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Calibration of Water Vapour Isotope Ratios for High Precision Measurements in the Tropics

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Due to the recent development of isotope ratio infrared spectroscopy (IRIS) analysers, measurements of $\delta^{18}O$ and $\delta^{2}H$ in water vapour can be made in real time with a high temporal resolution. This study is focussed on the development of a calibration device used to characterise such an analyser for measurement of the ambient H2O concentration observed in the Tropical Maritime location of Darwin NT, AUS. The calibration instrument was via experiments associated with injection tube material and vaporiser temperature. Initial findings indicated that system using a copper plate as an immediate injection surface was the most suitable due to both precision measurements and evaporative stability. With an appropriate measurement averaging time (10 to 20 minutes) the vaporiser system was able to meet precision measurements of $\delta^{18}O$ and $\delta^{2}H$ at 0.1‰ and 2‰ respectively over a H2O mixing ratio range of 5-45 mmol mol⁻¹. The calibration device designed in this study was compared against a calibration correction from a former calibration instrument utilised at the study site of Darwin. Data was contrasted between the two systems which revealed a discrepancy of up to ~11% for $\delta^{18}O$.

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Calibration of Water Vapour Isotope Ratios for High Precision Measurements in the Tropics

Graham Edwards 29th October 2013

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The information in this thesis is entirely the result of investigations conducted by the author, unless otherwise acknowledged and has not been submitted in part, or otherwise, for any other degree or qualification.

Graham Edwards 29/10/2013
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Due to the recent development of isotope ratio infrared spectroscopy (IRIS) analysers, measurements of δ\(^{18}\)O and δ\(^3\)H in water vapour can be made in real time with a high temporal resolution. This study is focussed on the development of a calibration device used to characterise such an analyser for measurement of the ambient H\(_2\)O concentration observed in the Tropical Maritime location of Darwin NT, AUS. The calibration instrument was via experiments associated with injection tube material and vaporiser temperature. Initial findings indicated that system using a copper plate as an immediate injection surface was the most suitable due to both precision measurements and evaporative stability. With an appropriate measurement averaging time (10 to 20 minutes) the vaporiser system was able to meet precision measurements of δ\(^{18}\)O and δ\(^3\)H at 0.1‰ and 2‰ respectively over a H\(_2\)O mixing ratio range of 5-45 mmol mol\(^{-1}\). The calibration device designed in this study was compared against a calibration correction from a former calibration instrument utilised at the study site of Darwin. Data was contrasted between the two systems which revealed a discrepancy of up to ~11% for δ\(^{18}\)O.
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Chapter One: Introduction

Stable isotope ratios in water vapour are powerful tracers with regard to the investigation into complex mechanisms occurring in the atmospheric water cycle (Yakir and Sternberg 2000; Wen et al. 2008; Iannone et al. 2010). These measurements can be used in a variety of research applications in such fields as; hydrology, ecology, meteorology and oceanography (Gat 1996; Yakir and Sternberg 2000; Kerstel et al. 2002; Farquhar and Gan 2003; Wen et al. 2008; Gupta et al. 2009; Sturm et al. 2009; Wang et al. 2009). In terms of expressing isotopic ratios in this study, δ notation is used as a departure from a reference ratio i.e.

\[ \delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \]  

R represents the ratio of the rare (heavier) isotopic concentration (i.e. \( ^2\text{H}^1\text{H}^{16}\text{O} \) or \( \text{H}_2^{18}\text{O} \)) to that of the concentration of the most abundant, lighter species (i.e. \( \text{H}_2^{16}\text{O} \)). Rstandard is the isotope ratio of the international reference standard; the internationally accepted primary standard is Vienna Standard Mean Ocean Water (VSMOW) (Gonfiantini 1978). The δ values are expressed here in units of per mil (‰) i.e. parts per thousand. A further international reference standard SLAP (Standard Light Antarctic Precipitation) is used to define the VSMOW/SLAP scale with a defined δ value.

The four stable isotopes of water vapour referred to most often in this study are deuterium \( (^2\text{H}) \) and oxygen-18 \( (^{18}\text{O}) \) which make up relative mass abundances of; 0.015% and 0.200% respectively when compared to their corresponding more common lighter isotopes i.e. \( ^1\text{H} \) and \( ^{16}\text{O} \) (Gat 2010). Such isotopes are termed stable as they do not decay over time unlike radioactive counterparts e.g. tritium \( (^3\text{H}) \) (Criss 1999). Ratios of stable isotopes in water
vapour are essential in understanding climatic processes in the atmosphere as they reflect exchange between water phases due to both kinetic and equilibrium effects explained later in this chapter (Worden et al. 2007). Therefore, stable isotopes are naturally available tracers of water phase transitions providing us with a vast array of knowledge regarding the atmospheric hydrological cycle, particularly in relation to transport and exchange processes including; rainfall re-evaporation (Worden et al. 2007; Kurita 2013), atmospheric mixing (Noone et al. 2011; Farlin et al. 2013) and sea surface evaporation (Pfahl and Wernli 2008).

For the measurement of temporal hydrological processes via isotopic ratios in water vapour, high frequency data is required (Wang et al. 2009; Aemisegger et al. 2012). With recent technological advancements in optical laser systems; real time measurements of stable isotopes in water vapour with a high precision, accuracy and temporal resolution have become possible (Wang et al. 2009; Rambo et al. 2011; Aemisegger et al. 2012). Through this improving technology, several laser based instruments have emerged recently in the field of isotope ratio infrared spectroscopy (IRIS). These IRIS instruments have become commercially available as well as compact and robust enough to be considered field deployable measurement devices (Lee et al. 2005; Lis et al. 2008; Gupta et al. 2009; Sturm and Knohl 2009). Several recent studies have characterised the accuracy, precision and limitations of multiple commercially available IRIS analysers [e.g. (Lee et al. 2005; Gupta et al. 2009; Sturm and Knohl 2009; Iannone et al. 2010; Schmidt et al. 2010; Wen et al. 2012)], therefore this type of assessment of the capabilities for IRIS analysers are not necessarily the main focus here.

This study is focussed on the development of calibration instrument for a laser based analyser used to measure stable isotopes of water vapour within the Tropical Western Pacific (TWP). The measurement site for this study is the TWP Atmospheric Radiation Measurement (ARM) climate facility located in Darwin, NT, AUS (12° 25' 28.56" S, 130° 53' 29.75" E). This site was selected in order to provide data which is representative of the maritime tropics for continuous measurements of isotopic ratios in water vapour. Tropical locations such as the ARM study site are prone to high water vapour content during the wet season resulting in difficulties and limitations for calibration of IRIS analysers. Throughout this study, the concentration of water vapour in the atmosphere is detailed by the mixing ratio, i.e. the number of molecules of water divided by the total number of molecules in a
mixture; represented in mmol mol\(^{-1}\) (Crosson 2008). The extent of H\(_2\)O mixing ratios observed in the western tropical pacific are the driving force behind the need for this study to be undertaken. Figure 1 shows the H\(_2\)O mixing ratio data collected from 17/8/2010 – 25/2/2012 (ARM 2013). Over this 18 month period, seasonal data oscillations reflect the monsoon, retreat of the monsoon and the dry season. While the data range is between 5.1 and 41.5 mmol mol\(^{-1}\), 26% of this data exceeds 30 mmol mol\(^{-1}\) which important for characterising this study.

![Figure 1 Mixing ratio (mol mol\(^{-1}\)) between 17/8/2010 – 25/2/2012 (ARM 2013)](image)

The Australian Nuclear Science and Technology Organisation (ANSTO) has been conducting continuous measurements of stable isotopes in water vapour at the ARM site over recent years via an analyser based on wavelength-scanned cavity ring-down spectroscopy [WS-CRDS; Picarro Inc., Sunnyvale, California, USA]. However, over this time frame, multiple calibration systems have been utilized in order to characterise this instrument for the ambient conditions, particularly in relation to H\(_2\)O range. However, none of the previous calibration systems have been able correct data at mixing ratios greater than 30mmol mol\(^{-1}\) which makes up for slightly over a quarter of all measurements from figure 1. Therefore a key goal for this study is to introduce a new calibration system able to span over all ambient mixing ratios seen in the tropics for the WS-CRDS located at the Darwin ARM site. However, in order to introduce the scope of this study further, a literature review focussing on
relevant studies and the background information regarding stable isotopes in water vapour has been compiled under the following headings of: physical principles of stable isotopes; atmospheric hydrology in the tropics; in-situ measurement techniques and calibration background.

1.1 Physical principles of stable isotopes

The variation in the global distribution of stable isotopes allows the analysis of isotopic features to be aligned with particular hydrological, atmospheric, meteorological and temporal influences (Criss 1999; Gat 2010). With this in mind, it is therefore necessary to diagnose the physical principles which govern isotope distribution and variability in atmospheric waters. The distribution of stable isotopes are essentially a product of fractionation processes involving the varying isotopic composition of an element in a compound through the transition from one physical state or chemical composition to another (Gat, 2000). As there are 9 stable Isotopologues of H2O with molecular mass ranging between 18 to 22g/mol, a large variety of physical and chemical processes discriminate against such isotopologues in differing ways (Kerstel et al. 2002). Such processes can generally be categorised into either kinetic (non-equilibrium) or equilibrium fractionation effects (Criss, 1999). According to Jouzel et al. (1997); equilibrium fractionation varies with the consideration of temperature and phase change. Equilibrium fractionation processes correspond to the ratio of $^{2}\text{H}/^{1}\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ respectively in the condensed phase related to the vapour phase; being fundamentally equal to the ratio of saturation vapour pressures of the corresponding molecules (Jouzel et al. 1997). Kinetic fractionation however, is based on the differences in dissociation energies of molecules composed of differing isotopes (Criss 1999; Gat 2010). As HDO has a lower molecular diffusivity in air than H2O; fundamental kinetic processes affect the rates of evaporation and condensation (Jouzel et al. 1997). The equilibrium isotopic effect is in the realm of 8 to 10 times the magnitude for HDO than it is for H2$^{18}$O; while kinetic effects are of the same order (Jouzel et al. 1997). This characteristic contributes to the importance for joint analysis of both isotopic species [e.g., Wen et al. (2008); Aemisegger et al. (2012); Schmidt et al. (2010)].
Termed the Global Meteoric Water Line (GMWL), Craig (1961) developed one of the original models characterising the observed depletion/enrichment of deuterium and oxygen-18 in terrestrial waters. The GMWL is defined as: \( \delta^2H = 8 \times \delta^{18}O + 10 \% \) with variations expressed in \% enrichments relative to Standard Mean Ocean Water (SMOW). Another important parameter worth mentioning here is deuterium excess (d); defined by Dansgaard (1964): \( d = \delta^2H - 8 \times \delta^{18}O \). Deuterium excess is inherited from the initial isotopic composition of an air mass determined by the sea-air interaction. As a result deuterium excess can therefore be used to predict prevailing conditions during evolution and mixing air masses before heading towards a precipitation site (Froehlich et al. 2002). In order to explain the distribution of stable isotopes in atmospheric water however, Rayleigh distillation processes must also be taken into account.

Dansgaard (1964) recognized four basic effects of atmospheric water which are generally attributed to the depletion of isotopic values explainable by Rayleigh distillation in which idealised models can be used to explain isotopic enrichment/depletion regimes. The first three processes essentially represent the nature of meteoric waters becoming progressively isotopically depleted with increasing distance from a water source through; altitude, latitude, distance from the coast. Yurtsever (1975) indicates that these moisture wringing-out effects result due to a progressively cooling air mass from the source with temperature being the central driving factor of the regime. The fourth and most complicated process; the ‘amount effect’ is an observed anti-correlation between the temperature at the cloud base and the proportion of the heavier isotopes in the precipitation regime (Dansgaard 1964; Risi et al. 2008). The idealised processes mentioned above however may not reflect actual events perfectly as such processes follow the Rayleigh distillation theory for an open system; i.e. water vapour is condensed into a liquid phase and is immediately rained out (Gat 1996; Lee et al. 2006). A second idealized process is described as a ‘closed system’ in which liquid and vapour phases reach a state of equilibrium (Gat 1996). Jouzel (1986) indicates that the closed system typifies the processes occurring in warm clouds as only limited enrichment/depletion can occur. The third model defined as the ‘partial rain out’ model however, is as the name suggests, a process somewhere between the two above idealized processes. In a 2003-2004 study conducted by Lee et al. (2006) at New England, USA, an 80% partial rainout model was approximated. A partial model is generally closer to
reality as an air mass is neither a fully open or closed system (Lee et al. 2006). Rayleigh type equations are useful indicators for general models of isotope distribution. However, for this study as we are concerned with tropical processes; care must be taken to look further than these idealised models and zone in on more relevant temporal and meteorological influences relevant for our study site of Darwin.

Simple Rayleigh models are generally inadequate for examining isotopic behaviour in such phenomena as convective storms and are only relevant for studies on idealized cloud processes (Jouzel et al. 1997). In order to explain why this is so; isotopic exchange between the falling rain droplets and the ascending air in the cloud is the basis of the general rain-out processes mentioned above. The resulting effect is precipitation which basically abandons the isotopic label of greatly depleted isotopic values imprinted by the in-cloud processes; therefore entrenching isotopic equilibrium with the ambient air (Gat, 1996). However, in the tropics this case does not fit the data accurately as the isotopic values in precipitation are more depleted than in true equilibrium precipitation (Gat, 1996). This is due to the strongly convective systems such as; deeply convective cumulonimbus clouds associated with the Inter-tropical convergence zone (ITCZ). Such systems are prevalent in the tropics and are defined by strong local downdrafts preventing a lack of interaction with ambient air and attaining only limited contact with a portion of in cloud air (Wells, 2011). Tropical systems are therefore characterized by complex meteorological phenomena which we look to quantify and relate to in this study by the analysis of $\delta^2$H, $\delta^{18}$O and deuterium excess regimes as well the subsequent mixing ratio. As limited atmospheric studies have been completed with in-situ continuous analysis for tropical regions (particularly in reference to our study site of Darwin), we hope to achieve a greater understanding of both tropical meteorology and hydrology; underlying processes of which, are explained in the following section.
1.2 Atmospheric Hydrology in the Tropics

The atmosphere receives three quarters of its heat energy from the release of latent heat due to precipitation; in which an estimated two thirds of this falls in the tropics (Kummerow 1998). Therefore, precipitation patterns and large scale weather events in the tropics have a highly significant global role in determining atmospheric and meteorological processes. Tropical atmospheric circulation is characterized by mean ascending and subsiding motions in the troposphere (Wells, 2011). The mean ascents are located over areas of convective instability in the ITCZ which migrates both north and south of the equator between seasons influencing the seasonal march of cloudiness, rainfall and the formation of tropical storms (Riehl 1955). Located at the latitudes 30° to 35° North and South of the equator, we see the subtropical high characterized by a general equator-ward return flow in the direction resulting in the trade winds (Riehl 1955). Generally, the trade winds are the prevailing wind regimes in the tropics with great consistency; blowing from east north east in the northern hemisphere and from east south east in the southern hemisphere due to the Coriolis effect (Riehl 1955).

The ARM tropical Western Pacific study site located at Darwin experiences three climatic patterns over an annual cycle: a dry continental regime between the months of May and September; a monsoon season between December and March; and, two transitional periods between these seasons through April-May and October-November (ARM 2013). During the wet season, large oceanic mesoscale convective systems are characterized by widespread rainfall (Pope et al. 2008). The wet season is dominated by marine winds as well as high temperature, humidity and precipitation. During the dry season, continental winds travel from the east and southeast during the morning and generally come from the northwest in the afternoon driven by sea breeze circulations (Pope et al. 2008). In terms of our study, wind regimes and other meteorological conditions may be assessed in order to incorporate trajectories of δ²H and δ¹⁸O through analysis of deuterium excess and the underlying processes affecting the isotopic species. In a study by Lawrence et al. (2004) isotope ratios were related to the intensity and degree of organization of storm systems 48 hours upwind from the collection site. Isotopic ratios were in near isotopic equilibrium with sea water during quiescent weather, with the lowest ratios measured in or downwind from organised storm systems.
As polar air masses move toward the equator over warmer surface waters convection may be established (Wells, 2011). Convection mixes a localised region vertically via both updraft and downdraft; however during precipitating storms a net updraft is the dominating influence (Sherwood et al. 2010). With weak vertical stability in the atmosphere throughout the ITCZ, convection may extend from the sea surface to the height of the tropopause. In such cases, deep convective cumulonimbus clouds will form; these clouds consist of water droplets in the lower troposphere and ice crystals in the upper troposphere (Wells, 2011). The decrease of isotopic ratios with increasing precipitation known as the amount effect (Dansgaard 1964) is observed if precipitation variations in the tropics arise from large scale vertical motion of the atmosphere (Gedzelman et al. 2003). However, if raindrops succumb to partial evaporation during descent, the air column below the cloud base will become enriched with isotopically light water vapour (Strong 2007). Through the analysis of isotopic ratios in tropical systems, we are able to characterise and determine atmospheric processes over both seasonal climatic and small scale events, however in order to measure such events over a temporal scale, continuous measurement techniques must be addressed.

1.3 In-Situ Measurement Techniques

Measurements of stable isotopes in water have been conducted for well over half a century as a method to interpret interactions within the hydrological cycle; however the vast majority of analysis has been executed with regard to the liquid phase (Gat 1996; Lee et al. 2005; Gupta et al. 2009; Rambo et al. 2011). Analysis of stable isotopes in the vapour phase has been considered both laborious and error prone, thus leading to a limited archive of direct and continuous global data for stable isotopes of water vapour (Wang et al. 2009; Helliker and Noone 2010; Rambo et al. 2011).

It must be noted however, that isotopic measurements gathered in the liquid state alone provide data with a limited temporal resolution (Wang et al. 2009; Iannone et al. 2010). Furthermore, greater insights into the hydrological system are possible via detail through both condensed and vapour phases (Lee et al. 2005). For example, (Iannone et al. 2010) reinforced findings from White and Gedzelman (1984) and He et al. (2001) showing that the isotope ratio of water vapour is highly correlated with the ambient moisture content therefore indicating that the vapour isotope ratio bears information on the condensation history of an air mass.
Originally, stable isotope analysis of water vapour was conducted with the use of isotope ratio mass spectrometry (IRMS); functioning on the ideal of the differing mass to charge ratio of isotopes (Horita and Kendall 2004). This type of technology involves either the liquid measurement of isotopes to be captured in discrete precipitation events or the need of water vapour samples to be condensed along with chemical conversion of H$_2$O into light gasses better suited for mass spectrometry (Schmidt et al. 2010). Liquid water samples captured in rain events or via cold trapped water vapour are generally discontinuous in nature; therefore such samples are only able to provide temporally coarse observations (Williams et al. 2004). The most accepted IRMS method for determining $\delta^2$H and $\delta^{18}$O water vapour involves cryogenic trapping, in which liquid nitrogen or dry ice is used to condense a sampled air stream. However, inefficient vapour trapping associated with this sampling technique is susceptible to measurement uncertainty particularly at low humidity (He and Smith 1999; Wang et al. 2009). Therefore, IMRS measurement campaigns are generally limited by the temporal resolution and the analytical precision due to the sampling procedure and the inability of continuous simultaneous measurements (Sturm and Knohl 2009; Wang et al. 2009; Helliker and Noone 2010; Schmidt et al. 2010; Rambo et al. 2011).

However, with technological advancements over recent years; the emergence of isotope ratio infrared spectroscopy (IRIS) has become invaluable for measurements of stable isotopes in water vapour (Helliker and Noone 2010). These laser spectroscopic systems use the structural differences in rotational-vibrational energy for different isotopic species, leading to known transition frequencies in the near-infrared region of the spectrum (Kerstel 2004). Therefore, IRIS permits the continuous simultaneous measurements of $\delta^2$H and $\delta^{18}$O in real time without the need for cumbersome external preparation systems traditionally encountered with measurements of water vapour (Sturm et al. 2009). Importantly, these laser based analysers have reached the point of commercial availability whilst also possessing the characteristics of ideal size, ruggedness and weight specifications to be considered field deployable (Gupta et al. 2009). With the increased ability to perform systematic continuous studies at many locations world-wide, the development of IRIS analysers greatly improves the global coverage of $\delta^2$H and $\delta^{18}$O data associated with hydrological and meteorological processes (Araguás-Araguás et al. 2000). At least three
commercial IRIS analysers are currently in use worldwide, including tuneable diode laser absorption spectroscopy [TDLAS; Campbell Scientific Inc., Logan, Utah, USA [see; (Lee et al. 2005; Wen et al. 2008), off-axis integrated cavity output spectroscopy [OA-ICOS; Los Gatos Research, Mountain View California (See; (Sturm et al. 2009; Wang et al. 2009; Aemisegger et al. 2012; Wen et al. 2012)] and wavelength-scanned cavity ring-down spectroscopy [WS-CRDS; Picarro Inc., Sunnyvale, California, (see; Sturm et al. (2009); Wang et al. (2009); Aemisegger et al.( 2012); Wen et al. (2012)). In this study, the WS-CRDS by Picarro is utilized as a means to test the effectiveness of an in-situ calibration device designed for the ambient conditions (i.e. the large annual humidity range) in tropical maritime locations, as presented by Darwin, NT, Australia. It must be noted that although the WS-CRDS instrument is used throughout this study, the intention and focus here is the actual calibration device. The WS-CRDS analyser by Picarro is therefore solely used in this study as a measurement device to characterise the ability of the vaporiser in terms of precision and accuracy.

1.4 Calibration Background

Laser based isotope ratio measurements are prone to systematic errors from drifts due to variations in environmental parameters such as pressure and temperature (Aemisegger et al. 2012). In order to achieve accurate and precise measurements of $\delta^2$H and $\delta^{18}$O in water vapour; calibration required to correct for such effects as well as to normalise isotopic measurements with respect to an international reference standard (e.g. VSMOW) (Gupta et al. 2009; Aemisegger et al. 2012). Such characterisation is particularly important for water measurements, as H$_2$O molecules have a high polarity and a subsequent high affinity to surfaces such as sampling lines and measurement chambers which in-turn dampens the response time and the measured isotope composition (Lee et al. 2005). Sturm and Knohl (2010) note that it is advantageous for an accurate calibration to be performed over the expected water vapour concentration range along with characterisation of sensitivity measurements to variations in water concentration. An ideal calibration method however can be further fine-tuned through the use of multiple isotopic standards delta values (Wen
et al. 2012). H$_2$O concentration dependence arises via a changing isotopic measurement when only the H$_2$O concentration has been altered in the system (Schmidt et al. 2010). Sturm and Knohl (2010) regard concentration dependence as the central factor which limits long term precision of isotope ratio analysis. In order to characterise the concentration dependence for the WS-CRDS analyser in this study, an appropriate range of H$_2$O mixing ratios must be used to coincide with the annual ambient values from the Darwin based study site.

As previously mentioned, the Tropical Western Pacific ARM site based in Darwin, is representative of an atmospheric water vapour concentration range generally between 5 - 40 mmol mol$^{-1}$ over the annual cycle (ARM, 2013). It should be noted however that the actual calibration applied to the Darwin based WS-CRDS analyser was performed over a H$_2$O mixing ratio range of 5-45mmol mol$^{-1}$ to counteract a measurement bias of the Picarro system at high H$_2$O concentrations. Therefore, to fulfil the aims of this project, our calibration device must coincide with this range of variability as well having robust enough characteristics to be used as a field deployable, remotely controlled instrument. Further, an assessment of the precision and accuracy of the coupled analyser and calibration system is also paramount in terms of validating effectiveness of the calibration device. To the best of our knowledge, no calibration device is available to conduct a suitable calibration at the high end of tropical water vapour mixing ratios; this is essentially reflects the need for development of such an apparatus in this study.

Previous studies have used a variety of systems and techniques used to calibrate laser based IRIS analysers for water vapour. All of these systems possess the collective aim to scale measured IRIS signals to the international Vienna Standard Mean Ocean Water (VSMOW) and the Standard light Antarctic Precipitation (SLAP) [e.g., Lee et al. 2005; Gupta et al. 2009; Wang et al. 2009; Sturm and Knohl 2010; Schmidt et al. 2010]. Over the span of these studies however; three widely used calibration system types have been identified including; a dew point generator as a Rayleigh distillation device, a liquid auto-sampler used in conjunction with an evaporator and finally a dripper/nebulisation type apparatus (Kurita et al. 2012)Schmidt et al. 2010, Wen et al. 2012).
Partial evaporation methods have been used in the past to calibrate IRIS analysers via the use of a dew point generator (Lee et al. 2005; Wen et al. 2008; Wang et al. 2009). Dew point generators work in such a way that dry air is bubbled through a water reservoir, producing a saturated air stream at a controlled temperature and pressure (Aemisegger et al. 2012; Wen et al. 2012). The liquid water in the reservoir is therefore continuously enriched in the heavy isotopes, following a Rayleigh distillation process (Aemisegger et al. 2012; Wen et al. 2012). The isotopic composition of the water vapour can be determined via the known composition of both the initial and residual isotopic water ratios along with the pre-set, controlled temperature (Schmidt et al. 2010; Aemisegger et al. 2012). Crucially however, dew point generators are not perfect Rayleigh distillation devices due to a minor deviation from the Rayleigh line. In a study undertaken by Wen et al. (2012) it was found that using a dew point generator as a Rayleigh distillation device for calibration was effective for $\delta^{2}H$ measurements, but not for $\delta^{18}O$. As this study, like many others is concerned with both $\delta^{2}H$, $\delta^{18}O$ and the subsequent deuterium excess measurements, a dew point generator was not considered when selecting an ideal calibration device.

The second IRIS calibration method encompasses a liquid auto-sampler used in conjunction with an evaporator (Wen et al. 2012). Calibration via an auto-sampler involves the injection of liquid water aliquots of a known isotopic composition into a vaporisation chamber undergoing complete and rapid vaporisation [see; Lis et al. (2008); Gupta et al. (2009); Schmidt et al. (2010)]. The subsequent water vapour is flushed from the evaporation chamber via a dry carrier gas to the sample cell, in which true and measured values are scaled through a linear fit for calibration (Wen et al. 2012). It has been noted by Schmidt et al. (2012) that this calibration method is well suited for a concentration range of 10 to 25 mmol mol$^{-1}$, with the possibility of extending the mixing ratio upper limit to 30 mmol mol$^{-1}$. Furthermore, liquid auto-samplers produce a limited quantity of calibration vapour which is not continuous in nature; therefore the field deployable possibility for extended calibration runs may be limited (Aemisegger et al. 2012). The premise of this study also requires an upper water vapour mixing ratio of at least 40 mmol mol$^{-1}$, which currently seen to be unachievable for an auto-sampler as a calibration device (Schmidt et al. 2010).

As a result, a continuous dripping system is likely to be the most favourable for a remote calibration designed to mimic ambient tropical conditions. This point is further reinforced by
Sturm and Knohl, 2009; indicating that directly adding liquid water to a dry air stream with complete rapid evaporation is the most promising way to develop water vapour standards. Various studies have been conducted on the calibration potential of a dripper type system regarding the calibration of laser based analysers for the measurement of stable isotopes in water vapour [see; (Lee et al. 2005; Lee et al. 2007; Sturm and Knohl 2009; Iannone et al. 2010; Rambo et al. 2011). Lee et al. (2005) incorporated a dripper type device which was able to operate effectively over the H$_2$O mixing ratio range wide range of 0.8-30 mmol$^{-1}$. As with previous studies however; a calibration device suitable for the higher mixing ratio calibrations is required for this study. In a study by Lee et al. (2007) a syringe pump was used which functioned as a dripping device, to administer a liquid standard to a vaporisation chamber. However, this test was not performed over a range of mixing ratios and is therefore not applicable to this study. Sturm and Knohl (2010) utilised a dripper type system which was employed to constantly inject water into an evaporation chamber to create water vapour with a known isotopic signature and homogenous concentration. Sturm and Knohl, (2010) used a Piezo injector as a nebulizer functioning via capillary tubing under shock waves generated via short electrical pulses (Iannone et al. 2009; Sturm and Knohl 2009; Iannone et al. 2010). Through this process, a miniscule droplet diameter of 65 microns is ejected from the nebulizer at a high acceleration allowing for a well-mixed water vapour sample. Sturm and Knohl (2010), note that periodically the nebulizer ceased functioning due to vapour bubbles in the glass capillary which requires manual set up of the apparatus. As our study requires long distance field deployment, such a scenario could put the entire project in jeopardy as re-calibrations may not be possible. Rambo et al. (2011) used a commercially available water vapour isotopic standard source (WVISS) manufactured by Los Gatos Research. This device also functioned on the premise of a nebuliser which injected known reference liquid into a heated chamber. This system was however only calibrated over the range of H$_2$O mixing ratio between 5.5 to 16 mmol $\cdot$ mol$^{-1}$. Tremoy et al (2011) was able to generate water vapour at a mixing ratio of 39 mmol $\cdot$ mol$^{-1}$ with a dripper system based on a syringe pump. However, only one sample was able to be produced at this mixing ratio which isn’t sufficient for this study as continuous measurements are required over the full range of H$_2$O mixing ratios.
As the above studies have shown, no known method can be incorporated from previous literature which possesses the characteristics to run a calibration at a mixing ratio maximum of at least 40 mmol mol\(^{-1}\). As dripper devices have the ability to adjust dynamically ensuring calibration vapour tracks ambient water mixing ratio; such a device likely the most suitable calibration method for our particular study. However, a simpler and more reliable dripping (described in the methods section) system in-lieu of a nebuliser is likely to increase the ability of field deployment and reduce manual operation.

1.5 Project Aims

The main aims of this project are therefore:

1. To assemble and test a new calibration system for the measurement of stable isotopes of water vapour specifically designed for measurement at high H\(_2\)O mixing ratios i.e. at least 40 mmol mol\(^{-1}\) and extendable to 45mmol mol\(^{-1}\)

2. Characterise the performance of the new calibration device regarding, optimisation, accuracy, precision, limitations and the H\(_2\)O concentration dependence.

3. To apply the calibration correction for H\(_2\)O dependence for measured data taken from the ARM study site, showing a comparison between the former calibration system (5-30 mmol mol\(^{-1}\)) and the system implemented in this study (5-45 mmol mol\(^{-1}\)). With the newly corrected data, focus can be made on both short term and longer term meteorological/hydrological trends comparing the difference between current and former calibration system.
Chapter Two: Materials and Methods

For the calibration of in-situ water vapour isotope analysers intended to be operated over a range of H₂O mixing ratios; a continuous flow calibration system which evaporates whole liquid water samples has been designed for field deployment. Whilst a number of systems have been designed for this purpose [e.g. Sturm and Knohl (2009); Iannone et al. (2010); Rambo et al. (2011)]; to the best of our knowledge, no system has the capability of producing unfractionated water vapour at mixing ratios observed in the maritime tropics (i.e. between 5 and 45 mmol mol⁻¹). The purpose of this work was therefore to design and test an apparatus capable of calibrating an IRIS analyser over H₂O mixing ratios spanning 5-40 mmol mol⁻¹ with an extendable calibration range of up to 45 mmol mol⁻¹. The intended aim is therefore producing a calibration device suitable for characterising the performance of the analyser in the Maritime Tropics.

The calibration system designed during this project; is based on a dripper-type device [see; (Lee et al. 2005; Lee et al. 2007; Sturm and Knohl 2009; Iannone et al. 2010; Rambo et al. 2011)] referred to here as a ‘vaporiser’. Operation of the vaporiser involves continuous injection of a liquid water standard of known isotopic composition into a stream of heated dry instrument air in order to produce vapour standards for calibration. Ideally, liquid H₂O injected into the vaporiser is evaporated immediately to prevent fractionation effects occurring within the system. The resulting water vapour should therefore have the same isotopic composition as that of the source water. The vaporiser design has been provided below, along with a brief outline of Picarro L1115-I WS-CRDS measurement device.
2.1 Vaporiser design

The following set-up design illustrates the final vaporiser configuration used in this study. In order to optimise the vaporiser apparatus, multiple experiments were undertaken involving controlled alterations of the vaporiser design. Such experiments are mentioned in detail during the ‘vaporiser experiments’ section addressed later in this chapter. Furthermore, any divergence from the following experimental design is detailed where appropriate.

Schematic diagrams of the vaporiser calibration system are shown in Figures 2, 3 and 4 while figure 5 shows a photographic cross-section for further detail of the system. Figure 2 shows the vaporiser in which all components are encased inside an aluminium block shown by figure 2-P. Figures 3 and 4 show cross-sections of the ‘back sector’ and the ‘front sector’ from figure 2 respectively. All the components of the vaporiser have been listed in Table 1, describing the component and the manufacturer where applicable.

To introduce water vapour standards into the WS-CRDS, source water was evaporated upon entry into the vaporiser which was mixed with heated instrument air within the vaporisation chamber. The subsequent water vapour exited the vaporiser via a heated copper line and was analysed by the WS-CRDS. The flow rate of compressed dry instrument air was controlled using a mass flow controller allowing for the gas flow to be adjusted for specific flow rates. Gas pressure from the instrument air cylinder was operated at 1 bar, with Teflon tubing supplying the dry instrument air to the vaporiser unit.
Tubing within the aluminium vaporising unit was copper to allow greater conductive heating of the air stream (Figure 2, A-D). The copper tubing was coiled around a 1” diameter solid copper cylinder in order to provide consistent heating of the gas line and an extended path length for the heating of the dry instrument air (Figure 2-F).

Three separate 200W heating elements; Figure 3–E, were inserted into drilled holes in the vaporiser to provide an evenly distributed heat source throughout the unit. The initial design, based around one 400W heating element was found to induce temperature fluctuations of ± 10°C which was regarded as too unstable for the calibration purposes related to this study. The three 200W heating elements functioned through a CAL: 3300 Proportional Integral Derivative (PID) controller (West Control Solutions, Gurnee, IL, USA) using a feedback loop from a Resistance Temperature Detector (RTD) sensor (Figure 2-K). Two of these heating elements were placed on either side of the copper coiled gas line (Figure 3–E). The third heating element was installed at a close proximity to both the vaporisation chamber and the RTD temperature sensor shown by Figure 4–E. In order to provide a constant source of heat when the heating elements had reached the set-point
temperature, a 24V (20W) adhesive backed heater mat was positioned around the vaporisation chamber with direct contact to the brass chamber (Figure 4-R).

**Back Sector**

![Diagram of vaporiser system: Back Sector](image)

An Instech P720/10K peristaltic pump supplied the vaporiser system with liquid H$_2$O standards. The peristaltic pump was connected to a collapsible PVC sample bag (Baxter Healthcare Ltd., Auckland, NZ); acting as the reservoir for the H$_2$O liquid standard. The peristaltic pump was adjustable in terms of liquid flow velocity, allowing for direct control over the H$_2$O mixing ratio attainable in the system. An Instech 0.38mm silicone tube-set was used as the peristaltic pump compression tubing; giving a flow rate range of 0.8-7.5 μL/min. Experiments were performed on the system to determine the optimum diameter of these tube-sets regarding precision of the instrument. Further detail is shown later in the ‘vaporiser optimisation’ section of this chapter.
Liquid water was injected via a tube into the vaporisation chamber. Throughout the vaporiser optimisation process a number different materials were used for the injection tube including stainless steel, Teflon and Teflon with a copper plate installation. The different materials are expected to alter the vaporisation process by changing the region and temperature range of where the onset of evaporation occurs which was later shown to effect measurement precision. Experiments were carried out regarding the injection tube material and temperature which are explained in more detail throughout the ‘vaporiser optimisation’ section later in this chapter.
The finalised setup of the vaporiser functioned with an injection tube composed of 1/16” OD; 1/32” ID Teflon. The H\textsubscript{2}O injection tube was introduced into the vaporiser through an airtight Polyethylene septum placed inside a 1/4” Swagelok stainless steel nut. This H\textsubscript{2}O injection tube was placed directly in contact with a copper plate (Figure 2–S) immediately inside the vaporiser. The presence of the copper plate allowed the injection tube to be placed directly on an adequately hot surface immediately upon entry into the vaporiser. As shown in the results section, the copper plate enabled greater consistency of evaporation rates (compared to other tested injection tube methods) whilst allowing the water vapour to flow freely into the vaporisation chamber upon evaporation. More detail is given in the
vaporiser optimisation section regarding the differing setup configurations for the injection tube.

Figure 5 Photographic cross-section of vaporiser design (same perspective as schematic from figure 2)

The vaporisation chamber was a brass 1” Swagelok T-piece. The large ~100ml volume of the vaporisation chamber is therefore designed to reduce variations in the signal of the water vapour mixing ratio, enabling a more consistently mixed stream of water vapour upon evaporation. However, an additional Swagelok buffer volume of 300ml (Figure 2–M) was added to the system to further reduce the variations of the water vapour mixing ratio signal.

Copper tubing (1/4”) exiting the vaporiser was wrapped with 15 W/m heating tape (Figure 2-L). All tubing downstream of the vaporiser unit was wrapped with this heating tape (including the buffer volume) in order to prevent condensation within the lines at high H$_2$O mixing ratios. A 1/4” T-piece was installed 4cm upstream of the WS-CRDS which allowed for excess gas from the vaporiser to be released to ambient air (figure 2-N). This T-piece was required as the WS-CRDS has a pump flow of 30ml/min while the supply of instrument air to the vaporiser was 200ml/min, therefore the T-piece allowed for a variable flow from the instrument air source without affecting the WS-CRDS. The measured values of; the H$_2$O
mixing ratio, $\delta^2$H and $\delta^{18}$O collected by the Picarro L1115 WS-CRDS analyser were analysed to evaluate the performance of the calibration system.

### 2.2 Picarro L1115-I cavity ring-down spectrometer

In order to investigate the performance of the vaporiser as a calibration system, a L1115-I cavity ring-down spectrometer (WS-CRDS); by Picarro, Inc., Sunnyvale, California is used here as the measurement device. A review of the functionality of the WS-CRDS Picarro analyser can be found elsewhere [e.g. (Crosson 2008)]. In terms of a basic system overview however, the analyser functions on the basis of a sample gas being drawn through a temperature and pressure controlled optical cavity. This optical cavity contains 3 highly reflective mirrors (>99.995%) set up in a ring formation allowing for the circulation of injected laser light. The high reflectivity of these mirrors results in a very large number of reflections within the cavity and therefore a long measurement path length (up to 12km) (Brand et al., 2009). The light inside the cavity builds up over time and is recorded via a photo detector; the ring-down measurement is then made by turning off the laser and measuring the light intensity inside the cavity as it decays over time (Brand et al., 2009). By scanning the wavelength over H$_2$O spectral features in conjunction with measurement of the ring-down time along with the laser wavelength; an optical spectrum is generated along with the concentration of individual isotopologues of H$_2$O. The L1115-I analyser scans over the spectral domain 7183.5–7184 cm$^{-1}$ (in 0.01 cm$^{-1}$ steps with a measurement frequency of 0.5Hz.

### 2.3 Vaporiser Experiments

Experiments were carried out regarding optimisation of the vaporiser system, measurement precision, measurement stability and characterisation of the H$_2$O dependence. Such experiments were undertaken in order to test and improve the vaporiser performance via altering various set-up configurations, showing whether the precision of the system was acceptable as a calibration instrument to characterise the H$_2$O dependency for the Picarro L1115-I WS-CRDS. The following descriptions indicate the methodology undertaken for all relevant experiments carried out on the vaporiser system. It should be noted here that liquid isotopic standards were not available for the majority of the vaporiser tests.
Therefore, the mean isotopic values were subtracted from the isotopic ratios for time series and average tests (where relevant) to show the disparity from zero. Isotopic standards were however available for the H2O concentration dependence tests applied to the WS-CRDS analyser located in the tropical study site of Darwin. The reader should also be aware that experiments involving peristaltic pump tube size, measurement stability and H2O concentration dependence were only performed for the copper plate setup.

2.3.1 Vaporiser Optimisation: Injection Tube material and vaporiser Temperature

The temperature of the vaporiser and the material used as the injection tube were tested over multiple experiments with differing vaporiser conditions in order to characterise optimum performance conditions for the calibration system. The relationship of vaporiser temperature and the injection tube material were tested against the standard deviations for the measurements of δ2H, δ18O, deuterium excess (d) and the H2O mixing ratio. This set of experiments were carried out in order to resolve issues of measurement scatter due to ineffective vaporiser configurations and to improve the functionality of the vaporiser. The standard deviation data for the isotopic measurements was later compared against the Picarro L1115-I WS-CRDS compliance specifications to validate the effectiveness of the vaporiser system as a calibration device.

In terms of experimental operating conditions; a dry air flow of 200mL/min was established from a source of instrumental air (<0.015mmol mol⁻¹ H2O). The peristaltic pump was set at an operating capacity of 66% (~4.7ul H2O/min). The expected H2O mixing ratio was therefore at the upper experimental level of ~41.0 mol mol⁻¹. Variables altered over this set of experiments were: the injection tube material (i.e stainless steel or Teflon), the temperature set point, the presence/absence of the 24V (20 Watt) heating mat and the presence/absence of the copper injection plate (which influenced the distance inside the vaporiser where evaporation occurs). The copper plate setup shown by figure 6 allowed rapid evaporation to occur at the point where liquid H2O enters the vaporiser. This was achieved by having the injection tube pressed up against the hot copper plate ~0.5mm below the septum. All other configurations (Teflon with/without heat mat and stainless Steel with/without heat mat) were set with the injection tube extending to the bottom of the mixing chamber, 10.5cm past the septum.
Figures 7 and 8 show the injection tube extending to the base of the vaporisation chamber for Teflon and stainless steel injection tube materials, both with and without the 20W heating mat. The temperature range for these experiments was between 85°C and 115°C spaced with increments of 3°C. This temperature range was selected in order to provide evidence of liquid water pooling at the lower temperatures (i.e. below the minimum adequate temperature range for vaporisation) and to capture higher temperatures without overheating the adhesive heat mat. Temperatures were allowed to stabilise for a minimum of 40 minutes at each temperature step in order to allow the inputs of energy, dry air and H₂O to reach equilibrium. Indicators of vaporiser performance were values of δ²H, δ¹⁸O, d (deuterium excess) the H₂O mixing ratio along with the subsequent standard deviations for all injection tube materials over the 30°C temperature range. The Pearson product-moment correlation coefficient ‘r’ was also used to gain further insight on the relationships between H₂O and δ²H. Data for the first five minutes of each temperature step was discarded to allow for temperature within the vaporiser to reach the recorded set-point.
2.3.2 Vaporiser Optimisation: Peristaltic Pump Tubing Size

By comparing the precision of the isotopic ratios generated via the vaporiser to that of the measurement precision specifications of the Picarro WS-CRDS, we are able to make an
assessment of the noise added to the system by the vaporiser calibration system. Detailed precision analysis for the vaporising system is a crucial step in assessing the effectiveness of the system as a whole. Addressing the variables which limit instrument precision however, allows for improvements to be made to the system. Throughout some preliminary tests, cycling effects were evident in both $\delta^2$H and $\delta^{18}$O at lower H$_2$O mixing ratios (i.e. under ~10 mmol mol$^{-1}$). Therefore, a set of experiments were performed to determine whether the overriding cyclic behaviour effect was the result of oscillations in the peristaltic pump flow rate.

Peristaltic pump tests were performed using a Teflon injection tube with the copper plate set-up along with the 24V (20W) heating mat in place. A dry air flow of 300mL/min was established along with a peristaltic pump operating capacity altered between the respective upper and lower H$_2$O mixing ratios of the vaporiser; ~42 and ~5 mmol mol$^{-1}$ (6.26 ul H$_2$O/min and 0.78ul H$_2$O /min respectively). Temperature was held stable at 105°C for the full experiment. Variables altered over the experiment were the diameter of peristaltic pump tube sets tubes i.e. small (0.38mm ID), medium (0.51mm ID) and large (0.79mm ID). Furthermore, a two point H$_2$O mixing ratio adjustment was performed for each tube diameter at ~42 and ~5 mmol mol$^{-1}$. Each of the six differing configurations were allowed to stabilise for ~30 minutes in order to allow the system inputs to reach equilibrium.

2.3.3 Measurement Stability

The stability of $\delta^2$H, $\delta^{18}$O and d was determined at mixing ratios of both 40 and 5mmol mol$^{-1}$ over a 24 hour measurement period. An Allan variance was performed over both data sets in order to attain a quantitative estimate of the precision over differing averaging times at both upper and lower H$_2$O mixing ratios. Proposed by Allan (1966) as a method to characterise instrument frequency stability, the Allan variance is given by:

$$\sigma_A^2(\tau) = \frac{1}{2n} \sum_{i=1}^{n} [y_{i+1}(\tau) - y_i(\tau)]^2$$

(2)
where $\tau$ is the averaging time, $y_i$ is the average value of the measurements over the averaging interval $i$, while $n$ is the total number of averaging intervals for the given $\tau$, describes the relationship between measurement precision and the averaging time. For a perfect instrument (i.e. no instrumental drift and only white noise), the Allan deviation (square root of equation (2)) decreases log linearly with the averaging time. Deviation from this linear relationship shows no further improvements are made to the measurement precision with averaging time (Werle 2011). Once the optimum averaging time is reached, instrumental drift dominates the averaged signal (Aemisegger et al. 2012). As we have previously mentioned, the Picarro WS-CRDS is used as the measurement device for the isotopic ratios generated via the vaporiser, therefore these averaged measured values can be compared against the Picarro compliance specifications. By using the Allan deviation we are able to indicate an averaging time necessary for the vaporiser to comply with these Picarro specifications, thereby characterising the of the vaporiser as a calibration system.

2.3.4 H$_2$O Concentration Dependence Characterisation

The purpose of the calibration system is to determine the H$_2$O dependence (concentration dependence) of in-situ stable isotope water vapour analysers for conditions observed in the maritime tropics. The water vapour concentration affects both the precision of the isotopic measurements and their bias. The H$_2$O dependence was characterised by adjusting the liquid injection rate so therefore the water concentration for the air stream exiting the vaporiser without changing the isotopic composition. The H$_2$O dependence was determined by decreasing the H$_2$O mixing ratio from 41 and 4 mmol mol$^{-1}$ and then increasing back to 41 mmol mol$^{-1}$ in approximately 1 mmol mol$^{-1}$ steps. This inverse “step-pyramid” method was utilised in order to ensure there was no hysteresis type behaviour.

ANSTO has deployed a second Picarro L1115-I WS-CRDS analyser located at the Darwin Tropical Western Pacific, ARM climate facility. Wen et al. (2012) notes that even two IRIS analysers of the same brand require separate calibration corrections to minimise error. Therefore, the vaporiser calibration system was transported to the Darwin ARM site to perform a H$_2$O dependence calibration on this second WS-CRDS instrument. The H$_2$O
concentration dependence was determined via a calibration run spanning a H$_2$O mixing ratio range of 5-45 mmol mol$^{-1}$ with known isotopic standards. The two calibration runs were compared in order to show the relevance for individual instrument calibrations.
Chapter Three: Results and Discussion

3.1 Vaporiser Optimisation

Before showing the results of the vaporiser temperature and injection tube experiments, the reasoning for such experiments to be carried out should be explained in further detail. The optimisation process was undertaken in order to have the vaporiser perform at its best achievable precision by varying temperature and the injection tube material. With adjustment of the temperature, differing evaporation processes become apparent which plays a part in selecting the most ideal vaporiser configuration for subsequent calibration runs.

Figure 6 shows a shortened time-series of Teflon with the 12V (20W) heater mat in use between 85°-106°C. This figure shows multiple evaporation regimes over the course of the experiment as the temperature was increased by 3°C every 40 minutes. Each grid line represents these increments, starting at 85°C and ending at 106°C; all other plots in this section show a 3°C increase at each 40 minute gridline operating over a temperature range.
of 85°-115°C. Below 91°C, partial evaporation processes are expected to be taking place based on Rayleigh distillation principles. This hypothesis can be explained by interpreting $\delta^2$H and $\delta^{18}$O processes at low temperatures. Both $\delta^2$H and $\delta^{18}$O initially (at 85°C) have slightly depleted values of $\sim$-6 and $\sim$-2 respectively below the zero line. These isotopic values switch from a light to a heavier regime which progressively becomes more enriched as the lighter isotopes are evaporated in preference during a period of water excess due to kinetic effects. As the H$_2$O values decrease; evaporation is reduced likely causing a water excess within the system thus causing a using a shift of $\delta^2$H and $\delta^{18}$O to a more depleted phase as the lighter isotopes again vaporise preferentially. This highly variable process is likely to continue until an adequate stable temperature is reached within the vaporisation chamber. An adequate temperature range appears to be seen between temperatures of 91° - 103°C. However, beyond 103°C a further clear evaporation regime is evident. It should be noted that at these temperatures and above; the evaporation front was visible (due to the transparent quality of the Teflon injection tube) outside of the vaporiser system, which was observed fluctuating within the injection tube ($\sim$2mm above point ‘x’ from figure 7). Therefore, the evaporation front had receded $\sim$10.5cm from inside the vaporiser where it was pressed against the bottom of the vaporisation chamber, to a point where evaporation was continuing externally from the vaporiser. The differing evaporation regimes observed over the 21°C temperature range in figure 9 indicate the need for vaporiser optimisation. Therefore, optimisation tests allow for quantification of the most suitable vaporiser configuration to be established in which further testing including precision and quantification of the H$_2$O dependence can be undertaken.
3.2 Vaporiser temperature and material of injection tube

A set of five experiments were conducted regarding vaporiser temperature and the material of the injection tube. The differing injection configurations included; stainless steel (SS), stainless steel with the 20W heating mat (SS HM), Teflon, Teflon with the 20W heating mat (Teflon HM) and Teflon injection with the copper plate installation (Cu). It should be noted that the Cu injection also had the 20W heating mat heat mat in use.

The relationship between the vaporiser temperature and standard deviation of the H$_2$O mixing ratio in the air stream produced by the vaporiser is shown in figure 10 for the different injection configurations. The standard deviation was calculated for measurements collected at each temperature and shows very different results for the different configurations. The H$_2$O standard deviation for the SS tube increases with temperature, whilst the SS HM, Teflon HM and Teflon show large peaks between 91-106°C. Teflon, Teflon HM and SS HM recorded the best standard deviations at 106°C (0.71 mmol mol$^{-1}$), 112°C (0.64 mmol mol$^{-1}$) and 103°C (0.64 mmol mol$^{-1}$), respectively. However, of all configurations Cu gave the best performance for H$_2$O at 103°C (0.12 mmol mol$^{-1}$) and was consistent up to 115°C.
The relationship between the H$_2$O mixing ratio values vs. temperature is shown in Figure 11. Under the SS configuration, a large unpredictable scatter is seen throughout the data. Teflon also has a large region of unpredictable scatter between temperatures between 94°-103°C. The two configurations of Teflon HM and SS HM show greater periods of stability compared to tests when the heat mat is not in use. The second change in the evaporation regime (i.e. when evaporation front recedes to a point where it is not occurring within the vaporiser –point X on figure 7) for SS HM, both initiates and ceases at lower temperatures than its Teflon counterpart. This is likely a result of greater heat conduction within the stainless steel material when compared to Teflon. The Cu system only has one single change in the evaporation regime which switches at 94°C (i.e. 2 hours into the test) and remains consistent. This is due to the functionality of the copper plate system allowing the injection tube to be placed directly on an adequately hot surface immediately upon entry into the vaporiser. Although the Cu configuration had the best standard deviation for H$_2$O, it is also clear that this configuration is the most stable and reproducible the range of tested temperatures.

Figure 10 H$_2$O Standard Deviation (mmol mol$^{-1}$) Vs. Temperature °C / Elapsed Time.
Figure 11 depicts the \( \delta^2 \)H mixing ratio values vs. Temperature °C / Elapsed Time.

Figure 12 shows the \( \delta^2 \)H standard deviation vs. Temperature. As with the \( \delta^2 \)H mixing ratio; SS shows a general increasing trend over the temperature series. SS HM, Teflon HM and Teflon all have large standard deviation peaks ~14 and 34‰ at temperatures between 90-108°C. In terms of lowest standard deviation statistics for each injection material, Teflon produced a standard deviation of 2.5‰ at 106°C; Teflon HM produced a standard deviation of 1.1‰ at 109°C. SS HM produced a standard deviation of 0.9‰ at 103°C. The copper plate setup achieved a standard deviation of <0.4‰ at all temperatures above 100°C.
Standard deviation data for $\delta^{18}$O vs. Temperature is displayed in figure 13. As with previous parameters, SS is shown to have consistently higher standard deviation outputs than all other injection materials (averaging ~3‰ over all temperatures). Teflon drops down to 1‰ at 106°C but is influenced by large amounts of erratic scatter above this temperature as observed in figure 13. Between temperatures of 106 and 115°C, Teflon HM has a standard deviation <0.6‰ with a minimum of 0.4‰ at 109°C. SS HM registered a minimum standard deviation of 0.4‰ for $\delta^{18}$O; however the standard deviation increased at 115° (1‰) due to the spike seen in figure 13. Between temperatures of 94-115°C, $\delta^{18}$O standard deviation for Cu remained below 0.4‰ with a minimum of 0.37‰ at 106° which consistently performed within the lowest standard deviation above 94°C.
Figure 13 δ¹⁸O Standard deviation (‰) vs. Temperature °C / Elapsed time

Figure 14 Deuterium excess (d) Standard deviation (‰) Vs. Temperature °C / Elapsed Time

Figure 14 shows the standard deviation for deuterium excess “d” vs. temperature. As with the previous analyses, SS shows a consistently higher standard deviation over the temperature range. SS had a lowest standard deviation of 9.6‰ at 88°C however it does not drop below 13‰ above 100°C. Teflon showed large d fluctuations in standard deviation; ranging between 7.5-25‰ throughout the test. Above 106°C d averaged ~10‰ for the
Teflon injection tube. SS HM had a minimum standard deviation of 3.5‰ at 103°C and mean standard deviation of 3.9‰ above this point. Teflon HM had a minimum standard deviation of 3.2‰ at 109°C with a mean standard deviation of 3.6‰ for temperatures greater than 109°C. Cu had a minimum standard deviation of 2.9‰ at 106°C with an average standard deviation of 3.1‰ for temperatures above this point.

The Pearson product-moment correlation coefficient ‘r’ was performed for the H₂O mixing ratio vs. δ²H as shown by figure 15. A correlation value of zero infers no correlation between the two variables, suggesting no fractionation of isotopes in the vaporisation process. SS HM and Teflon injection show large fluctuations in r over the 30°C temperature range (in excess of ± 0.5) which likely indicates the presence of undesired fractionation processes throughout these temperatures.

![Figure 15](image)

Figure 15  r correlation coefficient vs. Temperature°C / elapsed time for H₂O vs. δ²H 40 minute grid points on the x axis show 3°C temperature increases.

Between 105°C and 115°C, SS HM reaches an r value of 0.7 while Teflon has a maximum r of 0.5 over this 10°C temperature range. Over the same temperature range, Cu, SS and Teflon HM have a maximum r value of ± 0.1, indicating minimal correlation between H₂O and δ²H at these higher temperatures. This is a likely indication of minimal fractionation processes are occurring for Cu, SS and Teflon HM above temperatures of 106°C, while Cu performs within this range at temperatures greater than 97°C. Essentially, we are not able to quantify the
amount of fractionation occurring for each injection tube material from the correlation data seen in Figure 15. However, we are able to hypothesise that Cu, SS and Teflon HM are less susceptible to fractionation processes compared with SS HM and Teflon between temperatures of 85-115°C. As this correlation data only provides us with a rough guide of fractionation processes, we must investigate further to demonstrate vaporiser performance quantitatively by comparing measured data against the WS-CRDS instrument specifications.

As the Picarro WS-CRDS L1115-I analyser was used to measure the isotopic ratios from water vapour generated by the vaporiser system, comparing measured values to these specifications allows for great insight into the validation of the results from the vaporiser. Table 2 shows the standard deviations for each configuration at temperatures which provided the smallest standard deviation for the H₂O mixing ratio. These values are paired against Picarro L1115-I compliance specifications for each measured value.

<table>
<thead>
<tr>
<th>Vaporiser Configuration</th>
<th>Cu</th>
<th>SS HM</th>
<th>Teflon HM</th>
<th>SS</th>
<th>Teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaporiser Temp °C</td>
<td>103°C</td>
<td>103°C</td>
<td>112°C</td>
<td>109°C</td>
<td>106°C</td>
</tr>
<tr>
<td>H₂O Standard Deviation mmol mol⁻¹</td>
<td>0.07</td>
<td>0.11</td>
<td>0.41</td>
<td>5.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Measured δ²H Standard Deviation (30s Ave) (%)</td>
<td>0.19</td>
<td>0.32</td>
<td>0.61</td>
<td>4.2</td>
<td>1.3</td>
</tr>
<tr>
<td>δ²H Standard Deviation - Picarro Specs (30s Ave) (%)</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Measured δ¹⁸O Standard Deviation (30s Ave) (%)</td>
<td>0.14</td>
<td>0.17</td>
<td>0.18</td>
<td>1.5</td>
<td>0.54</td>
</tr>
<tr>
<td>δ¹⁸O Standard Deviation - Picarro Specs (30s Ave) (%)</td>
<td>0.067</td>
<td>0.067</td>
<td>0.067</td>
<td>0.067</td>
<td>0.067</td>
</tr>
<tr>
<td>Measured d Standard Deviation (30s Ave) (%)</td>
<td>1.2</td>
<td>1.4</td>
<td>1.4</td>
<td>9.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Measured d Standard Deviation - Picarro Specs, Quadrature (30s Ave) (%)</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 2 Vaporiser Configurations at lowest H₂O standard deviation for each configuration compared against Picarro L1115-I compliance data.
It should be noted however that the Picarro compliance data only gives specifications for H$_2$O mixing ratios between 8-24 mmol mol$^{-1}$, which is much lower than the tested values of $\sim$41 mmol mol$^{-1}$. Furthermore, the Picarro compliance values were averaged over 30 seconds while the measured data was taken at a 5 second (0.2 Hz) resolution. Therefore, the measured values from the vaporiser were appropriately averaged to coincide with the specification values of the compliance data. Further, d specs were not given from the Picarro compliance specifications but were attained via adding $\delta^{18}$O and $\delta^2$H by quadrature.

From table 2, measured values of Teflon and SS exceeded the all of the compliance specification values from Picarro; the closest measured value to that of the compliance data over these two configurations was Teflon’s $\delta^2$H value of 1.3‰ which was more than double the compliance value of 0.46‰. Cu and SS performed within the Picarro specifications of 0.46‰ for $\delta^2$H, registering 0.19‰ and 0.32‰ respectively. Teflon HM was above this level at 0.61‰. Cu, SS HM and Teflon HM configurations performed at a similar standard deviation for $\delta^{18}$O with values of 0.14‰, 0.17‰ and 0.18‰ respectively. However, all three configurations were well outside of the Picarro compliance data of 0.067‰. As a result, the d stats for Cu (1.2‰), SS HM (1.4‰) and Teflon HM (1.4‰) were also well outside of the quadrature calculated compliance data of 0.46‰. With measured values that are greater than the standard deviation specifications from the Picarro compliance data; we see an indication that noise is present in the system as a result of the vaporiser.

With this in mind, the Cu system out-performed all other configurations in terms of standard deviation analysis for all measured values. Further, the Cu system was also the most stable and consistent with only two separate evaporation regimes present (shown in figure 11). From the measured data calculated over the vaporiser temperature and injection material experiments, it is conclusive that the Cu system operated at 103°C is the best candidate for further experimental analysis including measurement stability and characterisation of concentration dependence. Before further experimental analysis was undertaken however, tests were performed on the Cu system to quantify precision statistics at lower H$_2$O mixing ratios.

Although vaporiser optimisation at the upper end of H$_2$O mixing ratios was the most
important factor for this study; showing the precision at the lower end of calibrated data also shows insight on the performance of the system. Standard deviation analysis was performed for \( \text{H}_2\text{O} \) mixing ratios at \( \sim 5 \text{ mmol mol}^{-1} \) shown by Table 3; with measured values contrasted against Picarro compliance standards for low mixing ratios (8mmol mol\(^{-1}\)). However this was only performed for the Cu injection tube at 103°C as this was the most ideal calibration configuration as shown in the previous data.

<table>
<thead>
<tr>
<th>Vaporiser Configuration</th>
<th>Copper Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>103°C</td>
</tr>
<tr>
<td>Vaporiser Temp °C</td>
<td></td>
</tr>
<tr>
<td>H2O Standard Deviation mmol mol(^{-1})</td>
<td>0.22</td>
</tr>
<tr>
<td>Measured δ(^{1})H Standard Deviation (30s Ave) (‰)</td>
<td>0.9</td>
</tr>
<tr>
<td>δ(^{1})H Standard Deviation - Picarro Specs (30s Ave) (‰)</td>
<td>0.33</td>
</tr>
<tr>
<td>Measured δ(^{18})O Standard Deviation (30s Ave) (‰)</td>
<td>1.3</td>
</tr>
<tr>
<td>δ(^{18})O Standard Deviation - Picarro Specs (30s Ave) (‰)</td>
<td>0.060</td>
</tr>
<tr>
<td>Measured d Standard Deviation (30s Ave) (‰)</td>
<td>9</td>
</tr>
<tr>
<td>Measured d Standard Deviation - Picarro Specs, Quadrature (30s Ave) (‰)</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 3 Copper plate configuration measurements at a mixing ratio of ~5mmol mol\(^{-1}\) compared against Picarro L1115-I compliance data

Table 3 shows that none of the measured values are within the compliance range for the Picarro specifications. Therefore, performing a 30 second averaged calibration at \( \sim 5 \text{ mmol mol}^{-1} \) with the vaporiser system (Cu setup) is not ideal in terms of acquired precision. However, by increasing measurement averaging times via Allan deviation (as shown in the measurement stability section later in this chapter); we are provided detail of an averaging time in which such precision requirements can be met.

### 3.3 Vaporiser Optimisation: Peristaltic Pump Tubing Size

As previously mentioned, a set of experiments were performed to determine whether an observed cyclic effect within the vaporiser system was a result of oscillations in the peristaltic pump flow rate. Measurements were collected for \( \text{H}_2\text{O} \) (mmol mol\(^{-1}\)), \( \delta^{2}\text{H} \) (‰) and \( \delta^{18}\text{O} \) (‰) at \( \text{H}_2\text{O} \) mixing ratios of ~42 mmol mol\(^{-1}\) (high) and ~5 mmol mol\(^{-1}\) (Low).
Figure 16 shows the H₂O data vs. elapsed time in minutes for both high and low H₂O mixing ratios. At the high H₂O mixing ratio, the large ID tube (0.79mm) averaged at 41.1 mmol mol⁻¹ with a standard deviation of 6.04 mmol mol⁻¹. Over an identical time frame the medium ID tube averaged at 42 mmol mol⁻¹ with a standard deviation of 0.32 mmol mol⁻¹ while the small ID pump tube had average H₂O concentration of 42 mmol mol⁻¹ with a standard deviation of 0.22 mmol mol⁻¹. As this high H₂O mixing ratio, a clear cyclic trend is evident for both the medium and large ID tubes, while the small ID tube appears to register within the instrument noise. In terms of results at the low mixing ratio (~5 mmol mol⁻¹), the large pump tube averaged at 11.2 mmol mol⁻¹ with a standard deviation of 3.42 mmol mol⁻¹. The medium ID tube averaged at 5.71 mmol mol⁻¹ with standard deviation of 1.15 mmol mol⁻¹, while the small ID pump tube averaged at 4.74 mmol mol⁻¹ with a standard deviation of 0.219 mmol mol⁻¹. As with the higher H₂O mixing ratios, the cyclic trend of the H₂O mixing ratio is clearly decreases in magnitude with decreasing tube size.

![Graph showing H₂O mixing ratio at ~42 mmol mol⁻¹ and ~5 mmol mol⁻¹ vs. Elapsed time for the three differing tubing sizes](image)

Figure 16 H₂O mixing ratio at ~42 mmol mol⁻¹ and ~5 mmol mol⁻¹ vs. Elapsed time for the three differing tubing sizes

δ¹⁸O data for upper and lower H₂O mixing ratios vs. elapsed time is shown in figure 17. At the upper H₂O mixing ratio, the large ID tubing averaged at -16.1 ‰, with a standard deviation of 0.73‰. The medium ID tubing recorded an average of -16.2‰ with a standard deviation of 0.41‰. The small ID tubing had an average of -16.4 ‰ with a standard deviation of 0.29‰. At the lower H₂O mixing ratio, the large ID tubing averaged at -16.33 ‰.
with a standard deviation of 2.89‰. The medium ID tubing had an average of -16.35‰ with a standard deviation of 2.18‰. The small ID tubing had an average of -16.88 ‰ with a standard deviation of 0.70‰.

Figure 17 δ¹⁸O (‰) at H₂O mixing ratios of ~42 mmol mol⁻¹ and ~5 mmol mol⁻¹ vs. Elapsed time for the three differing tubing sizes.

Figure 18 shows the δ³H data vs. elapsed time at the high and low H₂O mixing ratios respectively. At the high mixing ratio, the large ID tubing averaged at -17.4 ‰, with a standard deviation of 1.02‰, the medium ID tubing recorded an average of -17.6‰ with a standard deviation of 0.37‰. The small ID tubing had an average of -18.0 ‰ with a standard deviation of 0.39‰. At the lower H₂O mixing ratios, the large ID pump tube averaged at -19.2‰ with a standard deviation of 2.0 ‰. The medium ID tube averaged -20.8‰ with standard deviation of 1.81‰, while the small ID pump tube averaged at -21.4‰ with a standard deviation of 1.38‰.

In terms of what this data means for the limitations of the H₂O injection, a decrease in systematic cycling is clearly visible with decreasing tubing size indicated by both standard deviation statistics and graphically figures 16, 17 and 18. This decrease in the cyclic behaviour is evident as tubing size is sequentially decreased at both the high and low H₂O mixing ratios. Precision analysis of isotopic ratios throughout this study indicate that with
the vaporiser system in place, $\delta^2$H standard deviation figures are consistently much closer to the Picarro compliance specifications than $\delta^{18}$O measurements (shown in table 2). For $\delta^{18}$O (low H$_2$O mixing ratio) a 68% decrease in standard deviation was seen when comparing medium to small ID tubing, while only a 24% decrease in standard deviation was seen for $\delta^2$H when going from the medium to the small ID tube. This relationship is evident when comparing figures 17 and 18 the at the lower H$_2$O mixing ratios as $\delta^{18}$O shows a clear cyclic trend; whilst such a trend is much more difficult to see in $\delta^2$H. As the Picarro analyser has a much better measurement precision for $\delta^{18}$O than $\delta^2$H (0.46‰ compared to 0.067‰), it is for this reason that cycling trends appear much clearer in $\delta^{18}$O. However, this also helps explain why the vaporiser generally performs much better (in a relative sense) for $\delta^2$H measurements as these are close to being within the Picarro instrument noise. Therefore, low speed pump oscillations essentially hide the cyclic trend for $\delta^2$H in which tubing size greatly influences the system. Therefore, three options are available to improve the precision of $\delta^{18}$O for the vaporiser calibration device; increasing the averaging time (shown in the measurement stability section later in this chapter); further decreasing the pump tube diameter and; providing tests with a different pump (i.e. a syringe pump), which may be less susceptible to pulsing at lower pump speeds. The two latter options are addressed later in the conclusions and recommendations sections.

![Graph showing $\delta^{18}$O vs. elapsed time for H$_2$O mixing ratio at ~42 mmol mol$^{-1}$ for the three differing tubing sizes](image)

*Figure 18 $\delta^{18}$O vs. Elapsed time for H$_2$O mixing ratio at ~42 mmol mol$^{-1}$ for the three differing tubing sizes*
3.4 Measurement Stability
As previously mentioned, the stability of the H$_2$O, $\delta^2$H, $\delta^{18}$O, and $d$ in the vapour stream produced from the vapouriser was determined using Allan variance analysis via the Allan Deviation. Figure 19 shows the Allan deviation for H$_2$O, $\delta^2$H, $\delta^{18}$O and $d$ as a function of averaging time for analysis at the high H$_2$O mixing ratios (~40 mmol mol$^{-1}$). The precision at 30 seconds is 0.13 mmol mol$^{-1}$ for H$_2$O. At this same averaging time $\delta^2$H is 0.17‰, $\delta^{18}$O is 0.15‰ and $d$ is about 1.3‰. At an averaging time of 1 minute, H$_2$O is of a similar value at about 0.12 mmol mol$^{-1}$, $\delta^2$H is about 0.11‰, $\delta^{18}$O is 0.11‰ and $d$ is about 0.8‰. The optimum averaging time derived from this Allan deviation plot however is close to 20 minutes. The precision at 20 minutes is close to 0.08 mmol mol$^{-1}$ for H$_2$O, 0.05‰ for $\delta^2$H, 0.04‰ for $\delta^{18}$O and is about 0.3‰ for $d$.

Figure 20 shows the Allan plots at the low end of H$_2$O mixing ratio (~5 mmol mol$^{-1}$). The precision at 30 seconds is 0.35 mmol mol$^{-1}$ for H$_2$O, while being 0.9‰ for $\delta^2$H, 1.3‰ for $\delta^{18}$O and about 9‰ for $d$. However, at these lower mixing ratios, the Allan deviation unexpectedly increases over the next minute or so across all tested parameters due to short term variability within the measured data. The precision at 1 minute is 0.55 mmol mol$^{-1}$ for H$_2$O, 0.98‰ for $\delta^2$H, 1.45‰ for $\delta^{18}$O and almost 12‰ for $d$. As with Allan deviation stats at the higher H$_2$O mixing ratios, the optimum averaging time for the lower H$_2$O mixing ratios is also about 20 minutes. At this 20 minute averaging time, H$_2$O is about 0.02 mmol mol$^{-1}$, $\delta^2$H is about 0.14‰, $\delta^{18}$O is about 0.08‰ and $d$ is about 0.2‰.
Figure 19 Allan Deviation plots of H\textsubscript{2}O, δ\textsuperscript{2}H, δ\textsuperscript{18}O, and d for a mixing ratio of (~40 mmol mol\textsuperscript{-1}) as a measurement of signal stability. X axis is the Averaging time in minutes while the y axis is the Allan Deviation in (‰) for δ\textsuperscript{2}H, δ\textsuperscript{18}O, and d and mmol mol\textsuperscript{-1} for H\textsubscript{2}O

Table 4 has been provided below indicating the Picarro operating specifications for the L1115-I cavity ring-down spectrometer. Table 4 shows the optimum averaging time for the measured values averaged over 20 minutes along with 30 second averaged data so measured values can be directly compared to the Picarro compliance values. In terms of comparing the 30s averaged measured values to the 30s averaged Picarro compliance values, we see that at the measured values are compliant for δ\textsuperscript{2}H at both the 5mmol mol\textsuperscript{-1} and 40mmol mol\textsuperscript{-1} mixing ratios. At the 20 minute averaging time however, the precision of the vaporiser generally performed close to or at a better precision than the instrument specifications for all measured values. This insight therefore indicates that by increasing the averaging time of up to 20 minutes through calibration processes, the vaporiser is able to comply with the specifications of the Picarro instrument over the span of H\textsubscript{2}O mixing ratios 5-40 mmol mol\textsuperscript{-1}. At a 20 minute averaging time, the Picarro analyser coupled with the vaporiser system limits the measurement precision; beyond this point systematic noise is the dominating factor. Although such an averaging time would significantly increase the time needed to perform calibration runs with the vaporiser system (as opposed to 1 minute averaging times) it is essential to note that the vaporiser can perform within the compliance
specifications of the Picarro analyser if such accuracy is required. Wen et al. (2012) however notes that the typical Precision (and thus uncertainty tolerance) for $\delta^{18}$O and $\delta^2$H is 0.1‰ and 2‰ respectively. Taking these figures into account, an averaging time of 10 minutes would be sufficient over H$_2$O mixing ratio values spanning of 5-40 mmol mol$^{-1}$.

Figure 20 Allan Deviation plots of H$_2$O, $\delta^2$H, $\delta^{18}$O, and d for a mixing ratio of (~5 mmol mol$^{-1}$) as a measurement of signal stability. X axis is the Averaging time in minutes while the y axis is the Allan Deviation in (%) for $\delta^2$H, $\delta^{18}$O, and d and mmol mol$^{-1}$ for H$_2$O.
<table>
<thead>
<tr>
<th>Picarro Specification</th>
<th>Actual Experimental mixing ratio</th>
<th>Picarro Value (‰) 30 s Average</th>
<th>Experimental Value (%o) 30 s Average</th>
<th>Experimental Value (%o) 1 min Average</th>
<th>Experimental Value (%o) 20 min Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ²H Precision at low concentration (8 mmol mol⁻¹ H₂O)</td>
<td>5 mmol mol⁻¹</td>
<td>0.33</td>
<td>0.9</td>
<td>0.98</td>
<td>0.14</td>
</tr>
<tr>
<td>δ²H Precision at high concentration (24 mmol mol⁻¹ H₂O)</td>
<td>40 mmol mol⁻¹</td>
<td>0.46</td>
<td>0.2</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td>δ¹⁸O Precision at low concentration (mmol mol⁻¹ H₂O)</td>
<td>5 mmol mol⁻¹</td>
<td>0.060</td>
<td>1.3</td>
<td>1.45</td>
<td>0.08</td>
</tr>
<tr>
<td>δ¹⁸O Precision at high concentration (24 mmol mol⁻¹ H₂O)</td>
<td>40 mmol mol⁻¹</td>
<td>0.067</td>
<td>0.15</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>d Precision at low concentration (8 mmol mol⁻¹ H₂O)</td>
<td>5 mmol mol⁻¹</td>
<td>0.34</td>
<td>9</td>
<td>12</td>
<td>0.2</td>
</tr>
<tr>
<td>d Precision at high concentration (24 mmol mol⁻¹ H₂O)</td>
<td>40 mmol mol⁻¹</td>
<td>0.46</td>
<td>1.25</td>
<td>0.8</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3 averaged data at 40 mmol⁻¹ and 5 mmol⁻¹ compared against Picarro Compliance Specifications

### 3.5 Characterisation of the H₂O Dependence

The purpose of the calibration system is to determine the H₂O dependence of in-situ stable isotope water vapour analysers for conditions observed in the maritime tropics. The water vapour concentration affects both the precision of the isotopic measurements and their bias. Figure 21 shows the relationship between the average δ²H and δ¹⁸O values at each H₂O mixing ratio step along with the subsequent standard variation statistics. Over the average values, δ¹⁸O holds a much more stable trend with decreasing H₂O mixing ratio when compared to δ²H. Over the full 37 mmol mol⁻¹ range (4-41 mmol mol⁻¹), δ²H values have a range of 4.4 ‰, δ¹⁸O on the other hand has a range of 0.7 ‰. However, the standard deviation data shows a similar standard deviation trend for both δ²H and δ¹⁸O. H₂O mixing ratios below 15 mmol mol⁻¹ provoke an increase in the standard deviation for both parameters. δ¹⁸O had a standard deviation of 0.56 ‰ at 16 mmol mol⁻¹ which increased to 1.7‰ at 3.8 mmol mol⁻¹. δ²H, however, had a standard deviation of 0.6 ‰ at 16 mmol mol⁻¹ which increased to 1.9‰ at 3.8 mmol mol⁻¹.
Figure 21 Standard deviation and average values for $\delta^{2}$H‰ and $\delta^{18}$O‰ vs. H$_2$O (mmol mol$^{-1}$). Circles represent $\delta^{18}$O while plus signs represent $\delta^{2}$H concentration dependence data for the ANSTO based WS-CRDS analyser.

Figure 22 Standard deviation and average values for deuterium excess vs. H$_2$O (mmol mol$^{-1}$) - concentration dependence data for the ANSTO based WS-CRDS analyser.

Figure 22 shows the H$_2$O dependence for the deuterium excess (d) between ~41 and ~4 mmol mol$^{-1}$. A spike of 1.4‰ was observed between 30-35 mmol mol$^{-1}$ which is not fully understood at this point. Over the full experiment, average d values had a range of 3.3‰.
Using the concentration dependence data presented in figures 21 and 22, a comparison was able to be made between the concentration dependence for the ANSTO based WS-CRDS and the Darwin based instrument.

The vaporiser system was transported to the Tropical Western Pacific ARM site located in Darwin to calibrate a second Picarro WS-CRDS L1115-I instrument. For this calibration, known isotopic standards were used (SMOW: -20 for $\delta^2$H and -50 for $\delta^{18}$O) with data averaged over 1 minute. However, the average measured values were subtracted from both the Darwin and ANSTO instrument data (also averaged over 1 minute) in order to compare the concentration dependence for both instruments. The H$_2$O dependence for the Darwin and ANSTO Picarro analyser is shown in figure 23. Although the Darwin analyser was run over a calibration span between 5-45 mmol mol$^{-1}$ and the ANSTO based instrument spanned H$_2$O mixing ratios between 4-41 mmol mol$^{-1}$, a clear discrepancy in the slope characteristics is observed over this plot. Generally, the ANSTO based analyser held a more stable trend regarding the H$_2$O dependence with a smaller deviation from the zero line. At 40 mmol mol$^{-1}$ and 8 mmol mol$^{-1}$, $\delta^2$H was an average of $\sim$1.5‰ more enriched for the ANSTO based instrument with regard to the Darwin based instrument. For $\delta^{18}$O measurements, the Darwin based instrument was an average of $\sim$1‰ more enriched than the ANSTO based analyser at 40 mmol mol$^{-1}$ whilst being slightly more depleted ($\sim$0.25‰) at 8 mmol mol$^{-1}$. This discrepancy between the two concentration dependences observed over the two analysers of the same brand supports findings from Wen et al. (2012) indicating that separate characterisations are still required under such circumstances.
Figure 23 1 minute average values for $\delta^{2}H\%o$, deuterium excess ($d)\%o$ and $\delta^{18}O\%o$ vs. H$_2$O (mmol mol$^{-1}$) – concentration dependence data for both the ANSTO based WS-CRDS analyser (represented by red dots) and the Darwin based instrument (data represented by blue dots).

A H$_2$O concentration dependence correction was applied for the WS-CRDS instrument located in Darwin. In order to perform this correction, measurements of $\delta^{2}H$ $\delta^{18}O$ and were characterised using polynomial functions ($5^{th}$ and $7^{th}$ order for $\delta^{2}H$ and $\delta^{18}O$ respectively). Plots of the two polynomial fits vs. the H$_2$O mixing ratio and subsequent residuals for $\delta^{2}H$ and $\delta^{18}O$ are shown in the appendix.

Residual data gathered from the two polynomial equations allowed for standard deviation analysis to be performed for both raw and fitted data in order to compare the two. The standard deviation for residual data of $\delta^{2}H$ was 0.75‰ whilst the raw data had a standard deviation of 1.3‰, indicating the improvement made with the polynomial fit for the H$_2$O dependence. For $\delta^{18}O$, the standard deviation for the raw data improved from 0.8‰ to 0.31‰ upon characterising the data with the polynomial fit. The correction for deuterium excess was calculated by applying the equation ($\delta^{2}H - 8* \delta^{18}O$) for the corrected data of both $\delta^{18}O$ and $\delta^{2}H$.

From the above corrections, measured ambient data from the Darwin site was able to be corrected over the calibration range of 5-45 mmol mol$^{-1}$. As such, this new extended correction could be compared to the previous H$_2$O correction range of 5-30 mmol mol$^{-1}$ in
order to show the need for the new calibration system. In order to compare the two differing corrections, separate data plots were created for the two correction ranges. For the 5-45 mmol mol\(^{-1}\) correction, the concentration dependence correction was applied at all mixing ratios. For the 5-30 mmol mol\(^{-1}\) series, the data was corrected using the same function but only up to 30 mmol mol\(^{-1}\). For this second series above 30 mmol mol\(^{-1}\), the data was assumed to have a flat H\(_2\)O dependence so the offset between the raw measurements and VSMOW was assumed to be the same as at 30 mmol mol\(^{-1}\). With the acquisition of the former and current H\(_2\)O concentration dependency corrections (i.e. 5-30 mmol mol\(^{-1}\) and of 5-45 mmol mol\(^{-1}\)) the two can be contrasted for both short and long term measurements in order to show the importance of the new system.
Chapter Four: General Discussion

In the previous chapter, the performance of a new calibration system designed for the calibration of isotopic ratios in water vapour in the high humidity of tropical maritime regions was evaluated. A Picarro L1115-I WS-CRDS was used as a measurement device for the calibration system. Previous systems developed to calibrate the H$_2$O dependency of water isotope measurements have not been applied or were not capable of covering the whole humidity range observed in the tropics. With the introduction of the calibration system developed in this study, it is possible to evaluate the importance of characterising the H$_2$O dependence of water vapour isotope analysers at mixing ratios above 30 mmol mol$^{-1}$.

A second WS-CRDS analyser located in Darwin has been deployed in order to provide data which is representative of the maritime tropics for continuous measurements of isotopic ratios in water vapour. Measurements of H$_2$O, $\delta^{2}$H, $\delta^{18}$O and deuterium excess (d) have been collected via this instrument over 15 minute averages between December 19$^{th}$ 2012 and the 29$^{th}$ of July 2013; shown by figure 24. From the measurements obtained it was found that 70% of the raw H$_2$O data exceeded 30 mmol mol$^{-1}$. It must be noted that a humidity correction against a dew point generator (LI-610, Li-COR, Lincoln, Nebraska USA) reduced this figure from 70% to 53%. However, isotopic corrections from the WS-CRDS analyser can only be performed on the raw data measured by the WS-CRDS while the humidity correction is applied afterwards. Therefore, as H$_2$O mixing ratios may only reach a maximum of $\sim$40 mmol mol$^{-1}$ in reality (as shown by corrected H$_2$O data in figure 24 and ARM data from figure 1), a calibration range must span measured raw data from the WS-CRDS i.e. 5-45mmol.

Figure 24 shows the time series for these 2 corrected data series for the stable isotopes in water vapour measured in Darwin by the Picarro analyser. The data are 15 minute averages of the raw 0.2hz data collected by the instrument and cover the monsoon, retreat of the monsoon and the dry season between December 19$^{th}$ 2012 and the 29$^{th}$ of July 2013. As shown by figure 24, the H$_2$O mixing ratio between December and April averages at $\sim$34 mmol mol$^{-1}$ whilst dropping to an average of $\sim$25 mmol mol$^{-1}$ between April and August. This H$_2$O trend gives some indication of the extent of the water vapour influence over seasonal
variation. During the wet season, isotopic ratios show depletion regimes of much of a much greater extent than those seen during the dry season. Before the month of May we see depleted values of $-190\%$ for $\delta^2$H while after this period, a minimum value of $-140\%$ is observed for $\delta^2$H. The depletion of isotopic ratios during the wet season reflects the increasing convective activity due to the “amount effect” which dominates the composition of the regional water vapour (Dansgaard 1964; Tremoy et al. 2012). Isotopic ratios are generally depleted in regions of intense rainfall due to the fractionation of heavy isotopes during condensation which are preferentially removed from water vapour by precipitation (Gedzelman et al. 2003). The monsoon retreat beginning in May is characterised by enrichment in isotopic ratios as convective activity decreases, surface air therefore encounters fewer rainfall events causing the increase of isotopes in water vapour (Tremoy et al. 2012; Kurita 2013).

Figure 24 Time series plot of $\text{H}_2\text{O}$ (mmol mol$^{-1}$), $\delta^2$H‰, $\delta^{18}$O‰ and d‰ Vs. Date collected at the Darwin study site between December 19th 2012 and the 29th of July 2013. Red colour indicates the data corrected for values 5-30 mmol mol$^{-1}$ while the black colour represent data corrected 5-45 mmol mol$^{-1}$.

Without the implementation of the vaporiser calibration device developed in this study, $\text{H}_2\text{O}$ dependency corrections can only be applied to raw data between 5-30 mmol mol$^{-1}$. 
However, with the vaporiser calibration system, H₂O dependency corrections can be applied for values ranging 5-45 mmol mol⁻¹. The δ²H measurements from Figure 24 show that increasing the calibration range of the H₂O dependence from 30-45 mmol mol⁻¹ makes only a minor difference. The average difference between the two corrections for δ²H equates to 0.6‰ which represents a 0.4% range over the whole data set. δ¹⁸O values show a greater contrast between the two corrections at 0.9‰, equating to 5.3% discrepancy over the full range of data. The greatest variation between the 5-30 and 5-45 mmol⁻¹ corrections was observed with deuterium excess (d). The deuterium excess showed an average difference of 6.8‰ which was 16% of the data range. This 16% average discrepancy between the two corrections for the deuterium excess highlights the need to have a H₂O dependency correction over the range of expected ambient values. This statement is supported by Sturm and Knohl (2009) who regard concentration dependence as the central factor which limits long term precision of isotope ratio analysis.

In terms of what this means for the climate scale studies, figure 25 is provided showing deuterium excess vs. the H₂O mixing ratio for the two corrected datasets. As expected, both corrections overlay each other at H₂O mixing ratios lower than 30 mmol mol⁻¹. Beyond this point however, a clear offset exists which up to 14‰ at the highest mixing ratios, equating to a difference of 33%. Although the application of the two differing corrections show little difference for δ²H over this 8 month dataset, δ¹⁸O and d values induce respective discrepancies of 5.3% and 16%, highlighting the need for the extended 5-45 mmol mol⁻¹ calibration.
Whist a number of studies have been interested in investigating seasonal and interannual variations in stable isotopes (Jacob 1991; Lee et al. 2006; Tremoy et al. 2012) there is also an interest in using stable isotopes to gain insight into convective parameterisations (Bony et al. 2008; Risi et al. 2008; Risi et al. 2013). The high temporal resolution of an IRIS analyser may provide an important tool for these studies; with paired measurements of isotopes and water having provided interesting findings with regard to rainfall re-evaporation (Worden et al. 2007; Kurita 2013) and atmospheric mixing (Noone et al. 2011; Farlin et al. 2013). However, to accurately interpret these paired measurements, in-situ measurements must be accurately calibrated over the full range of measured ambient H₂O mixing ratios. To investigate the effect of not calibrating the Picarro analyser over all mixing ratios, we look at a wet season event where depleted stable isotope values were observed.

A wet season event was captured between the 7th to the 15th of March as shown by figure 26. To coincide with this data, Outgoing Longwave Radiation (OLR) was used as an indicator for meteorological properties; particularly in relation to convection. OLR is the amount of energy (W/m²) reflected from the earth back out to space, it a proxy for convective processes with areas of intense convection represented by low OLR values (Singh et al. 2013). Figure 27 shows the OLR measured from the Darwin ARM site (represented by the
pink marker) as of 8am on the 13th of January 2013. Arrows represent wind direction while the blue to red colour scale indicates a decreasing OLR value. From figure 27, winds from the east and west are seen to converge close to 130° E, resulting in thick cloud cover due to convective processes over the Darwin ARM site and surrounding regions. This coincides with the corrected 5-45 mmol mol⁻¹ data from figure 26 indicating a sharp depletion regime in the isotopic values just short of the 13th of January. During this period depleted values of -140‰ (from -80‰) for δ²H and -22‰ (from -17.5‰) for δ¹⁸O are evident, likely attributed to the “Amount effect” during periods of intense convergence as mentioned earlier. δ²H was plotted against d over this short term weather event for both corrections as shown in 28. A similar plot was performed by Kurita (2013) regarding sensitivity to relative humidity of measurements in which an apparent trend exists between lower δ²H values with an increasing d-excess. Although no such correlation was evident over this weather event, a large offset between the two corrections was up to 13 ‰. With this in mind, awareness of such a discrepancy is crucial for isotopic studies in water vapour in order to corrected measurements.

Figure 26 H₂O (mmol mol⁻¹), δ²H‰, δ¹⁸O‰ and d‰ Vs. Date collected at the Darwin study site between 7th to the 15th of March. Red colour indicates the data corrected for values 5-30 mmol mol⁻¹ while the black colour represents data corrected for over the 5 – 45 mmol mol⁻¹
Figure 27 Outgoing Longwave Radiation (W/m²) shown over latitude and longitude on the 13th of January 2013. Arrows represent wind direction while the pink marker represents the ARM study site.

Figure 28 $\delta^2$H vs. $d$ collected at the Darwin study site from the 7th to the 15th of January red dots represent data corrected for values 5-30 mmol mol$^{-1}$ while the black colour represents data corrected for over the 5 – 45 mmol mol$^{-1}$.
In terms of quantifying the short term discrepancies between the two correction values, we looked at data over timeframes of days rather than months. For \( \delta^2 \text{H} \), values of 3‰ were observed coinciding with high H\(_2\)O values of up to 40 mmol mol\(^{-1}\). This maximum 3‰ difference between the two corrections makes up only ~2% of the range exhibited by \( \delta^2 \text{H} \) values over the 7 month timeframe. \( \delta^{18} \text{O} \) values had a maximum difference between the two corrected values ~2‰ observed between February and March, however this accounted for ~11% of the total range for \( \delta^{18} \text{O} \) over the full dataset. The deuterium excess had a maximum discrepancy of ~14‰ during mid to late January and early to mid-March. This ~14‰ figure equates to a difference of 33% over the measured data. The large differences attributed to the two corrections of 5-30 mmol\(^{-1}\) and 5-45 mmol mol\(^{-1}\) indicate the necessity of applying the new calibration system developed in this study. As an ideal H\(_2\)O concentration dependence calibration must be characterised over the ambient values of the measured values (Schmidt et al. 2010), the vaporiser system has been able to achieve such values.
Chapter Five: Conclusions and Recommendations for Future Work

5.1 Conclusions

The central aim of this study was to develop a field deployable continuous flow calibration system which evaporates whole liquid water samples over H$_2$O mixing ratios up to 45 mmol mol$^{-1}$. This calibration range was selected in order to coincide with the ambient H$_2$O concentrations observed in maritime tropical water vapour. The purpose of developing the calibration device in this study was focussed on calibrating measured data from an IRIS analyser based on WS-CRDS, in order to correct measurements for H$_2$O concentration dependence. Over the course of this study, the following conclusions were drawn:

The calibration device was optimised via experiments associated with injection tube material and vaporiser temperature. Initial findings indicated that system using a copper plate as an immediate injection surface was the most suitable due to both precision measurements and evaporative stability (with regard to all other materials used). Standard deviation analysis further indicated that the ideal temperature to run the vaporiser calibration system (with the copper plate installation) was 103°C. Under these conditions the vaporiser device (when coupled with a Picarro L1115-I WS-CRDS) was able to produce δ$^{18}$O vapour over 30s averages with standard deviations of 0.15‰ and 1.3‰ at respective mixing ratios of ~40 mmol mol$^{-1}$ and ~5 mmol mol$^{-1}$. These results however did not match the compliance specifications supplied by the Picarro analyser (0.067‰), showing an indication of unwanted noise within the system. The vaporiser produced δ$^2$H vapour of 0.2‰ and 0.9‰ at respective mixing ratios of ~40 mmol mol$^{-1}$ and ~5 mmol mol$^{-1}$. The vaporiser data matched the compliance specifications for δ$^2$H (0.46‰) at ~40 mmol mol$^{-1}$ while not complying at ~5 mmol mol$^{-1}$. However, by increasing data averaging times to 10 minutes, it was found that over the concentration range of 5-40 mmol mol$^{-1}$ the vaporiser system was able to match the typical precision (Wen et al. 2012) of δ$^{18}$O and δ$^2$H at 0.1‰ and 2‰ respectively. However, a 20 minute averaging time was required for compliance with the Picarro specifications over concentration range of 5-40 mmol mol$^{-1}$.

Therefore, the vaporiser system was found to be an effective calibration device over the H$_2$O mixing ratios of 5-40 if appropriate averaging times are met. In terms of applying the
vaporiser system to measured data of from the Tropical Western Pacific ARM site located at Darwin; the calibration system developed in this system was used to characterise the data. This new calibration system, spanning $\text{H}_2\text{O}$ mixing ratio values of 5-45 mmol mol$^{-1}$ was compared to the former utilised calibration system (5-30 mmol mol$^{-1}$). By comparing these two datasets it was found that a discrepancy between the two corrections showed an average of 0.6‰ over the seasonal range while a maximum difference of 3‰ was observed during a short term weather event. For $\delta^{18}\text{O}$ the seasonal data showed an average difference of 0.9‰ between the two corrections with a maximum short term discrepancy of 2‰. Deuterium excess displayed the largest contrast between the two corrections with an average seasonal discrepancy of 6.8‰ with a maximum difference observed at 14‰ during a convective weather event. Therefore, this study reflects the need for calibration of a WS-CRDS analyser to be conducted over the full range of ambient $\text{H}_2\text{O}$ mixing ratios. Without such a procedure, error is seen as excessive for these high precision measurements particularly at high $\text{H}_2\text{O}$ mixing ratios as seen in the tropical maritime climate.

5.2 Limitations and Recommendations for Future work

Key limitations and recommendations for this study and future studies involving the calibration of laser-based instruments for measurements of isotopic ratios in tropical water vapour are represented in this chapter.

In terms of optimising the vaporiser calibration system, some essential steps are required in order to further validate the system as an accurate and precise calibration device. Firstly, known isotopic standards must be used to characterise the vaporiser system regarding systematic error and precision in order to completely characterise any possible fractionation effects within the system. Although known isotopic standards were used for the $\text{H}_2\text{O}$ concentration dependence characterisation for the Darwin based instrument, no such standards were available earlier for the optimisation experiments. To coincide with the use of isotopic standards for optimisation and precision analysis; cryogenic freezing of water vapour produced by the vaporiser is a technique which could be employed to further validate the vaporiser as an ideal calibration device. The cold-trapped water can be
compared to that of the known isotopic standard (source water) by Isotope ratio mass spectrometry (IRMS) (Sturm and Knohl 2009). By assuming no fractionation has taken place during the freezing process, this method can provide great insight into the presence/absence of fractionation processes within the calibration system.

As discussed in the results section, the peristaltic pump tubing diameter was mentioned as a source of uncertainty due to the cycling processes observed at lower pump speeds. This issue was hypothesised to limit the precision of the vaporiser system at the low H$_2$O mixing ratios (< 10 mmol mol$^{-1}$). In order to improve the precision of the vaporiser at these lower mixing ratios, further experiments should be undertaken involving the utilisation of a pump with less oscillating characteristics at low pump speeds or a completely different pump system all together (e.g. a syringe pump) (Tremoy et al. 2011). However, as an initial step; the sourcing of a peristaltic pump tube with a smaller diameter may be beneficial in further reducing the variation observed in the pump.

A further limitation was the usage of Picarro standards as a basis to compare precision data for the vaporiser system. Although these specifications give a good indication of noise within the system, the Picarro specifications are only a guide for this study as they are only applicable over H$_2$O mixing ratios of 8-24 mmol mol$^{-1}$. Regarding the calibration of a WS-CRDS analyser with the current vaporiser set up, it is recommended that an averaging time of at least 10 minutes is used for a full concentration dependence calibration for the tropical maritime. If focus is only made at higher mixing ratios i.e. > 30mmol mol$^{-1}$ this averaging time can be significantly reduced to ~2 minutes.

The vaporiser calibration device developed in this study was tested with a Picarro WS-CRDS analyser; however it was not specifically designed to be coupled with only this instrument. Therefore, figure 29 has been provided in order to demonstrate a possible conversion of the vaporiser system in order to improve its suitability for a calibration of a second commercial IRIS analyser. The Los Gatos instrument based on off-axis integrated cavity output spectroscopy has been selected to demonstrate such a conversion procedure.

The most important difference between the WS-CRDS system and the IRIS analysers is the discrepancy in the pump rate over the instruments. The Picarro WS-CRDS has a pumping rate of 30ml/min while the Los Gatos instrument has a pump rate between 500 and
800ml/min (Aemisegeger et al. 2012) Therefore, a larger capacity Mass flow controller (Figure 29-A) along with a pump with a greater flow rate to provide saturated water vapour for the larger volumes required.

**Figure 29 Amended design of vaporiser system**

Furthermore, Figure 29 shows some basic amendments which may be beneficial to improving the function of the vaporiser system. Such amendments include, a molecular sieve, used to completely desiccate instrument air. An increase in the length of the copper wire to ~3 times that of the current system has also been included to allow further heating of the air stream. This feature also involves having the water injection point injection point external to the main heat source (to prevent evaporation through the injection tube). An RTD sensor is also placed in close proximity to the region of evaporation (under the mixing chamber) to give greater control over the heat mat.
References


Appendices

Figure 30 5th order polynomial and subsequent residual for δ²H correction
Figure 31 7th order polynomial and subsequent residual for $\delta^{18}$O correction