\alpha_{cont}(\lambda)$ through calculation of the expected size parameter dependence of Q_{ext} from Mie theory. However, this calculation would require knowledge of the particle size distribution and particle composition and has not yet been achieved by BBCEAS in terms of ambient measurements. The ability of BBCEAS to make quantitative measurements of aerosol scattering via $\alpha_{cont}(\lambda)$ has however been shown through laboratory measurements by Washenfelder et al.,(132) and Zhao et al.(133) Here, $\alpha_{cont}(\lambda)$ measurements were performed using a vastly simplified system (compared to the ambient atmosphere) containing size selected particles (e.g. polystyrene latex spheres of known radius) of known composition, refractive index and number concentration. These laboratory experiments proved the ability of the BBCEAS technique to make quantitative measurements of aerosol extinction and the wavelength dependence of light scattering.

The equipment required to generate size selected aerosol was not available during the measurements contained in this thesis and therefore a different approach was taken to test the BBCEAS $\alpha_{cont}(\lambda)$ measurement via the Angstrom coefficient (Section 6.4.2).

This thesis presents measurement data from the deployment of two BBCEAS instruments. The larger, older "field" BBCEAS instrument is a fixed instrument that

remains at a stationary location during operation. This instrument was deployed at blue wavelengths to detect glyoxal and methyl glyoxal during an atmospheric chamber study (Chapter 3) and NO_2 in ambient urban air (Chapter 6). The field instrument was constructed such that it could be dismantled, transported and reassembled at different fixed locations with a minimal loss in performance. The field instrument is based on its predecessors, which were previously deployed for the measurement of urban NO_2 ,(129, 135) I_2 in the marine boundary layer,(124) and glyoxal, methyl glyoxal and NO₂ during an instrument intercomparison.(136) The newer, smaller "mobile" BBCEAS instrument was developed from a compact instrument previously constructed and configured by Daniels, (137) for the quantification of N₂O₅ produced from a calibration source and was originally used during the RONOCO campaign to measure losses of NO₃ and N₂O₅ in the inlet line of a three-channel BBCEAS system installed on the FAAM research aircraft.(138) The operation and performance of the instrument were modified to provide compact, mobile measurements of trace gas species in both the blue and green wavelength regions. The mobile BBCEAS instrument was deployed at green wavelengths to quantify emissions of I_2 by macroalgae into the MBL (Chapter 4 and 5) and at blue wavelengths to investigate the spatial and temporal distribution of NO₂ from an urban roadside (Chapter 6).

3 Atmospheric Simulation Chamber Measurements of Glyoxal and Methyl Glyoxal

3.1 Introduction

As discussed previously, in Section 1.2.5, glyoxal (GLY) and methyl glyoxal (MGLY) are oxygenated VOC (OVOC) intermediates that are produced by the OH and O₃ initiated oxidation of VOCs in the atmosphere. GLY is the oxidation product of a number of VOC sources and can therefore been used as a marker for oxidation chemistry in urban environments. GLY and MGLY are highly soluble in water, which enables their uptake onto aqueous aerosol particles and cloud droplets. A significant amount of scientific interest relates to their contribution to the formation of secondary organic aerosol (SOA). The field broadband cavity enhanced absorption spectroscopy (BBCEAS) instrument was applied to measurements of GLY, MGLY and NO₂ during atmospheric simulation chamber experiments performed as part of the PHOto-oxidation and Secondary Organic Aerosol 2 (Pho-SOA 2) campaign. Experiments were performed at the EUropean PHOto REactor (EUPHORE) atmospheric simulation chamber in Valencia, Spain during the period 02-07-2012 to 31-07-2012. These experiments investigated GLY and MGLY yields from VOC oxidations and the uptake of these alpha-dicarbonyls to seed aerosol particles (mainly ammonium sulphate). The instrument was deployed at blue wavelengths (430 - 486 nm) and provided high sensitivity measurements at a fast time resolution.

3.2 Atmospheric Chamber Studies

As discussed previously, monitoring reactive trace gases in the field is essential to determining the chemical composition of the atmosphere and for testing the current understanding of atmospheric processes. The high reactivity of the atmosphere means that the concentration of a target species *in situ* is likely to be influenced by a large number of contributing factors. Field measurements therefore generally require the deployment of multiple instruments at the same sampling location. However, the dynamic nature of the atmosphere also makes it difficult to ensure that all instruments are sampling the same gas mixture. This is particularly problematic when the target species have short atmospheric lifetimes or when the sampling location is heavily influenced by uncontrolled influxes from local emission sources.

Atmospheric simulation chamber experiments enable atmospheric processes to be observed in a controlled physical and chemical environment where initial reactants can be specifically selected and reaction conditions controlled to mimic real world conditions. Experiments can therefore be constructed to limit the number of variables in the monitored processes and make the interpretation of results easier. Another advantage of chamber studies is that multiple instruments can be deployed at the same location and enables the monitoring of different variables in a controlled homogeneous gas mixture. Chamber studies have therefore been widely applied to the validation of atmospheric processes including the oxidation of both anthropogenic and biogenic VOC emissions.(33, 35, 139) The multi instrument sampling of homogeneous chamber mixtures has also been applied to the assessment of atmospheric measurement techniques through instrument intercomparisons.(136, 140)

3.3 Pho-SOA 2

The first deployment of the field BBCEAS instrument was to measure GLY and MGLY as part of the Pho-SOA 2 campaign. The Pho-SOA 2 campaign aimed "to investigate the hypothesis that GLY and MGLY are responsible for the growth of particles" and "to determine the relationships between radiation and seed aerosol composition on SOA growth rate and yield, giving a mechanistic explanation."(141) Experiments were designed to provide "a better understanding of the mechanism responsible for heterogeneous uptake of GLY and MGLY onto pre-exisiting aerosol" and "an estimate of the atmospheric importance of heterogeneous uptake of GLY and MGLY."(141)

The measurement data presented in this chapter were obtained on location at the EUPHORE atmospheric simulation chamber in Valencia, Spain between 02-07-2012 - 31-07-2012. EUPHORE is a large-scale atmospheric simulation chamber that uses natural sunlight to investigate the mechanisms of photochemical atmospheric processes. Experiments were performed in one of two outdoor simulation chambers, formed by a half spherical Teflon bag (200 m^3). The chamber walls consisted of a fluorine-ethene-propene (FPE) foil (0.13 mm thick), which enabled the transmission of 80% sunlight in the near UV and visible range (280 - 640 nm). A mechanical roof was used to control the influx of natural solar radiation into the chamber and to initiate the chemical reactions that occur in the photo-oxidation processes in the atmosphere. The chamber

facility is operated by the Environmental studies centre for the Mediterranean (CEAM) and contains a range of permanent analytical instruments for monitoring the chemical composition and physical conditions that are experienced by the trace gas species contained within the chamber.(142)

An extensive description of the instruments and analysis techniques specifically assembled during the Pho-SOA 2 campaign is contained within Hamilton et al.,(143) and Pang et al,(144) and the following referenced sources. Briefly: a number of campaign specific instruments were deployed alongside BBCEAS including a proton transfer reaction mass spectrometry (PTR-TOF-MS, University of Leicester) instrument to detect gaseous organic compounds,(145) an aerosol time-of-flight mass spectrometer (A-TOF-MS, University of Leeds) for the online analysis of particles,(146) and a microfluidic lab-on-a-chip derivatisation technique for the quantification of GLY and MGLY (University of York).(144) Aerosol collected onto filters during chamber experiments were extracted and directly analysed through electrospray ionisation mass spectrometry (ESI-MS) and with prior separation using high performance liquid chromatography (HPLC, University of York).(147, 148)

3.4 BBCEAS Hardware

The configuration of the BBCEAS field instrument applied to atmospheric chamber measurements during the Pho-SOA 2 campaign is shown in Figure 3.1 and Figure 3.2. The instrument was operated at blue wavelengths to enable the simultaneous detection of the target species GLY, MGLY and NO₂.



Figure 3.1 Schematic of BBCEAS field instrument applied to atmospheric chamber measurements during the Pho-SOA 2 campaign



19 inch rack

Figure 3.2 Photograph of BBCEAS field instrument applied to atmospheric chamber measurements during the Pho-SOA 2 campaign

A blue high intensity LED light source (LED Engin, LZ1-10B205, 5 Watt, peak wavelength = 455 nm) was supplied with a current of 1.50 A from a regulated power supply (Thurlby, EL302). The LED was mounted on a Peltier cooled laser diode mount (Newport Corporation) and maintained at a constant temperature (18°C) by a temperature controller (Newport Corporation). The LED temperature was controlled to maintain its emission spectrum at a constant intensity across all wavelengths throughout experiments. A fibre optic cable (Ocean Optics; near IR/visible, 400 μ m fibre core diameter, 0.22 numerical aperture, length = 2 m) was used to direct light from the LED into the first optics enclosure.

An infinity corrected microscope objective lens (Leica) collimated light exiting the fibre to produce a well-defined beam for injection into the optical cavity and to reduce the amount of stray and scattered light inside the enclosure. The optical cavity was formed from two high reflectivity mirrors (Layertec, 1" diameter, 108621, 1000 mm radius of curvature, > 99.985% high reflectivity at 455 nm). The mirrors were housed in two custom-made bellows mounts, one in each optics enclosure, to enable their realignment if required to maximise cavity reflectivity. The mirrors were provided with a constant nitrogen gas (N₂) purge flow (0.2 standard litres per minute, slpm) provided from an N₂ cylinder and controlled using a mass flow controller (MFC, MKS). The mirror purge flow was applied to prevent the deposition of contaminants (e.g. aerosol particles) on the surface of the cavity mirrors and the loss of mirror reflectivity.

Light transmitted through the cavity output mirror was collected by an achromatic doublet lens (Thor labs Inc, 25.4 mm diameter, 40 mm focal length) and focussed into a second similar fibre optic cable (Ocean Optics). The outputted light was transported into the entrance slit of a USB spectrometer (Ocean Optics, HR2000, 50 μ m slit width, 407.0 – 491.2 nm wavelength range) and onto a linear array detector. The spectrometer was contained within a custom made Peltier cooled enclosure. The spectrometer was maintained at a constant temperature (13°C) to both reduce and also stabilise the intensity of spectrometer dark currents (Section 3.5.2) for the duration of experiments. The cooled enclosure was provided with a constant N₂ flow (\approx 1 slpm) to prevent the build up of condensation on the spectrometer.

Spectra were recorded on a laptop operating the SpectraSuite (Ocean Optics) software supplied with the HR2000 spectrometer. The laptop was connected to the HR2000 spectrometer via a USB cable. Spectra had a 100 ms integration time; 200 spectra were averaged in SpectraSuite, giving a net acquisition time of 20 s, before being saved on the laptop. Spectra were averaged and analysed using the Mathcad Prime 2.0 (PTC) software package and data processing routine as outlined in Section 3.5.

All optical components including the two mirror mounts were secured to two individual aluminium breadboards (Thorlabs, M6 threaded) and contained within two optics enclosures. The enclosures were attached to a support frame and stabilised by two anti-vibrational mounts. A 19-inch rack was used to store all components not contained within the optics enclosures and minimise the disruption to instrument configuration during transport.

Samples were analysed across a cavity constructed by a polytetrafluoroethylene (PTFE) tube (25.4 mm internal diameter), which was connected to the mirror mounts by two vacuum fittings (38.1 mm diameter). Gas was sampled from the chamber and into the cavity through a perfluoroalkoxy alkane (PFA) line (1.2 m length, 6.35 mm outside diameter, 2 slpm flow rate), which was connected to the cavity by a vacuum fitting (6.35 mm diameter). The inlet line protruded 40 cm above the chamber floor to ensure the sampling of gas that was well mixed and not influenced by chamber wall effects. Air was drawn from the chamber at 2 slpm using a diaphragm pump (KNF, N820.3FT.18) located downstream of the cavity and controlled by a MFC (MKS).

Reference $I_0(\lambda)$ spectra were obtained by swapping the cavity input line for another PFA line supplied with N₂ gas provided by a cylinder and regulated at 2 slpm by a MFC (MKS). A similar procedure was applied to obtain the reference, $I_{ref}(\lambda)$, spectra required for mirror reflectivity, $R(\lambda)$, and length factor, *LF*, calibrations (Section 3.5.3 and 3.5.4), where regulated flows of O₂, He or artificial air were provided through the cavity input (2 slpm) and mirror purge lines (0.2 slpm). The cavity was overflowed during the acquisition of reference spectra to ensure it was completely filled with the reference gas. The excess flow of approximately 0.2 slpm was sent to exhaust. Dark current spectra, $I_{dark}(\lambda)$, (Section 3.5.2) were recorded with a card blocking light entering the spectrometer collection fibre and hence no light was able to reach the photosensitive region of the device.

3.5 BBCEAS Spectral Analysis Procedure

The BBCEAS measurement data reported in this thesis were obtained using a custom built analysis routine written in the Mathcad Prime 2.0 (PTC) mathematical software package, which was developed from those previously reported by Hollingsworth,(135) and Daniels.(137) The analysis routine applied the DOAS fitting procedure, described previously in Section 2.2, to retrieve absorber concentrations from measured BBCEAS spectra, $\alpha(\lambda)$, as calculated by **Equation 3.1**. The observed, $I(\lambda)$, and reference spectra, $I_0(\lambda)$, were obtained by measuring the light intensity transmitted across the cavity when containing an absorbing sample and when flushed with non-absorbing N₂ gas respectively.

Equation 3.1

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right) \cdot \left(\frac{1 - R(\lambda)}{d}\right) \cdot LF$$

The $I(\lambda)$ and $I_0(\lambda)$ spectra were corrected by subtracting a dark current spectrum, $I_{dark}(\lambda)$, calculated through the procedure outlined in Section 3.5.2. The wavelength dependent mirror reflectivity, $R(\lambda)$, was determined by measuring the absorption spectrum of a reference sample of known composition, as outlined in Section 3.5.3. The length correction factor, *LF*, was applied to compensate for the artificial shortening of the cavity caused by the non-absorbing N₂ mirror purge flow. Application of the mirror purge flow restricts the sample from extending across the full cavity length. The net light extinction measured across the cavity must therefore be multiplied by the correction factor *LF* to accurately reflect the composition 3.5.4. The parameter, *d*, refers to physical path length between the cavity mirrors and was 1105 mm for the field BBCEAS instrument in this deployment. The following subsections describe the measurements and analysis procedures applied to the retrieval of absorber concentrations from measured BBCEAS spectra as outlined in Figure 3.3.


Figure 3.3 The analysis procedure applied to the retrieval of absorber concentrations from measured BBCEAS spectra

3.5.1 Spectrometer Calibration

As discussed previously, BBCEAS spectra were recorded using a HR2000 spectrometer (Ocean Optics) with a linear CCD array detector. The spectrometer was operated at a resolution and wavelength range as determined by the manufacturer (2048 pixels, 407.0 – 491.2 nm). The outputted data files consisted of two columns, which contained the wavelength assigned to each spectrometer pixel and a corresponding number of counts representing the measured light intensity at each pixel. The blue wavelength region of the electromagnetic spectrum was selected for analysis as it contained the overlapping absorption features of the two main target species GLY and MGLY. The previously described DOAS fitting procedure (Section 2.2) was used to quantify the contribution of overlapping structured absorbers, $\alpha_i(\lambda)$, and the underlying light absorption/extinction by other species (continuum absorption), $\alpha_{cont}(\lambda)$, in the BBCEAS spectra (Equation 3.2).

Equation 3.2

$$\alpha(\lambda) = \sum_{i} \alpha_{i}(\lambda) + \alpha_{cont}(\lambda) = c_{1} \cdot \sigma_{1}(\lambda) + c_{2} \cdot \sigma_{2}(\lambda) + \dots + \alpha_{cont}(\lambda)$$

The retrieval of absorber concentrations, c_i , using the DOAS method required the application of reference absorption cross sections, $\sigma_i(\lambda)$, which were obtained from compiled literature databases (e.g. the MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest).(149) The reference absorption cross sections were generally provided at a resolution higher than that of the HR2000 spectrometer and were therefore degraded onto the spectrometer wavelength scale and wavelength dependent line width. The line function and true wavelength scale of the spectrometer were experimentally determined using emission spectra recorded from argon and krypton lamps (Pen-ray), which contained well-defined lines across the full wavelength region of interest. The emission lamps were positioned in front of a fibre optic converging light to the HR2000 spectrometer. Absorption spectra were recorded at an integration time of 250 ms for argon and 60 ms for krypton, which enabled the capture of maximum light without saturating of the detector.

First, the lineshape of the detector was determined by fitting the individual emission lines with both a symmetric Gaussian (Equation 3.3) and an asymmetric (Equation 3.4) line shape function, where, λ_{cen} , and, w, are the centre wavelength (nm) and half width at half maximum (HWHM, nm) of the recorded peak respectively. The parameter, α , is a measure of asymmetry (no units), which when equal to zero, reverts the asymmetric function back to that of a symmetric Gaussian. The normalisation constant, N, was applied to ensure that the area under the fitted line shape function was equal to 1. The asymmetric instrument function was observed to provide the better simulation of the HR2000 detector line shape through comparison of the residual spectra of emission lines fitted with the two functions (Figure 3.4 and Figure 3.5). BBCEAS spectra of test NO₂ samples also produced smaller residuals when fitted with NO₂ cross sections degraded with asymmetric lineshapes.

Equation 3.3

$$lineshape_{sym}(\lambda) = N \cdot exp\left[\frac{-(\lambda - \lambda_{cen})^2 \cdot ln(2)}{w^2}\right]$$



Figure 3.4 An argon emission line (centre wavelength (NIST): 470.23 nm) measured by the HR2000 spectrometer and fitted with the symmetric Gaussian function centered at 470.17 nm (SD = standard deviation)

Equation 3.4



Figure 3.5 An argon emission line (centre wavelength (NIST): 470.23 nm) measured by the HR2000 spectrometer and fitted with the asymmetric function centered at 470.14 nm (SD = standard deviation)

Wavelength dependent line shapes were determined for the HR2000 detector through fitting of the asymmetric line shape function to emission lines recorded across the full wavelength range of the detector. Both the half width of the emission lines at HWHM and asymmetric parameter, α , displayed a clear wavelength dependency and were fitted with third order polynomial functions (Figure 3.6 and Figure 3.7). The fitted parameters were subsequently used to determine a wavelength dependent asymmetric instrument function for the HR2000 detector, which was applied to the determination of reference absorption cross sections during all BBCEAS deployments in this chapter (Section 3.3.5).



Figure 3.6 The wavelength dependent half width at half maximum (HWHM) for argon and krypton emission lines recorded between 410 – 490 nm by the HR2000 spectrometer



Figure 3.7 The wavelength dependent fitted asymmetric parameter for argon and krypton emission lines recorded between 410 – 490 nm by the HR2000 spectrometer

The true wavelength of the HR2000 spectrometer was subsequently determined through comparison of the measured centre wavelengths of the fitted asymmetric peaks with their expected centre wavelengths obtained from the NIST database.(150) The differences between the HR2000 measured central wavelength and the reference central wavelength were plotted against the HR2000 measured central wavelength for each emission line and fitted with a third order polynomial function (Figure 3.8). The parameters of the polynomial were used to adjust the manufacturer wavelength scale on each pixel to the true measured wavelengths over the BBCEAS spectral bandwidth. The reference absorber cross sections were linearly interpolated onto the new calculated wavelength scale prior to the differential fitting of the observed spectra.



Figure 3.8 Plotting the difference between expected and measured centre wavelengths of argon and emission peaks against measured centre wavelengths. Individual points were fitted with a 3rd order polynomial function to determine the true wavelength scale of the HR2000 spectrometer

3.5.2 Spectrometer Dark Current

In this context, the dark current, $I_{dark}(\lambda)$, refers to the spectra recorded by the HR2000 spectrometer when no light was passing into its entrance slit and hence no photons were incident of the photosensitive region of the detector. The dark current therefore contributes an amount of signal in the measured BBCEAS absorbance spectrum, which is completely independent from light exiting the output mirror of the BBCEAS cavity. The intensity of the dark currents produced by the HR2000 spectrometer was heavily

influenced by temperature. The spectrometer was therefore located in a custom-made Peltier cooled enclosure and maintained at a controlled temperature of 13°C to ensure the dark current intensity remained at a similar level throughout experiments. Some fluctuations in dark current were still observed however, owing to the delayed response of the Peltier cooler to changes in ambient temperature. The following analysis procedure was therefore applied, which enabled the determination of dark current intensity for $I_0(\lambda)$ and $I(\lambda)$ spectra measured at different temperatures.

Dark current spectra, $I_{dark}(\lambda)$, were recorded at varying intervals throughout the analysis by using a card to block light entering the spectrometer collection fibre and hence prevent all light from reaching the photosensitive region of the spectrometer. Dark currents were recorded at the same integration time as the $I_0(\lambda)$ and $I(\lambda)$ spectra (100 ms × 200) and subsequently averaged over 2 min intervals. The contribution of the dark current to both $I_0(\lambda)$ and $I(\lambda)$ spectra was approximated by utilising a previously identified grouping of dark pixels on the HR2000 linear diode array that were never illuminated. The seventeen dark pixels on the detector (pixels 7 to 23) never observed any light intensity, even during the recording of $I_0(\lambda)$ and $I(\lambda)$ spectra (Figure 3.9). The mean intensity of the seventeen dark pixels was observed to vary linearly with the mean intensity of the whole spectrum for all recorded dark currents (Figure 3.10).

Pixels 7 – 23 were therefore used as a proxy for temperature. A plot was created of intensity of each pixel on the detector versus the mean intensity in pixels 7 – 23 using the measured $I_{dark}(\lambda)$ spectra. The values determined by this plot meant that for $I_0(\lambda)$ and $I(\lambda)$ spectra that have light in pixels > 23, the mean of their initial 7 to 23 pixels could be used to inform what the dark current would be for each pixel across the detector. A synthetic dark current spectrum was therefore generated for and subtracted from all measured $I_0(\lambda)$ and $I(\lambda)$ spectrum.



Figure 3.9 $I_0(\lambda)$ and $I_{dark}(\lambda)$ spectra recorded by the HR2000 spectrometer showing the dark pixels 7 – 23, which were never illuminated



Figure 3.10 A linear relationship observed between the mean intensity of the seventeen dark pixels and of the whole $I_{dark}(\lambda)$ spectrum for dark currents measured on 03-07-2012. Each point represents 2 min of averaged $I_{dark}(\lambda)$ spectra (100 ms × 200 × 6)

3.5.3 Mirror Reflectivity Determination

As previously discussed in Section 2.2.2, the extinction due to absorption, $\alpha(\lambda)$, in BBCEAS measurements is obtained through measurements of $I_0(\lambda)$ and $I(\lambda)$ when both the distance between the cavity mirrors, d, and the wavelength dependent mirror reflectivity, $R(\lambda)$, are known. Equation 3.1 can be rearranged to calculate $R(\lambda)$ from measurements of light intensity, $I_{ref}(\lambda)$, transmitted across the cavity containing a known concentration of reference absorber where $\alpha_{ref}(\lambda) = \sigma_{ref}(\lambda) \times c_{ref}$ (Equation 3.5). It is important to note that all $I_{ref}(\lambda)$ spectra were measured while flushing the entire cavity with reference gas (including the mirror purge) and the length factor parameter was therefore equal to 1.

Equation 3.5

$$R(\lambda) = 1 - d \times \left(\frac{\alpha_{ref}(\lambda)}{LF}\right) \times \left(\frac{I_0(\lambda)}{I_{ref}(\lambda)} - 1\right)^{-1}$$

For a cavity free of absorbers (e.g. flushed with a non-absorbing reference gas such as nitrogen or helium), losses of light will only result from the interaction of light with the cavity mirrors and Rayleigh scattering owing to interactions of light with the reference gas molecules.(118) The mirror reflectivity values applied to the retrieval of absorber concentrations in this chapter were first determined from the changes in transmitted light intensity due to the Rayleigh scattering across a cavity flushed with nitrogen and then helium gas. Nitrogen and helium were selected because of the large difference between their Rayleigh cross-sections and hence significant distances between their respective $I_0(\lambda)$ and $I_{ref}(\lambda)$ spectra (Figure 3.11).



Figure 3.11 Dark corrected $I_0(\lambda)$ and $I_{ref}(\lambda)$ spectra measured by the field BBCEAS instrument across a cavity flushed with nitrogen and helium gas respectively

The wavelength dependent reflectivity was calculated through application of **Equation 3.5** where the $\alpha_{ref}(\lambda)$ parameter refers to the difference in the Rayleigh cross-sections of He,(151) and N₂.(108) The variation of Rayleigh scattering with wavelength for both gases is both slow and well defined and enabled the construction of a uniform measure of mirror reflectivity or "mirror curve" across the analysed wavelength region (Figure 3.12).



Figure 3.12 Example of a measured mirror reflectivity curve that describes the variation of mirror reflectivity with wavelength and the effective optical path length within the cavity (d = 1105) for the BBCEAS field instrument operating at blue wavelengths

The absolute measurement of mirror reflectivity was subsequently determined using BBCEAS spectra, $I_{ref}(\lambda)$, recorded across a cavity completely flushed with a pure oxygen reference gas. $I_{ref}(\lambda)$ is the intensity of light transmitted through the cavity when filled with a known concentration of the reference absorber (oxygen) where $\alpha_{ref}(\lambda)$ is the absorption spectrum of the reference absorber (O₂–O₂) calculated from a knowledge of its absorption cross sections and concentration. It is important to note that the O₂–O₂ absorption bands observed in the BBCEAS spectra are induced through the collision of two O2 molecules. Light is absorbed by the short lived O2-O2 collision complex formed by the interaction of two O₂ molecules.(152) Previous laboratory measurements have confirmed that the absorption of the collision complex varies with the square of the oxygen pressure (i.e. O₂ concentration).(153-155) In order to ascribe an absorption cross-section to the O₂–O₂ absorbance, the cross-section needs to be expressed in units that scale with the square of the O₂ concentration. Thus, the O₂-O₂ absorption crosssection is expressed in units of cm^5 molecule⁻² rather than the standard cross section units of cm^{-2} molecule⁻¹.(156) In this BBCEAS work, O₂ concentrations were obtained by fitting a reference O_2-O_2 absorption cross section, (155, 157) using the previously discussed DOAS fitting procedure. Oxygen's O2-O2 collision complex exhibits two absorption bands in the wavelength region of interest, centred at approximately 446 and 477 nm (Figure 3.13). Mirror reflectivity calibrations were performed both immediately before and after each chamber experiment and the obtained $R(\lambda)$ values either side of recording the $I(\lambda)$ spectra were averaged before being applied to the retrieval of absorber concentrations. The concentration of O₂–O₂ in a sample of pure oxygen was used to calculate a wavelength dependent scaling factor. The scaling factor multiplied $1-R(\lambda)$ until the retrieved oxygen concentration matched that for a sample of pure oxygen (i.e. O_2 mixing ratio = 1).



Figure 3.13 Example of a fitted O₂-O₂ BBCEAS absorption spectrum for a cavity flushed with O₂ as used to determine the wavelength dependent scaling factor $1-R(\lambda)$ applied to the previously calculated mirror curve (SD = standard deviation)

3.5.4 Length Factor Determination

During this deployment of the BBCEAS field instrument, a mirror purge flow of nonabsorbing nitrogen gas was supplied around each of the cavity mirrors when sampling the chamber and obtaining $I(\lambda)$ spectra. The small flow of nitrogen around the mirrors prevented the deposition of contaminants including aerosol particles on the surface of the cavity mirrors, which would result in a loss of reflectivity and a reduction in instrument sensitivity. The addition of non-absorbing nitrogen gas into the cavity also shortened the effective sample path length by reducing the amount of the cavity that contained absorbing sample gas. The length factor correction parameter, *LF*, was applied to the calculation of extinction due to absorption across the cavity, $\alpha(\lambda)$, (**Equation 3.1**) to compensate for the artificial shortening of the cavity by the mirror purge flow.

To determine the *LF* parameter, first a BBCEAS spectrum was recorded across a cavity completely flushed with artificial air (including the mirror purge regions) and the concentration of oxygen in the sample was retrieved by fitting its O_2-O_2 band. Another BBCEAS spectrum was then recorded with artificial air supplied to the cavity, but this time the cavity mirrors were supplied with the same nitrogen mirror purge flow as used

during chamber experiments. The concentration of oxygen was again retrieved but this time at a reduced amount as to what was contained in the artificial air sample. The difference observed between the two obtained oxygen concentrations was directly assigned to the reduction of oxygen in the cavity caused by the presence of the nitrogen mirror purge gas. The ratio of the retrieved oxygen concentrations was therefore used to determine the *LF* parameter.

3.5.5 Reference Absorption Cross-Sections

The DOAS fitting procedure (Section 2.2) was applied to quantify the fitted absorptions of several different overlapping target species and the underlying contribution to the unstructured continuum from other light scattering/absorbing species. Briefly: dark current corrected measurements of reference, $I_0(\lambda)$, and observed, $I(\lambda)$, spectra were used to calculate the optical depth, OD, across the absorption path of the BBCEAS instrument. The differential optical depth, $\triangle OD$, or differential spectrum was then calculated through subtraction of any smoothly varying contributions to the absorbance coefficient by non-absorbers. This was achieved by fitting a polynomial in wavelength of 8th order to the observed optical depth, $P(\lambda, 8)$. Absorption cross sections of the target atmospheric species were obtained from previous laboratory measurements and sourced from their referenced literature sources. The high resolution absorption cross sections of GLY,(158) NO₂,(159) and H₂O,(160) were convolved through application of the HR2000 spectrometer asymmetric instrument function with a wavelength dependent line width and degree of asymmetry as determined in Section 3.5.1. The MGLY,(161) and O_2-O_2 ,(157) reference cross-sections were not convolved prior to their application. Differential cross-sections were obtained by subtracting the previously applied $P(\lambda, 8)$ function from the reference absorption cross sections of the target absorbers. The concentrations of absorbers were then deduced through fitting the calculated differential cross-sections to the previously determined differential optical depth using a linear least squares fitting, singular value decomposition method. Figure 3.14 shows an example BBCEAS spectrum measured during the Pho-SOA campaign fitted for contributions by overlapping structured absorbers.



Figure 3.14 An example BBCEAS absorption spectrum (top panel) recorded over a 20 s integration time (100 ms × 20) during the Pho-SOA campaign on 16-07-2012. The measured BBCEAS absorption spectrum (red) was fitted for contributions from several overlapping structured absorbers (black) whose individual fitted spectra are shown with their corresponding retrieved concentrations and statistical errors in the panels below. Also shown are the continuum absorbance resulting from light extinction/absorption from other species (blue) and the residual spectrum with a standard deviation of 3.31×10^{-9} cm⁻¹ (green)

After the determination of individual structured absorbers, the contribution of the underlying extinction/absorption by other species (continuum absorption), $\sigma_{cont}(\lambda)$, was obtained through subtraction of the total fitted spectra from the measured spectra in absolute absorber units. The unstructured continuum absorption may contain contributions from variations in the reference, $I_0(\lambda)$, spectra and/or light scattering by

non-absorbing species (e.g. aerosol particles) contained within the cavity. Variations in the $I_0(\lambda)$ spectra are most likely the result from a change in the emission spectrum of the LED light source and/or a decline in the reflectivity of the cavity mirrors owing to the potential deposition of contaminants onto the mirrors or a misalignment of the cavity. Such variations were ruled out for experiments performed during the Pho-SOA 2 campaign by the retrieval of similar $I_0(\lambda)$ spectra and $R(\lambda)$ values from calibrations performed at the start and end of individual experiments. The variations in the absorption continuum were therefore assigned to light scattering by non-absorbing species and most likely Mie scattering by aerosol particles contained within the chamber mixture. The continuum absorbance measurement at 450 nm reported in this chapter was quantified over the 2 nm bandwidth 449 – 451 nm.

3.6 Determination of Instrument Detection Limits

3.6.1 Statistics of Baseline Spectra

In order to determine the performance of the BBCEAS instrument, statistical analyses were performed on a series of the baseline measurements of $I(\lambda)$, recorded in the laboratory at EUPHORE when the cavity was purged with N2 and was therefore free of all molecular absorbers.(129) The absence of molecular absorbers meant that any contributions to differential absorbance could therefore be assigned to instrument instability and random noise and hence be applied to the determination of instrument detection limits.(162) A large data set was assembled consisting of 2747 $I(\lambda)$ spectra, each with a 20 s (100 ms \times 200) integration time (54940 s of data, 15.26 h). The spectra were recorded overnight on 12-07-2012 and analysed through the data analysis procedure outlined in Section 3.5 and consistent with that applied to chamber measurements. The final 30 spectra of the 2747 spectra obtained were averaged together (600 s) and used for the $I_0(\lambda)$ reference spectrum. The retrieved concentrations of GLY, MGLY and NO₂ are shown as time series and corresponding histograms in Figure 3.15. The time series of all structured absorbers displayed a random distribution of concentrations around the mean concentration, which was directly assigned to the statistical error of fitting reference absorption cross sections to a spectrum of random noise. There is a small systematic upwards drift in concentrations of GLY and MGLY in the measurement data over the 15.3 h of analysis, which is not present in the NO₂ data. The retrieved 1σ standard deviation values can therefore be used to infer the BBCEAS instrument detection limits for each of the structured absorbers and continuum measurements. Baseline measurements show the BBCEAS instrument has a 1σ detection limit of 21.8 pptv for GLY, 338 pptv for MGLY and 27.5 pptv for NO₂ against a zero absorption background for an integration time of 20 s. The same determination was also applied to continuum measurements at 450 nm which had a 1σ detection limit of 0.124 Mm⁻¹ (1 megameter (Mm) = 1×10^8 cm).



Figure 3.15 The time series and corresponding histograms of GLY, MGLY and NO₂ concentrations retrieved through fitting of baseline spectra when the cavity was purged with nitrogen using an integration time of 20 s

3.6.2 Allan Variance Analysis

The baseline measurements of GLY, MGLY and NO₂ were also subjected to Allan variance analysis, which investigates the reduction in measurement uncertainty which could be achieved through signal averaging.(129, 162) The standard variance (Equation 3.6) and Allan variance (Equation 3.7) analysis was calculated for the baseline GLY, MGLY and NO₂ time series shown in Figure 3.15. Equation 3.6 and Equation 3.7 were used to split the time series up into sections of data with different integration times, t_{int} . The parameter, $y_i(t_{int})$, represents the i = 1 to m individual concentrations of each absorber obtained for the integration time, t_{int} , and μ is the mean baseline concentration of each absorber for the whole time series.

Equation 3.6

$$\sigma^{2}{}_{S}(t_{int}) = \left(\frac{1}{m-1}\right) \sum_{i=1}^{m} [y_{i}(t_{int}) - \mu]^{2}$$

Equation 3.7

$$\sigma_A^2(t_{int}) = \left(\frac{1}{2(m-1)}\right) \sum_{i=1}^{m-1} [y_{i+1}(t_{int}) - y_i(t_{int})]^2$$

The standard deviation and Allan deviation, (the square root of standard variance and Allan variance, respectively) for retrieved baseline concentrations of GLY, MGLY and NO₂ are shown in Figure 3.16. Here, the standard deviation provides a measurement of the instrument's detection limit at a given integration time. In contrast, the Allan variance is the time average of the variance between adjacent measurements in a time series. At short integration times, the measurements are dominated by random noise and the Allan variance and the standard variance track each other closely. Also for random white noise the Allan deviation reduces with the square root of the integration time (gradient = -0.5 in the plots in Figure 3.16). The minima in the Allan deviation plots (2500 s for GLY, 1500 s for MGLY and 2500 s for NO₂) represent the optimum integration times, the measurements become affected by instrument drift and the averaging of measurements no longer increases the sensitivity of the instrument to measure absorber concentrations.



Figure 3.16 Standard deviation and Allan deviation plots for GLY (top panel), MGLY (middle panel) and NO₂ (bottom panel) concentrations retrieved through fitting of baseline spectra when the cavity was purged with N₂ using an integration time of 20 s

3.7 Application to Chamber Experiments

The high sensitivity of the BBCEAS instrument and its fast 20 s integration time enabled GLY, MGLY, NO₂ and aerosol extinction to be followed in detail during chamber experiments at EUPHORE aimed at investigating the uptake of low molecular weight α -dicarbonyls by aerosols.(143) Three experiment types were devised to investigate the uptake of GLY onto ammonium sulphate (AS) aerosol. Type 1 were dark experiments which involved the direct injection of GLY into the chamber containing AS seed aerosols with no natural light. Figure 3.17 shows the BBCEAS time series of GLY, MGLY, NO₂ and aerosol extinction retrieved during the direct injection experiment on 03-07-2012. Gas phase GLY was introduced at 10:45 into a chamber already containing AS seed aerosol particles. Scanning mobility particle sizer spectrometer (SMPS) measurements reported in Hamilton et al.,(143) observed a steady increase in aerosol growth for an extended period of \approx 16 h until the experiment end and the chamber was flushed with scrubbed and filtered air. The gradual decrease observed in the BBCEAS aerosol extinction measurement was likely the result of aerosol loss through chamber dilution and/or chamber wall losses.



Figure 3.17 Time series of BBCEAS measurement data obtained during the direct GLY injection experiment on 03-07-2012 (Experiment type 1). Scan 1 highlights the GLY concentration retrieved from the fitted spectrum in Figure 3.22

In order to estimate a rate constant for the heterogeneous uptake of GLY onto AS aerosol from the GLY measurement data in Figure 3.17, the loss rate of GLY through

other mechanisms (e.g. chamber dilution and wall reactions) was also calculated. The rate constant for the loss of GLY owing to wall reactions $(1.03 \times 10^{-5} \text{ s}^{-1})$ was estimated from the first order decay of GLY directly injected into a clean, aerosol free, chamber during the experiment on 26-07-2012. Chamber dilution was monitored by the first order decay of chemically inert sulphur hexafluoride (SF₆) injected into the chamber at the start and during each experiment. The concentration of SF₆ was measured by Fourier transform infrared spectroscopy (FTIR, CEAM). Figure 3.18 (bottom panel) shows the determination of rate constants for the loss of GLY, SF₆ and aerosol from the chamber during the experiment on 03-07-2012. Rate constants were estimated through calculation of the slope of the natural logarithm of the measured time series for each species during the time period 17:02 to 02:51 (31852 to 67162 s) when chamber conditions had stabilised following the second addition of SF₆.



Figure 3.18 Top panel: Time series of BBCEAS (GLY and aerosol extinction) and FTIR (SF₆) measurement data obtained during the direct GLY injection experiment on 03-07-2012. Bottom panel: Calculation of the rate of loss for each species from the gradient of the linear regression of a plot of the natural logarithm of each time series for a selected time period

The calculated GLY loss rate $(5.03 \times 10^{-5} \text{ s}^{-1})$ was significantly faster than that of SF₆ $(7.67 \times 10^{-6} \text{ s}^{-1})$ and aerosol $(1.55 \times 10^{-5} \text{ s}^{-1})$ and indicated either the uptake of GLY onto aerosol or the loss of GLY through other mechanisms. Extra GLY loss mechanisms are limited during dark experiments as GLY photolysis and the reaction of GLY with OH are prevented by the lack of sunlight. The faster decline in aerosol compared to SF₆ indicates extra aerosol loss mechanisms (e.g. deposition onto chamber walls and/or the coagulation of small particles).

The rate constant for the heterogeneous uptake of GLY onto AS aerosol during the experiment on 03-07-2012 was estimated as $3.23 \times 10^{-5} \text{ s}^{-1}$ through subtraction of the calculated loss rate of GLY through chamber dilution ($7.67 \times 10^{-6} \text{ s}^{-1}$) and wall reactions ($1.03 \times 10^{-5} \text{ s}^{-1}$) from the measured GLY loss rate ($5.03 \times 10^{-5} \text{ s}^{-1}$). This equates to an associated GLY lifetime of 516 min and is longer than the estimated lifetimes for the reaction of GLY with OH radicals (300 min) and GLY photolysis (221 min), previously discussed in Section 1.2.1.

Experiment type 2 involved the formation of GLY from the oxidation of acetylene (C_2H_2) in light. The experiment was designed to investigate the impact of OH radicals on the uptake of GLY onto AS aerosol particles. Here, OH radicals were formed from the photolysis of directly injected HONO. Figure 3.19 shows the experiment from 18-07-2012 where the direct injection of HONO between Time = 10:26 - 11:02 is reflected by an increase in NO₂ in the chamber. The chamber was opened at Time = 11:11 to initiate HONO photolysis and produce OH radicals, which subsequently reacted with C₂H₂ (previously added at Time = 07:23) to produce GLY.



Figure 3.19 Time series of BBCEAS measurement data obtained during the C₂H₂ + HONO + light experiment on 18-07-2012 (Experiment type 2). Scan 1 and 2 highlight the GLY concentrations retrieved from the fitted spectrum in Figure 3.20 and Figure 3.21 respectively. Scan 3 and 4 are discussed in Section 3.7.1

Experiment type 3 again involved the formation of GLY from the reaction of C_2H_2 with OH but this time the reaction was in the dark with the chamber roof closed. In this experiment, OH radicals were formed without sunlight through the ozonolysis of trans-2-butene. Experiments were also designed to investigate the VOC systems initiated by the reactions of acetylene, isoprene and propyne with OH radicals. These data are not shown here but exist and are available to any modeller who wished to use, for example the Master Chemical Mechanism,(163) to explore GLY & MGLY product yields from first- and later-generation products. The combination of the detailed experimental data produced here and future modelling may potentially provide new insights into VOC oxidation mechanisms. A series of calibration experiments were also performed, where the BBCEAS instrument was deployed to provide the reference measurement to test a micro-fluidic derivatisation instrument designed for the detection and quantification of glyoxal and methyl glyoxal. These data are not shown here but are contained in the publication by Pang et al.(144)

3.7.1 Determination of BBCEAS Measurement Uncertainties

The BBCEAS spectral analysis procedure outlined in Section 3.5 produced a concentration (mixing ratio) for each fitted absorber and two corresponding uncertainties in its concentration termed the statistical and overall error. The statistical errors (precision) represented the uncertainty with which, for example, a GLY signal could be retrieved from the BBCEAS spectrum. Statistical error was directly determined by the ability of the fitting procedure to isolate the structured absorption signal of GLY from the combined BBCEAS absorption spectrum. The statistical error therefore differed for every concentration retrieved from a BBCEAS measurement. This was applied to comparisons of how GLY concentration at Time_1 compared to GLY concentration signal owing to a low absorber concentration generally returned a systematic error that was close to the previously determined instrument detection limit (GLY $1\sigma = 21.8$ pptv, Section 3.6.1). Figure 3.20 demonstrates this for a measured GLY spectrum obtained during the experiment on 03-07-2012 (Figure 3.17). A statistical error of ± 32.5 pptv was obtained for a retrieved GLY concentration of 159 pptv.



Figure 3.20 A measured absorption spectrum of GLY (Figure 3.19, Scan 1) where the fitted concentration is close to the detection limit and the statistical error is the significant source of measurement error

The retrieval of stronger absorption signals due to the presence of increased absorber concentrations, as shown in Figure 3.21, generally produced statistical errors < 1% for GLY. The retrieval of GLY at 19.44 ± 0.038 ppbv shown in Figure 3.21 was during the experiment on 18-07-2012 (Figure 3.19) and in the presence of a relatively low absorbance continuum measurement of 1.81 Mm⁻¹ at 450 nm. Here the statistical error represents 0.2% of the total fitted GLY concentration. This is compared to the retrieval of a similar GLY 19.40 \pm 0.105 ppbv concentration (Figure 3.22) in the presence of a much larger continuum absorbance of 162 Mm⁻¹ during the experiment on 03-07-2012 (Figure 3.17). Here, the larger concentration of light scattering non-absorbers has reduced the effective absorption path length of the cavity and resulted in an increase in statistical error to 0.5% of the total retrieved GLY concentration. The presence of other fitted absorbers at higher concentrations will also increase the statistical error because the competing extinctions will also reduce the effective cavity path length. This was observed for GLY concentrations retrieved at Scan 3 (54.41 \pm 0.049 ppbv) and 4 $(54.30 \pm 0.072 \text{ ppbv})$ in Figure 3.19 in the presence of NO₂ concentrations of 4.078 ± 0.0452 ppbv and 67.33 ± 0.0769 ppbv respectively. Here the statistical error increases from 0.09% to 0.13% of the retrieved GLY concentration with an increase in NO₂ of \approx 63 ppbv.



Figure 3.21 A measured absorption spectrum of GLY (Figure 3.19, Scan 2) in the presence of aerosol extinction of 1.81 Mm⁻¹ at 450 nm



Figure 3.22 A measured absorption spectrum of GLY (Figure 3.17, Scan 1) in the presence of aerosol extinction of 162 Mm⁻¹ at 450 nm

The overall error (accuracy) of BBCEAS measurements consists of the combination of the previously discussed statistical errors with systematic errors. Here, the systematic errors contain contributions from the uncertainties in determination of mirror reflectivity, the length factor parameter and the reference absorption cross-sections. They therefore affect every retrieved concentration of a given absorber by the same percentage and are not influenced by the amount of the absorber contained within a sample. The uncertainty in the determination of mirror reflectivity was generally between 3 – 5% and was calculated from the combined errors of the two $R(\lambda)$ determination methods described in Section 3.5.3. The error in mirror reflectivity was therefore a combination of (i) the difference between the mirror curve and the difference in the Rayleigh scattering cross-sections of He and N₂ and (ii) the difference in the scaling factors applied to retrieve the reference O₂ concentration at the start and end of each experiment. The uncertainty in the length factor was determined by the uncertainty in fitting oxygen's O₂-O₂ collision complex in the reference artificial air sample spectrum (generally 1 - 2%). The uncertainties in reference absorption cross sections were estimated by their referenced sources and were 3% for GLY,(158) 7.5% for MGLY,(161) and 3% for NO₂.(159)

3.8 Conclusion

The field BBCEAS instrument obtained high sensitivity measurement data of GLY, MGLY, and NO₂ and provided detailed (20 s integration time) time series during experiments performed in the EUPHORE atmospheric simulation chamber as part of the Pho-SOA 2 campaign. Experiments were designed to investigate the formation of GLY and MGLY from VOC oxidation and their potential uptake onto seed aerosol particles (mainly ammonium sulphate). 1^o detection limits were obtained of 22 pptv, 340 pptv, and 27.5 pptv (20 s integration time) for GLY, MGLY and NO₂ respectively, and corresponded well with the instrument's performance during an extensive instrument inter-comparison exercise for GLY, MGLY and NO₂ held at the EUPHORE chamber a year earlier.(136) This thesis also reported the first measurements aerosol extinction made by one of our BBCEAS instruments. A detection limit of 0.124 Mm⁻¹ was obtained for aerosol extinction at 450 nm from quantifying changes in the unstructured continuum absorbance between 449 - 451 nm. High quality BBCEAS measurement data of GLY, MGLY and aerosol extinction were provided for a publication investigating the potential uptake of GLY by aerosols.(143) Experiments were also performed investigating the VOC systems initiated by the reactions of acetylene, isoprene and propyne with OH radicals. BBCEAS also provided the reference measurement to test a micro-fluidic derivatisation instrument designed for the detection and quantification of GLY and MGLY.(144)

4 In Situ Measurements of I₂ Emissions from Macroalgae

4.1 Introduction

Seaweeds are the dominant source of iodine emitted into the atmosphere at coastal locations. They are known to emit both iodocarbons,(164) and molecular iodine to combat the various stress factors experienced when exposed to air.(77) I₂ emissions have been shown to dominate those of iodocarbons through the measurement of significantly higher concentrations of I₂ in the MBL despite the photo-dissociation of I₂ $(J(I_2) = 0.143 \text{ s}^{-1})$ being more rapid than for organic iodine compounds (e.g. $J(CH_2I_2) = 4.7 \times 10^{-3} \text{ s}^{-1}$).(85) Iodine atoms produced by photolysis go on to react with O₃ to produce iodine oxides (IO and OIO) which have a significant impact on the abundance and partitioning of HO_x and NO_x in the marine troposphere.(165) Iodine oxides may also combine to form higher oxides (I_2O_n , where $n = 2 \rightarrow 5$) which have been shown to nucleate larger iodine containing clusters and hence aerosol particles. A fraction of these particles can act as cloud condensation nuclei (CCN) leading to enhanced cloudiness and a potential climate effect.(85) Knowledge of I₂ emission rates exhibited by seaweed species, growing in their natural habitat, is therefore essential for atmospheric modelling and to improve the understanding of gas phase halogen chemistry and the formation of particulate matter. This chapter presents in situ measurements of I₂ emissions made directly above Laminaria digitata and Ascophyllum nodosum seaweed beds in the inter tidal zone at Roscoff in Brittany, France on the separate visits between September 2012 and June 2013.

4.2 Previous In Situ Measurements of I₂

Direct spectroscopic measurement of I_2 in ambient air was first reported from Mace Head, Ireland. Long path differential optical absorption spectroscopy (LP-DOAS) measurements made during the NAMBLEX campaign,(77) subsequently led to the general consensus that I_2 emissions are the major source of gaseous reactive iodine, as opposed to organic iodine-containing compounds, as was previously supposed (Section 1.3.4). I_2 has since been observed at other coastal locations containing macroalgae, as summarised by Table 4.1.

Location	Max I ₂ / pptv	Method	Spatiality	Local seaweed species	Reference
Mace Head (Ire)	93 ± 5	LP-DOAS	8.4 km	Not reported	Saiz–Lopez & Plane, 2004 (77) (NAMBLEX)
	94 ± 20	BBCRDS	Single point in situ	$\approx 100 \text{ m to } L.$ digitata	Bitter et al, 2005 (86) (NAMBLEX)
	61 ± 12	LP-DOAS	14.4 km	Not reported	Peters et al, 2005 (80) (PARFORCE)
	140.7 ± 5.6	Denuder derivatisation & GC-MS	Single point in situ	5 cm to unspecified species	Huang et al, 2010 (91)
	94.4	LP-DOAS	13.6 km	N/A	
Mweenish Bay (Ire)	302 ± 4	Denuder	Single point in situ	5 cm above A. nodosum and F. vesiculosus	Huang et al, 2010 (91)
	547	Denuder	Single point in situ	≈ 5 to 10 cm to L. digitata	
	290	Denuder	Single point in situ	5 cm to A. nodosum and F. vesiculosus	Huang et al, 2013 (92)
Roscoff (Fr)	52 ± 4	LP-DOAS	6.7 km	N/A	Mahajan et al, 2009 (79) (RHaMBLe)
	50 ± 10	BBCRDS	Single point in situ	$\approx 30 \text{ m to}$ A. nodosum and F. vesiculosus	Leigh et al, 2010 (93) (RHaMBLe)
Ria de Arousa (Sp)	300 ± 100	Fluorescence	Single point in situ	≈ 5 to 10 m to <i>Laminaria</i> species	Mahajan et al, 2010 (73)(LEGOLAS)
California (USA)	4.0 ± 0.6	APCI-MS-MS	Single point in situ	Not specified	Finley & Saltzmann, 2008 (94)

Table 4.1 Previous measurements of I₂ in ambient air reported in literature

LP-DOAS = long-path differential optical absorption spectroscopy; BBCRDS = broadband cavity ringdown spectroscopy; APCI-MS-MS = atmospheric pressure chemical ionisation tandem mass spectrometry

When seaweed plants are exposed to oxidative stress factors (high irradiance, desiccation and atmospheric O_3) at times of low tide, significant levels of iodide are released to the thallus surface of the plant. Γ reacts with and detoxifies aqueous

oxidants (e.g. H_2O_2 and O_3). Such reactions lead to the release of I_2 directly into the atmosphere or indirect release via the production of HOI which disproportionates with Γ to produce I_2 (HOI + Γ + $H^+ \rightleftharpoons H_2O + I_2$) (Figure 4.1).(166)



Figure 4.1 (a) Iodine metabolism in *Laminaria* species when submerged (Γ released into aqueous phase in response to H₂O₂/ROS, so no volatilisation of I₂), and (b) when exposed to oxidative stress (I₂ emissions into gas phase) (from Küpper et al.)(166)

The daytime chemistry of reactive iodine species (atomic iodine, iodine oxides, and iodine oxide particles) in the MBL is therefore primarily initiated by the rapid photolysis of I_2 emitted by seaweed. *In situ* measurements close to the I_2 emission source are essential in developing an understanding of the contribution of seaweed's emissions to the overall chemistry of the troposphere. However, measurements of I_2 emissions are often limited to those made over the open ocean through LP-DOAS,(77, 79, 80) or in the laboratory, as detailed in Chapter 5 of this thesis, as a result of the logistical challenges connected to deployment of instrumentation close to intermittently exposed seaweed beds. The highest I_2 concentrations reported in the ambient atmosphere have been obtained through single point *in situ* measurements, made within a few centimetres,(91, 92) to metres,(73) above the macroalgal emission source. The contrasting concentrations observed between measurements made directly above and further removed from seaweed beds are a result of dilution effects and the photolysis lifetime of I_2 (\approx 15 s).(167, 168) LP-DOAS techniques are further disadvantaged when reporting I_2 emissions, as measurements are averaged over light paths of many kilometres in length that typically extend over mostly open water, with only a small percentage (≈ 10 %) over exposed seaweed beds. Emissions must also be vertically mixed by a few metres before intersecting the DOAS light path.

Previous in situ I₂ measurements have mainly been performed at locations nearby seaweed beds of Laminaria species, which have been shown through laboratory studies (Section 5.2) to produce the strongest I_2 emissions when exposed to air. Peak concentrations observed in situ above Laminaria beds are typically observed to correlate with times of low tide (Section 1.3.4). Huang et al.,(92) combined denuder diffusion tube sample collection a few centimetres from the emission source, with laboratory gas chromatography-mass spectrometry (GC-MS) analysis, to provide in situ measurements of I₂ emissions from mixed A. nodosum and F. vesiculosus seaweed beds. I₂ concentrations increased gradually with exposure time, reaching a peak value of one order of magnitude higher than the initial concentration after approximately 6 h (Figure 4.2), and are consistent with results observed through laboratory incubation experiments (Section 5.2). Laboratory incubation experiments of L. digitata are typically characterised by a strong initial I₂ burst after exposure, followed by an exponential decline. In contrast, A. nodosum and F. vesiculosus plants produce I₂ emissions of a significantly lower concentration, with a gradual increase in emission rates observed with time.



Figure 4.2 I₂ mixing ratio measured above *A. nodosum* and *F. vesiculosus* mixed seaweed beds by Huang et al.,(92) at Mweenish Bay, Ireland, as a function of algal exposure time and solar irradiation. Each data point represents the mean value over a 30 min period

4.3 Application of BBCEAS to In Situ Measurements

The detection and quantification of I₂ and other atmospheric absorbers in ambient air was performed using a mobile broadband cavity enhanced absorption spectroscopy (BBCEAS) instrument, previously constructed and characterised at red wavelengths (640 - 674 nm) by Daniels.(137) The instrument had previously been designed to quantify N₂O₅ produced from a custom-built calibration source. The instrument was used to determine N2O5 and NO3 wall losses for another BBCEAS instrument measuring N₂O₅, NO₃ and NO₂ from Facility for Airborne Atmospheric Measurements (FAAM) aircraft during the ROle of Nighttime chemistry in controlling the Oxidising Capacity of the AtmOsphere (RONOCO) campaign.(120) One of the design requirements for the RONOCO deployment was that the BBCEAS and N₂O₅ source were portable to transport quickly to/from the side of the aircraft to perform pre-flight and post-flight calibrations. The measurements reported in this chapter utilised that portability to obtain high sensitivity, direct spectroscopic detection of I₂ concentrations at green wavelengths (520 - 570 nm). This section details the BBCEAS instrumentation used, its deployment above seaweed beds and the specific data analysis procedure applied to the detection and quantification of *in situ* I₂ emissions.

4.3.1 Experimental design

The mobile BBCEAS instrument was deployed from the in-shore research vessel "Aurelia" operated by the Station Biologique de Roscoff (SBR) (Figure 4.3). The boat was maneuvered into position above the seaweed bed and anchored before the plants were exposed to air by the ebbing tide. The boat was grounded on the seaweed bed around the tidal minimum, and then refloated as the incoming tide covered the seaweed.



Figure 4.3 Experimental setup for *in situ* measurements of I₂ emissions above seaweed beds by BBCEAS including schematic layout of equipment on board the boat (left panel) and photographs taken at *L. digitata* measurement site (right panel). Photo credit: Wilfreid Thomas (SBR)

4.3.2 BBCEAS Hardware

A green high intensity LED light source (ILS OSLON1 PowerStar green, 2.24 Watt, peak wavelength = 528 nm) was supplied with a current of 0.75 A from a regulated power supply (Thurlby, EL301). The LED was mounted on a Peltier cooled laser diode mount (Thorlabs; TCLDM9) and its temperature was maintained at 20°C by a benchtop temperature controller (Thorlabs; TED200C). The LED temperature was controlled to ensure that the output of the LED was consistent throughout experiments. Light emitted by the LED was directed into a fibre optic cable (Ocean Optics; near IR/visible, 400 μ m fibre core diameter, 0.22 numerical aperture, length = 2 m) and collimated on output by an infinity-corrected microscope objective lens (Leica).

The collimated light beam was directed by two turning mirrors (Newport 1" UV 10D20AL.2, > 90% average reflectivity at 250 - 600 nm) into an optical cavity (cavity length = 590 mm) formed by two high reflectivity mirrors (Layertec 1" diameter, part

number: 111078, 1000 mm radius of curvature, > 99.98% high reflectivity at 520 - 560 nm) which were held in place by two custom-made bellows mounts.

Light exiting the cavity through the output mirror was focussed by an achromatic doublet lens (12.7 mm diameter, 30 mm focal length) into another similar fibre optic cable (Ocean Optics), which was directly coupled to a custom-made round to linear fibre (Anglia Instruments). The round to linear fibre consisted of seven fibres (each 100 μ m fibre core diameter, 0.22 numerical aperture) arranged in a daisy bundle at the "round" input end, which were rearranged in a linear stack at the fibre output. This arrangement enabled the efficient delivery of collimated light from the cavity output fibre into the entrance slit inlet of the fibre-coupled spectrometer (Ocean Optics; HR4000, 504.8 – 581.9 nm, linear diode array of 3648 pixels). The spectrometer was housed in a custom-built Peltier-cooled enclosure, also referred to as the spectrometer at a constant, low temperature helped reduce the dark current in the spectrometer output and also stabilised the intensity of the dark current for the duration of the experiments.

Ambient air was drawn by a diaphragm pump from approximately 30 cm directly above the seaweed bed and into the BBCEAS instrument through Teflon tubing (6 m length, 6.35 mm outside diameter, 3.6 litres/min flow rate). Samples were contained within a PTFE cavity (12.7 mm internal diameter), which was secured between the mirror mounts by two 25.4 mm diameter vacuum fittings. Gas was transported in and out of the cavity by two 1/8 inch diameter vacuum fittings, separated by 385 mm.

Spectra were recorded on a laptop using the SpectraSuite (Ocean Optics) software supplied with the HR4000 spectrometer. The laptop was connected to the HR4000 spectrometer via a USB cable. Spectra had a 500 ms integration time; 10 spectra were averaged in Spectrasuite giving a net acquisition time of 5 s, before being saved on the laptop. Spectra were averaged and analysed using the Mathcad Prime 2.0 (PTC) software package as outlined in Section 3.5.

The LED mount and all optical components were attached to an aluminium breadboard (Thorlabs; $880 \times 150 \times 12.7$ mm, M6 threaded), which was mounted on two antivibrational mounts in order to maintain the alignment of the cavity whilst during operation and transport. The breadboard and all other components were housed within an aluminium frame (890 mm W \times 390 mm D \times 300 mm H), which was contained within a Zarges box (950 mm W \times 450 mm D \times 380 mm H). Figure 4.4 and Figure 4.5 show a schematic representation and an annotated photograph of the BBCEAS instrument used.



Figure 4.4 Schematic of the mobile BBCEAS instrument deployed for *in situ* measurements of I₂ emissions above seaweed beds



Figure 4.5 Photograph of the mobile BBCEAS instrument deployed for *in situ* measurements of I₂ emissions above seaweed beds. Photo credit: Wilfreid Thomas (SBR)

For autonomous operation on-board the boat, the BBCEAS was powered by a custom built power supply. In September and November 2012 the power supply consisted of two leisure batteries $(2 \times 12 \text{ V}, \text{ DC}, 100 \text{ Ah}, \text{ Elecsol})$ and a unit combining an inverter (1000 W, 230 V, AC) and 3-stage battery charger (10 A) (Caravan and Leisure Technology). This configuration provided power sufficient to run the BBCEAS instrument, laptop and detector fridge for approximately 3 h 30 min. For deployment in June 2013, the power supply was expanded to house four leisure batteries $(4 \times 12 \text{ V})$, DC, 100 Ah, Elecsol), a multi-stage battery charger (60 A, Caravan and Leisure Technology) and a pure sine wave inverter (700 W, 230 V, AC, Antares). This setup powered the BBCEAS instrument, spectrometer fridge and ozone monitor for approximately 5 h 30 min. The power supply was housed within an aluminium frame (890 mm W \times 390 mm D \times 300 mm H), which was contained within a Zarges box (950mm W \times 450 mm D \times 380 mm H) of identical size to the BBCEAS instrument's Zarges box. During September and November 2012, the power supply box was also used to house the spectrometer fridge. For measurements made in June 2013 the spectrometer fridge was housed in a new aluminium frame (550mm W \times 495 mm D \times 495 mm H), which was contained within a third separate Zarges box (550 mm W \times 550 mm D \times 590 mm H). The box also contained a small power supply consisting of one leisure battery (12 V, DC, 70 AH, Premium Batteries) and the combined inverter (1000 W, 230 V, AC) and 3-stage battery charger (10 A) unit (Caravan and Leisure Technology) previously deployed in September and November 2012. This supply was sufficient to keep the fridge cool during transit from SBR to its installation on Aurelia.

A backup petrol generator was deployed to maximise analysis time during *L. digitata* experiments performed in September and November 2012 and the longer *A. nodosum* experiments in June 2013. Battery power was highly preferred to that of the petrol generator due to the latter's NO₂ emissions. The generator did not adversely affect measurements of I_2 concentrations through BBCEAS, because I_2 is spectrally distinct from NO₂, however knowledge of ambient concentrations of NO₂ was useful to inform the atmospheric composition of the region. Variability in the generator's output was also observed to cause the BBCEAS pump to stop functioning at various intervals when powering the BBCEAS instrument directly, specifically during the first *L. digitata* experiment performed on 17-09-2012. Since then the generator was only used to power to the detector fridge and laptops with the BBCEAS system only powered by batteries.

The generator was always positioned downwind from the BBCEAS inlet, either at the back of the boat during *L. digitata* measurements or on the shore when possible during *A. nodosum* experiments.

4.3.3 HR4000 Spectrometer Calibration

The HR4000 spectrometer (Ocean Optics, 504.8 - 581.9 nm) was used to record absorption spectra for all BBCEAS measurements of seaweed emissions presented in Chapter 4 and 5 of this thesis. The green visible region of the electromagnetic spectrum was selected because this is where the main target species, I₂, exhibits its major structured absorbance features. As discussed previously, BBCEAS determines the concentration of overlapping absorbers through the DOAS fitting procedure and application of reference absorption cross sections (Section 2.2). The reference absorption cross sections applied to measurements in this chapter (Section 4.3.6) were degraded through application of the experimentally determined HR4000 true wavelength scale and line functions. Calibration of the spectrometer was performed at the start and end of each campaign month through a similar procedure applied to measurements in the blue spectral region (Section 3.5.1).

The HR4000 spectrometer was calibrated using light from an argon emission lamp (Pen-Ray), as it exhibited well-defined lines in its emission spectrum, which could be individually assigned. The emission lamp was positioned in front of a fibre optic (Ocean Optics) converging light to the HR4000 spectrometer. Emission spectra were recorded at an integration time of 500 ms, which enabled the capture of maximum light without any saturation of the detector. The emission lines were fitted with a symmetric Gaussian line shape function (Equation 4.1, Figure 4.6) in order to determine the lineshape of the HR4000 spectrometer, where λ_{cen} and w are the centre wavelength (nm) and half width half maximum (nm) of the emission line shape respectively.

Equation 4.1

$$lineshape_{sym}(\lambda) = N \cdot exp\left[\frac{-(\lambda - \lambda_{cen})^2 \cdot ln(2)}{w^2}\right]$$


Figure 4.6 An argon emission line (centre wavelength (NIST): 542.14 nm) measured by the HR4000 spectrometer and fitted with the symmetric Gaussian function centered at 542.18 nm (SD = standard deviation)

An asymmetric line shape function (Equation 4.2, Figure 4.7) was also fitted to the emission lines, where the parameter, α , is a measure of asymmetry (no units), which when equal to zero, reverts the asymmetric function back to that of a symmetric Gaussian. The asymmetric instrument function was observed to provide the best simulation of the HR4000 spectrometer line shape through comparison of the residual spectra of emission lines fitted with the two functions (e.g. Figure 4.6 and Figure 4.7). This was the same result as observed for calibrations of the HR2000 spectrometer described in Section 3.5.1.

Equation 4.2

$$lineshape_{asym}(\lambda) = N \cdot exp\left[\frac{-(\lambda - \lambda_{cen})^2 \cdot ln(2)}{[w \cdot (1 + \alpha \cdot (\lambda - \lambda_{cen}))^2]}\right]$$



Figure 4.7 An argon emission line (centre wavelength (NIST): 542.14 nm) measured by the HR4000 spectrometer and fitted with the asymmetric function centered at 542.17 nm (SD = standard deviation)

The width and asymmetry of the line shape varied somewhat across the HR4000 spectrometer's bandwidth. Figure 4.8 shows the wavelength dependent line shapes determined for the HR4000 spectrometer by fitting the asymmetric line shape function to emission lines recorded across the full wavelength range of the spectrometer. The wavelength dependencies of half width at half maximum and the asymmetric parameter, α , were fitted with a third order polynomial function (Figure 4.8 and Figure 4.9) similar to that of the HR2000 spectrometer (Section 3.5.1). The fitted parameters were subsequently used to determine a wavelength dependent asymmetric instrument function for each pixel of the HR4000 spectrometer. These line shapes were then used to degrade the I₂, NO₂ and H₂O reference cross sections for fitting the BBCEAS spectra in this chapter and Chapter 5.



Figure 4.8 The wavelength dependent half width at half maximum (HWHM) for argon emission lines recorded between 505 – 582 nm by the HR4000 spectrometer



Figure 4.9 The wavelength dependent fitted asymmetric parameter for argon emission lines recorded between 505 – 582 nm by the HR4000 spectrometer

The true wavelength of the HR4000 spectrometer was determined through comparison of the measured centre wavelengths of the fitted asymmetric peaks with their expected centre wavelengths obtained from the NIST database.(150) The difference between the measured central wavelength and the reference central wavelength was plotted against the measured central wavelength for each emission line and fitted with a third order polynomial function (Figure 4.10). The parameters of the polynomial were used to adjust the manufacturer wavelength scale on each pixel to the true measured wavelengths over the 519.84 - 570.07 nm spectral bandwidth. The reference absorber cross sections were linearly interpolated onto the new calculated wavelength scale prior to the differential fitting of the observed spectra.



Figure 4.10 Plotting the difference between expected and measured centre wavelengths of argon emission peaks against measured centre wavelengths. Individual points were fitted with a 3rd order polynomial function to determine the true wavelength scale of the HR4000 spectrometer

4.3.4 HR4000 Dark Current Determination

The HR4000 dark currents were located through the same process outlined for the HR2000 spectrometer in Section 3.5.2. The contribution of the dark current to both $I_0(\lambda)$ and $I(\lambda)$ spectra was approximated through the recording of $I_{dark}(\lambda)$ spectra (500 ms × 10) at varying intervals throughout the analysis. $I_{dark}(\lambda)$ spectra were recorded with a card blocking light entering the spectrometer collection fibre and hence no light was able to reach the photosensitive region of the device. The HR4000 detector, by chance, has fifteen dark pixels which were never illuminated, even during the recording of $I_0(\lambda)$ and $I(\lambda)$ spectra (Figure 4.11). The ten dark pixels (pixels 7 to 16) shown in Figure 4.11 were used as a proxy for temperature and applied in the same way as those

identified for the HR2000 spectrometer in Section 3.5.2 to generate a synthetic dark current spectrum to be subtracted from every measured BBCEAS $I(\lambda)$ spectra.



Figure 4.11 $I_0(\lambda)$ and $I_{dark}(\lambda)$ spectra recorded by the HR4000 spectrometer showing the dark pixels 7 – 16, which were never illuminated

4.3.5 Mirror Reflectivity Determination

As discussed previously, measurements of absorber concentrations, $\alpha(\lambda)$, by BBCEAS requires detailed knowledge of how the mirror reflectivity varies with wavelength across the detection bandwidth. Mirror reflectivity calibrations were performed in the laboratory both immediately before and after transportation of the BBCEAS instrument to and from the measurement sites. The $R(\lambda)$ parameter was determined through application of **Equation 4.3** using the same method applied to the BBCEAS field instrument in Section 3.5.3.

Equation 4.3

$$R(\lambda) = 1 - (\alpha_{ref}(\lambda) \cdot d) \cdot \left(\frac{I_0(\lambda)}{I_{ref}(\lambda)} - 1\right)^{-1}$$

A first estimate of mirror reflectivity was calculated through comparison of the light transmitted across a cavity flushed with helium and then with nitrogen $(\alpha_{ref}(\lambda) = \sigma_{He} - \sigma_{N_2})$. Knowledge of the Rayleigh scattering cross-sections of

He,(151) and N₂,(108) enabled a uniform measurement of mirror reflectivity (mirror curve) to be constructed across the analysed wavelength range (Figure 4.12).



Figure 4.12 Example of a measured mirror reflectivity curve and the effective optical path length within the cavity (d = 590 mm) for the BBCEAS mobile instrument operating at green wavelengths

The absolute measurement of mirror reflectivity was subsequently determined using BBCEAS spectra, $I_{ref}(\lambda)$, recorded across a cavity completely flushed with a pure oxygen reference gas. Here $\alpha_{ref}(\lambda)$ is the absorption spectrum of the reference absorber (O₂–O₂) calculated from knowledge of its absorption cross section and concentration. A scaling factor was applied to the previously calculated mirror curve until the retrieved intensity of oxygen's O₂–O₂ absorption matched that expected for the reference sample of 100 % oxygen.

4.3.6 Reference Absorption Cross Sections

Ambient gas-phase concentrations were determined through application of the DOAStype fitting procedure outlined in Section 3.5. In this case the differential spectrum was calculated by fitting a polynomial in wavelength of 6th order to the smoothly varying contributions to the absorbance coefficient by non-absorbers. Reference absorption cross sections were fitted for I₂ (adapted from (167)), NO₂,(169) H₂O/water vapour,(160) oxygen's O₂–O₂ collision complex,(157) and OIO,(170) between 520 and 570 nm. The I₂ reference absorption cross section published by Saiz-Lopez et al,(167) was available at a resolution of 0.1 nm. A high resolution I₂ spectrum was therefore calculated using the PGOPHER simulation package,(171, 172) with an average line width appropriate to the HR4000 spectrometer. The same calculation was previously applied to BBCEAS detection of I₂ by Ball et al.(124) The new synthetic I₂ spectrum was subsequently put on an absolute (cm² molecule⁻¹) scale by scaling to the original Saiz-Lopez cross-section.(167) Figure 4.13 shows an example of a fitted BBCEAS spectrum decomposed into the various absorption contributions from the different structured absorbers.



Figure 4.13 Examples of fitted BBCEAS spectra recorded in ambient air during the experiment on 18-09-2012 at 13:51:57 with a 20 s integration time (Figure 4.23). The statistical error in the fitted amount for each absorber is shown. OIO is not shown because the retrieved concentration was below the instrument detection limit

4.3.7 Instrument Detection Limits

The precision (statistical error) and accuracy (overall error) of BBCEAS measurements were determined through the same methodology as described in Section 3.6.1. The uncertainties summarised here applied to the absorber concentrations determined from BBCEAS measurements in both Chapter 4 and 5 of this thesis. The overall error was again determined from the combined net systematic and statistical uncertainty of the BBCEAS measurement. The sources of systematic uncertainty were uncertainties in the mirror reflectivity (3 - 5%) and the absorption cross sections of 15% for I₂,(167) 3% for NO_2 ,(169) and 15% for OIO.(170) The statistical uncertainty was again determined by the ability of the fitting procedure to isolate the structured absorption signal of an individual absorber (e.g. I₂) from the combined BBCEAS absorption spectrum. When fitting a very weak absorption signal owing to a low absorber concentration, the retrieved statistical error was \pm the instrument detection limit (Section 4.3.7.1). When retrieving stronger absorption signals owing to an increased absorber concentration, the statistical uncertainty increased but was insignificant in comparison to the net systematic error. For example, the statistical error generally remained at < 1% when retrieving larger concentrations of the main target absorber I2. The detection limits and stability of the BBCEAS instrument were calculated through the Allan variance method, as previously applied to measurements reported in Section 3.6.

4.3.7.1 Statistics of Baseline Spectra

Statistical analyses were performed on a series of the baseline measurements of $I(\lambda)$, recorded in the laboratory at SBR, when the cavity was purged with N₂ and therefore was free of all molecular absorbers.(129) The absence of molecular absorbers meant that any contributions to differential absorbance therefore resulted from instrument instability and random noise(162). 7756 $I(\lambda)$ spectra, each with a 5 s (500 ms × 10) integration time (38780 s of data, 10.8 h), were recorded overnight on 09-06-2013. These spectra were averaged to produce 20 s spectra through the data analysis procedure outlined in Section 3.5 in order to be consistent with the 20 s net acquisition time used in the analysis of ambient air BBCEAS spectra. The final 120 spectra of the set of 7756 spectra were averaged together (600 s) and used for the $I_0(\lambda)$ reference spectrum. The retrieved concentrations of the target absorbers, I₂, OIO and NO₂ are shown in the upper panels of Figure 4.14.



Figure 4.14 The time series and corresponding histograms of I₂ (top panel), OIO (middle panel) and NO₂ (bottom panel) concentrations retrieved through fitting of baseline spectra when the cavity was purged with nitrogen using an integration time of 20 s

Baseline measurements show the BBCEAS instrument has a 1σ detection limit of 3.62 pptv for I₂, 1.10 pptv for OIO and 92.6 pptv for NO₂ against a zero absorption background for an integration time of 20 s. The time series of all structured absorbers displayed a random distribution of concentrations around the mean concentration which was directly assigned to the statistical error of fitting reference absorption cross sections to a spectrum of random noise. The retrieved 1σ standard deviation values can therefore be used to infer the BBCEAS instrument detection limits for each of the structured absorbers. The baseline tests in Figure 4.14 were performed under ideal conditions in the lab. One might expect therefore the detection limits achievable when operating in the field to be higher. Here the fitted BBCEAS spectra in Figure 4.13 provides a useful comparison; the fitted errors on the I_2 (4 pptv) and NO₂ (100 pptv) are actually very close to the detection limits inferred from the baseline histograms for I_2 (3.62 pptv) and NO_2 (92.6 pptv). This further indicates that the retrieval errors produced by fitting individual BBCEAS spectra are reproducible of detection limits established in the baseline tests (at least for lower absorber amounts where the statistical fitting errors dominate).

4.3.7.2 Allan Variance analysis

The standard deviation and Allan deviation were calculated for retrieved baseline concentrations of I₂ OIO and NO₂ through application of the same analysis procedure previously applied to measurements in Section 3.6.2. The minima in the Allan deviation plots shown in Figure 4.15; ≈ 2400 s for I₂, ≈ 1500 for NO₂ and ≈ 700 s for OIO, represent the optimum integration time of the BBCEAS instrument for fitting the individual absorbers. The analysis showed lower detection limits could be achieved (e.g. < 1 pptv for I₂) but would require the instrument to operate at a much longer integration time. In the work presented in this thesis, the primary aim was to capture I₂ emission at fast time responses and hence further averaging was not desirable.



Figure 4.15 Standard deviation and Allan deviation plots for I_2 (top panel), OIO (middle panel) and NO₂ (bottom panel) mixing ratios retrieved from baseline measurements made for a time series recorded flowing N₂ (zero absorption background)

4.4 Other Data Sets

4.4.1 Sea Level and Wind Measurements

Sea level information was reported in 10 min averages, as recorded by the REFMAR collection system at Port de Bloscon (near ferry terminal) operated by Service hydrographique et océanographique de la marine (SHOM) (48 43.10, -003 57.944).(173) Wind speed and direction data was recorded in 30 min intervals at the Astan measurement buoy, operated by SBR, located NE of the Ile de Batz, approximately 3 km from SBR, close to the route of the cross channel ferries (Figure 4.20) (48 46.40, -003 56.15).

4.4.2 Ozone Measurements

Ozone concentrations were measured on board the research vessel "Aurelia" for June experiments only, using a model 202 ozone monitor (2B Technologies). Air was drawn at approximately 990 cc/min through a 575 mm long, 6.35 mm outside diameter Teflon line connected to the main BBCEAS inlet line via a T-piece. Ozone measurements were reported over a 1 min integration time.

In order to check for losses of ozone on the inlet line, a series of calibrations of the ozone monitor were performed in the laboratory using a model 306 ozone calibrator (2B Technologies). Set ozone concentrations between 0 and 100 ppbv were analysed in 10 minute intervals under the usual flow rate drawn by the ozone monitor. The lengths of Teflon tubing used to directly connect the ozone monitor and the calibrator were varied between 0.4 m and 9.4 m and connected with chemically resistant PFA fittings. Actual ozone concentrations were determined through the averaging of monitor readings when the ozone concentration had stabilized. No systematic variation of intercept values was observed with tube length and a mean > 95% transmission was assigned for all tube lengths and applied to measurements made in the field. Interestingly no point losses of ozone were observed during experiments where stainless steel fittings were used.

4.4.3 Calculation of Photolysis Rates

As previously discussed in Section 1.2, photochemistry is the driving force behind much of the atmospheric radical chemistry and hence the overall reactivity and composition of the troposphere. Photolysis rate constants, also known as J values, are dependent on three factors as described by Equation 4.4 where, Φ , represents the quantum yield for photolysis of a species with an absorption cross-section, σ , described both as a function of wavelength, λ , and temperature, *T*. The solar spherical or point irradiance, $F(\theta, \lambda)$, represents the flux of photons available to enable the photolysis of a species. The quantity, θ , is the solar zenith angle, which describes the angle between the sun and the vertical.

Equation 4.4

$$J = \int \phi(\lambda, T) \,\sigma(\lambda, T) F(\theta, \lambda) d\lambda$$

 I_2 is a very short lived species because it absorbs light most efficiently between approximately 420 and 600 nm which coincides with the Sun's strongest output radiation experienced in the lower troposphere of between approximately 400 and 700 nm. The diurnal profiles of the photolysis rates of various atmospheric species, previously measured by a spectral radiometer (Met Com) in Roscoff during the RHaMBLe field campaign, are shown in Figure 4.16. The local midday peak photolysis rates reported for reactive iodine species are $J(I_2) = 0.143 \text{ s}^{-1}$, $J(IO) = 0.147 \text{ s}^{-1}$, and $J(OIO) = 3.7 \times 10^{-2} \text{ s}^{-1}$.



Figure 4.16 Photolysis rates calculated from spectrally-resolved irradiance radiometer measurements grouped according to their photolability on 10th September 2006 during the RHaMBLe campaign (from McFiggans et al.)(85)

The photolysis rates of iodine $J(I_2)$ reported in this thesis were calculated from sunlight measurements recorded using a fibre-coupled USB650 Spectrometer (Ocean Optics Red Tide) (September 2012) and USB650-UV-VIS Spectrometer (Ocean Optics Red Tide) (November 2012 and June 2013). Both have a modest 2 nm optical resolution over the wavelength ranges 350 - 1000 nm and 200 - 850 nm respectively. The true wavelength of the spectrometers were assigned by records of emission lines of an argon lamp (Pen-Ray) and comparing the wavelengths of the lines with their known wavelength from the NIST database.(150)

The spectrometers were connected to a collection optic attached to the roof of the boat, which pointed vertically upwards, through a UV-visible fibre (2m, 400 μ m diameter, Ocean Optics). Measurements made in 2012 used a collection optic constructed from a neutral density filter, (1.0 optical density, 1.0 inch diameter, Newport) which from the experiment on 18-09-2012, also had a double layer of lens tissue placed over the filter to act as a sunlight diffuser and prevent spectrometer saturation. In June 2013, a cosine-corrected diffuser (OceanOptics) was used in place of the filter and paper diffuser. Measurements were made at integration times of 5 s, 20 s, and 10 s in September 2012, November 2012 and June 2013 respectively, dependent on the intensity of sunlight and transmission characteristics of the diffuser/collection optics. J(I₂) values were calculated from the combined intensity of the recorded spectra, I₂ absorption cross section and I₂ quantum yields using Equation 4.4.

An absolute radiometric calibration of collection optics and the spectrometer's response was not attempted. Instead the $J(I_2)$ values recorded at peak sunlight levels through each instrumental setup on each month of the campaign were scaled based on $J(I_2)$ values previously observed at Roscoff (0.15 s⁻¹).(47)

The validity of this approach was tested through comparison of sunlight levels recorded by the USB650UV spectrometer in its June 2013 setup with spectral radiometer (Specrad, described in full detail by Edwards et al.(174)) measurements made at the University of Leicester. The Specrad uses a 2π sr quartz dome collection optic to collect photons from different incident angles to enable the calculation of actinic flux. Photolysis rates were calculated using Equation 4.4 and scaled to Specrad J(I₂) values, recorded between 29-07-2014 and 31-07-2014 at UoL (Figure 4.17 shows an example plot of the middle one of these three days). A good correlation ($R^2 = 0.7691$) was observed between Specrad and USB650UV measurements made between 05:00 and 21:00 across the three days (Figure 4.18). The agreement between the two instruments was very good around midday. The poorest agreement was observed around times of sunrise and sunset, where the USB650UV spectrometer under measured J(I₂). This was attributed to the failure of the collection optic to sample solar radiation at high solar zenith angles.

For all the boat measurements, solar zenith angles were calculated from their GPS points using an online solar elevation angle calculator.(175) The solar zenith angle between the Sun and the vertical was observed to result in an underestimation of photolysis rates by the USB650UV spectrometer at angles above approximately 50° but this was determined not to be a problem for the majority of measurements made during boat experiments. Figure 4.19 shows the calculated solar zenith angles for the days of the boat experiments reported in this chapter. The markers indicate the start and end of the sunlight measurements made by the USB650UV on each of the days. The solar zenith angle ranges calculated for the boat experiments (except for 15-11-2012) were where the Specrad and USB650UV data agree well. An added instability in J values obtained during the boat experiments may also result from the rocking of the boat on the waves and hence the collection optic prior to being grounded by the outgoing tide.



Figure 4.17 $J(I_2)$ measurements recorded by Specrad at University of Leicester on 30/07/2014 and comparison with values estimated from USB650UV measurements



Figure 4.18 Correlation between Specrad $J(I_2)$ and scaled USB650UV $J(I_2)$ values recorded between 05:00 and 21:00 between 29/07/2014 and 31/07/2014 at the University of



recorded between 05:00 and 21:00 between 29/07/2014 and 31/07/2014 at the University of Leicester

Figure 4.19 Solar Zenith angles for sampling sites at Roscoff on boat experiment days. Markers indicate the start and end of sunlight measurements

4.5 Measurement Sites

Measurements were taken off the coast of Roscoff in Brittany (Figure 4.20) in the north-west of France in September and November 2012 and June 2013, enabling an inter-seasonal comparison of I_2 emissions. The Roscoff intertidal zone extends more than 5 km in length and approximately 1 km wide, and consists of large areas of extensively characterised high biological activity containing a variety of different seaweed species growing in bands.(176) We chose to study *L. digitata* and *A. nodosum*

through *in situ* measurements, however other species were also studied through laboratory incubation experiments described in Chapter 5. Previous measurements made as part of the RHaMBLe campaign had observed high levels of reactive iodine species, coastal photochemistry and iodine mediated particle formation in the region, corresponding with the exposure of seaweed at low tide.(85)



Figure 4.20 Map of Roscoff, France showing key experimental locations



Figure 4.21 Photographs of *A. nodosum* (Asco 2) measuring site (left panel) and *L. digitata* measuring site (right panel). Photo credit: Wilfreid Thomas (SBR)

The tidal range at Roscoff is large (≈ 9 m) and therefore the exposure time of seaweed varies significantly with location, owing to the very wide inter-tidal zone. Individual measurement sites were selected which contained a high abundance of single dominant species of seaweed (either *L. digitata* or *A. nodosum*) and which were accessible by boat. *L. digitata* was selected because it is known to be a large emitter of I₂ and particle nucleation events are often attributed to this species in other studies. In comparison *A. nodosum* is an intermediate emitter and was selected as it provided a contrast to the *L. digitata* measurements. The measurements also tested the assertion by Huang et al.,(92) that *A. nodosum* provides a significant contribution to coastal iodine.

An individual location above a seaweed bed containing *L. digitata* (90%) and *L. hyperborea* (10%) at Sainte Barbe (48 43.512, -003 58.056/7), referred to as the *L. digitata* site, was chosen for analysis, where the majority of plants were exposed for no longer than 2 h on a selection of days in each month. Six experiments were performed at the *L. digitata* site in total: three in September 2012, one in November 2012 and two in June 2013. The boat was positioned at the same GPS reading to within 00.001 minutes for each experiment. Two *Ascophyllum nodosum* (100%) sites (*Asco 1*: 48 43.857, -003 59.096 and *Asco 2*: 48 43.842, -003 59.226), were analysed on days close to the tidal maximum, 10-06-2013 and 24-06-2013 respectively. At these locations the majority of *Ascophyllum* plants were exposed for over 5 h, twice daily.

4.6 Results: Laminaria digitata

4.6.1 Introduction to Results

The data presented in the following figures were recorded *in situ*, above a *L. digitata* seaweed bed (90% *L. digitata*, 10% *L. hyperborea*) from the same location at San Barbe, as determined by GPS. Six experiments were performed over three seasons. Blue diamonds in Figure 4.22 to Figure 4.27 indicate the times and hence tidal heights when seaweed immediately below the BBCEAS sampling inlet were exposed and resubmerged by the tide. The blue square represents the recorded tidal minimum. The first deployment on 17-09-2012 was something of a test day. Some BBCEAS data from the experiment on 17-09-2012 has been removed due to the intermittent failure of the instrument pump, which was assigned to the use of a petrol generator (Section 4.3.2). The use of a generator may also account for the higher than average NO₂ concentrations and increased activity in the instrument continuum observed during this particular experiment.



Figure 4.22 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 17-09-2012. BBCEAS I₂ (top panel), and BBCEAS NO₂ and aerosol extinction (2nd panel). All BBCEAS results reported at 20 s integration time. J(I₂) from USB650 spectrometer's sunlight spectra (3rd panel) reported at 5 s int. time. Wind speed and wind direction from ASTAN buoy (bottom panel) at 30 min intervals. Tide (top panel) at 20s interpolated from REFMAR observations



Figure 4.23 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 18-09-2012. The panel contents are the same as Figure 4.22. Scan at 13:51:57 was obtained from the fitted BBCEAS spectra shown in Figure 4.13



Figure 4.24 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 19-09-2012. The panel contents are the same as Figure 4.22



Figure 4.25 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 15-11-2012. The panel contents are the same as Figure 4.22 except J(I₂) from USB650 spectrometer's sunlight spectra (3rd panel) reported at 20 s int. time



Figure 4.26 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 25-06-2013. The panel contents are the same as Figure 4.22 except O₃ from model 202 monitor at 1 min int. time. J(I₂) from USB650 spectrometer's sunlight spectra (3rd panel) reported at 10 s int. time



Figure 4.27 Summary of *in situ* measurements made above a *L. digitata* seaweed bed on 26-06-2013. The panel contents are the same as Figure 4.26. Box indicates anti–correlation in measured NO₂ and O₃ concentrations discussed in Section 4.6.3

4.6.2 Iodine and its Tidal Dependence

A strong anti-correlation between I_2 concentration and water depth was observed for all six *in situ* experiments. During a typical experiment, a small initial amount of I_2 was seen above background levels, whilst the blades of the seaweed plants were floating on the water surface. A consistent increase in I_2 of several hundred pptv was observed during all experiments, within a few minutes of the plants' stipes breaking the surface and the first blades coming to rest on rocks out of the water. I_2 concentrations increased further as the tide ebbed, peaking around the times of low tide (Figure 4.28). The largest I_2 concentrations were observed on 15-11-2012, peaking at 2.08 ppbv, which was on the day with the lowest tidal minimum (0.77 m).



Figure 4.28 I₂ emissions measured *in situ* above a *L. digitata* seaweed bed. The time shown is relative to tidal minima

For the most part, I_2 concentrations were extremely low (below 50 pptv) before the seaweeds beneath the sampling inlet were uncovered. The profiles of I_2 on the 18th and 19th September 2012 sat on a smoothly-varying background which was attributed to I_2 transported from other more-distant seaweeds, whose emissions were better–mixed into the atmosphere. The highest background concentrations of I_2 , of over 100 pptv, were observed on all experiment days in September 2012, when the wind was coming from a NW to SW direction (Table 4.2). Air was potentially transported from seaweed beds located to the west of the *L. digitata* site, which had been uncovered prior to the

Laminaria species. The wind speeds were notably high on 18-09-2012 and therefore potentially enabled the transport of other seaweed emissions to the sampling site rapidly and before they could be photolysed. On experiment days in November 2012 and June 2013 with lower background levels, the wind was coming from a NE direction, across the open water, and had not travelled over any nearby seaweed beds.

Table 4.2 A summary of I_2 concentrations, wind measurements and tidal information recorded during all *in situ L. digitata* experiments. Tide information was interpolated onto BBCEAS integration time (20 s) from REFMAR (originally 10 min intervals)

Date	17/09/12	18/09/12	19/09/12	15/11/12	25/06/13	26/06/13
Tidal minimum / m	0.926	0.843	0.919	0.772	0.806	0.915
Time exposed & submerged /	13:22 -	13:56 -	14:42 -	12:15 -	13:55 -	14:45 -
hh:mm	14:39	15:25	16:01	13:52	15:25	16:10
Duration of exposure / hh:mm	01:17	01:29	01:19	01:37	01:30	01:25
Peak I ₂ / ppbv	0.770	1.16	0.428	2.08	1.01	0.553
Mean I_2 exposed to air / ppbv	0.535	0.462	0.192	0.576	0.492	0.120
Mean I ₂ under water / ppbv	0.380	0.178	0.100	0.0633	0.0460	0.0241
[I ₂] (ppbv) × Time (s) for duration of exposure	93.6	124	45.3	167	138	29.3
Average wind speed / ms ⁻¹	6.05	12.39	5.55	1.58	6.29	6.05
Average wind direction / $^\circ$	209	318	293	47.6	27.6	47.2

It is important to note that tide height was by far the dominant factor in determining the amount of I_2 in the atmosphere, as demonstrated by the strong repeated anti-correlation observed between tide height and concentration. Figure 4.29 shows the relationship between the mixing ratio of I_2 measured above the *L. digitata* bed and tide height on each of the individual experiment days. A strong tidal dependence is observed for each experiment owing to more *L. digitata* plants being exposed at lower tide heights and hence increasing the number of contributing plants to overall I_2 emissions.



Figure 4.29 [I₂] vs. tide height for all L. digitata in situ experiments

The peak I₂ concentrations observed here are three to five times greater than the maximum amounts recorded above/closeby Laminaria beds in previous studies: 300 pptv max in O Grove, Galicia, Spain(73), and 547 pptv max at Mweenish Bay, near Mace Head, County Galway, Ireland.(91, 92) In part, the larger peak concentrations seen here are a consequence of deploying a fast response instrument very close to the source which enables the high temporal variability of emissions to be captured with fewer temporal averaging and dispersion effects and minimises the photolysis losses for I_2 . Nevertheless, the I_2 concentrations averaged over the time when the plants were uncovered were still typically several hundred pptv, suggesting Laminaria beds are even larger emitters of I₂ into coastal atmospheres than previously thought. Figure 4.30 demonstrates the effect of averaging on the I2 concentration time series recorded on 15-11-2012. The concentration profiles measured at shorter integration times were more structured and show higher peak concentrations. For example the peak I₂ concentration for all experiments (3.18 ppbv), was observed at the shortest integration time of the BBCEAS instrument (5 s), in this deployment. It is important to note that when the data were averaged up to 5 min (at an integration time that is comparable to instruments in previous studies), the I2 concentration retrieved on 15-11-2012 was still greater than 1 ppbv and is larger than the amounts of I₂ previously observed *in situ*.



Figure 4.30 I₂ concentrations observed above a *L. digitata* seaweed bed on 15-11-2012 at integration times of 5 s, 20 s, 1 min and 5 min. The blue diamonds indicate the times and hence the tide heights at which the seaweed immediately below the sampling inlet were exposed and submerged by the tide

4.6.3 O₃ and NO₂

Ozone measurements were available for the two experiment days in June 2013. Some anti-correlation ($R^2 = 0.398$) was observed between I₂ and O₃ concentrations above the Laminaria beds during the 25-06-2013 experiment (Figure 4.26) with an approximate 5 ppbv decrease in O_3 coinciding with an approximate 1 ppbv increase in I_2 . No significant changes in NO₂ concentration were observed around the times of ozone depletion to indicate the NO + $O_3 \rightarrow NO_2 + O_2$ reaction which might explain O_3 loss owing to NO from fresh pollution. The reduction in O₃ was therefore assigned to iodine chemistry initiated by the photolysis of the I₂ released from the exposed L. digitata plants. As discussed previously, (Section 1.3.1) I_2 is photolysed to produce two I atoms, which will react with O₃ to form IO. We therefore would expect to lose 2 ppbv of O₃ for every 1 ppbv of I₂ emitted. However, the O₃ loss observed here was somewhat higher. This may be the result of some downstream IO chemistry losing O_3 , but this is unlikely given the very short reaction times. Perhaps more likely is the enhanced physical deposition of O_3 onto the seaweed's surface, where only one molecule of O_3 is required to react with Γ to produce each molecule of I₂. However, this would still be short of explaining the total change in O₃ concentration and may therefore indicate the formation of other products from the reaction of O_3 and seaweed that are not I_2 (e.g. HOI production).

An anti-correlation in NO₂ and O₃ concentrations was observed at around 13:50 on 26-06-2013 (box on Figure 4.27), where a significantly high NO₂ peak concentration of 33.2 ppbv corresponded to a loss in O₃ of approximately 8 ppbv. This sharp increase in NO₂ indicated the transport of fresh pollutants by the northerly wind and directly corresponded to the passing Roscoff to Plymouth ferry which left port at 13:45. On this day, no obvious reduction in O₃ was observed corresponding to the increased levels of I₂.

4.6.4 OIO and Particle Nucleation

No light extinction was observed which could be attributed to the formation of new iodine oxide particles. However, this was not unexpected because such newly nucleated particles are too small to influence the absorption continuum at the BBCEAS instrument's operating wavelengths. Interestingly no OIO was observed above the

BBCEAS detection limits despite large quantities of I₂ and the expected good BBCEAS sensitivity (1 σ detection limit = 1.10 pptv) reported in Section 4.3.6. This is therefore presumably the result of sampling so close to the I₂ source (distance between sampling inlet and seaweed = 30 cm) and hence the required photochemistry hadn't yet had time to form OIO. The time taken for I₂ to travel the distance from its emission source to the sampling inlet (< 1 s) is faster than the previously determined photolysis lifetime of I_2 at midday ($J_{12} = 0.15 \text{ s}^{-1}$, lifetime $\approx 7 \text{ s}$) and the lifetimes of the following additional reactions required for OIO formation. The reported rate coefficient for the $I + O_3 = IO + O_2$ reaction is $k = 1.3 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹.(177) During the boat measurements in June 2013, O₃ was measured at \approx 30 ppbv \approx 7.5 \times 10¹¹ molecule cm⁻³, which are amounts typical of ocean background.(85) Hence the reaction lifetime for $I + O_3$ was ≈ 1 s. The reported rate coefficient for the subsequent IO + IO = OIO + I reaction is $k = 9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.(177)$ IO concentrations were not measured during the boat experiments but assuming an IO concentration of 10 ppbv (FAGE [IO] = 10 ppbv, previously measured at Roscoff),(79) which corresponds to $\approx 2.5 \times 10^8$ molecule cm⁻³, the reaction lifetime for IO + IO is ≈ 40 s.

Additionally, in semi-polluted environments, such as the locations of measurements reported in this chapter, the self-reaction of IO radicals to form OIO will also compete with the reactions of IO and both NO (IO + NO = I + NO₂, $k = 1.95 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),(177) and NO₂ (IO + NO₂ + M = IONO₂, $k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Section 1.3.1).(177) For the mean NO₂ concentration of 1.21 ppbv (3.03 × 10¹¹ molecule cm⁻³) observed during all *in situ* experiments in this chapter, the reaction lifetime for IO + NO₂ is ≈ 0.5 s. Thus the presence of NO_x at our sampling sites may strongly suppress OIO formation.



Figure 4.31 I₂ and OIO concentration time series observed above a *L. digitata* seaweed bed on 18-09-2012. The error bars in the bottom panel represent BBCEAS instrument statistical (fitting) error. OIO was not observed above statistical errors

4.7 Results: Ascophyllum nodosum

4.7.1 Introduction to Results

The data presented in in Figure 4.32 and Figure 4.33 was recorded *in situ*, above two, nearby *Ascophyllum nodosum* seaweed beds (*Asco 1*: 48 43.857, -003 59.096 and *Asco 2*: 48 43.842, -003 59.226, Figure 4.20) in June 2013. Blue diamonds indicate the times and hence tidal heights when seaweed immediately below the BBCEAS sampling inlet were exposed and submerged by the tide. The blue square represents the recorded tidal minimum. Two small breaks in the 10-06-2013 data series for I₂ were removed because the instrument's inlet was lowered to within approximately 5 cm of the seaweed bed. Concentrations of I₂ were increased by up to four times (max: 0.821 pptv) from those observed at the usual sampling height of 30 cm. Such differences were accounted for by the averaging/dispersion effects and rapid photolysis losses for I₂ after its emission into the troposphere.



Figure 4.32 Summary of *in situ* measurements made above an *A. nodosum* seaweed bed on 10-06-2013. The panel contents are the same as Figure 4.26. The box indicates an anti-correlation between NO₂ and O₃ discussed in Section 4.7.3



Figure 4.33 Summary of *in situ* measurements made above an A. nodosum seaweed bed on 24-06-2013. The panel contents are the same as Figure 4.26

4.7.2 Iodine and its Tidal Dependencies

Figure 4.34 shows I_2 emission profiles from the *A. nodosum* experiments on 10-06-2013 and 24-06-2013 overlaid on the same plot. Similar I_2 emission profiles were observed for both *in situ* experiments, even though they were two different measuring sites. I_2 emissions increased gradually after exposure, peaking immediately prior to being recovered by the incoming tide. Peak concentrations were approximately three times the background levels. I_2 concentrations returned to background levels within 45 min of the seaweeds immediately below the boat being recovered. These observations correspond to those *in situ* measurements reported in literature from denuder data from Mweenish Bay, where I_2 levels peaked after several hours of exposure, in some cases reaching mixing ratios one order of magnitude higher than initial concentrations after 6 h.(91, 92)



Figure 4.34 I_2 emissions measured *in situ* above *A. nodosum* seaweed beds. Time = 0 corresponds to the time when the plants immediately below the sampling inlet were exposed by the outgoing tide

Figure 4.35 shows correlation plots of I_2 concentrations versus tide height for 10-06-2013 and 24-06-2013 overlaid on the same plot. The time series appear to match each other more closely when I_2 is plotted against time (Figure 4.34) than when it is plotted against tide height (Figure 4.35). This may indicate that desiccation time is a bigger driver than tide height when it comes to I_2 emissions. It is important to note than *A. nodosum* grows over a large tidal range (< 4 m to > 6 m). Therefore the outgoing and
incoming tide takes a long time to uncover and re-submerge neighbouring plants, whose emissions may also contribute to the measured I_2 emissions.

The iodine concentration profiles observed here increase more gradually relative to those observed over *L. digitata* beds, and peak at significantly lower concentrations (215 pptv compared to 2.08 ppbv). It is important to note that the experimental exposure times of *A. nodosum* were up to 6 times those observed for *L. digitata* and hence the total quantity of iodine emitted during one experiment is actually similar for both species. Integration of the area below the concentration vs. time emission profiles during times of exposure demonstrates how the modest concentrations of I₂ released by *A. nodosum* for a long time (126 mean, Table 4.3) are of a similar quantity to a strong short burst from *L. digitata* (99.5 mean, Table 4.2).



Figure 4.35 [I₂] vs. tide height for both A. nodosum in situ experiments

Date	10/06/13	24/06/13
Tidal minimum / m	2.17	0.894
Time exposed & submerged / hh:mm	11:31 - 16:45	10:29 - 16:53
Duration of exposure / hh:mm	05:15	06:24
Peak I ₂ / ppbv	0.215	0.180
Mean I_2 exposed to air / ppbv	0.143	0.104
Mean I2 under water / ppbv	0.0792	0.0472
[I ₂] (ppbv) \times Time (s) for duration of exposure	131	120
Average wind speed / ms ⁻¹	5.07	9.13
Average wind direction / °	151	283

Table 4.3 A summary of I_2 concentrations, wind measurements and tidal information recorded during both *in situ A. nodosum* experiments

A. nodosum plants at the sampling locations are also subjected to over 5 h exposure every day (Figure 4.34), compared to the seldom exposed *L. digitata* beds which are exposed for no longer than 2 h on a selection of days in each month (Figure 4.33) and it can therefore be assumed that their overall contribution to atmospheric iodine concentration is much larger. Table 4.4 provides a comparison of the percentage time in each month in which the seaweed plants directly below the BBCEAS instrument inlet were exposed to air. The tide heights at which seaweed plants were exposed were calculated from exposure times observed during experiments and the reported REFMAR tide heights.

 Table 4.4 The approximate percentage time at which seaweed plants are exposed to air

 per month at each boat experiment measurement site

Measurement site	Growing height at site (m)	Time uncovered (%) Sept 2012	Time uncovered (%) Nov 2012	Time uncovered (%) June 2013	
L. digitata	1.19	1.70	1.06	1.55	
Asco 1	4.79	44.10	41.28	42.40	
Asco 2	5.52	52.49	50.35	51.51	



June 2013: Tide height & L. digitata exposed to air

Figure 4.36 The tide height in Roscoff, France in June 2013, as measured by the REFMAR collection system with calculated exposure times for *L. digitata* growing at a range heights



Figure 4.37 The tide height in Roscoff, France in June 2013, as measured by REFMAR with calculated exposure times for *A. nodosum* growing at a range of heights

An anti-correlation between I₂ and O₃ was observed during the 24-06-2013 experiment (Figure 4.33). O₃ remained at a constant concentration of approximately 25 ppbv for the time period when the seaweed immediately below the sampling inlet was exposed to air. An immediate increase in O₃ concentrations of approximately 5 ppbv was observed to coincide directly with the re-submerging of plants and an immediate I₂ decrease of approximately 0.1 ppbv. NO₂ concentrations remained around the baseline, which appeared to rule out the reaction of O₃ with fresh pollution (NO + O₃ \rightarrow NO₂ + O₂) being the cause of this O₃ loss. The 5 ppbv loss in O₃ for only a 200 pptv increase in I₂ potentially suggests a dominant catalytic loss of O₃ and/or physical O₃ deposition over the more extensive *A. nodosum* seaweed beds. Anti-correlation between NO₂ and O₃ was observed for multiple NO₂ emission peaks on 10-06-2013 (Figure 4.32), most noticeably at around 11:02 where a peak NO₂ concentration of 17.0 ppbv was observed

to coincide with a 15 ppbv decrease in O_3 . At this time the wind was coming from an easterly direction and may therefore have transported emissions from the shipping port/shipping lane located approximately 2000 m in this direction. This theory was further supported through the observation of two ferries in dock when our research vessel "Aurelia" departed port at approximately 10:00. A significant increase in NO_2 (4.39 ppbv peak) was also observed to coincide with a modest decrease in O_3 concentrations of approximately 5 ppbv around 11:55 on 24-06-2013 (Figure 4.33). ASTAN measurements at this time show a wind emanating from a NW direction (towards Ile de Batz), with observations noted at the measurement site of a light wind from an approximate westerly direction but also from SE when very slack, with the potential of transporting emissions from the shipping port/path of the Ile de Batz ferry. Supporting evidence for fresh (shipping) pollution comes from aerosol spikes observed at the same time as NO_2 spikes because we expect shipping to produce both NO_2 and aerosol.

4.8 Aquarium Experiments

A series of desiccation experiments were performed in outside aquarium tanks, in order to recreate the *in situ* boat experiments under controlled conditions. Air was sampled from 0.12 m above submerged plants of a single species of known biomass, previously harvested and stored in the SBR aquarium. Water was then drained from the tank to expose the seaweed to air, before the tank was refilled with seawater to mimic the outgoing and returning tides experience by the plants when growing in situ. An advantage of this approach was the ability to measure I₂ emissions whilst retaining ambient temperature and light conditions. The main disadvantage was that the experimental setup was not a closed system and therefore whilst it was possible to measure the concentration of I2 above the seaweed plants, it was not possible to convert concentrations to emission rates (picomoles of I₂ emitted per min per gramme fresh weigh of seaweed, pmol gFW⁻¹ min⁻¹) for individual samples. A. nodosum samples were harvested from waters located between the SBR and Asco 1 and 2 boat experiment sites (Figure 4.20) and transported back to the aquarium in seawater. The A. nodosum were either used immediately or kept submerged in fresh, filtered, running seawater. L. digitata plants were collected during boat experiments and kept submerged for between 1 and 3 days in a neighbouring tank before the aquarium experiments.



Figure 4.38 Aquarium seaweed desiccation experiment: photograph and schematic of experimental setup

4.8.1 Laminaria digitata

A large spike in I_2 was observed when the plants were first uncovered during all *L. digitata* experiments (Figure 4.39). This was followed by an immediate slowing/stopping of emissions after 15 min. This profile corresponds with laboratory incubation experiments previously reported in literature (Section 5.2) and subsequently in this thesis (Section 5.5.1), which typically observed low activity when *L. digitata* plants were under water, followed by an immediate large spike after exposure and a rapid stopping/slowing of emissions. The spike and decline profiles observed during aquarium experiments can be explained by the localised and immediate desiccation effects of the concerted exposure to air of all plants in a flat-bottomed tank. In contrast the bell-shaped emission profiles observed around low tide *in situ* (Figure 4.28) can be assigned to the natural uncovering of plants at different times and the repeat desiccation and re-wetting of the plants by the lapping motion of the sea waves.

Sample	Number of		Mass (g)			Recovery time in aquarium since
date	plants	Total	Min	Med	Max	collection (days)
21/09/12	8	1400	15	117	334	3
22/09/12	11	1400	15	117	334	1
16/11/12 a	20	1351	4	224	224	1
16/11/12 b	21	1061	3	148	148	1



Figure 4.39 Measured I₂ concentrations and water heights during *L. digitata* aquarium seaweed desiccation experiments

4.8.2 Ascophyllum nodosum

The I_2 concentration profiles observed during the two *A. nodosum* aquarium experiments increased gradually following exposure with peak concentrations observed after 57 min (22-09-2012) and 48 min (18-11-2012). A sharp decline in emissions was observed following the re-submerging of plants in both experiments. I_2 concentrations observed *in situ* were more prolonged than those in the aquarium experiment and can be assigned to the natural uncovering of plants at different times by the out-going tide and the repeat desiccation by the sea waves. The difference between *A. nodosum* and *L. digitata* experiment time series were assigned to the differences in how often the species are exposed to the atmosphere by the outgoing tide which in turn determines how individual plants must store and emit iodine to combat oxidative stress.

Sample date	Total mass (g)	Recovery time in aquarium since collection (h)
22/09/12	5325	0
18/11/12	7475	0.5

Table 4.6 A. nodosum aquarium desiccation experiment sample details



Figure 4.40 Measured I₂ concentrations and water heights during *A. nodosum* aquarium seaweed desiccation experiments

4.9 Measurements of NO₂

This section combines BBCEAS measurements of ambient NO₂ and ASTAN meteorological data to establish the climatology of the environment at Roscoff. Previous RHaMBLe measurements of NO_x and wind direction and speed were recorded from a jetty located immediately to the north of the SBR during September 2006. Wind roses were produced (Figure 4.41) which show the largest ambient concentrations of NO corresponding with a wind from a SE direction and potentially resulting from emissions from the nearby town. NO₂ levels however were similar from both SE and SW directions, which indicated the influx of more processed polluted air. NO₂ concentrations between 1 and 2 ppbv were observed for winds from the NE direction, which did not pass over any land and were assigned to emissions from the ferry port located to the NE of the measurement site. NO_x levels were significantly lower from the NW but still at a higher than expected for marine background. Air from this direction may have passed over the Ile de Batz, an inhabited island 1 km NW of the measurement site.



Figure 4.41 NO_x and O₃ concentrations observed throughout the RHaMBLe campaign during September 2006 in Roscoff, France. The wind roses show concentrations of NO_x and the directions from which they result. The lower panel shows median diurnal cycles for NO (blue), NO₂ (red) and O₃ (black) for air that had broadly passed over the land from the south (filled symbols) and the sea from the north (open symbols). Figure from McFiggans et al.(85)

On the days of experiments in this study, the mean NO_2 concentrations measured by BBCEAS at the boat experiment locations ranged from 0.115 to 4.41 ppbv with a 1.37 ppbv overall mean. These pollution levels are low for urban centres but high for open ocean environments and indicate that the manmade emissions from the Roscoff town, local shipping (e.g. fishing, Isle de Batz foot passenger ferry) and ferry port may have a significant influence the coastal environment. Mean O_3 concentrations varied between 25 and 30 ppbv, levels typical for marine environments and consistent with those previously observed in Roscoff during the RHaMBLe campaign.(79)

The NO₂ and ozone time series recorded during measurements reported in this thesis are shown in and are summarised by Table 4.7. NO₂ concentrations obtained on 17-09-2012 have been omitted due to use of a petrol generator located on the boat during the experiment. The lowest peak NO₂ concentrations were observed on days when the wind was travelling over the sea from a mainly NW direction (18-09-2012, 19-09-2012 and 24-09-2013), corresponding to measurements made during the RHaMBLe campaign. A prolonged emission peak of between 1 and 2 ppbv for approximately 30 min was observed on 18-09-2012 (Figure 4.23) and was potentially indicative of well mixed pollutants. The days with the most structured NO₂ and aerosol extinction time series, (10-06-2013, 25-06-2013 and 26-06-2013) had a wind direction emanating from a N to NE direction, where emissions from the nearby ferry/shipping port were likely to be transported to the measurement site. Spikes in the aerosol absorption coefficient were observed on all experiment days, which often correlated with increases in NO₂ and were therefore attributed to local emissions.

Date	18-09-12	19-09-12	15-11-12	10-06-13	24-06-13	25-06-13	26-06-13	
Location		L. digitata		Asco 1	Asco 2	L. digitata		
Mean [NO ₂] (ppbv)	0.238	0.115	4.41	2.46	0.222	0.175	0.882	
Peak [NO ₂] (ppbv)	2.31	31 1.07 6.84		19.0	4.39	5.75	33.2	
Mean [O ₃] (ppbv)	-	-	-	24.6	25.1	29.8	26.4	
Mean wind direction (°)	318	293	47.6	151	283	27.6	47.2	
Mean wind speed (ms ⁻¹)	12.39	5.55	1.58	5.07	9.13	6.29	6.05	

Table 4.7 Summary of BBCEAS NO₂ and UV absorption O₃ measurements made during boat experiments

4.10 Conclusion

Extremely large I₂ concentrations were observed in situ above L. digitata macroalgae growing in their natural habitat. Observed peak concentrations (2.08 ppbv) at a 20 s integration time were significantly higher than those previously reported in literature (0.547 ppbv), owing in part to the deployment of a fast response instrument very close to the emission source. L. digitata and A. nodosum emission profiles were markedly different with significantly higher I₂ concentrations observed above L. digitata than over the A. nodosum seaweed beds. I₂ emission profiles over L. digitata species were strongly correlated with tide height, with peak concentrations observed around low tide. In comparison, measurements above A. nodosum observed a gradual build-up of collective emissions from plants, peaking immediately prior to the seaweed being resubmerged by the incoming tide. Controlled aquarium experiments, using pre-harvested L. digitata seaweed samples produced more immediate, short term emissions, similar to those of previous reported laboratory incubation experiments, resulting from a more immediate desiccation of plants than which occurs in situ. A. nodosum aquarium experiments showed a slower build up of emissions, similar to those observed during lab experiments and in situ. Despite high concentrations of I2, no OIO was observed above the BBCEAS instrument detection limits, which may indicate that our observations were made so very close to the emission sources that downstream chemistry (I2 photolysis, the reaction of IO with O3 and the IO self-reaction) had not yet had sufficient time to generate OIO. An anti-correlation between I_2 and O_3 concentrations was observed for certain experiments over both *L. digitata* and *A. nodosum* seaweed beds, with a 5 ppbv decrease in O_3 coinciding with peak I_2 concentrations of 1.01 and 0.180 ppbv, respectively.

5 Quantifying I₂ Emitted by Seaweeds: Laboratory Incubation Experiments

5.1 Introduction

As previously discussed in Section 1.3.3, seaweeds accumulate iodide from seawater and store it as an inorganic antioxidant to protect the algal thallus surface and cell wall against oxidative stress.(166) Courtois,(178) first discovered iodine, in the ashes of *Laminaria* and *Fucus* species of brown macroalgae in 1813. More recently, *Laminaria* species, and specifically *L. digitata*, have become the focus of numerous laboratory studies, because they are known prodigious accumulators of iodide: up to 30,000 times the concentration found in seawater and approximately 1% of their dry weight.(65) The release of molecular iodine (I₂) by seaweed was first observed in the nineteentwenties,(69, 70). More recently, seaweeds were assigned as the largest source of iodine in to the marine boundary layer (MBL) in coastal regions owing to the observation of significantly higher concentrations of I₂ than iodocarbons above exposed kelp beds, despite the more rapid photolysis rates of I₂.(47, 53)

Around low tides, macroalgae are exposed to the atmosphere for a period of time that depends on their growing height relative to the tidal minimum. On exposure, iodide (Γ) is released to the plant surface to combat stress factors experienced by the seaweed including tropospheric ozone (O₃), desiccation and high irradiance by sunlight (Section 1.3.3). The reaction of Γ with O₃ in the air, and/or with aqueous phase reactive oxygen species (ROS) such as H₂O₂ produced by the plants' own metabolism, results in the production of hypoiodous acid (HOI), which further reacts with iodide resulting in the emission of I₂ into the MBL. Simultaneous emissions of iodocarbons (RI) also occur but at a much smaller rate than I₂ and hence their influence on tropospheric chemistry is less significant. As discussed previously in Section 1.3.1, I₂ emissions significantly impact the gas phase chemistry of the MBL through their photolysis to iodine atoms, which subsequently react with O₃ to produce iodine oxide radicals (IO). The formation of IO has implications for the catalytic loss of O₃, partitioning reactions of HO_x (HO₂ \rightarrow OH) and NO_x (NO \rightarrow NO₂) species, and the nucleation of new iodine oxide particles (IOPs).

The emissions of I_2 from different species of seaweed therefore impact on both the key radical reactions of the troposphere and climate through the formation of new particles. Knowledge of the quantities of I₂ emitted by the major widespread species of seaweed is therefore essential to improve the understanding of these atmospheric processes and to inform future atmospheric modelling. Laminaria species are known to be the largest emitters of I₂, as observed through the in situ measurements of atmospheric I₂ reported in Section 4.6 of this thesis and in other previous in situ and laboratory incubation experiments reported in literature. Other brown algae, including Ascophyllum nodosum (Section 4.7), Saccharina latissima and Fucus species (e.g. F. vesiculosus and F. serratus) emit I_2 at lower concentrations but the mechanism by which I_2 is emitted may differ significantly from species to species. Such differences were evident from the contrasting I₂ concentration profiles shapes and peak I₂ concentrations observed in situ above L. digitata and A. nodosum in Chapter 4 of this thesis. The fraction of time that a seaweed plant is exposed to the atmosphere per tidal cycle (lunar month) will also vary significantly from species to species. This will potentially have a significant impact on the amount of I2 released into the MBL by an individual species and its relative contribution to the atmospheric chemistry of iodine.

In situ observations directly above seaweed beds are scarce owing to the logistical difficulties of locating and operating the sampling instrument. Important exceptions include the denuder data of Huang et al.(91, 92) Most measurements of atmospheric I_2 are made some distance from the source, hence the observed I_2 concentrations are reduced by dilution and photolysis.(93) Meteorological factors including wind speed and direction, the distance of measurements from the emission source and the intensity of sunlight/cloud cover can all impact the concentrations of I_2 observed at the measurement site as previously discussed in Section 4.2. *In situ* measurements reported in the literature are also often non-species specific, as seaweed beds often contain a mixture of species and plants of different ages, health and conditions. It is therefore extremely difficult to quantify emissions from individual seaweed plants from I_2 concentrations observed *in situ* and thus the determination of accurate emission rates requires the use of a closed system and a known sample composition. A number of laboratory incubation experiments have been reported in literature, which enabled the quantification of species dependent Γ contents and I_2 emissions.

5.2 A Review of Seaweed Laboratory Measurements

The first quantification of the accumulation of iodide by different species of seaweed was performed by Eschle in 1897,(179) who investigated the iodine content of F. vesiculosus (0.02 % DW) and L. digitata (0.37 – 0.75 % DW). Since then a number of laboratory incubation experiments have reported the Γ content and I₂ emissions of various macroalgal species. With I₂ having been identified as the most important source of reactive iodine in the coastal troposphere, (47) the earlier laboratory studies tended to focus on I_2 emissions from L. digitata, owing to the high Γ content of its biological material and intense I₂ emission rates. Kupper et al.,(65) and Gall et al.,(66) observed the average accumulation of iodide by seaweed of about 1% of their dry weight. They also demonstrated that brown macroalgae, specifically L. digitata were the strongest accumulators of iodine among all marine biota, with the potential to volatilise significant concentrations of reactive iodine into the troposphere. Palmer et al.,(180) investigated the release of halocarbons and I₂ emissions from L. digitata plants as a response to chemical stresses, specifically H₂O₂, O₃ and a solution of oligoguluronates, known to elicit an oxidative burst in brown algae. Maximum I2 emissions were observed in the presence of O₃, which were at significantly higher levels than those of iodocarbons in response to atmospheric levels of O₃. I₂ emission rates measured from unstressed plants peaked at 3.7 pmol gFW^{-1} min⁻¹ and particle formation was only observed in the presence of O3. These results indicated that emissions of I2 as opposed to organic iodine released by exposed seaweeds were the major source of iodine initiated new particle formation in coastal regions. A further study by Sellegri et al.,(181) as part of the BIOFLUX campaign, observed a direct correlation between particle number concentrations and I₂ emitted from seaweeds collected at Mace Head, Ireland. Concentrations of particles and gas phase I₂ concentrations also showed a direct positive correlation with seaweed mass (Figure 5.1), with 24 pptv of I₂ observed per kg of seaweed (0.797 pmol min⁻¹ gFW⁻¹).



Figure 5.1 Positive correlation observed between total and 3 - 3.4 nm particle concentration, I_2 and seaweed mass observed during chamber experiments by Sellegri et al.(181)

Using x-ray absorption spectroscopy (XAS), Kupper et al.,(166) showed that the only detectable form of iodine stored in *L. digitata* plants was the iodide ion (Γ). This study also demonstrated that the detoxification of O₃ and aqueous oxidants by Γ , occurred on the thallus surface and in the apoplast (cell wall) of the seaweed plant. Emissions of I₂ and subsequent particle formation were again observed following the exposure of seaweed to air and the reaction of Γ with O₃.

The first interspecies comparison of I_2 emissions was performed by Ball et al.(124) This study used BBCEAS to make fast time resolution (7.5 s) measurements of the I_2 emissions from seven species of seaweed (*L. digitata*, *L. hyperborea*, *S. latissima*, *A. nodosum.*, *F. vesiculosus*, *F. serratus* and *Dictyopteris membranacea*) harvested in Roscoff, France. Significant differences were observed between both the quantity and profile of I_2 emissions for different species. The two *Laminaria* species (*L. digitata* and *L. hyperborea*) were observed to be the largest emitters, producing an intense initial emission when first exposed to air (Figure 5.2). Very large emissions of up to 26.9 ppbv of I_2 and additional particle formation were observed during an additional set of *L. digitata* stress experiments, where O_3 (90 ppbv) and oligoguluronates (recognised by algae as pathogen attack indicator) were present.



Figure 5.2 Time series of I₂ mixing ratios and emissions rates observed from *L. digitata* and *L. hyperborea* by Ball et al.(124) The insets show I₂ mixing ratios plotted on a logarithmic scale

 I_2 emissions from *A. nodosum* and *S. latissima* samples were significantly lower and displayed broader emission profiles (Figure 5.3). No I_2 emissions were observed for *Fucus* species (*F. vesiculosus* and *F. serratus*) and *D. membranacea* above the instrument detection limit of 25 pptv.



Figure 5.3 Time series of I₂ mixing ratios and emissions rates observed from *A. nodosum* and *S. latissima* by Ball et al.(92)

An overall ranking of species was established based on the emission rates of I_2 from plants exposed to ambient air: *D. membranacea* < *F. serratus* < *F. vesiculosus* < *A. nodosum* < *S. latissima* < *L. digitata* < *L. hyperborea*. These findings are further discussed and compared with those of another study by Kundel et al.(182) in Table 5.1 later in this subsection. I_2 emission rates from plants with varying levels of decomposition were also compared: for example, mean I_2 emission rates of 0.55, 0.055 and 0.015 pmol min⁻¹ gFW⁻¹ respectively were observed for healthy, partly decayed and decayed plants of *S. latissima*, suggesting that healthy plants emit more strongly. In sharp contrast, mean I_2 emission rates from a partly decayed *L. hyperborea* plant (19.3 pmol min⁻¹ gFW⁻¹) were 29 times higher than those observed for a healthy plant (0.67 pmol min⁻¹ gFW⁻¹). These results suggest different species and different plants within the same species have different I_2 emission responses depending on the stress factors and/or the plants' health.

Dixneuf et al.,(123) later performed a series of air chamber experiments on *L. digitata*, harvested from Cork Harbour in southern Ireland. Emissions of I_2 were initiated by exposing the plants to ambient air and were measured at a 10 s integration time by BBCEAS. High variability was observed across all long-term experiments (n = 16): all samples emitted intense bursts of I_2 but the emission profiles were not reproducible between samples. Figure 5.4 shows two examples of time series from Dixneuf et al.(123) One sample in Figure 5.4(a) shows a quasi-regular repeating pattern of bursts (at 25 min intervals), whereas another sample (Figure 5.4(b)) shows few, larger bursts with no obvious pattern. The authors proposed that keeping seaweed plants in a closed tank potentially enabled the rapid increase of bacteria and hence artificially influenced stress levels experienced by the seaweed but these conditions may represent those experienced by seaweed plants growing in rock pools.



Figure 5.4 Time-dependences of the I₂ mixing ratio [nmol mol⁻¹] from *L. digitata* reported by Dixneuf et al.(123) The inserts show the first 30 min of measurements. The traces left and right of the vertical dashed lines refer to the scales on the left and right axes respectively. The traces are connected at the dashed line

Nitschke et al.,(125) investigated the emission of I₂ from specific regions of *L. digitata* plants (the stipe, the meristematic area and the distal blade, shown in Figure 5.5) under low light and dark conditions. I₂ was again quantified by BBCEAS (detection limit $\approx 7 \pm 2$ ppbv at a 10 s integration time). All thallus parts exhibited emission profiles

similar to those previously observed for whole plants with large I_2 emissions appearing immediately after air exposure. I_2 emission rates of all thallus parts were then significantly reduced by 70 – 80% between 60 and 180 min of exposure. The stipes were observed to emit ten times the amount of I_2 (molar ratio) than for the meristematic area and the distal blade. I_2 emission rates measured within the first 30 min of exposure to air were highest for stipes (median values: 2999 and 5222 pmol gDW⁻¹ min⁻¹ in low light and dark, respectively) and one order of magnitude higher than those measured from both the meristematic area and distal blade. A high variability of I_2 emission rates produced by samples of the same species was again observed with reported values ranging from 3 to 14,976 pmol min⁻¹ gFW⁻¹.



Figure 5.5 I₂ emissions rates vs. time for different parts of the thallus of the strongest I₂ emitting specimens of *L. digitata* exposed to air in both low light (a) and dark (b) conditions

Ashu-Ayem et al.,(126) performed an extensive study of I₂ emissions from twenty-five *L. digitata* samples using BBCEAS to detect I₂ (30 s integration time). The authors characterised the emission profiles into four distinct stages (1) moderate emissions when the plant was partially submerged; (2) large emissions when the plants were fully exposed; (3) a slowing or stopping emissions; and (4) later pulses of I₂ for some samples. Emission rates again displayed high sample-to-sample variability and ranged between 7 – 616 pmol min⁻¹ gFW⁻¹ in O₃-free air (median value of 55 pmol min⁻¹ gFW⁻¹ observed over 20 samples). As for Ball et al.,(124) a relationship between increased O₃ concentrations and I₂ emission rates was not observed and was again potentially masked by the high variability between individual samples.



Figure 5.6 Iodine emission profiles (black) and calculated emission rates (blue) of two *L*. *digitata* plants in experiments performed by Ashu-Ayem et al.(126) The four stages of the iodine emission profile described in the above paragraph are shown in the gray shaded area above the plot

A further interspecies comparison of I_2 emissions was presented by Kundel et al.,(182) who determined the emission rates and profiles of eight different seaweed species using time-of-flight mass spectrometry (ToF-MS) to quantify I_2 at a 2.5 min integration time (detection limit of 250 pptv at a time resolution of 1 min). Figure 5.7 shows time profiles for six seaweed species (*Chondrus crispus* and *Delessaria sanguinea* were close to or below detection limit and are not shown). Total iodine content of the seaweed samples was determined through microwave-assisted tetramethylammonium hydroxide extraction followed by inductively coupled-plasma MS analysis. Table 5.1 compares the mean and peak emission rates measured by Kundel et al.(182) with those from Ball et al.(124)



Figure 5.7 Time-resolved I₂ emission profiles from six different seaweed species at 50 ppbv O₃ harvested at Helgoland measured by ToF-MS (by Kundel et al.)(182)

Experiment	I ₂ emission rates (pmol n	nin ⁻¹ gFW ⁻¹)	I ₂ emission rates (pmol min ⁻¹ gFW ⁻¹)			
details	by Ball et al.(12	24)	by Kundel et al.(182)			
Spacios	Sample means exposed to	Sample	Mean of samples exposed	Species		
species	air for < 60 min	peaks	to air for 60 min	peak		
D.membranacea	0.0012	Below DL	N/A	N/A		
F. serratus	0.0039	Below DL	0.648	1.25		
F. vesiculosus	0.0079	Below DL	0.308	1.35		
A. nodosum	0.063 0.104		1.15	2.3		
S. latissima	0.55.0.055.0.015	1.01, 0.099,	2 19	53		
5. <i>iaissina</i> 0.55, 0.055, 0.015		N/A	2.17	5.5		
L. digitata	3.17	9.03	2.66	20.2		
L. hyperborea	19.3 and 0.67	35.6 & 5.45	2.79	42.1		

Table 5.1 Comparison of I_2 emission rates measured for different species in laboratory incubation experiments by Ball et al.,(124) and Kundel et al.(182)

Laminaria species were again observed to emit large quantities of I_2 immediately following exposure to air, which quickly decreased within 20 min. *S. latissima* and *F. serratus* emissions peaked within 30 min of exposure and were followed by a more gradual decrease than observed for the *Laminaria* species. *A. nodosum* and *F. vesiculosus* emissions increased gradually with time and leveled off after 45 and 90 min respectively. The gradual increase in emission rates with exposure time observed for *A. nodosum* and *F. vesiculosus* again indicated that they may have a much more substantial impact on I_2 concentrations in the MBL than was previously determined, and may explain particle formation previously observed at Mweenish Bay, Ireland, where they are the dominant species.(91) Similar emission trends were observed for indocarbon emissions, however their emission rates were one or two orders of magnitude lower than those of I_2 .

It is notable that, notwithstanding sample-to-sample variability and the different geographical locations (Helgoland, Germany versus Roscoff, France), Kundel et al.,(182) produced the same ranking of species based on their emission rates as Ball et al.,(124) (*F. vesiculosus/F. serratus < A. nodosum < S. latissima < L. digitata < L. hyperborea*). Quantitatively, the mean and peak emission rates agree well for the kelp species across these two studies. The emission rates observed by Kundel et al.,(182) are an order of magnitude larger for the *Fucus* sp. and for *A. nodosum*. However, as will be confirmed by the results in this thesis (Section 5.5), emissions from these seaweed species typically peak one hour after exposure to air, whereas Ball et al.,(124) recorded emission profiles for these species lasting only \approx 20 minutes and thereby likely underestimated the true emission rates.

A recent study by Huang et al., (92) measured I_2 emissions from *A. nodosum*, *F. vesiculosus* and *L. digitata* seaweed plants harvested at Mweenish Bay, Ireland. Denuder sampling with GC-MS quantification was applied to chamber experiments where samples were exposed to ambient air containing O_3 at concentrations between 35 - 40 ppbv. Figure 5.8 shows emissions within periods of up to 20 min and is a natural consequence of the detection method being less sensitive that previous BBCEAS studies. Early and late 5 - 20 min bins were selected for comparison to show the gradual build up of *A. nodosum* and *F. vesiculosus* emissions over time and the immediate bursts of *L. digitata*. Emissions measured from *A. nodosum* and *F. vesiculosus* after a prolonged exposure (up to 360 min) were observed to be comparable with those from *L. digitata* after their initial exposure period of 20 - 30 minutes and the authors emphasised the importance of considering non-*Laminaria* species as a significant source of reactive iodine species in the MBL.



Figure 5.8 Time-dependent I₂ emission rates of *A. nodosum*, *F. vesiculosus* and *L. digitata* at daytime and nighttime when exposed to ambient air in a flow chamber at Mweenish Bay by Huang et al.(92)

5.3 Aims of this Study

A significant proportion of reported seaweed laboratory studies have focused on L. digitata plants as a result of their high intensity I_2 emissions produced immediately following exposure to air. The observed emission profiles are broadly consistent across collection locations: emissions from most L. digitata samples are characterised by an immediate strong release when first exposed to air, followed by an approximately exponential decline and an eventual slowing/stopping of emissions. However, only a few laboratory studies have characterised I2 emissions from a variety of seaweed species, and such studies are often limited by small sample sizes (i.e. few repeats) and a lack of sample characterisation (e.g. Γ content, how long the seaweeds have been kept since harvesting and how well the storage conditions mimicked their natural growing conditions). Emission profiles are also often not measured over exposure times as long as those experienced by the seaweed species when exposed by tidal cycles in their natural habitats. Also to date, there has been no investigation into (i) whether I₂ emissions from different species vary with season, or (ii) whether emissions from plants of the same species vary depending on where the plants are growing within the tidal range.

This chapter presents results from an extensive laboratory study of I₂ emissions from five seaweed species (two Fucales, A. nodosum and F. vesiculosus, and three kelp species, L. digitata, L. hyperborea and S. latissima). Results are also presented from a small number of other experiments involving F. serratus, Dictyopteris membranacea and Grateloupia turuturu. A total of eighty-three incubation experiments were performed at the Station Biologique in Roscoff (Brittany, France) in September 2012, November 2012 and June 2013 to quantify species-dependent I₂ emission rates in response to progressive air exposure, mimicking low tide, and to investigate any seasonal differences. The mixing ratios of I₂ produced by individual seaweed samples were recorded by BBCEAS using a 5 s integration time and averaged to 20 s for reporting in this chapter, enabling highly detailed I₂ emission rate profiles to be obtained for each sample. The breadth of this study aimed to provide detailed statistical information on the variability in the emission profiles and total I₂ amounts across multiple samples of the same species. It also considered how the emission profiles and I₂ amounts changed with species, season, growing height and total iodine content of the algal samples. The results have applications for quantifying iodine fluxes into the atmosphere and for investigations into the physiology of macroalgae.

5.4 Experimental

The same BBCEAS hardware was deployed for these laboratory experiments as for the *in situ* experiments detailed in Section 4.3.2. The equipment was powered from the laboratory's 230V AC mains wall sockets in place of the portable battery power supply. The same wavelength calibration and spectrometer line shapes determined for the HR4000 spectrometer in Section 4.3.3 were applied to measurements in this chapter. The same methods were applied to determine the dark current corrections and mirror reflectivity as reported in Section 4.3.4 and 4.3.5 respectively. Dark current spectra, N₂ purge spectra and O₂ and He calibration spectra were recorded both immediately before and after BBCEAS spectra sampling the I₂ emissions from each individual seaweed sample. The detection limits reported in Section 4.3.7 also apply to measurements reported in this chapter.

5.4.1 Sample Collection

Experiments were conducted in the visitors' laboratory on the ground floor of the Station Biologique de Roscoff (SBR) in Brittany, France. The SBR building is located within approx. 20 metres of the shoreline. This location enabled the collection of fresh samples, directly for their natural growing habitat. The experiments also benefitted from the local expertise to identify the best sites to harvest seaweeds and on-site facilities for handling and storing seaweed samples. Experiments were conducted using fresh, fully-intact seaweed samples collected from a variety of locations and growing heights, spanning most of the Station Biologique de Roscoff (SBR) inter–tidal zone (Figure 5.9). Samples were labelled in the format '*Species_xy*' where *x* referred to the month (x = no number for September 2012, 2 for November 2012 and 3 for June 2013) and *y* increased sequentially with the number of samples analysed. For example, the second *A. nodosum* sample analysed in June 2013 was labelled '*asco_32*'. If a repeat analysis of the same sample was performed, the sample was labelled '*asco_32*'.



Figure 5.9 (a) General collection locations for samples used in laboratory incubation experiments in relation to the SBR, aquarium and *L. digitata* boat experiment site.
Rectangle shows approximate range of *A. nodosum* and *F. vesiculosus* samples. (b)
Collection locations, as recorded by GPS, for selected samples used in laboratory incubation experiments during June 2013

The majority of A. nodosum and F. vesiculosus thalli and some samples of S. latissima were collected whilst still submerged on an ebbing tide, from the beach or rocky outcrop directly in front of the SBR (white rectangle, Figure 5.9(a)). These samples were transported back to the laboratory in a bucket of seawater. Most samples were used immediately; where this was not possible the samples were stored in an outdoor aquarium, like the kelp samples below. All L. digitata and L. hyperborea and some S. latissima samples were collected by the SBR Service Mer from deeper waters not accessible by foot or collected from the same site as the in situ boat experiments (L. digitata, Figure 5.9(a)). The kelp samples were stored in an outdoor aquarium, submerged in running, filtered seawater, and were analysed within a few days of collection. Storage in the aquarium meant that the seaweed samples were not exposed to oxidative stress and continued to experience both ambient light and temperatures. Analysis of all samples took place immediately following their transport from the beach/aquarium to the laboratory. Time between sample collection and the start of sampling was approximately 10 to 15 min, during which time the sample remained completely submerged by seawater and was not exposed to air. Experiments were conducted under ambient light levels. The 10 L translucent Nalgene sample bottle was placed next to the laboratory's window but shaded from direct sunlight (a window blind was used to block sunlight entering through the laboratory's West-facing windows in the late afternoon). Experiments were generally performed with the room lights turned off, except for experiments that begun in the late evenings (all visits) or early mornings in November. For overnight experiments involving F. vesiculosus or A. nodosum, the room lights were turned off after we departed the laboratory. The SBR laboratory was well ventilated with temperatures ranging from 19.0 - 24.0°C (21.0°C mean) in November 2012 and 18.0 – 25.5°C (20.6°C mean) in June 2013. Temperatures were recorded in November and June by an EL-USB-2 temperature and RH logger (RS components, 490-1064). Room temperature was lowest in the early morning and increased through the day, especially in the mid-afternoon when the lab was illuminated by sunlight through its large West-facing windows. Ambient ozone concentrations in the laboratory were recorded by model 202 ozone monitor (2B Technologies) during experiments in June 2013 with measured concentrations ranging from 3 - 55 ppbv (23.5 ppbv mean).

5.4.2 Laboratory Incubation Experiments

A total of eighty-three experiments on eight different species of seaweed were performed on three visits to the SBR between September 2012 and June 2013 (Table 5.2). Samples were characterised by their species, season of harvesting, fresh weight, estimated growing height and measured iodide content (Table 5.3).

Table 5.2 The	number of	laboratory	incubation	experiments	conducted	on each	seaweed
in each season							

Species	Number of experiments							
species	Sept 2012	Nov 2012	June 2013	Total				
Fucus vesiculosus	3	3	5	11				
Ascophyllum nodosum	6	6	13	25				
Saccharina latissima	3	3	4	10				
Laminaria digitata	6	3	9	18				
Laminaria hyperborea	4	2	9	15				
Fucus serratus	1	0	1	2				
Dictyopteris membranacea	1	1	0	0				
Grateloupia turuturu	2	0	1	0				
Total	26	18	42	83				

Table 5.3 Summary of fresh weight, growing height and iodide content of samples used in
the laboratory incubation experiments during all seasons (minimum, median, maximum)

Spacies	Fresh weight (g)			Estimate	Iodide content (ppmv)				
species	Min	Med	Max	Min	Max	Mean	Min	Med	Max
Fucus vesiculosus	311	452	1076	2.61	5.13	3.94	8	52	259
Ascophyllum nodosum	378	587	1413	3.77	6.25	4.86	35	296	4200
Saccharina latissima	51	88	305	1.19	1.87	1.42	552	2862	5219
Laminaria digitata	6	152	462	-	1.19	1.19	2349	6308	13091
Laminaria hyperborea	11	77	208	-	1.19	1.19	1010	3430	10262
Fucus serratus	412	773	593	-	2.21	2.21	-	-	71
Dictyopteris membranacea	-	-	210	-	-	-	-	-	107
Grateloupia turuturu	-	-	193	-	-	-	-	-	105

Seaweed samples were contained inside a 10 L Nalgene bottle (actual volume 11.2 litres). Ambient "laboratory" air was drawn through the bottle, into the BBCEAS cavity, and exhausted through a mass flow controller connected to the diaphragm pump on the BBCEAS instrument (3.6 slpm flow rate; residence time inside Nalgene bottle =

2 min 47 s). A Teflon tube (6.35 mm external diameter, approx 2 m length) conveying gas to the cavity was connected through a fitting in the Nalgene bottle's screw cap. The bottle's screw cap contained a second fitting, which was open to allow gas sampled into the cavity to be replenished with ambient air.

Sampling began with seaweed samples fully submerged in seawater (Figure 5.10a). Water was drained after 15 min (b), exposing the sample to desiccation effects and mimicking the effects of the outgoing tide. Samples were exposed for up to 360 min (c), and when possible, for exposure times relative to the typical time period that the plants are exposed in their natural habitat. The samples were then re-submerged in fresh seawater (d). Fresh weights of individual seaweed samples were determined by weighing the sample on an electronic balance immediately following incubation experiments, after first shaking any excess seawater from the sample. Samples were then immediately labelled, frozen at -20° C and stored to enable future analysis of the samples' iodide content.



Figure 5.10 Schematic of the desiccation and re-submerging of seaweed samples during laboratory incubation experiments

The concentration of I_2 (mol mol⁻¹) in the bottle headspace was measured continuously during steps (a) to (d) by BBCEAS at an integration time of 20 s. I_2 mixing ratios (mol mol⁻¹) were converted to emission rates (pmol min⁻¹ gFW⁻¹) through Equation 5.1, where *n* was the number of molecules per cm³, as determined through the Ideal Gas Law, the *flowrate* was determined by the BBCEAS pump (3600 cm³ min⁻¹), and *FW* was the fresh weight of the seaweed sample in grams. Figure 5.11 shows the conversion of I_2 mixing ratio to emission rate for an example *A. nodosum* incubation experiment time series.

Equation 5.1



Figure 5.11 An example of the conversion between I₂ mixing ratio and emission rate. Time series for the *A. nodosum* incubation experiment performed on 07-06-2013 (asco32)

This thesis uses box and whisker plots to present the maximum, minimum (coloured circles) and median (black line) emission rates observed for an individual or groups of samples. Such plots are a convenient way to visualise the often high variability in I_2 emission rates. The box represents the interquartile range and is constructed from the upper (75th percentile) and lower quartile (25th percentile). Percentiles indicate the value below which fall a given percentage of observations in a group of observations.

5.4.3 Iodine Content Determination

Immediately following their use in an incubation experiment, seaweed samples were labelled and stored frozen at -20° C. The samples' total iodide contents were later determined at the Departement d'Analyse Elementaire, Service Central d'Analyses, Centre National de la Recherche Scientifique (Vernaison, France) through the same

method as deployed by Kupper et al.(67) Briefly: after complete combustion in a Schoninger flask, the ashes of each individual seaweed sample were analysed using established anion-exchange chromatography techniques, with UV detection employed to determine concentrations of iodide relative to the dry weight of the sample. Iodine contents reported here for *L. hyperborea*, *L. digitata* and *S. latissima* were obtained through analysis of the blade of the plant.

5.4.4 Growing Height Determination

Growing heights relative to the tidal datum, as reported in Table 5.3, were estimated as follows. Most samples harvested "on foot" from the beach in front of SBR were collected whist still submerged in 10 to 50 cm of seawater on an ebbing tide; the water depth and time of collection were noted. Tide height measurements from REFMAR,(173) were then used to find the height of the tide above datum at the time when a sample was collected. REFMAR measurements are made every 10 minutes; tide heights at intermediate times were obtained from an interpolation (cubic spline) through the REFMAR data. The growing height of the seaweed sample was calculated by subtracting the water depth noted at collection from the tide height given by REFMAR. The growing height of A. nodosum and L. digitata, L. hyperborea and S. latissima samples collected from the same sites as the in situ boat experiments were obtained by noting the times the seaweeds immediately surrounding the boat were uncovered and recovered by the tides, and then finding the tide height at those times in the REFMAR dataset. The uncertainty in these methods is estimated to be ± 10 cm for the June 2013 samples and for samples from boat measurements sites on all three visits. The growing heights of samples collected "on foot" in the September and November 2012 visits are larger (est ± 50 cm) owing to the less detailed notes made of the water depth and precise time when the samples were collected. Estimated growing heights are reported for these samples only where collection notes contain sufficient information to merit an estimate and/or to closely co-locate the sampling site to a location used again in June 2013. Additionally the GPS location of sampling sites in June 2013 were measured using a handheld GPS instrument (Garmin GPS map 76CSx) – see Figure 5.9(b). The GPS instrument also reported a height above sea level, however its stated accuracy of 3 m was too coarse to be useful in this study. Indeed the GPS instrument commonly reported differences of 4 m for samples harvested from the same location on different days. A detailed analysis of the seaweeds' I_2 emission rates against the samples' growing heights is reported in Section 5.6.3.

5.5 Results from laboratory incubation experiments

The I_2 emission profiles produced by individual seaweed samples are presented in Sections 5.4.1 to 5.4.6; one section for each species. The time series are further grouped based on the month of analysis (e.g. September 2012, November 2012 and June 2013) and peak I_2 emission rates (if required) to aid interpretation. We begin with *L. digitata*, previously the most widely studied species.



Figure 5.12 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from *L. digitata* samples in September 2012 (top two panels), November 2012 (third panel) and June 2013 (bottom two panels)

The typical I_2 emission profile observed for the majority of *L. digitata* samples consisted of an intense immediate rise in I_2 emissions soon after exposure, broadly consistent with profile previously reported in the literature.(123-126, 182) Peak emission rates were typically observed in either a single broad peak or multiple short high intensity bursts within the first 30 min after exposure. A rapid decrease in emissions was then observed until up to 60 min of exposure, where emission rates became approximately 10% of peak emissions. During further exposure from 60 to 180 min, emission rates remained relatively constant, with additional short intense emission bursts observed for some samples at irregular intervals. Samples which did not emit their I_2 starting with a large initial burst were generally lower emitters (peak I_2 emissions < 1.08 pmol min⁻¹ gFW⁻¹) and were only seen in June 2013.

The amount of I₂ emitted by *L. digitata* samples was highly variable during all three months, with peak I₂ emission rates for individual samples ranging between 0.386 – 62.5 pmol min⁻¹ gFW⁻¹. No seasonal trends were observed in peak emissions. The box and whisker plots for individual samples in Figure 5.13 shows that the scatter of results within each season is as large as the scatter across all seasons. I₂ emission rates were typically most intense soon after exposure: between 0 – 60 min the mean emission rate calculated from all data shown in Figure 5.12 was 2.81 pmol min⁻¹ gFW⁻¹, compared to a mean of 1.03 pmol min⁻¹ gFW⁻¹ in the following 60 – 120 min period and a mean of 1.41 pmol min⁻¹ gFW⁻¹ between 120 – 180 min. These peak and first-hour mean values are consistent with emission rates recorded in the first 20 - 52 min of exposure by Ball et al.,(124) (peak I₂: 4.27 – 22.1 pmol min⁻¹ gFW⁻¹, mean I₂: 2.59 pmol min⁻¹ gFW⁻¹, mean I₂: 2.66 pmol min⁻¹ gFW⁻¹).



Figure 5.13 Box and whisker representation of I₂ emission rates from *L. digitata* samples for (a) 0 to 60 min and (b) 0 up to 180 min of exposure to air





Figure 5.14 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from *L. hyperborea* samples in September 2012 (top two panels), November 2012 (third panel) and June 2013 (bottom two panels)
I₂ emission profile shapes produced by *L. hyperborea* samples were generally similar to those observed during *L. digitata* experiments in the previous subsection and for other *L. hyperborea* samples in literature.(124, 182) An intense immediate rise in I₂ emissions was observed, soon after exposure, which typically peaked within 15 min. I₂ emissions decreased to approximately 14% of peak emissions within 120 min of exposure. Additional short intense emission bursts were observed for some samples at irregular intervals. Some seasonal differences were observed between the emission profiles. Samples in June 2013 generally produced strong initial bursts of I₂, similar to those observed for *L. digitata*. Emission profiles produced in September 2012 also contained strong bursts but they occurred 15 to 60 min after exposure (with the exception of lami_h2). Samples in November 2012 didn't produce their largest emission levels until after the first 60 min. After this point, lami_h22 emissions reach a similar intensity to those observed for samples in the other months and lami_h21 remains a low emitter throughout the experiment.

The intensity of emissions were significantly higher than those observed for *L. digitata* samples, with peak emissions observed between 3.31 - 221 pmol min⁻¹ gFW⁻¹. The highest emission rates were typically observed between 0 - 60 min (mean = 10.2 pmol min⁻¹ gFW⁻¹), compared to between 60 - 120 min (mean = 5.49 pmol min⁻¹ gFW⁻¹) and 120 - 180 min (mean = 4.40 pmol min⁻¹ gFW⁻¹) of exposure. The measured emission amounts corresponded with those reported by Ball et al.,(124) in up to 57 min of exposure (peak I₂: 5.45 - 35.6 pmol min⁻¹ gFW⁻¹, mean I₂: 10.32 pmol min⁻¹ gFW⁻¹) and the first 60 min of exposure by Kundel et al.,(182) (peak I₂: 42.1 pmol min⁻¹ gFW⁻¹, mean I₂: 2.79 pmol min⁻¹ gFW⁻¹). Figure 5.15 shows the distribution of I₂ emission rate data for the individual *L. hyperborea* samples recorded over the first 60 and up to 180 min of exposure to air.



Figure 5.15 Box and whisker representation of I₂ emission rates from *L. hyperborea* samples over (a) 0 to 60 min and (b) 0 up to 180 min of exposure to air



Figure 5.16 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹) from *S.latissima* samples in September 2012 (top panel), November 2012 (middle panel) and June 2013 (bottom panel)

The I₂ emission rate profiles produced by *S. latissima* differed significantly from *L. digitata* and *L. hyperborea*. They are characterised by intense bursts of I₂ occurring at irregular emission rates and exposure times. Only one sample, lami_s33 (June 2013), produced an initial strong emission burst. Peak I₂ emission rates ranged from 0.209 – 8.14 pmol min⁻¹ gFW⁻¹ and were typically observed between 0 – 120 min of exposure to air. Mean I₂ emission rates of 0.587, 0.672 and 0.642 pmol min⁻¹ gFW⁻¹ were observed between 0 – 60 min, 60 – 120 min and 120 – 180 min of exposure, respectively. All three samples analysed in November produced similar emission profiles, with repeating bursts of I₂ observed at approximately 15 min intervals during the first 120 min of exposure. The emission profile shapes observed here correspond to

those observed by Kundel et al.,(182) which peaked at 5.3 pmol min⁻¹ gFW⁻¹ after 7.5 min of exposure and showed further irregular bursts of a lower intensity. Ball et al.,(124) observed similar average emission rates recorded up to 36 min of exposure (mean peak I₂: 0.555 pmol min⁻¹ gFW⁻¹, mean I₂: 0.206 pmol min⁻¹ gFW⁻¹). Figure 5.17 shows the distribution of I₂ emission rate data recorded for individual *S. latissima* samples over the first 60 and up to 180 min of exposure to air.



Figure 5.17 Box and whisker representation of I₂ emission rates from *S. latissima* samples over (a) 0 to 60 min and (b) 0 to up to 180 min of exposure to air



Figure 5.18 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from *A. nodosum* samples in September 2012 (top two panels), November 2012 (third panel) and June 2013 (bottom two panels)

A. nodosum is the most extensively studied species in this work. The A. nodosum I_2 emission rate profiles differed significantly from those observed for L. digitata, L. hyperborea and S. latissima. A typical emission profile was broad, consisting of a gradual increase in I_2 emissions following exposure to air, a peak in the emissions between 60 and 180 min after exposure, and a subsequent decline to modest emission rates at long exposure times (less than a quarter of peak emissions after 240 min exposure). Often (and particularly for the samples in June 2013), irregular spikes/bursts were superimposed on the broad emission envelope; in some cases this structure was present for the full 360 min of exposure.

Emission rates typically peaked between 60 and 180 min (mean I_2 : 0.586 pmol min⁻¹ gFW⁻¹) compared to 0 - 60 min (mean I₂: 0.208 pmol min⁻¹ gFW⁻¹) and 180 - 360 min (mean I₂: 0.172 pmol min⁻¹ gFW⁻¹). High variability was observed between individual samples with peak emissions ranging between 0.0107 -4.86 pmol min⁻¹ gFW⁻¹. These emission rates are significantly higher than those reported by Ball et al.,(124) (peak I_2 : 0.104 pmol min⁻¹ gFW⁻¹, mean I_2 : $0.063 \text{ pmol min}^{-1} \text{ gFW}^{-1}$): however their experiments only recorded emissions from one plant and only for its first 17 min of exposure, i.e. a time period too short for a typical A. nodosum plant to reach its max emission rate. The mean emissions rate observed for the first 17 min for the A. nodosum samples in this study was 0.0700 pmol min⁻¹ gFW⁻¹, which compares well with the one observation from Ball et al., (182) also observed similarly low emissions during the first 15 min after exposure (mean I₂: 0.04 pmol min⁻¹ gFW⁻¹) and a gradual increase to wide emission peak (mean I₂: 2.3 pmol min⁻¹ gFW⁻¹) after approximately 48 min for that study's one reported sample. The emission rates measured here are also similar to those of Huang et al.,(92) who reported significantly higher mean I_2 emissions from A. nodosum after both 65 - 85 min $(\approx 1.25 \text{ pmol min}^{-1} \text{ gFW}^{-1})$ and 340 - 360 min ($\approx 3.5 \text{ pmol min}^{-1} \text{ gFW}^{-1}$) of exposure to air when compared to initial emissions between $0 - 20 \text{ min} (\approx 0.25 \text{ pmol min}^{-1} \text{ gFW}^{-1})$. Figure 5.19 shows the distribution of I₂ emission rate data for the individual A. nodosum samples recorded over up to 360 min of exposure to air.



Figure 5.19 Box and whisker representation of I₂ emission rates from *A. nodosum* samples over up to 360 min of exposure to air





Figure 5.20 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from *F. vesiculosus* samples in September 2012 (top panel), November 2012 (middle panel) and June 2013 (bottom panel)



Figure 5.21 Box and whisker representation of I₂ emission rates from *F. vesiculosus* samples over up to 360 min of exposure to air, analysed through laboratory incubation experiments

A typical emission profile for *F. vesiculosus* was broad, consisting of a gradual increase in I_2 emissions following exposure to air, a peak in the emissions between 60 and 180 min after exposure, and a subsequent decline to modest emission rates at long exposure times (less than a quarter of peak emissions after 240 min exposure). The I_2 emission rate profiles produced by *F. vesiculosus* samples corresponded most closely in shape to those from *A. nodosum* but were less intense and did not feature any irregular emission spikes

Emission rates produced by F. vesiculosus samples increased gradually following exposure and were typically largest between 60 and 180 min (mean I₂: \min^{-1} gFW^{-1}) compared to 0 – 60 min 0.0818 pmol (mean I_2 : 0.0391 pmol min⁻¹ gFW⁻¹) and 180 – 360 min (mean I₂: 0.0320 pmol min⁻¹ gFW⁻¹). The distribution of emission rate data is shown in Figure 5.21. The sample-to-sample variability observed here appears to be less than for the other species (excluding Fucus_v32). Peak emissions ranged between 0.00485 and 0.419 pmol min⁻¹ gFW⁻¹. The emission rates reported here were significantly higher than those reported by Ball et al.,(124) (mean L: 0.0079 pmol min⁻¹ gFW⁻¹). But again, as for A. nodosum, the Ball et al. experiments only observed emissions for a very short period of time (the first 10 min of exposure, i.e. before F. vesiculosus plants have reached their peak emissions) - the mean emission rate recorded in the present study for the first 10 minutes of exposure $(0.0206 \text{ pmol min}^{-1} \text{ gFW}^{-1})$ are somewhat closer to that of Ball et al. The emission rates observed by Kundel et al.,(182) for F. vesiculosus also increased with time after exposure but were roughly an order of magnitude larger than those found in the present study: mean $I_2 = 0.308$ pmol min⁻¹ gFW⁻¹ over the first 60 min of exposure increasing to a broad maximum of approximately 1.35 pmol min⁻¹ gFW⁻¹ after 90 - 120 min.

5.5.6 Other species



Figure 5.22 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from *F. serratus*, *D. membranacea* and *G. turuturu* samples analysed in September 2012 (fucus_s and dict_m), November 2012 (grat_t21) and June 2013 (fucus_s31)

A small number of laboratory incubation experiments were also performed for samples of *F. serratus*, *D. membranacea* and *G. turuturu*. Given the lack of repeats, no robust conclusions can be draw for these species' emission rates. However the results are presented here for completeness. *F. serratus* emissions remained relatively constant across 180 min of exposure, albeit the one plant tested in June 2013 (mean I₂: 0.0337 pmol min⁻¹ gFW⁻¹) produced an order of magnitude higher emissions than the one plant tested in September 2012 (mean I₂: 0.00545 pmol min⁻¹ gFW⁻¹). *G. turuturu* had a small burst of emissions (peak I₂: 0.0548 pmol min⁻¹ gFW⁻¹) after approximately 15 min of exposure which gradually declined for the remainder of the experiment. The I₂ signal observed from *D. membranacea* remained essentially constant throughout the experiment (mean = 0.00559 pmol min⁻¹ gFW⁻¹) and was close to the detection limit of the BBCEAS instrument, like in the Ball et al. study. Thus we cannot determine with any certainty whether *D. membranacea* emits or not, because such a small, constant I₂ signal could conceivably arise from residual I₂ remaining in the sampling lines from an earlier experiment.

5.6 Discussion

5.6.1 Species Dependent I₂ Emissions

To facilitate comparisons between different species, average I_2 emission profiles were calculated for *L. hyperborea* (n = 15), *L. digitata* (n = 18), *S. latissima* (n = 10), *A. nodosum* (n = 25) and *F. vesiculosus* (n = 11) using the aggregated results from all samples of each species for all three seasons. The averaged profiles for *L. hyperborea*, *L. digitata* and *S. latissima* were calculated for up to 180 min after exposure because these species are generally exposed to air for shorter times than this *in situ*. The profiles for *A. nodosum* and *F. vesiculosus* were calculated for longer – up to 360 mins after exposure because these species are typically exposed for longer times *in situ*. These averaged emission profiles are shown in Figure 5.23. The total amounts of I₂ emitted from the moment of exposure up to time T were calculated by summing the averaged emission rates between times 0 to T minutes – the equivalent of integrating under the emission profiles in Figure 5.23.

It is important to note that not all experiments lasted for the full 180 or 360 min and a reduction in the number of samples averaged to produce the mean I_2 emission rate time series caused discontinuities in the averaged time series. The *S. latissima* mean I_2 emission rates after T = 142.67 min were multiplied by the scaling factor, 2.21. The scaling factor was calculated from the ratio of the mean I_2 emission rate at 141.33 min for all samples (n = 10) and for samples analysed for the full 180 min (n = 6). The *F. vesiculosus* mean I_2 emission rates after T = 180 min were multiplied by the scaling factor, 0.606. The scaling factor was calculated from the ratio of the ratio of the mean I_2 emission rate at 179.67 min for all samples (n = 11) and for samples analysed for the full 360 min (n = 5).

The mean I_2 emission profile of *L. digitata* was characterised by an intense initial emission in the first 30 mins of exposure (4.18 pmol min⁻¹ gFW⁻¹), followed by a decline in emissions to an average rate of 1.22 pmol min⁻¹ gFW⁻¹ between 30 – 180 min. Occasional spikes appear in the averaged profile (e.g. at 50 mins and 150 mins) from large, belated emission burst in individual samples, although these spikes contribute rather little to the integrated I_2 amount. The average profile of *L. hyperborea* I_2 emissions also showed a strong initial burst within the first 30 min after

exposure. Several later bursts are also evident (notably after ≈ 50 minutes) arising from the delayed emission bursts of the samples tested in September 2012 and November 2012, suggesting that the emission profiles of *L. hyperborea* vary with season. The average profile for *L. hyperborea* has a mean emission rate of 10.2 pmol min⁻¹ gFW⁻¹ over the first 60 minutes slowing to 3.99 pmol min⁻¹ gFW⁻¹ between 60 – 180 min. The averaged profile for *S. latissima* increases over the first 30 min after exposure and then attains a plateau extending out to the end of the calculation at 180 min, albeit with a small amount of structure arising from the structured emissions in the individual samples' time series (Figure 1.16). The mean emission rate over the period 30 – 180 min is 0.740 pmol min⁻¹ gFW⁻¹. By comparison the average emission profiles for *A. nodosum* and *F. vesiculosus* are rather smooth, largely because the emission profiles of the individual samples are broad themselves. Averaged I₂ emissions increased gradually between 0 – 60 min with mean emission rates of 0.208 (*A. nodosum*) and 0.391 pmol min⁻¹ gFW⁻¹ (*F. vesiculosus*), which increased to 0.618 and 0.0837 pmol min⁻¹ gFW⁻¹ between 60 – 180 min respectively.



Figure 5.23 Mean I₂ emission rates and integrated total I₂ amounts calculated from all *L. hyperborea*, *L. digitata*, *S. latissima*, *A. nodosum* and *F. vesiculosus* samples across all three seasons

A ranking of species' propensity to emit I_2 was generated using their mean I_2 emission rate profiles from Figure 5.23. These averaged profiles were used to produce box and whisker plots (Figure 5.24) for a "standard" 180 min exposure time and a typical exposure time of each species given the harvesting locations of the samples obtained around Roscoff. In the latter case, the typical exposure times were obtained by referencing the average growing heights of each species' samples against the REFMAR tide data,(183) for June 2013 for those days when the samples would be exposed by the tides at Roscoff. These times were then rounded to the nearest 30 min (*L. hyperborea* and *L. digitata*: 90 min, *S. latissima*: 120 min, *A. nodosum*: 360 min, *F. vesiculosus*: 240 min). Note that this calculation does not seek to imply that e.g. *L. digitata* is exposed for 90 minutes around each low tide – in fact, most tidal minima are not low enough to expose L. digitata at the sampling sites used in this study (see also the next paragraph). A more detailed description of how exposure times were determined is given in Section 5.6.3 wherein an analysis is presented of I₂ emissions versus the growing height for individual seaweed samples used in this work.



Figure 5.24 Box and whisker representation of mean I₂ emission rates a calculated from all L. hyperborea, L. digitata, S. latissima, A. nodosum and F. vesiculosus samples over 180 min (left panel) and representative average exposure times for tides that are sufficiently low to expose these species at the Roscoff sampling sites (right panel)

A clear ranking of species was observed (*L. hyperborea* > *L. digitata* > *S. latissima* > *A. nodosum* > *F. vesiculosus*) for mean and maximum I₂ emitted over 180 min exposure times amongst the five species examined in this work (Figure 5.24 left panel). This ranking corresponds to those observed in previous interspecies comparisons by both Ball et al.,(124) and Kundel et al.(182). The ranking remains in the same order when, instead, one considers the I₂ emitted over the typical exposure times of each species – the major difference between the two plots in Figure 5.24 is that the strong, fast emitting seaweeds have produced larger I₂ amounts. However in both plots, the

strongest emitter (*L. hyperborea*) emits more than two orders of magnitude more I_2 than the weakest emitter (*F. vesiculosus*).

It is important to note however, that the amount of time seaweed plants are exposed each month *in situ* varies significantly from species to species (Figure 5.25). The relationship of growing height and exposure was calculated for growing heights between 0 - 10 m using REFMAR tide data from September and November 2012 and June 2013. The relationship is consistent across all three months of analysis. According to the average growing heights of individual samples of each species used in this study and measured tide heights, *A. nodosum* and *F. vesiculosus* samples were exposed 58 times during June 2013 and spent approximately 44.9 and 33.8% of the month exposed to air. This equates to an approximate mean exposure time of 346 and 260 min per exposure event for *A. nodosum* and *F. vesiculosus* respectively. In comparison, the analysed *L. hyperborea* and *L. digitata* samples were exposed to air, which equates to a mean exposure time of 94 min per exposure event. The analysed *S. latissima* samples were exposed for 10 times in June 2013 and spent approximately 2.56 % of the month exposed to air, which equates to a mean exposure time of 114 min per exposure event.



Figure 5.25 Growing height above tidal minimum vs. percentage of time exposed to air for seaweed plants growing in the inter-tidal zone at Roscoff, France in September and November 2012 and June 2013 (top panel) and in June 2013 with markers showing mean growing height and percentage exposure for individual species (bottom panel)

A rough estimate of the amount of I_2 emitted (per unit weight) by each species in June 2013 was calculated from the estimated number of exposure events and exposure times during the month and mean integrated I_2 amounts released by each species over specific time periods. The calculated I_2 amounts were 1630 pmol gFW⁻¹ for *L. digitata*, 6250 pmol gFW⁻¹ for *L. hyperborea*, 916 pmol gFW⁻¹ for *S. latissima*, 6680 pmol gFW⁻¹ for *A. nodosum* and 891 pmol gFW⁻¹ for *F. vesiculosus*. A new ranking was

assigned for total I_2 emitted per month *A. nodosum* > *L. hyperborea* > *L. digitata* > *S. latissima* > *F. vesiculosus*. Weighting emission rates according to exposure times therefore leads to a different conclusion about which species of seaweed are the most important I_2 sources.

5.6.2 Seasonal Differences in I₂ Emissions

Data regarding the seasonal variation of iodine in seaweed is scarce. One analysis of the iodide content of *Laminaria* species exists, however no seasonal investigation into I_2 emission rates have previously been performed. Gall et al.,(66) observed that the average iodide contents of *L. digitata* samples, the majority of which were collected in Brittany, France, were lowest in summer months (June, July and August) and highest in late autumn (October and November) and in winter (December, January and February). The lowest iodide contents observed in summer coincided with stronger solar irradiances and a higher prevalence of epiphytes and endophytes (other plants or bacteria/fungi which grow on the seaweed). This section utilises seasonal mean I_2 emission rate profiles calculated for our samples of each species in September (early Autumn) and November (late autumn) 2012 and June 2013 (early summer) (Figure 5.26 to Figure 5.30) to investigate whether there was a trend in I_2 emission rates with season. The shapes of I_2 emission profiles across each of the three months were compared and the significance of any differences between mean monthly I_2 emission rates were determined through statistical analyses.

The statistical significance of the differences in the observed I_2 emission rates in the three months was assessed through application of the Mann-Whitney test. The Mann-Whitney test is a nonparametric test that compares two unpaired groups (e.g. I_2 emission rates recorded in Sept and Nov 2012). The test calculates whether the medians of the two datasets are significantly different from one another. It does not require that the data are normally distributed but it does require that both datasets are the same shape. The test proceeds by first ranking all the values from low to high (1 to *n*, where *n* is the total combined number of values in the two groups), whilst paying no attention to which group each value originates. The average ranks in each group are subsequently compared and if the means of the ranks in the two groups are very different, the probability of randomly getting the observed results from the sample groups (*p* value)

will be small. If the *p* value is greater than 0.05, the difference is not statistically significant and is likely to be a result of chance. However, if the *p* value is less than 0.05, the difference is significant and not likely to be the result of chance and the null hypothesis is rejected. By using the 5% significance level we would expect to be correct in rejecting the null hypothesis 95% of the time. Tests were performed using calculated mean I_2 emission rates for each month shown in Figure 5.26 to Figure 5.30 using time series of identical lengths (e.g. *L. digitata* September and November 2012 were compared using the first 113 min of available data). It is important to note that the maximum amount of data available were used for comparisons (e.g. *L. digitata* November 2012 and June 2013 were compared using 180 min of available data).



Figure 5.26 Mean I₂ emission profiles calculated for *L. digitata* samples in September and November 2012 and June 2013. Note that for ease of comparison, each months' data are shown on common Y1 and Y2 axis scales



Figure 5.27 Mean I₂ emission profiles calculated for *L. hyperborea* samples in September and November 2012 and June 2013



Figure 5.28 Mean I₂ emission profiles calculated for *S. latissima* samples in September and November 2012 and June 2013



Figure 5.29 Mean I₂ emission profiles calculated for *A. nodosum* samples in September and November 2012 and June 2013



Figure 5.30 Mean I₂ emission profiles calculated for *F. vesiculosus* samples in September and November 2012 and June 2013

The mean I₂ emission profile shapes calculated for *L. digitata* across all three months displayed the typical, intense increase in emissions immediately following exposure, with a rapid slowing in emissions within 30 to 60 min (Figure 5.26). Among *L. digitata* there was no statistically significant difference between mean I₂ emission rates obtained in September (median = 1.58) and November 2012 (median = 1.50) over 112.67 min of exposure; U = 62261, p = 0.0598. Therefore we fail to reject the null hypothesis that there is no difference in I₂ emission rates from *L. digitata* in September 2012 (median = 1.58) and November 2012. However, among *L. digitata* in September 2012 (median = 1.58) and June 2013 (median = 0.769) over 112.67 min of exposure, there was a statistical significant difference between I₂ emission rates; U = 94835, p = < 0.001. Emission rates obtained in November 2012 (median = 1.64) and June 2013 (median = 0.945) over 180 min exposure were also significantly different; U = 248941, p = < 0.001.

In contrast, the shapes of the L. hyperborea emission profiles showed distinct differences across the three months (Figure 5.27). The high variability between individual samples tested in September and November 2012 produced mean emission profiles containing high intensity peaks at irregular times across the full 180 min exposure time of the experiments. Much less variability was observed between the individual samples tested in June 2013 (even though the sample size n = 9 was larger in June), which produced in a mean emission profile similar in shape similar to that observed for L. digitata samples. Among the L. hyperborea samples, a statistically significant difference was found between mean I2 emission rates obtained in September (median = 9.74) and November 2012 (median = 1.21) over 114.67 min of exposure; U = 110765, p = < 0.001. Therefore we reject the null hypothesis that there is no difference in I₂ emission rates from L. hyperborea samples between September and November 2012. Further statistically significant differences were observed between mean I_2 emission rates obtained in November 2012 (median = 1.21) and June 2013 (median = 3.23) over 114.67 min of exposure (U = 28656, $p = \langle 0.001 \rangle$) and between September 2012 (median = 8.22) and June 2013 (median = 1.66) over 180 min of exposure (U = 260176, p = < 0.001).

High variability was also observed for *S. latissima* emission profile shapes across all three months, which consisted of high intensity peaks of irregular sizes observed at irregular exposure times. Significant statistical difference was observed between mean

I₂ emission rates obtained for *S. latissima* in September (median = 1.22) and November 2012 (median = 0.787) over 142.33 min of exposure; U = 146052, p = < 0.001, between September 2012 (median = 1.22) and June 2013 (median = 0.198) over 142.33 min of exposure; U = 177596, p = < 0.001 and between November 2012 (median = 0.667) and June 2013 (median = 0.157) over 180 min of exposure; U = 266204, p = < 0.001.

Mean emission profile shapes calculated for A. nodosum across all three months showed a gradual increase in emissions, reaching their maximum between 60 - 180 min, followed by a gradual decline. Emission profiles all consisted of irregular I₂ bursts of varying intensities for the duration of exposure (although after averaging the samples within a given month, this irregular structure typically comprised less than 20% of the emitted I₂). Among the A. nodosum samples, there was no statistical significant difference between mean I_2 emission rates obtained in September 2012 (median = (0.707) and June 2013 (median = 0.558) over 187.67 min of exposure; U = 164448, p = 0.3236. Therefore we fail to reject the null hypothesis that there is no difference in I₂ emission rates from A. nodosum samples between September 2012 and June 2013. However, mean emission rates were significantly lower (by one order of magnitude) in November 2012 than for the two other months. A. nodosum samples in September (median = 0.707) and November 2012 (median = 0.0384) showed a statistically significant difference between I₂ emission rates over 187.67 min of exposure; U = 318096, p = < 0.001. There was also a statistically significant difference between I₂ emission rates A. nodosum samples in November 2012 (median = 0.0232) and June 2013 (median = 0.193) over 360 min of exposure; U = 90345, p = < 0.001.

F. vesiculosus emission profile shapes were consistent across all three months and all gradually increased with exposure to a peak at 60 - 180 min. The mean emission profile calculated for *F. vesiculosus* in June 2013 was corrected after 180 min due to a sharp increase in calculated mean emissions, owing to the averaging of some samples that were not analysed for the full 360 min. Among *F. vesiculosus* there was no statistically significant difference between mean I₂ emission rates obtained in September (median = 0.0460) and November 2012 (median = 0.0495) over 130.33 min of exposure; U = 82222, p = 0.0892. Therefore we fail to reject the null hypothesis that there is no difference in I₂ emission rates from *F. vesiculosus* samples between September and November 2012. However, among *F. vesiculosus* samples in September (median =

0.0460) and June 2013 (median = 0.105) over 130.33 min of exposure, there was a statistical significant difference between I_2 emission rates; U = 35063, p = < 0.001. There was also a statistical significant difference between I_2 emission rates *A. nodosum* samples in November 2012 (median = 0.0474) and June 2013 (median = 0.108) over 184.67 min of exposure; U = 52494, p = < 0.001.

According to the analysis presented here, no seasonally specific trend has been identified that applies to I₂ emissions consistently across all species (Figure 5.31). No statistical significant differences were observed for samples of both L. digitata and F. vesiculosus between samples analysed in the autumn months of September and November 2012 or for A. nodosum between samples analysed in September 2012 (early autumn) and June 2013 (early summer). These three species also retained very similar emission profile shapes across all three months of analysis when compared to the high variability in shapes of L. hyperborea and S. latissima. The A. nodosum and F. vesiculosus species may show more similar profiles month-on-month and between individual samples (Figure 5.18 and Figure 5.20) because they are exposed almost every day. According to the table of typical growing heights in the Roscoff intertidal zone contained in Leigh et al., (93) L. digitata does not inhabit the deeper waters (minimum growing height: -1 m) that is dominated by *L. hyperborea* (minimum growing height: -20 m) and some S. latissima (minimum growing height: -2 m). It is therefore conceivable that the persistent emission rates produced by L. digitata may result from their adaptation to life at higher growing heights where they are exposed more frequently compared to the less frequent exposure of L. hyperborea and S. latissima in the deepest parts of the macroalgal zone. Comparison of the growing heights in Leigh et al., (93) and the values calculated in this study (Figure 5.25) also shows that the S. latissima plants used in experiments appear to have been collected from unusually shallow waters for the species.



Figure 5.31 Comparison of mean I₂ emission rates from *L. hyperborea*, *L. digitata*, *S. latissima*, *A. nodosum* and *F. vesiculosus* samples in September and November 2012 and June 2013

5.6.3 Growing Height and I₂ Emissions

Different species of seaweed are commonly observed growing in distinct bands on rocky shores, with each species growing at a specific height in the inter-tidal (littoral) zone. In coastal environments the littoral zone describes the region, which extends from the high water mark to the permanently submerged shoreline. The system developed by Stephenson and Stephenson, (184) and later modified by Lewis, (185) divides the littoral zone into three distinct regions as connected by their respective zone fringes. The supralittoral zone describes the highest region above high tide marks, which may be subject to sea spray in rough weather. The supralittoral fringe joins the supralittoral and midlitorral zones and is determined by the height of high tide, which only reaches the lower part of this zone. This zone features the highest growing species of macroalgae relative to the tidal minimum and is commonly home to selected species of *fucales*. The midlittoral zone is highly influenced by tides and is usually exposed and submerged on a daily basis. This zone is home to the majority of *Fucus* and *A. nodosum* species. The infralittoral fringe connects the midlitorral and infralittoral zone and is commonly inhabited by Laminaria species, which are only exposed at the major low tides, and often only in calm weather. This region extends down to the extreme low water level of spring tides, or to the lowest level visible between waves. The infralittoral zone is the region below the extreme low water level of tides and represents the lower limit of seaweed growth. This region is predominantly home to deep water *L. hyperborea*. Figure 5.32 shows an example of the growth banding of seaweed species, in this case observed at Mace Head (Ireland), and shows distinctive belts of shallow water *fucales* (*F. serratus* and *A. nodosum*) growing in the supralittoral fringe and midlittoral zone and deep water kelps (*L. digitata*) growing in the infralittoral zone and sublittoral fringe. It is important to note that Roscoff has a larger tidal range than that observed at Mace Head (9 m versus 5 m) and hence the zonation of different species of seaweed is more subtle at Roscoff.



Figure 5.32 The variation of seaweed species with growing height at Mace Head, Ireland. Photo credit: S. M. Ball

The littoral zone at Roscoff is dominated by brown macroalgae species including the shallow water, regularly exposed species of *Fucales* (e.g. *F. serratus, F. vesiculosus* and *A. nodosum*) and deeper water, seldomly exposed *Laminariales* (e.g. *L. digitata, L. hyperborea, S. latissima* and *L. ochroleuca*), growing in distinct groups and regions on the coastline, as surveyed by Leigh et al,(93) in Figure 5.33. *Fucus* and *A. nodosum* were observed to grow in mixed beds (65:35, *Ascophyllum:Fucus*) and were mapped together.



Figure 5.33 The mapped distribution of *L. digitata* (green), *L. hyperborea* (purple), *L. ochroleuca* (orange), *S. latissima* (yellow), *Fucus* and *A. nodosum* (red) in the Roscoff intertidal zone by Leigh et al.(93)

The tidal cycle experienced on the coast at Roscoff exposes macroalgae to air and varying degrees of biotic and abiotic stress factors up to two times daily. Levels of stress experienced by macroalgae therefore vary significantly with its geographical location and more specifically its height relative to the tidal minimum. The major driving force behind species growing in distinct bands at specific heights is the ability of an individual species of seaweed to combat the stress factors (e.g. temperature, irradiance, dehydration, and mechanical forces caused by wave action) experienced in different regions of the littoral zone. Macroalgae which inhabit upper littoral zones, (e.g. *Fucales*) are exposed to the atmosphere for significantly longer periods than those which grow in lower zones (e.g. *Laminariales*) and are therefore evolved to better withstand and recover from extended periods of exposure related stress.

This section investigates whether the growing height, and hence amount of exposure to air, influences the total amounts of I_2 emitted by seaweed plants and whether plants growing at different heights exhibit peak emissions at different times. Growing heights relative to the tidal minimum were estimated using the depth of seawater at the time and location where samples were collected, and the measured REFMAR tide heights.(173) GPS information was used to provide an accurate record of collection. GPS points were available for the *L. digitata* boat experiment site described in Section 4.6 across all three

months of analysis and selected samples harvested collected from shallow waters directly in front of SBR in June 2013 (Figure 5.9).

As previously discussed, the height at which a seaweed plant grows relative to the tidal minimum directly determines the amount of time it will be exposed to the atmosphere. The relationship of growing height and exposure (Figure 5.25) was calculated for growing heights between 0 - 10 m using REFMAR tide data from September and November 2012 and June 2013. The relationship is consistent across all three months of analysis. Figure 5.34 shows the growing height and percentage time exposed to air for samples harvested in June 2013. The solid lines represent the minimum and maximum growing heights/exposure times for individual species.



Figure 5.34 Growing height above tidal minimum vs. percentage of time exposed to air for seaweed plants harvested in June 2013

The relationships between total amounts of I_2 emitted after 60 min and 180 min of exposure and growing height for individual seaweed samples are presented in Figure 5.35. A negative trend is observed between total I_2 emitted and growing height along with a clear grouping in terms of both the total emissions and growing heights of the *Laminariales* and *Fucales*. These groupings arise because the shallower water species were generally the weaker emitters. Analysis of the scatter between total emissions and growing height was only possible for *A. nodosum* and *F. vesiculosus*

owing to the collection of *Laminariales* all from the same height at the *L. digitata* boat experiment site (at least for those samples where the exact growing heights were known). No trends were observed within individual species, potentially a result of the previously discussed high variability between individual samples (Figure 5.36).



Figure 5.35 Total I₂ emitted after 60 min (left panel) and 180 min (right panel) for individual seaweed samples plotted against the growing height relative to tidal minimum at which they were harvested



Figure 5.36 Total I₂ emitted after 180 min for *A. nodosum* samples plotted against the growing height relative to tidal minimum at which they were harvested (uncertainty in gradient = \pm 48.9)

The mean I_2 emission profiles calculated for different species in Section 5.6.1 show a clear relationship between the time and intensity of peak emissions with average growing heights. *L. digitata* and *L. hyperborea* for the most part display peak emissions

immediately following exposure whereas the *A. nodosum* and *F. vesiculosus* display emissions of a significantly lower intensity which peak between 60 and 180 min of exposure. Figure 5.37 shows how samples that grow in deeper waters tend to exhibit their peak emissions at a shorter exposure time than those exposed for extended periods. Again however, no trends were able to be assigned within individual species.



Figure 5.37 The time of peak emission rate after exposure vs. growing height for individual seaweed samples. Marker size is proportional to the intensity of the peak emission rate in relation to other samples within a species (e.g. the largest light blue circle represents the *A. nodosum* sample with the largest peak emission of all plotted *A. nodosum* samples)

5.6.4 Iodide Content and I₂ Emissions

As discussed previously in Section 5.2, seaweed accumulate significant quantities of iodide from seawater at levels around 1% of their dry weight. *L. digitata* is the most studied species in terms of its iodide content because it is known to transfer large amounts of iodine from seawater into the atmosphere. Only a small number of studies have investigated the variation in iodide content between different species and the impact of other variables on iodide accumulation. This section investigates whether iodide content influences the total amounts of I₂ emitted by seaweed plants and whether there were any variations of iodide levels with species, season and growing height. The iodide contents of individual seaweed plants were determined relative to the dry weight of the seaweed sample in grams (gDW) through the method outlined in Section 5.4.3.

Küpper et al.,(65) assayed the iodide content of L. digitata and observed iodide contents which ranged from 0.4% DW in adult plantlets (3 - 4 yr old) to up to 4.7 % in young plantlets less than 15 cm in length. The higher accumulation by young plantlets was assigned to their higher surface to volume ratio, which is approximately six to ten times higher that that of adult plantlets. The data obtained during this study was applied to investigate the correlation between iodide content and plant age/size. Figure 5.38 shows the blade iodide content of L. digitata, L. hyperborea and S. latissima plants plotted against their individual plant mass. Here, the measured fresh weights of individual plants were used as an indicator for plant size. Smaller plants were observed to generally contain more iodide per DW than larger plants, however the correlations were not particular strong ($R^2 = 0.150 - 0.410$). It is important to note that the size of samples used in experiments were self-limited because plants were only used if they were small enough to fit into the 10 L Nalgene bottle. Kelp plants are likely to grow to much larger sizes than those analysed here, however these are most likely to be deep water species that are never exposed to air. There are therefore subtle differences that exist between biological trends and the trends that matter for I₂ emitted into atmosphere.



Figure 5.38 The iodide content of individual samples of *L. digitata*, *L. hyperborea* and S. *latissma* vs individual plant mass

Table 5.4 provides a comparison of the results of iodide content analysis performed in this study with those reported by Kundel et al.,(182) and Küpper et al.(67) Here, the percentage of total iodine emitted as I_2 was calculated from the ratio of total I_2 emitted during laboratory incubation experiments (mol gFW⁻¹) and the experimentally

determined iodide content of each sample (mol gDW⁻¹) assuming that two moles of I⁻ make one mole of I₂. To enable the comparison, iodide content was first converted from $\mu g \; g D W^{-1}$ to $\mu g \; g F W^{-1}$ through multiplication of a scale factor (1/6.66). This scale factor was applied based on the assumption that FW is approximately 6.66 times heavier than DW, or in other words seaweeds are 85% water. The kelps, L. digitata, L. hyperborea and S. latissima were observed to contain larger amounts of iodide than A. nodosum and the Fucus species. The ranking of species based on iodide content was different from that assigned through total I2 emissions with L. digitata and not L. hyperborea observed to have the largest iodide content (L. digitata > L. hyperborea > S. latissima > A. nodosum > F. vesiculosus). The results are consistent with the previously observed high iodide accumulation and content of L. digitata plants. The distribution of iodide content data across five orders of magnitude is shown in Figure 5.39. The median iodide contents of the five species varied across three orders of magnitude, the same as for the total I₂ emissions data. Similar amounts of variation in iodine content and I₂ emission data were also observed within individual species (across one to three orders of magnitude).

Table 5.4 The mean iodide content and percentage of total stored iodine emitted as I_2 for different species of seaweed and a comparison to other studies. Data were aggregated over all three seasons

	Mean of all samples		Kundel et al.(182)		Küpper et al.(67)
Seaweed species (sample size)	Iodide content (μg gDW ⁻¹)	% of stored iodine emitted as I ₂	Iodide content (μg gDW ⁻¹)	% of stored iodine emitted as I ₂	Iodide content (μg gDW ⁻¹)
<i>L. hyperborea</i> (n = 11)	4512	0.0317	1,946	0.0106	N/A
<i>L. digitata</i> (n = 17)	7225	0.00654	1,886	0.0036	N/A
S. latissima ($n = 10$)	2875	0.00738	1,281	0.0123	N/A
A. nodosum $(n = 18)$	740	0.114	553	0.0138	1600
<i>F. vesiculosus</i> $(n = 8)$	100	0.113	494	0.0129	N/A
<i>F. serratus</i> $(n = 1)$	71	0.0162	365	0.0119	890
G. turuturu (n = 1)	105	0.00423	N/A	N/A	N/A



Figure 5.39 Box and whisker representation of the mean iodide content (left panel) and % total stored iodine emitted as I₂ (right panel) for the five different species of seaweed

Only a very small fraction of the total iodide stored by the plants was emitted as I_2 during exposure to air. Therefore one exposure event was observed to use up only a very small fraction of the iodide stored in a plant. Figure 5.40 shows the lami_d2 and lami_d2a time series from Figure 5.12. The lami_d2a sample is a repeat experiment using the lami_d2 sample after it had been allowed to recover in the aquarium for ≈ 48 h. One exposure of the example of the lami_d2 plant did not exhaust the seaweed's ability to emit I_2 and the second emissions are, if anything, stronger than the first.



Figure 5.40 I₂ emission rate profiles (pmol min⁻¹ gFW⁻¹ vs. time) from two experiments using the same *L. digitata* sample (lami_d2 and lami_d2a) in September 2012

A seasonal comparison of measured iodide contents was also performed between samples collected in the three different visits to Roscoff. Figure 5.41 shows the distribution of iodide contents of L. hyperborea, L. digitata, S. latissima, A. nodosum and F. vesiculosus determined in September and November 2012 and June 2013. The highest median iodide content was observed in November 2012 for all species except L. hyperborea. This is consistent with the findings of Gall et al.,(66) who observed that the average iodine contents of L. digitata samples (the majority of which were collected in Brittany, France) were lowest in summer months (June, July and August) and highest in late autumn (October and November) and in winter (December, January and February). Only a few of the groupings in Figure 5.41 had sample sizes large enough to perform viable Mann-Whitney Tests. Among L. digitata there was no statistically significant difference between mean iodide contents (µg gDW⁻¹) obtained in September 2012 (median = 6133) and June 2013 (median = 6483); U = 19, p = 0.689. Therefore we fail to reject the null hypothesis that there is no difference in the iodide contents of L. digitata samples between September 2012 and June 2013. However, among A. nodosum in November 2012 (median = 1118) and June 2013 (median = 210), there was a statistical significant difference between iodide contents; U = 3, p = 0.00236.



Figure 5.41 Box and whisker representation of the iodide content for samples of the five different species of seaweed in September and November 2012 and June 2013

The relationships between total amounts of I_2 emitted after 60 min and 180 min of exposure and iodide content for individual seaweed samples are presented in Figure 5.42. A negative trend was observed between total I_2 emitted and iodide content along

with a clear grouping in terms of both the total emissions and iodide contents of the *Laminariales* and *Fucales*. As for the I_2 emissions versus growing height plots (Section 5.6.3), no trends were observed within individual species and potentially a result of the previously discussed high variability between individual samples. However, here the different coloured spots are grouped more tightly than for Figure 5.35. It is important to note that this analysis is only semi-qualitative because different species have different biological mechanisms of iodine uptake and emission.



Figure 5.42 Total I₂ emissions by seaweed samples after 60 min (left panel) and 180 min (right panel) of exposure to air vs. iodide content

5.6.5 Ozone Concentration and Temperature

The relationship between the total amount of I_2 emitted by individual seaweed samples after 180 min of exposure and room temperature and O_3 concentration was investigated for all seaweed species analysed in June 2013. No trends were observed within individual species; potentially a result of the variability between the emissions of individual samples previously discussed in Sections 5.6.1 to 5.6.4. Figure 5.43 shows correlation plots of total amount of I_2 emitted after 180 min of exposure versus O_3 (left panel) and temperature (right panel) for *L. digitata* and *A. nodosum* samples analysed in June 2013. No correlations are apparent and the R^2 correlation co-efficients were all close to zero.



Figure 5.43 Total I₂ emitted after 180 min for *L. digitata* and *A. nodosum* samples plotted against the mean O₃ concentration (left panel) and mean temperature (right panel) measured in the laboratory during individual experiments

5.7 Conclusion

Results were presented from an extensive laboratory study of the I₂ emissions from the seaweed species: L. digitata, L. hyperborea, S. latissima, A. nodosum and F. vesiculosus. The BBCEAS instrument produced high sensitivity data over a short integration time (I₂ detection limit of 3.62 pptv at 20 s integration time), which enabled the calculation of high frequency average I₂ emission profiles for the five species. A clear ranking of species was observed (L. hyperborea > L. digitata > S. latissima > A. nodosum > F. vesiculosus) for I_2 emitted that was consistent over both 180 min of exposure to air and the typical exposure times of each species in situ. The strongest emitter (L. hyperborea) was observed to emit more than two orders of magnitude more I_2 than the weakest emitter (F. vesiculosus). No seasonally specific trend was identified that applied to I2 emissions consistently across all species. However, no statistical significant differences were observed for samples of both L. digitata and F. vesiculosus between samples analysed in September and November 2012 or for A. nodosum samples analysed in September 2012 and June 2013. The emission profiles of the A. nodosum and F. vesiculosus species may show more similarities both month-onmonth and between individual samples because they experience regular (daily) exposure. A negative trend was observed between total I₂ emitted and growing height along with a clear grouping in terms of both the total emissions and growing heights of the *Laminariales* and *Fucales*. However, no trends were observed within individual species. The ranking of species based on iodide content was consistent with that assigned for I_2 emissions except *L. digitata* and not *L. hyperborea* plants were observed to have the largest average iodide content. A similar distribution of the iodide content data across the five species was observed as for the total I_2 emission data, with the strongest accumulator (*L. digitata*) observed to contain more than two orders of magnitude more iodine than the weakest accumulator (*F. vesiculosus*). One exposure event was observed to use up only a very small fraction of the iodide stored in a plant for all species. A negative trend was observed between total I_2 emitted and iodide content, however no trends were observed within individual species.
6 Measurements of Urban NO₂ and Particulate Matter

6.1 Introduction

Following its atmospheric simulation chamber deployment (Chapter 3), the "field" BBCEAS instrument was used to quantify NO₂ and aerosol optical extinction in ambient air in the urban environment. Both NO₂ and aerosol particles have large vehicle traffic emission sources and therefore significantly impact the chemistry of urban air (Section 1.2.3 and 1.2.4). This chapter presents BBCEAS measurement data obtained at the Leicester University UK Automatic Urban and Rural Monitoring Network (AURN) site between March and July 2014. A comparison was performed between the direct spectroscopic BBCEAS measurements of NO₂ and concentrations obtained using the indirect, but very widely used, molybdenum catalyst chemiluminescence (CL) technique. The ability of BBCEAS to measure ambient levels of aerosol via the unstructured continuum contributions to spectra was also assessed by comparing BBCEAS data with three commercial particle analysers. In a separate set of experiments the mobile BBCEAS instrument, previously applied to detect I₂ emissions (Chapter 4 and 5), was applied to high frequency (1 s) roadside measurements of emissions of NO₂ and PM from vehicle traffic. The ability of the roadside BBCEAS instrument to capture and interrogate the composition of exhaust plumes from individual vehicles was applied to investigate the temporal and spatial distribution of a short-lived species like NO₂ from the roadside.

6.1.1 Controlled Urban Air Pollutants

Air pollution is a major environmental risk to health.(20) Air pollutants have been shown to increase the incidence of heart disease and respiratory illness including asthma, bronchitis and lung cancers.(23) The levels of pollutants are therefore directly linked to the long- and short-term respiratory and cardiovascular health of a population. Those most at risk of the detrimental health effects of poor air quality often reside in urban areas where a significant amount of harmful emissions emanate from vehicle traffic exhausts.(186) Potentially harmful species may either be directly emitted from vehicle combustion engines or formed through subsequent secondary reactions of emissions in the atmosphere (Section 1.2.3 and 1.2.4). The harmful effects of emissions on air quality are controlled by protocols,(21) which limit the concentrations of air

pollutants in ambient air over both hourly and annual averaging periods. Table 6.1 shows the current European limit values and World Health Organisation (WHO) guidelined for NO₂, particulate matter (PM_{10} and $PM_{2.5}$), and tropospheric O₃.

Table	0.1	WHO	guidelines,(186)	and	European	limit	values,(21)	Ior	ambient
concen	tratio	ons of NO	D ₂ , O ₃ , PM ₁₀ and F	PM _{2.5} .					

	Amonoging	Limit value	e (µg m ⁻³)	Downitted exceedences	
Pollutant	Averaging	WHO	EU	Perinitied exceedances	
	period	guidelines	standards	per year (EU)	
Nitrogen dispide (NO)	One hour	200	200	18	
(NO_2)	One year	40	40	-	
$O_{7000}(O_{1})$	Maximum daily	100	120	25	
$OZOIIe(O_3)$	eight hour mean	100	120	25	
Particulate matter < 10 µm	One day	50	50	35	
(PM_{10})	One year	20	40	-	
Particulate matter $< 2.5 \ \mu m$	One day	25	-	-	
(PM _{2.5})	One year	10	25	-	

6.1.2 Chemiluminescence Measurements of NO₂

Measurements of ambient NO₂ concentrations are essential to implement and enforce the limit values shown in Table 6.1. Of the various in situ techniques used to quantify NO₂, arguably the most prevalent ones are CL NO_x instruments.(187) Indeed, CL is the standard detection technique for the measurement of NO₂ across the UK AURN (Section 6.2.2). CL NO_x instruments operate over two modes which determine the concentration of NO and total NO_x in an ambient air sample respectively.(188) First, the concentration of NO is determined through its reaction with O₃ produced inside the instrument to form an electronically excited molecule of NO2 (NO2*). The NO2* molecule is then detected through its fluorescence at visible and near IR wavelengths. The second mode determines the total NO_x concentration and operates by first flowing the ambient air sample over a solid molybdenum oxide catalyst to reduce all NO₂ contained in the sample to NO. The same method of detection is then applied as for the NO mode, where the fluorescence produced now represents the amount of NO in ambient air combined with that produced by the reduction of NO₂. The concentration of NO₂ can be indirectly calculated from the difference in NO concentrations determined by the two sampling modes. The instrument comparison reported in this chapter (Section 6.4.1) uses NO₂ measurement data generated using a molybdenum catalyst CL NO_x monitor. It is important to note that alternative less commonly deployed photolytic conversion CL detectors are also available, which employ a photolytic converter (e.g.

LED or Xenon lamp) in place of the molybdenum catalyst to reduce NO_2 to NO.(189, 190)

Chemiluminescence (CL) instruments are commonly used to measure NO_x species in air quality monitoring applications because they are sensitive, simple to operate and have low running costs owing to their few operating parts. The main disadvantage of the CL technique however is that it can be subject to interference, specifically an overestimation of the NO₂ concentration resulting from the conversion of molecules other than NO₂ (e.g. NO_y = HONO, N_2O_5 , PAN etc.) to NO by the heated molybdenum catalyst.(187) Such interferences may result in the overestimation of NO₂ concentrations measured at air monitoring sites and thereby increase the likelihood that a region will fail to comply with prevailing NO₂ legislative limit values. Dunlea et al.,(187) investigated the performance of CL NO_x monitors by comparing a spectroscopic instrument (tunable infrared laser differential absorption spectroscopy, TILDAS) at a range of location types in the heavily polluted urban atmosphere of Mexico City. The TILDAS technique was used to provide the reference NO₂ measurement that directly determined NO₂ concentrations from its absorption spectrum and were therefore assumed to be free from interferences. Observed CL NO2 concentrations often exceeded TILDAS NO2 concentrations which indicated a positive interference in the CL instrument; also the CL NO₂ interferences were larger at inner city locations than at urban background sites where pollution levels were lower. Such interferences accounted for an overestimation in NO2 concentrations retrieved by CL by up to 50% (Figure 6.1).



Figure 6.1 NO₂ measurements retrieved by a CL NO_x monitor and TILDAS instrument at Pedregal in Mexico City in 2002 showing highlighted CL NO_x monitor interference (by Dunlea et al.)(187)

Interferences were most significant in the afternoon and coincided with measured peak concentrations of ambient O_3 . The causes of CL NO_x monitor interferences were assigned as nitric acid (HNO₃), and alkyl nitrates (RONO₂). The measured concentration of O_3 was used as a marker for the levels of photochemistry in the local atmosphere and hence the levels of oxidised nitrogen (NOy) species, which may interfere with the CL technique. For example, the photochemical production of O_3 and HNO₃ may occur on a similar time scale in the urban atmosphere as both involve the reaction of NO₂ (previously discussed in Section 1.2).

$$NO_2 + hv (\lambda < 420 \text{ nm}) \rightarrow NO + O(^{3}P)$$
 R1.12

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
 R1.13

$$OH + NO_2 + M \rightarrow HNO_3 + M$$
 R6.1

Alkyl nitrates and O_3 are also both products of NO_x photochemistry involving the reaction of NO with peroxy radicals (R6.3 and R6.2 respectively).

$$RO_2 + NO \rightarrow NO_2 + RO$$
 R6.2

$$NO_2 + hv (\lambda < 420 \text{ nm}) \rightarrow NO + O(^3P)$$
 R1.12

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
 R1.13

$$RO_2 + NO + M \rightarrow RONO_2 + M$$
 R6.3

Dunlea et al.,(187) observed a fair correlation between CL NO_x monitor interference and measured ambient concentrations of O₃ at all locations ($R^2 = 0.19 - 0.54$).

A further field comparison performed by Villena et al.,(190) at urban background locations in Santiago, Chile, compared CL NO_x monitor measurements with direct spectroscopic NO₂ measurements made using the DOAS technique by Elshorbany et al.,(191) (Figure 6.2). A clear difference was again observed between NO₂ concentrations obtained by the CL NO_x instrument and the spectroscopic technique. NO₂ concentrations determined by CL were overestimated by up to 25 ppbv during the day and between 5 – 10 ppbv at night (Figure 6.2a). CL NO_x monitor interferences again showed a positive correlation with measured levels of O₃ (R² = 0.82, Figure 6.2b).

HONO was assigned as the major nighttime interfering species through subtraction of its measured concentrations from NO_2 interferences (red points, Figure 6.2b).



Figure 6.2 (a) Campaign averaged NO and O diurnal profiles in Santiago de Chile, 2005; The error bars show the 1σ error of the average of all 10 min NO₂ data. (b) Correlation of

the NO₂ interference of the CL instrument (CL [NO₂] – DOAS [NO₂]) with [O₃]. In addition, the NO₂ interference corrected for HONO and PAN interferences ("corr. NO2interference"). Figure by Villena et al.,(190) using results by Elshorbany et al.(191)

6.1.3 Roadside Measurements of NO₂

In addition to monitoring NO₂ at a number of point measurement sites, the implementation of NO₂ limit values also requires an assessment of where high exposure is likely to occur.(192) For example the implementation of hourly limit values may require the application of roadside measurements whereas urban background measurements may be used to infer annual averages. Knowledge of the variability and dispersion of NO₂ from a roadside is therefore required to determine where high exposures are likely to occur. The high-density deployment of diffusion tubes, first developed by Palmes et al.,(193) is a commonly used cheap method, to determine the spatial distribution of NO₂ from a roadside.(194) The major disadvantages of diffusion tubes are their long acquisition times (> 1 week) that fail to capture the short-term variations in NO₂ concentrations and positive biases including within-tube NO₂ production. The previously discussed CL instruments provide data over much shorter sampling periods but generally sample at fixed-point locations and therefore do not offer any spatial information.

Zavala et al.,(195) compared emissions from different vehicle types in Mexico City through a combination of fleet average measurements, vehicle chase experiments, and most relevant to this chapter; roadside stationary sampling. The roadside experiments captured emissions from individual mobile vehicles through the deployment of high sensitivity and high time resolution (1 - 2 s) instrumentation (including a CL NO_x monitor, a Condensation Particle Counter (CPC) and a Multi Angle Absorption Photometer (MAAP)). The capture of emissions was highly dependent on wind direction and speed at the time of the exhaust event and signatures of individual plumes typically only lasted for a few seconds as a result of the short distance between the source and instrument inlet. The deployment of multiple instruments enabled the characterisation of several pollutants in individual emission plumes. HGVs were the most significant emitters of NO₂ and PM and a large variability was observed between emissions of gaseous pollutants and PM even within individual vehicle types.

Chaney et al.,(192) applied mobile instrumentation to investigate the distribution of NO₂ at increasing distances from an urban roadside. A mobile laboratory containing analytical instrumentation including a CL NO_x monitor and UV absorption O₃ detector was used to measure the variation in pollutant concentration as a function of distance from the roadside. Concentrations of NO₂ were measured at locations within 10 and 500 m of two different major urban roads in Leeds along suburban residential side roads with limited traffic (Figure 6.3). Concentrations of NO_x were highest at locations closest to the roadside and decreased with an increasing distance from the source. Concentrations of NO decreased more rapidly than total NO_x owing to the slower decay of NO₂ and the reaction NO + O₃ \rightarrow NO₂ + O₃. NO₂ was the dominant source of NO_x after approximately 100 m.



Figure 6.3 Variation in NO_x and O_3 concentrations as a function of distance from the centre of the Otley Rd in Leeds. The lines have no physical significance, but act as a guide to the eye (by Chaney et al.)(192)

Wang et al.,(196) also examined the gradients of NO and NO₂ emissions with distance from a roadside for the purpose of informing atmospheric dispersion models. Concentrations were measured at multiple distances downwind of the roadside source and fitted with exponential decay curves (y = a + b exp(-cx)). Here x is downwind distance from the roadside (metres), y is measured concentration of the pollutant (ppbv), a is urban background concentration (ppbv), b is roadside increment (concentration at site nearest to roadside – a in ppbv) and c is the decay constant (metres⁻¹). Values of c obtained during experiments ranged between 0.00328 and 0.04529 m⁻¹.

6.2 Experimental: Instrument Comparison

6.2.1 BBCEAS Field Instrument

Measurements of NO_2 and aerosol scattering in ambient air were performed at the Leicester University AURN site alongside the consortium of commercial atmospheric monitoring instrumentation detailed in the following subsections. The same BBCEAS hardware was deployed for the *in situ* measurements in this chapter as for the atmospheric simulation chamber experiments detailed in Section 3.4. However, owing to the spatial constraints of the AURN site, the field instrument was deployed in a new "vertical" arrangement (Figure 6.4).



Figure 6.4 The "vertical" arrangement of the field BBCEAS instrument for deployment in the Leicester University AURN site

The same wavelength calibration and spectrometer line shapes determined for the HR2000 spectrometer in Section 3.5.1 were applied to measurements in this chapter. The same methods were also applied to determine the dark current corrections, the wavelength dependent mirror reflectivity, and the length factor correction parameter as reported in Section 3.5.2, 3.5.3, and 3.5.4 respectively. Dark current spectra, and N₂ reference, and O₂ and He calibration spectra were recorded approximately two times in every seven-day period. The detection limits reported in Section 3.6.1 also apply to measurements reported in this chapter.

Ambient air was drawn by a diaphragm pump from above the AURN site roof and approximately 4 m above ground level and into the BBCEAS instrument through Teflon tubing (4 m length, 6.35 mm outside diameter, 2 litres/min flow rate). The BBCEAS sampling inlet was separated from those of the commercial instruments by a lateral distance of 1.5 m.

Spectra were recorded on a desktop PC using the SpectraSuite (Ocean Optics) software supplied with the HR2000 spectrometer. Spectra had a 100 ms integration time; 50 spectra were averaged in Spectrasuite giving a net acquisition time of 5 s, before being saved on the PC. Spectra were averaged and analysed using the Mathcad Prime 2.0 (PTC) software package as outlined in Section 3.5.

6.2.1.1 Measurement Errors

The same statistical and systematic uncertainties in retrieving NO₂ concentrations from measured BBCEAS spectra apply here as previously stated for the field BBCEAS instrument in Section 3.6.1. The sources of systematic uncertainty were uncertainties in the mirror reflectivity (3 - 5%), the length factor (1 - 2%) and the absorption cross section of NO₂ (3%).(169) The statistical uncertainty was again determined by the ability of the fitting procedure to isolate the structured absorption signal of NO₂ from the combined BBCEAS absorption spectrum. When fitting a very weak absorption signal owing to a low absorber concentration, the retrieved statistical error was \pm the instrument detection limit. When retrieving stronger absorption signals owing to an increased absorber concentration, the statistical uncertainty increased but was insignificant in comparison to the net systematic error. For example, the statistical error generally remained at < 1% when retrieving larger concentrations of NO₂.

6.2.2 Leicester University AURN Site

The AURN is the UK's largest air monitoring network for determining compliance against the previously discussed European ambient air quality directives (Table 6.1). The network currently consists of 122 air-monitoring sites, which measure ambient concentrations of specific pollutants at different location types across the UK. All data reported in this chapter, as part of the instrument comparison, were provided by instruments deployed at the Leicester University AURN. Instruments were housed within a brick building located on the main university campus. Ambient air was sampled through inlets located on the site roof at a height of 4 m above ground level. The area surrounding the site was open and contained university buildings, a sports field, a cemetery and a regional road all within a 40 m radius (Figure 6.5). The measured concentrations of pollutants were therefore not significantly influenced by any one individual source, but rather the combined contribution from all sources upwind of the station. The site was classified as an urban background location and provides pollutant concentrations representative for an area of several square kilometres. Table 6.2 provides a summary of the instrumentation deployed at the AURN site to which BBCEAS was compared. All measurement data were provided by the University of Leicester except for O_3 data, which were obtained from Defra.(197)



Figure 6.5 Photograph of the University of Leicester AURN air-monitoring site (top panel) and its mapped location (bottom panel)

Table 6.2 A summary of the instrumentation deployed within the Leicester UniversityAURN air-monitoring site used in the instrument comparison

Instrument	Pollutant measured	Time resolution (min)	Units
CL NO monitor	NO ₂	15	ppbv
$CL NO_x$ monitor	NO	15	ppbv
UV absorption O ₃ monitor	O ₃	60	ppbv
Ultrafine particle (UFP) monitor	Particle number concentration (20 - 30 nm, 30 - 50 nm, 50 - 70 nm, 70 - 100 nm)	30	$\# \mathrm{cm}^{-3}$
Nanoparticle Surface Area Monitor (NSAM)	Surface area of particles that would be deposited in the alveolar region of a human lung	30	$\mu m^2 cm^{-3}$
Multi Angle Absorption Photometer (MAAP)	Black carbon concentration	30	μg m ⁻³

6.2.3 Chemiluminescence NO_x Monitor

A molybdenum catalyst CL NO_x monitor (Model T200 Nitrogen Oxide Analyzer, Teledyne) was deployed to provide measurements of NO, NO₂ and total NO_x. The instrument operated by the same procedure outlined previously in Section 6.1.2. NO and total NO_x concentrations were individually determined through R6.4 and R6.5 respectively. The difference between the measured NO and NO_x concentrations was used to indirectly determine the ambient concentration of NO₂. The instrument manufacturers stated an instrument detection limit of 0.4 ppbv and an accuracy of \pm 0.2 ppbv for concentrations between 0 – 50 ppbv and \pm 0.5 % for concentrations above 50 ppbv.

$$NO + O_3 \rightarrow NO_2^* + O_2 \xrightarrow{\text{fluorescence}} NO_2$$
 R6.4

$$NO_2 \xrightarrow{\text{catalyst}} NO \xrightarrow{O_3} NO_2^* + O_2 \xrightarrow{\text{fluorescence}} NO_2$$
 R6.5

6.2.4 UV Absorption Ozone Monitor

Measurements of ambient O₃ were provided by a UV photometric O₃ analyser (Model 49*i*, Thermo Scientific). The instrument applied Lambert-Beer's law to retrieve concentration of O₃ from its absorbance at 254 nm. Ambient air was drawn into the instrument and split into a reference and a sample gas flow to determine $I_0(\lambda)$ and $I(\lambda)$ respectively. The reference gas flow was first directed through an O₃ scrubber to remove all O₃ and provide a measurement of the UV light intensity transmitted through

a sample without O_3 . The sample gas flow was then used to determine the intensity of UV light intensity transmitted through an ambient air sample containing O_3 .

6.2.5 Ultrafine Particle Monitor

An ultrafine particle monitor (UFP, Model 3031, Trust Science Innovation) provided measurements of the size distribution and number concentration of particles in ambient air between 20 - 100 nm over four size resolution channels: 20 - 30 nm, 30 - 50 nm, 50 - 70 nm, 70 - 100 nm. The instrument operated by first charging all particles in an ambient air sample positive using a diffusion charger. The charged particles were then classified according to their mobility in an electric field using a differential mobility analyser (DMA).

6.2.6 Nanoparticle Surface Area Monitor

A nanoparticle surface area monitor (NSAM, Model 3550, Trust Science Innovation) provided measurements of the surface area of particles of diameters (1 - 500 nm) that if inhaled, would be deposited in the alveolar region of a human lung. The technique therefore did not measure the total surface area of particles suspended in air but the combined surface area of the particles that would be deposited in the alveolar region of the human respiratory tract. The instrument operated by using a selective ionizer to impart a positive charge on particles of a certain size that would be deposited in the alveolar region of a human lung. The charged aerosol particles were then measured by an electrometer, where the measured charge was directly proportional to the combined surface area of the measured particles.

6.2.7 Multi Angle Absorption Photometer

A multi angle absorption photometer (MAAP, Model 5012, Thermo Scientific) determined the concentration of ambient black carbon (BC) through aerosol related light absorption. The instrument operated by drawing an ambient air sample through its inlet and into a detection chamber where it was deposited onto a filter tape. A 670 nm light source was aimed towards the deposited aerosol and the light transmitted through and reflected back from the sample was measured by a series of photo-detectors. The

concentration of BC was determined from measurements of light transmitted and reflected by the deposited aerosol in a known air sample volume.

6.3 Experimental: Roadside Measurements

6.3.1 Mobile BBCEAS Instrument

The mobile BBCEAS instrument deployed here for *in situ* roadside experiments was the same as deployed for the *in situ* boat experiments detailed in Section 4.3.2 but modified for the detection of NO₂ at blue wavelengths. All instrument hardware was the same as stated in Section 4.3.2 except for the LED light source, cavity mirrors and spectrometer. A blue high intensity LED light source (LED Engin, LZ1-10B205, 5 Watt, peak wavelength = 455 nm) was supplied with a current of 1.50 A from a regulated power supply and maintained at a constant temperature of 18°C. The optical cavity was formed from two high reflectivity mirrors (Layertec, 1" diameter, 108621, 1000 mm radius of curvature, > 99.985% high reflectivity at 455 nm). A custom-made round to linear fibre (Anglia Instruments) transported the light transmitted through the cavity output mirror into the inlet slit of the fibre-coupled spectrometer (Ocean Optics; HR2000, 407.0 -491.2 nm, linear diode array of 2048 pixels). In this deployment, the spectrometer was not temperature controlled and instead housed in an aluminium bracket attached to the aluminium breadboard to which the BBCEAS optical components were also attached. The Zarges box containing the BBCEAS instrument was stacked on top an identical Zarges box containing a battery power supply. The battery power supply consisted of four leisure batteries (4×12 V, DC, 100 Ah, Elecsol), a multi-stage battery charger (60 A, Caravan and Leisure Technology) and a pure sine wave inverter (700 W, 230 V, AC, Antares). The boxes were mobilised on a rough terrain platform trolley (Model: 550/RH/TC127P/1, The Handling & Storage Shop). Ambient air was sampled through a PFA inlet line (1 m) from a height of 150 cm to correspond with the approximate average human adult mouth and nose height. Measurements of wind speed and direction were provided at a 10 s time resolution by a combined weather meter (Kestrel 4500 pocket weather tracker) and portable vane mount (Kestrel) mounted on the platform trolley (Figure 6.6).



Figure 6.6 Deployment of the mobile BBCEAS instrument, power supply and Kestrel weather meter during measurements of NO₂ at an urban roadside location

The same wavelength calibration and spectrometer line shapes determined for the HR2000 spectrometer in Section 3.5.1 were applied to measurements in this chapter. The same methods were also applied to determine the dark current corrections and mirror reflectivity as reported in Section 3.5.2 and 3.5.3 respectively. Dark current spectra, N₂ reference and O₂ and He calibration spectra were recorded in the laboratory immediately before and after transporting the instrument to and from the roadside measurement site. Dark current spectra were also recorded on location during measurements in the field. The same statistical and systematic uncertainties in BBCEAS measurements of NO₂ apply here as reported in Section 6.2.1.1, apart from uncertainties associated with the application of a length factor correction parameter. No N₂ mirror purge flow was used for roadside measurements with the mobile BBCEAS instrument and hence the only sources of systematic error were uncertainties in the mirror reflectivity (3 – 5%) and the absorption cross section of NO₂ (3%).(169)

6.3.2 Measurement Site Locations

The mobile BBCEAS instrument sampled ambient air from measurement sites located at distances between 1 and 190 m from a busy urban through road (B568, Victoria Park Road in Leicester, UK, Figure 6.7). A pedestrian footpath through Victoria Park, Leicester was used to provide the mobile BBCEAS instrument measurement sites (red line in Figure 6.7). The pathway runs southeast to northwest from the side of the B568

source road to the University of Leicester campus and is lined on both sides by trees that did not have any leaves at the time of measurements. The source road was open and lined by a row of detached houses on the opposite side of the road. The B568 traffic flow was relatively constant across all days of experiments. Regular average vehicle counts were performed every 5 min and observed an average traffic flow of 20 vehicles per min consisting of a mixture of cars, LGVs, HGVs and buses. No significant variation in traffic flows were observed during the measurement of individual transects.



Figure 6.7 Mapped location of the roadside measurement transect (red line) in relation to the University of Leicester AURN site

Three individual experiments were performed on 20^{th} January, 23^{rd} February and 12^{th} March in 2015. Each transect consisted of six measurement sites at increasing distances from the roadside. Ambient air was sampled at each location for 10 - 20 min over a total experiment time of 1 - 2 h. Sites were not visited in sequential order of either increasing or decreasing distances from the roadside. The mobile BBCEAS instrument was situated downwind from the roadside during all experiments to ensure a successful capture of emissions from the source road.

6.4 Results: Instrument Comparison

6.4.1 Comparison of BBCEAS and CL NO₂ Measurements

In order to compare the NO₂ concentrations obtained by the BBCEAS and CL instruments, the BBCEAS NO₂ data (5 s) were interpolated onto the 15 min time resolution of the CL instrument. The interpolation resulted in two NO₂ concentration time series that shared a common 15 min time resolution and were therefore able to undergo a statistical comparison. Figure 6.8 shows the BBCEAS (5 s) and CL (15 min) NO₂ concentration time series obtained on 13-03-2014 and the subsequent interpolation of the BBCEAS data onto the common time resolution provided by the CL instrument. The 15 min averaged NO₂ concentration data from both instruments were subsequently used to construct x–y correlation plots to compare the NO₂ concentrations retrieved by both analysis techniques (Figure 6.8 inset). These correlation plots were used to assess the level of agreement between the two instruments for measurements made across specific time periods of interest.



Figure 6.8 BBCEAS and CL NO₂ concentration time series obtained on 13-03-2014 showing the interpolation of BBCEAS 5 s data onto a common 15 min time resolution provided by the CL instrument and the subsequent statistical comparison (inset)

Figure 6.9 shows NO₂ measurement data for both instruments across an example eleven-day period. The NO₂ data have been averaged onto the same 15 min sampling time grid. The two data sets exhibit strong similarities ($R^2 = 0.966$). The BBCEAS instrument generally measured lower NO2 concentrations than the CL monitor (86% of data points during selected time period). Figure 6.10 shows an x-y correlation plot generated using the combined 15 min NO₂ concentration data retrieved across the full BBCEAS instrument deployment. The instruments again showed good agreement (R² = 0.919) across the extended period. The linear least square fit of CL NO₂ concentration versus BBCEAS NO2 concentration again produced a positive offset (1.83 ppbv) and indicated that CL technique on average retrieved higher NO2 concentrations over the duration of the deployment (CL $[NO_2] > BBCEAS [NO_2]$ for 67% of total data points). It is important to note that on some occasions during the deployment the BBCEAS instrument also measured higher NO2 concentrations than the CL monitor. These negative interferences were potentially the result of an atmospheric species drawn into the CL monitor which either (i) chemically decreased the measured concentration of NO₂ through reaction with NO and/or NO₂ or (ii) enhanced quenching of the electronically excited molecule of NO_2 (NO_2^*). Another very mundane (but quite possible) explanation could be an offset error in calibration of the CL NO₂ channel.



Figure 6.9 A comparison of CL (15 min) and interpolated BBCEAS (15 min) NO₂ concentration time series obtained between 12-03-2014 and 23-03-2014 (top panel). Time series were compared by x–y correlation plot (top panel inset). The difference between NO₂ concentrations retrieved by the two techniques is shown in the bottom panel



Figure 6.10 Correlation plot of CL and BBCEAS NO₂ concentration measurements obtained across the full BBCEAS deployment (between 11-03-2014 and 18-07-2014)

The retrieval of larger NO₂ concentrations by the CL instrument is consistent with the findings of the previously discussed studies by Dunlea et al.,(187) and Villena et al.(190) In those studies, the overestimation of NO₂ concentration by the CL technique was assigned to interfering oxidised nitrogen (NO_y) species, which were converted to NO by the molybdenum catalyst and wrongly assigned as NO₂. These species would therefore not interfere with the direct BBCEAS measurement of NO₂. In this thesis the source of the false positives in the CL instrument measurements was therefore investigated using the BBCEAS instrument to provide the reference NO₂ concentration.

Equation 6.1

$$CL NO_x$$
 monitor interference = $[NO_2] (CL) - [NO_2] (BBCEAS)$

The calculated CL NO_x monitor interference levels were compared with measurements of ambient O₃ made by the UV absorption ozone monitor also located at the AURN site for the reasons discussed in Section 6.1.2. Figure 6.11 shows a comparison of the NO₂ measurement data retrieved by the BBCEAS and CL instruments over a seven-day period (01-04-2014 to 08-04-2014) where particularly high levels of CL NO_x monitor interference were observed. Here, positive interferences were observed of up to 6.70 ppbv (04:00 on 02-04-2014) and were significantly larger than the BBCEAS measurement errors reported in Section 6.2.1.1. The largest positive interferences were generally observed when NO₂ concentrations were low. This was consistent with a possible correlation offset error on the CL instrument which would have the largest effect when the NO₂ concentration was low. This may also be indicative of a chemical interference (e.g. NO_y) because the NO₂ concentration would likely be high if the instruments were measuring fresh, unprocessed pollution. A statistical comparison of the interference data and measured O₃ concentrations was performed for the time period shown in Figure 6.11. The interference time series data (15 min) was interpolated onto the common time base of the O₃ data from the AURN UV absorption instrument (1 h) in order to produce the x-y correlation plot shown in Figure 6.12. A fair correlation $(R^2 = 0.509)$ was observed between the measured CL NO_x monitor interference levels and O₃ concentrations obtained across this seven-day period. The strength of the interference versus O₃ correlation observed here slightly exceeded that observed by Dunlea et al., (187) ($R^2 = 0.19$ to 0.54) but was lower than that observed by Villena et al.,(190) ($R^2 = 0.82$). It is important to note that the correlation between interference and O_3 observed here was only observed for specific periods of large interferences and no correlation was observed when plotting the aggregated measurements obtained across the full BBCEAS instrument deployment.



Figure 6.11 NO₂ concentration time series 15 min data retrieved by the BBCEAS and CL instruments between 01-04-2014 – 08-04-2014 (top panel) and a comparison of positive CL NO_x monitor interferences (15 min) and retrieved O₃ concentration time series data (60 min) during the same time period (bottom panel)



Figure 6.12 Correlation plot of the CL NO_x monitor interference and O₃ concentration data shown in Figure 6.11

6.4.2 BBCEAS Measurements of Aerosol Extinction

The ability of BBCEAS to measure ambient levels of aerosol via the unstructured continuum contributions to spectra was assessed by comparing BBCEAS data with three commercial particle analysers. The BBCEAS field instrument was previously applied to determine aerosol levels during the atmospheric simulation chamber experiments described in Chapter 3. A detection limit of 0.124 Mm^{-1} was obtained for aerosol extinction at 450 nm from quantifying changes in the unstructured continuum absorbance between 449 – 451 nm (Section 3.6.1). This subsection applies ambient air measurement data obtained at the AURN site to investigate what aerosol parameters the BBCEAS field instrument measures through its aerosol extinction. For ambient air measurements, the most likely contributor to extinction and the reduction in cavity path length is aerosol.(121)

As discussed in Section 2.2, in principle, the wavelength dependence of the $\alpha_{cont}(\lambda)$ measurement provides some information about particle size. In this section, the Angstrom coefficient was used to retrieve particle size information from BBCEAS ambient measurements made at the AURN site. The Angstrom coefficient, *A*, is an empirical coefficient which describes the power dependence of the scattering of light by aerosol with wavelength.(198) Different sized particles produce different *A* values and hence the calculated value of *A* can be used to infer basic information about aerosol size. The spectral extinction by particles may be approximated using Equation 6.2

where, $\tau(\lambda)$ is the aerosol extinction at wavelength, λ , and $\tau_1(\lambda)$ is a function of the aerosol loading of the atmosphere known as the turbidity coefficient.

Equation 6.2

$$\tau(\lambda) = \tau_1 \lambda^{-A}$$

Measurements of aerosol extinction at two or more wavelengths can be applied to calculate *A* by taking the logarithm of Equation 6.2:

Equation 6.3

$$log_{10}\tau(\lambda_i) = log_{10}\tau_1 - Alog_{10}\lambda_i$$

The Angstrom coefficient can therefore be calculated from the gradient of the linear regression of a plot of aerosol extinction versus wavelength. As an example, Figure 6.13 (top panel) shows BBCEAS aerosol extinction measurement data obtained at 440, 450, 460, 470 and 480 nm during morning rush hour (between 06:00 and 09:00) on 13-03-2014. This time period contained a peak of high aerosol extinction at 06:13 probably caused by the BBCEAS instrument sampling aerosol from an especially polluting vehicle using the nearby roadside. Angstrom coefficient The (Figure 6.13, middle panel) was calculated from the slope of the linear regression of a plot of BBCEAS aerosol extinction (measured on every detector pixel between 440 and 480 nm) versus wavelength. Three example plots of aerosol extinction versus wavelength at 06:13, 07:30 and 07:58 are shown in Figure 6.13 (bottom panel).



Figure 6.13 BBCEAS aerosol extinction time series data (1 min) measured at 440, 450, 460, 470 and 480 nm obtained on 13-03-2014 (top panel) and the corresponding calculated
Angstrom coefficient values (middle panel). The bottom panel shows three example plots of aerosol extinction versus wavelength at 06:13, 07:30 and 07:58

The A = 3.03 value calculated for the high extinction event at 06:13 was larger than the mean A = 2.31 value calculated for the full 3 h period and potentially indicates an increase in the proportion of smaller particles in the sample. One would expect new unprocessed vehicle exhaust emissions to contain many small particles, freshly nucleated from the hot condensable exhaust gases. The A = 1.97 value calculated at 07:58 is slightly lower than average for the selected time period and is indicative of another type of aerosol. The Angstrom coefficient values observed here ($A \ge 2$) are typically assigned to size distributions which are dominated by particles with radii

 $\leq 0.5 \ \mu\text{m}$ and are typically associated with urban pollution and biomass burning.(199, 200) Angstrom coefficient values of less than one are typically indicative of particle size distributions which consist of mainly coarse mode aerosols (e.g. dust and sea salt of radii $\geq 0.5 \ \mu\text{m}$).(201)

BBCEAS continuum measurements at 450 nm were compared with measurements of particle number, surface area and particle mass made by the commercial particle monitors also located within the AURN site. BBCEAS aerosol extinction measurement data (5 s) were interpolated onto the common time base already shared by the UFP, MAAP and NSAM particle instrument data (30 min, Figure 6.14). This generated a BBCEAS aerosol extinction time series (30 min) that could be statistically compared to those of the commercial instruments through x–y correlation plots.



Figure 6.14 BBCEAS aerosol extinction and UFP 70 – 100 nm time series data obtained on 13-03-2014 showing the interpolation of BBCEAS data (5 s) onto a common time resolution provided by the UFP instrument (30 min)

The data shown in Figure 6.15 was measured over a seven-day period where the BBCEAS aerosol extinction measurement, showed a good agreement with the measured particle quantities of the three commercial instruments. The selected time period was characterised by a three-day period of larger aerosol amounts followed by four days of

lower aerosol levels. The strongest correlation was observed between BBCEAS aerosol extinction and black carbon measurements ($R^2 = 0.751$), followed by surface area measurements of particles with diameters 1 nm – 500 nm ($R^2 = 0.708$) and the number of particles counted in the UFP 70 – 100 nm size distribution ($R^2 = 0.628$). The BBCEAS aerosol extinction was also compared to the number of particles counted in the different size distributions of the UFP instrument over the same time period (Figure 6.16). The x–y correlation plots showed that the BBCEAS continuum was most heavily influenced by larger particles between 70 – 100 nm ($R^2 = 0.628$), followed by 50 – 70 nm ($R^2 = 0.559$), 30 – 50 nm ($R^2 = 0.399$) and 20 – 30 nm (no correlation).



Figure 6.15 Comparison of BBCEAS aerosol extinction time series data with UFP 70 – 100 nm (top panel), MAAP BC (middle panel), and NSAM Alveolar (bottom panel) time series data retrieved between 12-03-2014 – 18-03-2014



Figure 6.16 Correlation plot of BBCEAS aerosol extinction and UFP time series data for individual particle size distributions obtained between 12-03-2014 – 18-03-2014

The same statistical analysis was applied to the collected measurement data obtained across the full BBCEAS instrument deployment. However, the x-y correlation plot produced low R² values owing to the instability of the BBCEAS aerosol extinction measurement. Periods of significant drift were observed in the continuum measurements at random times during the deployment, which were not associated with changes in the levels of ambient aerosol. As discussed previously, in Section 3.6, the BBCEAS absorption continuum measurement is more susceptible to instability caused by variation in the BBCEAS $I_0(\lambda)$ spectrum than the retrieval of fitted absorber concentrations. Here, the variation in the $I_0(\lambda)$ spectrum was most likely the result of a loss in mirror reflectivity caused by deposition onto the cavity mirrors.

BBCEAS NO_2 measurements were also compared with the particle number concentrations observed in each of the different size categories of the UFP instrument. As discussed previously, in Section 6.1, NO_2 and aerosol particles both share a large vehicle traffic emission source. The comparison investigated whether the BBCEAS measurement of NO_2 could be used to indicate vehicle traffic particle emissions, even in the absence of expensive and specialist particle measuring instruments. The BBCEAS NO₂ (5 s) data were interpolated onto the common time base of the UFP instrument (30 min) using the same method applied previously to the absorption continuum measurements. The increased stability of the BBCEAS NO₂ measurement enabled correlation plots to be produced using the aggregated data obtained across the full BBCEAS deployment (Figure 6.17). BBCEAS measurements of NO₂ showed the strongest correlation with larger particles between 50 – 70 nm (R² = 0.315), and 70 – 100 nm (R² = 0.303), followed by 30 – 50 nm (R² = 0.263) and 20 – 30 nm (R² = 0.141).



Figure 6.17 Correlation plot of BBCEAS NO₂ concentration and UFP time series data for individual particle size distributions obtained across the full BBCEAS deployment (11-03-2014 and 18-07-2014)

The correlation of ambient particles and NO₂ was also investigated for different time periods that were determined to be likely to have different traffic flow intensities on the nearby roads. Table 6.3 compares the R^2 values obtained from x-y plots using the aggregated measurement data obtained at weekends (Saturday – Sunday), weekdays (Monday – Friday), during the weekday morning rush hours (06:00 – 09:00 on

Monday – Friday) and at all other non-rush hour times. The strongest correlations were observed for plots of particle number versus NO₂ using data from the larger UFP size distributions (50 – 70 nm and 70 –100 nm) over all time periods except for the morning rush hour. During rush hour the BBCEAS NO₂ measurement correlated strongest with the UFP counts of smaller particles (20 – 30 nm, $R^2 = 0.419$). This may suggest that a proportion of the measured NO₂ and particles between 20 – 30 nm were transported from a common vehicle traffic emission source, which was increased in size at times of large traffic flow.

Table 6.3 R² values produced from x–y correlation plots of UFP particle number (# cm⁻³) versus BBCEAS NO₂ (ppbv) for specific time periods

UFP particle size (nm)	Weekday	Weekend	Non rush hour ^a	Rush hour ^b
20-30	0.1597	0.0854	0.1152	0.4188
30 - 50	0.2766	0.2146	0.2529	0.3066
50 - 70	0.3348	0.2644	0.3247	0.2685
70 - 100	0.3218	0.2358	0.3155	0.2490

^a Non rush hour = All hours excluding 06:00 – 09:00 UK time Monday – Friday

^b Rush hour = 06:00 - 09:00 UK time Monday – Friday

6.5 Results: Roadside Measurements

The mobile BBCEAS instrument was applied to high frequency roadside measurements of emissions of NO₂ and PM from vehicle traffic at varying distances from an urban roadside. For a period of 10 - 20 min during each experiment, the instrument was situated at a stationary sampling location approximately 1 m from the traffic flow and sampling the emission plumes of passing vehicles. The close to source location and fast integration time (1 s) of the measurement data enabled the capture of individual vehicle traffic emission plumes at times when the road was not too heavily travelled or overly congested. Figure 6.18 demonstrates in principle the ability of roadside BBCEAS instrument to capture and interrogate the composition of exhaust plumes from individual vehicles. For example, the highlighted NO₂ and aerosol extinction peaks at 15:01:45 represent an emission plume, which contains both NO₂ and particulate matter.



Figure 6.18 Roadside measurement time series of NO₂ and aerosol extinction retrieved by the mobile BBCEAS instrument positioned at a stationary sampling location 1 m from the roadside. Highlighted peaks at 15:01:45 represent an emission plume which contains both NO₂ and particulate matter

This ability was applied to investigate the temporal and spatial distribution of a shortlived species like NO2 from the roadside. NO2 concentration data (1 s) were averaged for the full duration of measurements made at individual stationary sampling sites at varying distances from the roadside. Each experiment consisted of six stationary sampling locations. Figure 6.20 shows the concentration profile observed along the measurement pathway for three individual experiments. Concentrations are shown both as a function of the path distance from the roadside and the distance between the road and sampling site along the vector of the predominant wind direction. For each experiment the predominant wind direction was calculated from wind measurements averaged over the full experiment duration. As expected, concentrations at the nearest sampling site (1 m) to the source road were the highest and NO₂ emissions decayed to background levels with increasing distance from the roadside. For the three experiments, the decrease in concentrations with distance was broadly similar with a decline of \approx 5 ppbv NO₂ observed within 110 m (path distance) of the roadside. Figure 6.19 shows the measured NO₂ concentrations relative to the concentration measured at the nearest sampling site (1 m) to the source road also plotted as a function of both the path and downwind distance from the roadside.



Figure 6.19 Variation in NO₂ concentrations relative to the concentration measured at the nearest sampling site (1 m) to the source road as a function of path distance (left panel) and downwind distance (right panel) from Victoria Park Road

The measured NO₂ concentrations plotted as a function of distance from the roadside were subsequently fitted with exponential decay curves of the form $y = a + b \exp(-cx)$, for both path distance and downwind distance from Victoria Park Road (Figure 6.20). The values of a (urban background concentration), b (roadside increment) and c (decay constant) calculated for each experiment are shown in Table 6.4 and Table 6.5. The cvalues obtained here were relatively consistent $(0.01 - 0.03 \text{ m}^{-1})$ and those obtained through application of downwind distances $(0.00976 - 0.02716 \text{ m}^{-1})$ corresponded to previously NO NO_x those obtained for and Wang al.,(196) by et $(0.00328 - 0.04529 \text{ m}^{-1}).$



Figure 6.20 Variation in NO₂ concentrations as a function of path (left panel) and downwind (right panel) from Victoria Park Road fitted with exponential decay curves of the form $y = a + b \exp(-cx)$

Date of experiment	a (ppbv)	b (ppbv)	c (m ⁻¹)	R ²	Roadside [NO ₂] (ppbv)	Wind speed (m/s)	Wind direction (°)
20/01/2015	$20.775 \pm$	$5.8884 \pm$	$0.02303 \pm$	0.905	26.3	0.67	174
20/01/2013	1.24	1.17	0.0123				
22/02/2015	6.8519 ±	$3.8976 \pm$	$0.01975 \pm$	0.908	11.0	2.14	204
25/02/2015	0.526	0.581	0.00814				
12/02/2015	$10.054 \pm$	$5.664 \pm$	0.03031 ±	0.055	15.8	1.69	150
12/03/2013	0.392	0.535	0.00807	0.955			138

Table 6.4 Experimental results fitted using path distance from Victoria Park Road

Table 6.5 Experimental	results fitted us	sing downwind	distance from	Victoria 1	Park Road

Date of experiment	a (ppbv)	b (ppbv)	c (m ⁻¹)	R ²	Roadside [NO ₂] (ppbv)	Wind speed (m/s)	Wind direction (°)
20/01/2015	20.632 ± 1.86	5.9543 ± 1.74	0.01796 ± 0.013	0.861	26.3	0.67	174
23/02/2015	6.702 ± 0.5151	4.1321 ± 0.531	0.00976 ± 0.00336	0.940	11.0	2.14	204
12/03/2015	10.024 ± 0.535	5.5186 ± 0.701	0.02716 ± 0.00943	0.925	15.8	1.69	158

6.6 Conclusion

The field BBCEAS instrument was successfully applied to the quantification of NO₂ and aerosol optical extinction in ambient air at the Leicester University AURN site. The comparison of BBCEAS NO₂ measurements with those made by the commercial CL technique showed a strong correlation ($R^2 = 0.919$). However, the CL instrument was observed to overestimate NO2 concentrations compared to BBCEAS for sustained periods. The interferences in the CL measurement technique correlated with measured O_3 concentrations over certain periods of high interferences (e.g. $R^2 = 0.508$ for 01-04-2014 to 08-04-2014). The ability of BBCEAS to measure ambient levels of aerosol via the unstructured continuum contributions to absorption spectra was also assessed by comparing BBCEAS data with three commercial particle analysers. A good correlation was observed between the BBCEAS continuum and measurements of black carbon ($R^2 = 0.751$) and particles of diameters 1 – 500 nm ($R^2 = 0.708$) over a sevenday period (12-03-2014 to 18-03-2014) where the continuum measurements remained free from instrument drift. Comparison of the continuum measurement and particle numbers in the different size regions of the UFP instrument indicated that larger particles (70 - 100 nm) had the most impact on light scattering within the cavity. It was concluded that the BBCEAS continuum measurement could be used to provide information of ambient aerosol, however optimum instrument performance was required through, for example regular cleaning of the cavity mirrors. The BBCEAS measurement of NO₂ with commercial particle measurements showed a fair to good correlation ($R^2 = 0.141 - 0.315$) with particles between 20 – 100 nm measured by the UFP over long measurement periods with the strongest correlation observed with the larger particles between 50 - 100 nm. For measurements made during the morning rush hour period of high traffic flow (06:00 - 09:00) the strongest correlation was observed between NO₂ and the smaller particles between 20 - 30 nm, which may suggest a common vehicle traffic emission source.

The ability of the mobile BBCEAS instrument to capture and interrogate the composition of exhaust plumes from individual vehicles was observed through measurements made at a stationary site next to an urban roadside. Measurements of NO_2 made at various locations downwind of the same road were applied to investigate the temporal and spatial distribution of NO_2 . NO_2 concentrations were plotted as a function of distance from the roadside and fitted with exponential decay curves with *c*

values $(0.01 - 0.03 \text{ m}^{-1})$ that corresponded to those previously observed by Wang et al.(196)

7 Conclusions and Prospects for Future Work

The work presented in this thesis has explored various aspects of tropospheric source gases at or very nearby their emission sources. The common factor in these studies was the application of broadband cavity enhanced absorption spectroscopy (BBCEAS) to make highly sensitive, fast time resolution measurements of the target gases and aerosol extinction. Two BBCEAS instruments were used in this thesis. The larger, older "field" BBCEAS instrument developed in previous work, (124, 129, 135) was used for experiments at the EUPHORE atmospheric simulation chamber (Chapter 3) and as a reference instrument sited in the AURN monitoring station on the university campus (Chapter 6). This instrument was deployed in essentially the same "tried-and-tested" configuration as described by Daniels.(137) The iodine studies in Chapters 4 and 5 and the roadside dispersion studies in Chapter 6 used a newer, smaller "mobile" BBCEAS instrument. This instrument was constructed by Daniels,(137) for the quantification of N₂O₅ produced from a calibration source and was originally used during the RONOCO campaign to measure losses of NO₃ and N₂O₅ in the inlet line of a three-channel BBCEAS system installed on the FAAM research aircraft.(138) A key design feature of the mobile BBCEAS instrument was that it could be easily transported to and from the FAAM aircraft on the airport apron immediately before and after RONOCO flights. Further technological developments achieved during the period of my PhD studies (e.g. greatly extending the battery life; exchanging optical components to access different wavelength regions) enabled this instrument to also be used for ambient atmospheric measurements for the first time. In particular, deploying the instrument on movable platforms enabled it to be manoeuvred into position close to emission sources in order to make the novel observations described in this thesis.

7.1 Application of BBCEAS to Atmospheric Chamber Studies

The field BBCEAS instrument was applied to measurements of glyoxal, methyl glyoxal, and NO_2 during experiments performed in the EUPHORE atmospheric simulation chamber as part of the Pho-SOA 2 campaign. These experiments investigated GLY and MGLY yields from VOC oxidations and the uptake of these alpha-dicarbonyls to seed aerosol particles (mainly ammonium sulphate). The instrument was deployed at blue wavelengths (430 – 486 nm) and provided high sensitivity measurements at fast time resolution. Detection limits were obtained through

fitting baseline measurements recorded across a cavity flushed with N2 for individual structured absorbers. 1^o detection limits of 22 pptv, 340 pptv, and 27.5 pptv (20 s integration time) were achieved for GLY, MGLY and NO₂ respectively, and corresponded well with the instrument's performance during an extensive instrument inter-comparison exercise for GLY, MGLY and NO₂ held at the EUPHORE chamber a year earlier - see Thalman et al.(136) However, for the first time, the Pho-SOA 2 work included in this thesis reported measurements of the aerosol extinction made by one of our BBCEAS instruments. A detection limit of 0.124 Mm⁻¹ was also obtained for aerosol extinction at 450 nm from quantifying changes in the unstructured continuum absorbance between 449 - 451 nm. Statistical errors produced by fitting individual BBCEAS spectra were shown to be representative of the detection limits established in the baseline tests (at least for absorber amounts where the statistical fitting errors dominate). High quality time series of GLY, MGLY and aerosol extinction were provided for a publication investigating the potential uptake of low molecular weight α -dicarbonyls by aerosols.(143) Experiments were also performed investigating the VOC systems initiated by the reactions of acetylene, isoprene and propyne with OH radicals. These data exist and are available to any modeller who wished to use, for example the Master Chemical Mechanism,(163) to explore GLY & MGLY product yields from first- and later-generation products. The combination of the detailed experimental data produced here and future modelling may potentially provide new insights into VOC oxidation mechanisms. BBCEAS also provided the reference measurement to test a micro-fluidic derivatisation instrument designed for the detection and quantification of GLY and MGLY.(144)

7.2 Measurements of Urban NO₂ and Particulate Matter

Following its EUPHORE deployment, the field BBCEAS instrument was used to quantify NO₂ and aerosol optical extinction in ambient air in the urban environment. The instrument was located at the Leicester University AURN site between March and July 2014 enabling a comparison of BBCEAS to be performed with commercial NO_x and PM instrumentation. A strong correlation ($R^2 = 0.919$) was observed between the direct spectroscopic BBCEAS measurements of NO₂ and NO₂ concentrations obtained using the indirect, but very widely used, molybdenum catalyst chemiluminescence (CL) technique. The CL instrument was observed to overestimate NO₂ concentrations

compared to BBCEAS for sustained periods. Such "false-positive" CL interferences have been previously identified in work by Dunlea et al.,(187) and Villena et al.,(190) and linked to the presence of interfering oxidised nitrogen (NO_y) species. As previously discussed in Section 6.1.2, both studies used O₃ as a marker for levels of NO_y species. Excess NO₂ measured by CL over that from BBCEAS correlated with measured O₃ concentrations over certain periods (e.g. $R^2 = 0.508$ for 01-04-2014 to 08-04-2014). The investigation of CL interferences was limited by the absence of a direct measurement of NO_y species and the consequent reliance upon O₃ as a tracer molecule, which may be influenced by other sources and sinks. Future investigation of CL monitor interferences would benefit from the deployment of NO_y instrumentation alongside the BBCEAS and CL instruments, for example the four-channel thermal dissociation laser induced fluorescence (TD-LIF) instrument for NO₂, peroxy nitrates, alkyl nitrates and HNO₃ deployed during the RONOCO campaign.(202)

The ability of BBCEAS to measure ambient levels of aerosol via the unstructured continuum contributions to spectra was also assessed by comparing BBCEAS data with three commercial particle analysers. The stability of the continuum measurements was found to be susceptible to changes in BBCEAS instrument performance (e.g. any degradation in the reflectivity of the cavity mirrors). A seven-day period (12-03-2014 to 18-03-2014) where the continuum measurements remained free from instrument drift was used for the comparison. For this period, a good correlation was observed between the BBCEAS continuum and measurements of black carbon and particles of diameters $(0.001 - 0.5 \ \mu\text{m})$ that would be deposited in the alveolar region of a human lung. Comparison of the continuum measurement and aerosol in the different size regions of the UFP instrument indicated that larger particles $(0.07 - 0.1 \ \mu m)$ had the most impact on light scattering within the cavity. The BBCEAS continuum measurement can be used to provide information of ambient aerosol, however optimum instrument performance must be ensured through, for example regular cleaning of the cavity mirrors. The BBCEAS also provides direct data on aerosol extinction, which reflects the undesirable reduced visibility caused by aerosol in situ.

The BBCEAS measurement of NO₂ showed a fair to good correlation with particles between $0.02 - 0.1 \mu m$ over long measurement periods with the strongest correlation observed with the larger particles between $0.05 - 0.1 \mu m$. For measurements made
during the morning rush hour period of high traffic flow (06:00 - 09:00) the strongest correlation was observed between NO₂ and the smaller particles between $0.02 - 0.03 \mu m$. These particles and NO₂ are both known to have large vehicle traffic sources. As discussed previously, there are good but imperfect existing CL methods for measuring NO₂ but the hardware required to measure the different types of aerosol is more expensive and specialist. The results in this thesis show that high frequency NO₂ data, especially where individual traffic emission spikes can be identified, could be used to indicate vehicle traffic particle emissions, even in the absence of particle measuring instruments.

The mobile BBCEAS instrument was successfully applied to high frequency (1 s) roadside measurements of emissions of NO₂ and PM from vehicle traffic. The roadside deployments presented in this thesis demonstrate in principle the ability of roadside BBCEAS instrument to capture and interrogate the composition of exhaust plumes from individual vehicles. This ability was applied to investigate the temporal and spatial distribution of a short-lived species like NO₂ from the roadside. NO₂ concentrations plotted as a function of distance from the roadside were fitted with exponential decay curves with *c* values (0.01 – 0.03) that corresponded to those previously observed by Wang et al.(196) Future repeat experiments are required where measurements are performed on days with different wind speeds and directions, and with and without leaves on the trees, to test how representative the preliminary results are.

7.3 Measurements of I₂ Emitted by Seaweeds

The mobile BBCEAS instrument was successfully applied to measure I_2 emissions from macroalgae in the coastal environment of Roscoff in Brittany, France. For this work, the instrument was operated for the first time in the green spectral region (520 – 570 nm) in order to capture the highly structured absorption features of I_2 . Baseline tests using the cavity flushed with N₂ yielded 1 σ detection limit of 3.62 pptv for I_2 , 92.6 pptv for NO₂, and 1.10 pptv for OIO over a 20 s integration time. The statistical errors achieved in field observations of I_2 and NO₂ were very close to these detection limits, indicating that the retrieval errors produced by fitting individual BBCEAS spectra were again representative of the instrument's detection limits. In particular, the figure for I_2 represents a significant improvement on the detection limit of ~25 pptv I_2 in 7.5 s achieved previously by Ball et al,(124) using an early version of the larger field BBCEAS system deployed for the work in Chapter 3 and 6 of this thesis.

The addition of a battery power supply enabled the instrument to be deployed in a novel way – in this case from an inshore research vessel to quantify I_2 concentrations in situ directly above seaweed beds. Extremely large I2 concentrations were observed above L. digitata macroalgae growing in their natural habitat. Observed peak concentrations (2.08 ppbv at 20 s) were significantly higher than any previously reported in literature (0.547 ppbv),(92) owing in part to the deployment of a fast response instrument very close to the emission source. The I₂ time profiles observed over L. digitata species were strongly correlated with tide height, with peak concentrations consistently observed to coincide with low tide. In contrast, measurements above A. nodosum observed a gradual build-up of collective I2 emissions from multiple nearly plants, peaking immediately prior to the seaweed being re-submerged by the incoming tide. Somewhat surprisingly, despite the high concentrations of I2, no OIO was observed above the BBCEAS instrument detection limits. A possible explanation for this is that our observations were made so very close to the emission sources that downstream chemistry hadn't yet had sufficient time to generate OIO. A clear anti-correlation between I_2 and O_3 concentrations was observed for certain experiments over both L. digitata and A. nodosum seaweed beds, with a 5 ppbv decrease in O_3 coinciding with peak I_2 concentrations of 1.01 and 0.180 ppbv, respectively.

The same instrument was deployed in the laboratory for an extensive study of I_2 emissions from five seaweed species (two Fucales, *A. nodosum* and *F. vesiculosus*, and three kelp species, *L. digitata*, *L. hyperborea* and *S. latissima*). The mixing ratios of I_2 produced by individual seaweed samples were reported using a 20 s integration time enabling highly detailed I_2 emission rate profiles to be obtained for each sample. Moreover, the number of repeat measurements enabled this study to provide statistical information on the variability in the emission profiles and total I_2 amounts across multiple samples of the same species. To facilitate comparisons between different species, average I_2 emission profiles were calculated for *L. hyperborea* (n = 15), *L. digitata* (n = 18), *S. latissima* (n = 10), *A. nodosum* (n = 25) and *F. vesiculosus* (n = 11) using the aggregated results from all samples of each species for all three seasons. A clear ranking of species was observed (*L. hyperborea* > *L. digitata* >

S. latissima > A. nodosum > F. vesiculosus) for mean and maximum I_2 emitted over 180 min exposure times amongst the five species examined in this work; this ranking persisted when, instead, one considers the I_2 emitted over the typical times each species is exposed by the tides. This ranking corresponds to those observed in previous interspecies comparisons by both Ball et al.,(124) and Kundel et al.(182) Science was advanced through application of significantly larger sample sizes (i.e. more repeats) and an improved sample characterisation (e.g. Γ content, sample growing height, season harvested).

Data regarding the seasonal variation of iodine in seaweed is scarce and therefore the statistical significance of the differences in the I2 emission rates observed for September, November and June were assessed through application of the Mann-Whitney test. According to the analysis presented in this thesis, no seasonally specific trend in I₂ emissions could be identified that applies consistently across all species. Statistically significant differences were observed for I₂ emissions for L. hyperborea and S. latissima samples observed across all seasons. L. digitata and F. vesiculosus I2 emissions in June, and A. nodosum I₂ emissions in November were also significantly different from emissions observed for the species in the other months of experiments. In other cases, no statistically significant seasonal differences were observed: for example for samples of both L. digitata and F. vesiculosus between samples analysed in the autumn months of September and November 2012, or between A. nodosum samples analysed in September 2012 (early autumn) and June 2013 (early summer). It was proposed that F. vesiculosus and A. nodosum showed the most similarities month on month and between individual seaweed samples because these plants were exposed to air by the tides almost every day in their natural habitats.

A negative trend was observed between total I_2 emitted and growing height in a correlation plot of data spanning all samples of all species. Most likely, this trend was driven by species-to-species differences, which reflect each species' particular adaptations to grow at specific water depths. No correlations between I_2 emissions and growing height were found in similar correlation plots using data from just one species, although the limited range of sampling heights meant this test was only possible for *A. nodosum* and *F. vesiculosus*.

Analysis of the iodide content of the biological material of individual samples enabled the ranking of species based on iodide content (*L. digitata* > *L. hyperborea* > *S. latissima* > *A. nodosum* > *F. vesiculosus*). Smaller plants were generally observed to contain more iodide per gram dry weight than larger plants, however the correlations weren't particular strong. The selection of plants analysed in this thesis was self-limited because analysis was restricted to only plants that were small enough to fit in the Nalgene bottle. *A. nodosum* and *F. vesiculosus* generally do not grow to sizes larger than the Nalgene bottle. This was therefore of more significance for the kelp species because samples were restricted to < 462 g. Analysis showed that one exposure event uses up only a very small fraction of the iodide stored in a plant. Median Γ content was highest for all species in November 2012 (except *L. hyperborea* potentially due to a small sample size). This result was consistent with Gall et al.,(66) who observed that the average iodine contents of *L. digitata* samples were lowest in summer coinciding with stronger solar irradiances and a higher prevalence of epiphytes and endophytes.

7.3.1 Future work

The average I_2 emission profiles from this work should be combined with data on the species specific geographical distribution of each seaweed species to estimate the total flux of iodine emitted in a particular coastal region. Such calculations have already been done by Leigh et al,(93) for Roscoff using the seaweed emission profiles from the early work of Ball et al.(124) These showed an input of 1.7×10^{19} molecules s⁻¹ over the 100 km^2 region around Roscoff during the lowest tides. The work in this thesis has provided better constrained profiles for kelp species and longer time series for A. nodosum and F. vesiculosus than those used by Leigh et al. The work in this thesis has shown that emissions from A. nodosum and F. vesiculosus increase with time to reach a peak after a few hours, whereas Leigh et al. assumed the emissions from these species remained constant at their initial low values throughout the period when these plants were uncovered. The calculations of Leigh et al. should therefore be re-run using the emission profiles produced in this thesis, in particular to substantiate the proposal of Huang et al., (92) that A. nodosum and F. vesiculosus play larger roles in the aggregate I_2 emissions into the atmosphere than previously supposed. The observations made here in September, November and June should also be incorporated separately into the Leigh et al. model to examine if any seasonal differences can be discerned in the net I₂ inputs.

Either the representative I_2 emission profiles from seaweeds from this work or net source strengths from calculations such as those proposed in the previous paragraph should be incorporated into models of tropospheric halogen chemistry. These models can then be applied to evaluate the effect of seaweed-derived iodine on HO_x and NO_x chemistry, the atmospheric oxidizing capacity (via increased fraction of HO_x available as OH), and on aerosol nucleation (e.g. von Glasow et al).(203) In order to calculate the impact of seaweed-derived I₂ emissions on a larger geographical scale (e.g. across northern Europe or globally) further observational data on seaweed distributions and speciation would be required like the existing mapping of Laminariales (kelp) off the west coast of Ireland,(204) and *A. nodosum* in the Outer Hebrides.(205)

7.4 Extension of BBCEAS to other trace gases.

Nitrous acid (HONO) is a major precursor of OH radicals in the troposphere but its emission sources and chemistry in the atmosphere are not well understood. Current atmospheric models cannot reproduce the concentrations of HONO observed by field measurements in the boundary layer without the inclusion of additional large (order of magnitude) HONO sources. HONO will be the next trace species to be targeted by the field BBCEAS instrument. The older field instrument previously participated in the Formal Inter-comparison of Nitrous Acid instrumentation (FIONA) campaign held at the EUPHORE chamber in 2010,(206) and achieved HONO limit of detection of \approx 130 pptv in 1 min. A new NERC-funded project is about to begin investigating Sources of Nitrous Acid in the Atmospheric Boundary Layer (SNAABL). One of the major aims of this project is to detect HONO from vehicle emissions using the field BBCEAS instrument. Experiments will be performed in a road tunnel (Figure 7.1) to enable the sampling of a well-defined vehicle subset and restrict the sources of HONO to those inside the tunnel.



Figure 7.1 The road tunnel location for detecting HONO in vehicle traffic emissions during the upcoming SNAABL campaign

The field BBCEAS instrument will provide measurements from a static sampling location over an approximate four-week period with the aim of linking retrieved HONO concentrations to different vehicle types (e.g. petrol versus diesel; and different vehicle ages). Additionally, BBCEAS provides a direct spectroscopic NO_2 measurement in same spectral region as HONO. The simultaneous measurement of both species will be applied to investigate how much HONO interferes with the NO_2 concentrations retrieved by a CL NO_x instrument.

8 **Bibliography**

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