Using high temporal resolution δD, $\delta^{18}O$ to determine groundwater and surface water interactions in tropical catchments

Submitted by

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Statement of Originality

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

01/08/2015

Nicholas K. E. Rockett Date

Abstract

This Master thesis focuses on the deployment of newly developed instruments capable of monitoring the isotopic composition of water continuously and in-situ in a remote, pristine, rainforest location in the Daintree region of Far-North Queensland. Over a series of four rain-system events, towards the end of the tropical wet season 2013, two Picarro, Cavity Ring-Down Spectrometers, incorporating Diffusion Sampling units (DS-CRDS), were operated simultaneously over an extended period, to measure rainwater and creekwater isotope values at sub-minute temporal resolution. Over the series of experiments, successful methods and operational strategies were developed to cope with the often-challenging conditions faced. One storm occurrence was successfully monitored by both CRDSs during a field trip in early March 2013. Two significant rain events occurred during the transition of this system: one very intense flood event, recording a fall of 7.55 ‰ VSMOW in rainwater values and a second, less intense event, over a protracted period, with a fall of 9.68 ‰ VSMOW. The second instrument simultaneously recorded creek water isotope values, recording a fall of 1.6 ‰ VSMOW over the course of the second event. Comparison of rain intensity and ambient air temperature with isotope value, over the two events showed no significant positive correlation, confirming previous research. The simultaneous monitoring results, from the second event demonstrate the superiority of high temporal resolution methods in monitoring and modeling the water cycle and streamflow generation. Comparing mean isotope values for both event and creek water, real time values for event-water/mean values for creek-water and real time values for event-water/ 15-minute discreet values for creek-water, indicated that high resolution, in conjunction with the extra component, can highlight subtle changes to creek contribution over time. Using statistical mean values to calculate relative contribution of event water to discharge results in an input of 0.03 %. When calculated using the mean contribution values of real time analysis, the event water contributions are: 3.88 %, using mean fixed value creek/groundwater and 5.53 % using mean 15-minute values for creekwater and fixed value groundwater. These results suggest that higher temporal resolution monitoring components may produce greater accuracy in discharge contribution values.

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1. Introduction

The identification of preferential flowpaths can suggest strategies for managing a catchment, and a more effective management plan may help mitigate disaster and provide environmental and economic benefits. The application of high temporal resolution monitoring instruments can help us better define the mechanisms and processes occurring in catchments and therefore assist in the development of effective management strategies.

Towards the end of the Australian tropical Wet Season, March/April, 2013, a series of hydrological experiments were conducted at the Daintree Research Observatory, near Cape Tribulation, in Far-North Queensland. The experiments sought to gain a deeper understanding of the ground/surface water interactions taking place during storm events in this pristine rainforest catchment.

The research objective were to:

A. Successfully operate a field experiment under challenging conditions, over an extended period, using a suite of high temporal resolution loggers. This instrument suite incorporated newly developed 'continuous', real time monitoring, of creek and rainfall isotopes, using Diffusion Sampling units, supplying water vapour to Picarro, Cavity Ring-Down Spectrometers (DS-CRDS) (Munksgaard et al., 2011) and,

B. Demonstrate simultaneous 'continuous' analysis of rain and creek-water isotope values so as to better understand short-term variability and investigate any short-term interactions in streamflow generation.

The experiments sought to characterise the water from various sources using the stable isotopes of hydrogen and oxygen. Isotopic tracers occur naturally, with the ratio of isotopes changing according to fractionation mechanisms such as evaporation or condensation. These mechanisms result in the water's isotopic state being dependent on its derivation; it's provenance. These experiments used a Picarro Isotope Analyser

L2120-i for high temporal precision measurements of $\delta^{18}O$ (ratio of ^{18}O:^{16}O) and δD (ratio of ^{2}H: ^{1}H) values. With end-members defined according to these values, the identification of flow mechanisms, pathways and fluxes within the catchment could be suggested.

A pilot study, conducted in March 2012 (page 47) indicated that, during wet season storm events, each end-member: rainwater, soil-water, bore-water and creek-water, had a distinctly different isotopic signature suggesting that a detailed investigation could provide useful results.

Logistic and Scientific Challenges

The use of new, untested technologies in conjunction with a multiple loggers and samplers, operated under demanding conditions, can present many challenges. During this series of experiments, operational configuration and methods were adjusted to achieve the greatest chance of success. Methods were developed to face challenges presented by flash flooding, white tailed rats and limited power supply, among others. Solutions will be discussed and recommendations suggested for the benefit of any similar research projects that are undertaken in the future (page 78).

Simultaneous Operation of DS-CRDS: Rain/Creek Water

In 2012 Munksgaard et al. described "extreme and rapidly changing" isotope values in rainfall in Far-North Queensland after analysing nine rain events over an eight-month period using the high temporal resolution capabilities of the Picarro DS-CRDS. By deploying similar instruments to analyse both rain and creek-water simultaneously, any corresponding patterns of variability between rain and creek-water could be identified, whilst modeling creek contribution at such resolution would highlight its importance for describing realistic values throughout an event.

High temporal resolution data can reveal processes that are obscured by data of a coarser resolution. An objective of the experiment was to simultaneously monitor water isotope values, in 'real time', from both rain and creek-water, during a flood event. I report on the simultaneous data set of both rain and creek $\delta^{18}O$, at very high temporal resolution (15-second integrated), with corresponding (15-minute) discreet samples of creek water, collected during a storm event in early March 2013.

Document Outline

This document begins with a literature review (page 14) reporting on the significance, history and contemporary developments in the field of water isotope monitoring, including the technological advances that resulted in new instruments with the ability to sample and monitor isotope values in 'real time'. The literature review section is followed by a site description (page 31) of the Daintree Research Observatory (DRO) and a methods section (page 35) describing both the conventional and new technologies employed during the experiment series. The results (page 52) and discussion (page 78) sections are structured according to the research objectives (page 11): **A**. challenges, solutions and suggestions and **B**. the successful, continuous, simultaneous monitoring of rain/creekwater isotopes.

2. Literature Review

> "From a drop of water a logician could infer the possibility of an Atlantic or a Niagara without having seen or heard of one or the other. So all life is a great chain, the nature of which is known whenever we are shown a link of it."
>
> - Sir Arthur Conan Doyle, A Study in Scarlet

Isotopes have been employed as powerful tools in the environmental sciences for over fifty-five years (Koehler & Wassenaar, 2011). Their highly conservative nature makes them ideal as tracers to identify sources and flux between water compartments. Traditional mass spectrometer laboratory analysis of discreet samples has been expensive and time consuming, and therefore limiting (Buttle, 1994; Brand, 2009; Gkinis et al., 2010; Munksgaard et al., 2011). This review investigates the advances in isotope analysis instrumentation that are making field deployment and 'real time' analysis under difficult conditions a reality. Combined with robust and reliable in-field data loggers and sonde water quality monitors, which can be deployed at high temporal resolutions, instruments are revealing a much more detailed picture of catchment hydrological processes.

The worlds tropical regions have proved a challenge to hydrology research. Flash flooding, caused by torrential rainfall in highly responsive catchments, can result in the movement of large volumes of water. These floods can be a threat to life, property, crops and livestock. Intense rainfall has resulted in rapid increases in streamflow (flash flooding) at Thompson Creek and many other rainforest streams in Far-North Queensland (Bass et al., 2011; Bass et al., 2014). Due to historical bias, difficult physical access and lack of resources much of our understanding of hydrological processes in tropical regions relies on modeling (developed in temperate regions), rather than empirical data (Wohl, 2012). With the use of high resolution, field deployable isotope analysers, researchers in the tropics finally have the opportunity to gain detailed, high temporal resolution data, promoting quantification of sources, storage and fluxes within tropical catchments.

2.1 Hydrology in the Tropics

Tropical regions, those lying between 25 degrees North and South of the Equator (Wohl, 2012), have significantly different climate regimens to the mid latitude and polar regions. The widely used Köppen climate classification scheme, an empirical system based on vegetation, divides the tropical regions into three sub-climate regions that all have temperatures above 18 °C in their coldest month:

- Tropical rainforest climate - Aseasonal regions directly adjacent to North and South of the equator (usually within five to ten degrees latitude)

- Tropical monsoon climate – Biseasonal regions that are subject to a hot, wet period during summer and a cooler dry season

- Tropical wet and dry savanna climate – Usually found in the outer margins of the tropical zone, these regions have a much longer and more intense dry season

(Encyclopaedia Britannica, 2013)

During the summer months most of the tropics becomes meteorologically very active. Unfortunately, with the historical development of atmospheric and hydrological sciences in mid-latitude regions, and the inherent difficulties accessing many areas, especially in the tropical 'wet season', much of the tropics have been relatively insufficiently studied.

The tropics have a lack of data on rainfall intensity, duration and frequency, which is crucial to understanding runoff processes (Bonell, 2004). So, in the regions that are subject to the highest energy in terms of rainfall there is a paucity of useful data, limiting the understanding of key hydrological interactions (Wohl, 2012).

Many tropical regions are subject to extreme annual rainfall, for instance, the regions of the northeast coast of Australia between Cardwell and Cooktown have an annual rainfall of between 2000 and 8000 mm, with 60 % of that rainfall arriving between December and March (Bonell, 2008). Short-term rain intensities can be up to two orders of magnitude greater than those in temperate regions (Bonell, 2008).

As global temperatures rise, due to predicted climate change (IPCC, 2013), the capacity of the atmosphere to hold moisture will increase resulting in an increase in hydrological activity in tropical regions (Wohl, 2012). Increased intensity, duration and frequency of significant rain events is likely in many parts of the tropics and these changes will impact on terrestrial hydrological mechanisms and processes. To adapt to these changes understanding the processes and mechanisms occurring in a rapidly changing landscape is a priority. Advances in instrumentation, allowing researchers to record isotope values in 'real time', in challenging situations, are helping them understand the highly energetic and rapidly changing tropical regions hydrological systems.

2.2 Environmental Tracers

Tracers are materials that are either naturally occurring in the water body or are deliberately introduced into the system in order to determine the waters pathways, flow and flux. Naturally occurring tracers include oxygen 18 (^{18}O), hydrogen 2 (deuterium/^{2}H), radon (^{86}Ra) and various ions. An example of one of the simplest and most effective tracers being salt, as expressed as salinity, and measured as electrical conductivity. Salinity tends to be greater in groundwater, due to the dissolution of minerals, than in rainwater, consequently this characteristic can be used to determine the source of water samples.

The most useful tracers behave conservatively (Dincer & Davis, 1984), reacting minimally within the water body, and have a discernible variation between end members. There are many naturally occurring tracers but this review will be looking at the use of hydrogen and oxygen stable isotopes (D (^{2}H)/H and $^{18}O/^{16}O$).

D and ^{18}O are two of the most useful and important tracers in hydrological research (Gat, 1996). They occur naturally in all waters as various isotopologues (molecules that differ in isotopic composition, such as the water molecules; $H_2{}^{18}O$, $H_2{}^{16}O$, $HD^{16}O$) and behave with extreme conservatism, generally only changing concentration ratios during phase shifts when fractionation processes occur.

These isotopes have been used effectively for over 55 years (Koehler & Wassenaar, 2011) in meteorological as well as surface and groundwater studies (Craig, 1961a; Dansgaard, 1964; Clark & Fritz, 1997). Although environment tracers alone cannot determine the physical mechanisms of ground/surface water interactions (Anderson, 1978; Buttle, 1994; Elsenbeer et al., 1995), they are ideal for determining gross storage and fluxes within/between compartments under the high spatial heterogeneity within catchments (Buttle, 1994).

Buttle (1994) summed up the benefits of using stable isotopes as environmental tracers in catchment research:

- They are applied relatively evenly across the catchment (Sklash, 1990) and represent a "synthesis of spatially distributed processes occurring across the basin" (Buttle, 1994)

- They are conservative - not reacting chemically with other materials in the catchment (Dincer and Davis, 1984)

- They undergo fractionation during phase changes resulting in the identifiable 'fingerprints' of different waters (Dansgaard, 1964)

- The isotopic signature of old water tends to be a homogeneous mixture of input waters over time (Sklash, 1990), producing a powerful tool for investigating mixing of old/new waters.

2.3 Water Isotopes as Tracers

The water molecule is constructed of hydrogen and oxygen atoms. These atoms each have a number of isotopes of different atomic weights (Table 1).

Table 1. The abundance and weight of the isotopes of oxygen and hydrogen

Isotope	Alternate Name	Symbol	Abundance (%)	Weight (u)
Oxygen 16		^{16}O	99.76	15.9949
Oxygen 17		^{17}O	0.04	16.9991
Oxygen 18		^{18}O	0.20	17.9991
Hydrogen 1	Protium	^{1}H	99.98	1.00794
Hydrogen 2	Deuterium	^{2}H	0.015	2.0141
Hydrogen 3 (Radiogenic)	Tritium	^{3}H	Trace	3.0160

Having different molecular weights, isotopologues behave differently during phase changes, resulting in different ratios in the resulting phase (mass-dependent isotopic fractionation). This behavior is what makes water isotopes ideal as environmental tracers. For example, heavier isotopic water preferentially condensing from clouds as rain, will result in the clouds containing a higher ratio of light isotopes to that of the rainfall, whilst evaporation from water bodies will result in the opposite effect. The ratios resulting from this physical fractionation can be used to deduce the historical processes that have acted on the sample. The most useful isotope ratios to researchers of natural hydrological systems are $^{16}O/^{18}O$ and $^{1}H/^{2}H$ (D), as ^{17}O is of very low abundance and ^{3}H is a radiogenic isotope. Instruments such as isotope-ratio mass spectrometers and cavity ring-down spectrometers are used to determine the ratios of heavy to light isotopes – these instruments will be discussed later.

The International Standard

To compare isotopic values effectively from different sites across the globe an international standard reference has been agreed upon. The original reference for both hydrogen and oxygen was developed in the 1960s. Named Standard Mean Oceanic Water (SMOW), it was defined by the U.S. National Bureau of Standards and was based on a mixture of deep ocean water samples taken from the Pacific, Indian and

Atlantic oceans, at depths of between 500 and 2000 m (Craig, 1961B). In 1995 this international standard was updated to the current Vienna Standard Mean Oceanic Water (VSMOW) (Coplen, 1995). VSMOW is a recalibration of the original SMOW and is maintained by the International Atomic Energy Agency (IAEA).

Delta Values

The waters isotopic values are expressed as delta (δ) values, representing parts per thousand (per mil or ‰) variation from the standard (VSMOW). The equation for this is shown below:

$$\delta^{18}O \text{ or } \delta D = [(R_{sample} - R_{SMOW)})/ R_{SMOW}] \times 10^3$$

Where $\delta^{18}O$ and δD are the relative difference from VSMOW in isotope ratios expressed in per mil (‰), R_{sample} is the ratio of heavy to light isotopes in the sample, R_{SMOW} is the ratio of heavy to light isotopes in the VSMOW international standard. This equation gives a per mil enrichment according to the VSMOW standard (Craig, 1961B).

The Global Meteoric Water Line

The Global Meteoric Water Line is an equation that represents the average values for $D/^{18}O$ of terrestrial waters worldwide. It can be used to define and interpret local values, which may show deviations from the line (IAEA(C)). Smaller regions will have their own Local Meteoric Water Line (LMWL), which may deviate from the GMWL and can be used to interpret local variability.

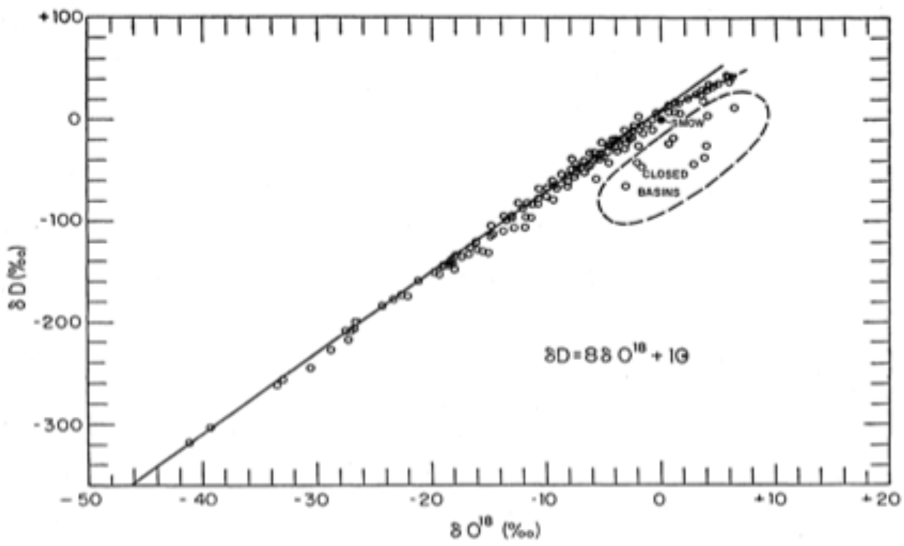

Figure 1. *Craig's original Global Meteoric Water Line - " Deuterium and Oxygen-18 variations in rivers, lakes, rain and snow, expressed in per millage enrichments relative to "standard mean oceanic water (SMOW) " (Craig, 1961a)*

The Global Meteoric Water Line (Figure 1) was originally defined by Harmon Craig (1961A) and relates the average terrestrial water delta values for oxygen and hydrogen worldwide. The $\delta^{18}O$ and δD data derived from 400 samples (≈40 % of which were collected in the North America and the rest from around the world), were found to be linearly related, with the equation:

$\delta D = 8\ \delta^{18}O + 10$

With an R^2 value = 0.95, indicating the intimate relationship between oxygen and hydrogen isotope values.

Global Network of Isotopes in Precipitation (GNIP)

The largest and longest running coordinated isotope collection program, GNIP, is a joint project between the International Atomic Energy Agency (IAEA) and World Meteorological Organisation (WMO). This program has been operating since 1961. It collects monthly samples from more than 800 meteorological stations in 101 countries (IAEA (A)). The Global Network of Isotopes in Rivers (GNIR) is a recent program launched to complement GNIP. This program was initiated between 2002 and 2006 using data from 20 rivers. Participation is voluntary with samples, once again, collected on a monthly basis. The data for GNIP and GNIR are freely available from the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval (WISER) (IAEA (B))

These two programs are invaluable assets to researchers in various fields, but recent advances in analytical methods and instrumentation are facilitating data collection and promoting much greater temporal and spatial resolutions. Although high-resolution, event scale, studies have been conducted using auto-samplers, they are rare. Expensive analysis of bulk discreet samples and the inconvenience of the required laboratory processing make such studies impractical, more especially in isolated tropical catchments. In-field analysis of isotope values and virtual continuous monitoring (sub-minute sampling) is now becoming a reality, making such event scale studies manageable. Higher temporal resolution may identify dynamic processes that were previously obscured by more coarse resolution.

The next section of this review will discuss these advances in an historical context and look at their possible applications.

2.4 Advances in Instrument Technology

Isotope-Ratio Mass Spectrometry

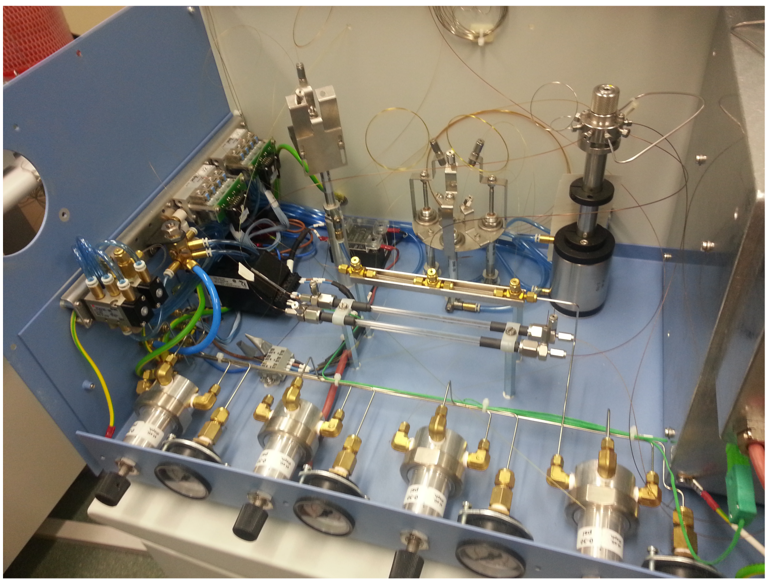

Figure 2. *Internal workings of an isotope-ratio mass spectrometer (IRMS)*

Isotope-ratio mass spectrometers (IRMS) (Figure 2) are used to determine the relative abundance of isotopes in a given sample. The instrument uses an electric and/or magnetic field to alter the trajectory of ionic particles according to their mass/charge ratios. The resulting spectra can be used to identify the isotopic composition of the sample by comparison with a standard. Isotope-ratio mass spectrometry has, until recently, been the preferred method used for measuring the stable isotopes of water (Gupta, 2009).

Cavity Ring-Down Spectrometry

Figure 3. *Two Picarro DS-CRDS instruments, field deployed, automatically analysing rainfall and creek water isotopes in a tropical rainforest*

A more recent development, cavity ring-down spectroscopy (CRDS), also known as cavity ring-down laser absorption spectroscopy (CRDLAS) uses the decay (ring-down) of a laser signal over time to identify isotopic concentration (Figure 3). To identify an isotopes concentration a laser signal is introduced into a thermally controlled cavity containing two or more highly reflective mirrors. The signal is bounced between the mirrors for many kilometers resulting in a small loss due to mirror inefficiency and leakage through to a photo-detector. The signal measured by the detector is proportional to that of the signal within the cavity. After the signal is first built up to a threshold, it is turned off and the detector measures the time it takes for the signal to decay (ring-down) to optical extinction. This process is repeated with the laser tuned to the target gas species, which absorbs the signal and accelerates the decay. By tuning the laser to wavelengths where the light is and isn't absorbed the signals can be compared. The resulting data from this comparison is robust, as it is independent of signal fluctuations and absolute power. With regular analysis of standards the results can be compensated for drift, calibrated to VSMOW and an error budget created (Brand et al., 2009; Gupta et al., 2009; Picarro Inc. 2013).

Comparisons and Innovations: IRMS/CRDS

Although accurate and proven technology, IRMS analysis is relatively expensive, time consuming and complicated (Buttle 1994; Brand et al., 2009; Gupta, 2009; Gkinis et al., 2010; Munksgaard et al., 2011). With analysis requiring the collection of discreet samples, a significant laboratory turn around time and skilled technicians necessary to operate the instrument, the analysis of multiple samples in the field is impossible. Furthermore, delivery of samples to the laboratory and the cost of analysis can be prohibitive. With IRMS analysis taking days to weeks, depending on location, and financial constraints, sampling has been necessarily low definition.

Using a Picarro CRDS isotope analyser (L1102-i) and Delta XL isotope ratio mass spectrometer, Brand et al. (2009), found statistically identical results (precision of the mean for IRMS - ± 0.22 ‰ δD; ± 0.05 ‰ $\delta^{18}O$ and for CRDS - ± 0.15 ‰ δD; ± 0.03 ‰ $\delta^{18}O$). Contamination with methanol and ethanol proved to be problematic, with significant alteration of results. This was expected to be remedied with the introduction of a high-resolution wavelength monitors within the instrument to allow for fine-tuning of the laser and the addition of methanol/ethanol standards to a spectral library. IRMS is more robust in dealing with contaminants, as size is related to concentration of contaminant and isotope composition. Brand et al. (2009) stated, "For pure water samples, the data produced by the CRDS system are very precise, rivaling the best mass spectrometer performance in the field".

Where no reliable method has so far been found to analyse liquid water using IRMS due to phase conversion methods reducing precision (Brand, 2009), laser spectroscopy is now able to analyse isotopic values of water vapour as a continuous stream in real time (Gkinis et al., 2010) and is relatively portable and inexpensive (Koehler & Wassenaar, 2011). Up until recently the factor limiting the application of CRDS in hydrological field research has been the phase conversion of liquid water to water vapour. As partial evaporation results in fractionation, complete evaporation of the sample is required to measure a representative isotope ratio. The necessity for complete evaporation constrains the instrument to discreet, individual samples. This, unavoidably, requires the attention of an operator to service the sample input device, limiting the instruments independence during field deployment (Koehler & Wassenaar, 2011).

Gupta et al (2008) demonstrated that a bench-top CRDS (Picarro L1102-i) could be used for the measurement of water isotopes automatically and with minimal preparation. The experimental set-up used an auto-sampler to inject water into a vapouriser, from where it was passed to the CRDS cavity for analysis. This configuration, although simplifying sample preparation and automating/accelerating the processing, was still not sampling in 'real time' or designed for field deployment.

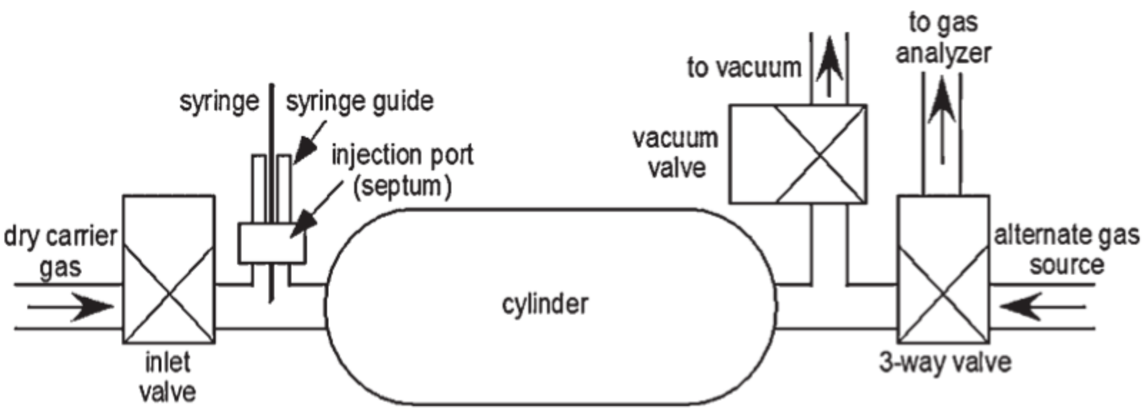

Figure 4. *Schematic of Liquid evaporator (from Gupta et al., 2009)*

Further development and testing by Gupta's team resulted in an updated publication in 2009 that involved the field deployment of the instruments. These tests measured ambient air, water vapour isotopes, but relied on an auto-sampler and flash evaporator cylinder to process the liquid standards and reference samples for calibration and drift analysis (Figure 4). Gupta et al. concluded:

- CRDS performance matched or exceeded that of IRMS
- CRDS was easier to use than IRMS
- CRDS was cheaper to operate than IRMS
- CRDS had unmatched drift free performance
- Memory effect within the instrument, and evaporator, increased sampling time

These tests highlighted the suitability of CRDS for field deployment and unmonitored operation, but continuous 'real time' analysis of liquid water was still not possible.
Also in 2009, Berman et al. tested a field-deployable analyser based on the Los Gatos Research Liquid Water Isotope Analyser (LWIA). An evaporative type analyser relying on discrete liquid samples, the LWIA is compact, rugged and designed for field deployment. This instrument normally processed a maximum of 29 samples/day but with Berman's modifications, a relatively high frequency sample rate of 90 per day was achieved. With external water source sampling capabilities using pumps and an auto-sampler, the researchers were able to simultaneously collect rainfall and creek isotope data. Precision for this instrument was found to be $\delta^{18}O$ ±0.17 ‰; $\delta D <$ ±0.32 ‰ (1SD) over a 48 hr period. Although having relatively high frequency sampling and field deployability the instrument was still relying on discrete sampling and required daily servicing to change injection septa and filters.

In 2010, Gkinis et al. designed a continuous flow evaporator capable of monitoring isotope ratios in liquid water (Figure 5). This instrument was designed to measure the continuous melting of water from ice cores. A low volume flow (0.5 µl/min) of liquid water was introduced into an evaporation chamber, where it was completely evaporated to produce an optimal instrument gas flow rate of 30 ml/min (20 000 ppmv) for the CRDS. The researches reported minimal instrument drift and a precision equal to that of IRMS. As with Gupta et al. (2009) the researchers reported that memory effects may have resulted in lower resolution, this was to be looked at in subsequent tests. Gkinis et al. suggested that further reduction in transfer line volume might reduce this memory effect. Although flow rate and memory limitations may be manageable for the low volumes involved in ice core melt, application to measuring the rapid changes and large volumes of hydrological features such as rainfall and creek flow would be limited. These instruments were also determined to be too delicate and too complex for reliable field application (Koehler & Wassenaar 2011).

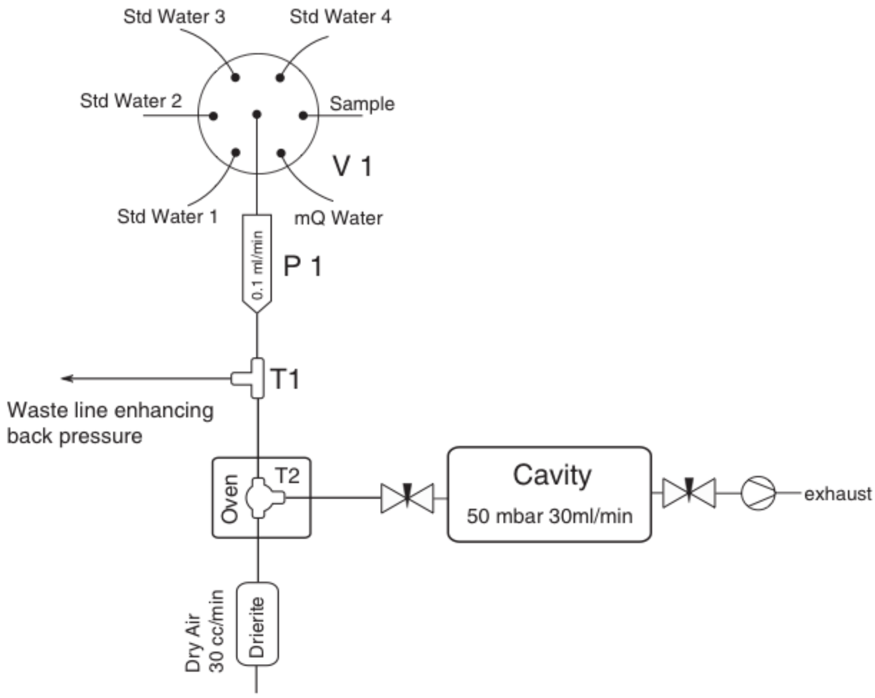

Figure 5. *Schematic of CFA-CRDS system (from Gkinis et al., 2010)*

To facilitate the conversion of liquid to vapour phase Koehler and Wassenaar, (2011), experimented with liquid vapour equilibrators. Two types of in-house custom-built equilibrators were constructed using commercially available showerheads to inject a fine spray into a sampling chamber (figures 6 & 7). To further increase the water/gas interface, one chamber was filled with beads, and the other, a reduced flow device, a 'drip screen'. These devices were compared with a commercially available equilibrator, a Membrana MiniModule (Model G-542). These devices are used to measure dissolved gases from industrial production waters. The modules 7400 Celgard® micro-porous hollow polytetrafluoroethylene (PTFE) fibers allow the liquid water phase inside the fiber to equilibrate with the vapour phase in the chamber. Gas transfer efficiency within this device was found to be close to 100 % and near instantaneous. The resultant vapour was analysed using a Picarro L1115-I wavelength scanned cavity ring-down spectrometer.

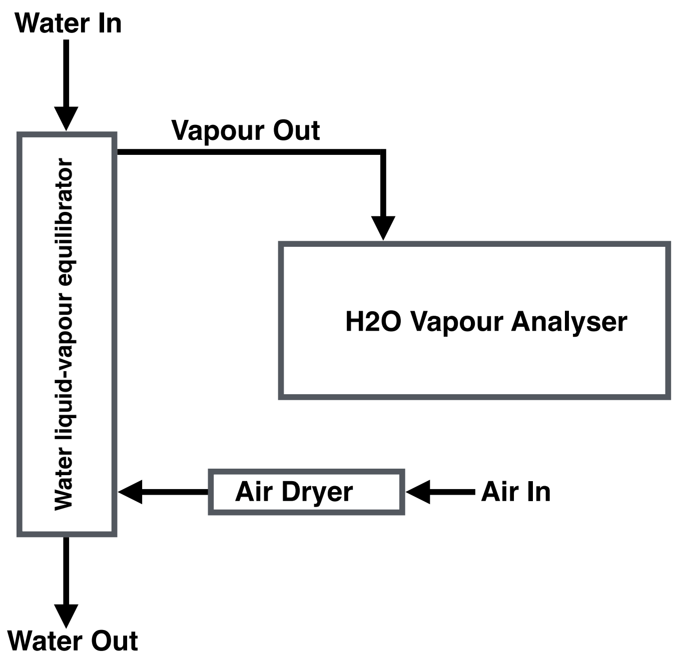

Figure 6. *Liquid vapour equilibrator - flow diagram (After Koehler and Wassenaar, 2011).*

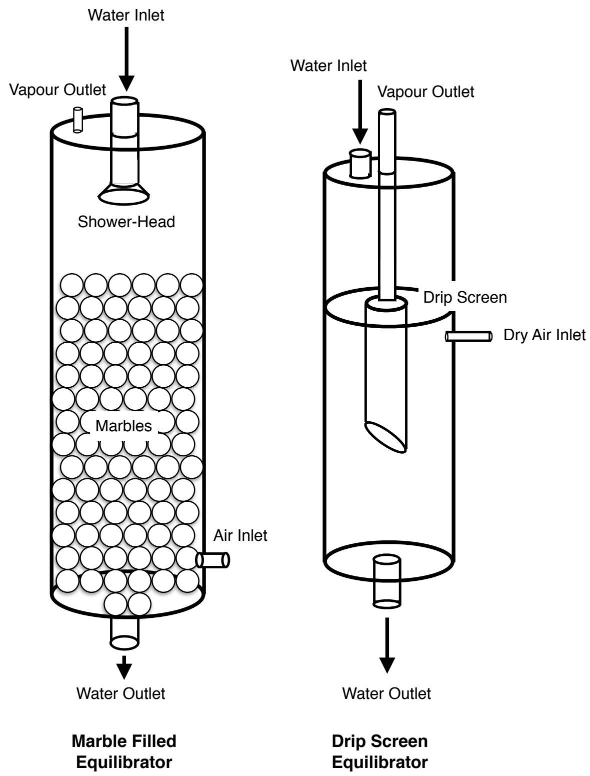

Figure 7. *Shower head type equilibrators (After Koehler and Wassenaar, 2011).*

Koehler and Wassenaar recorded stability in isotopic values across the optimal flow rate of the mini-module (0.2 to 3 l/min), leading them to conclude that the flow rate had no effect on isotopic results. The researchers expected similar results from the custom built equilibrators. For higher volume field deployment in hydrological applications this was an improvement on the continuous flow evaporator. The researchers also found that rapid changes in isotopic values were recorded within < 30 s of injection, indicating a minimal memory effect. One drawback of these instruments was the requirement for individual reference standards to be independently analysed using IRMS to normalise the data to VSMOW, although this could be done at a later stage after returning from the field. Although Koehler and Wassenaar's tests were conducted in a laboratory they suggest that unattended field operation of this instrument is possible.

Later that same year a team at James Cook University in Cairns, Australia developed a simple 'diffusion cell' unit, based on porous PTFE (expanded polytetrafluoroethylene) surgical tubing (Munksgaard, 2011). Similar to the mini-module, but using a single tube, sample water was passed through PTFE tubing from which the vapour diffused into a cavity. This vapour was subsequently mixed with dry air (introduced via a Drierite (Ca SO_4), desiccant) to produce the optimum water concentration for diffusion sampling – cavity ring down spectroscopy (DS-CRDS) analysis.

As a test the instrument was deployed for the unattended measurement of rainfall over three rain events at a site in Far North Queensland, Australia. The rainwater was collected from an inclined plastic sheet, with a float switch device automatically switching between rain and reference water to maintain flow and provide data for drift calibration when rain was absent (Figure 8).

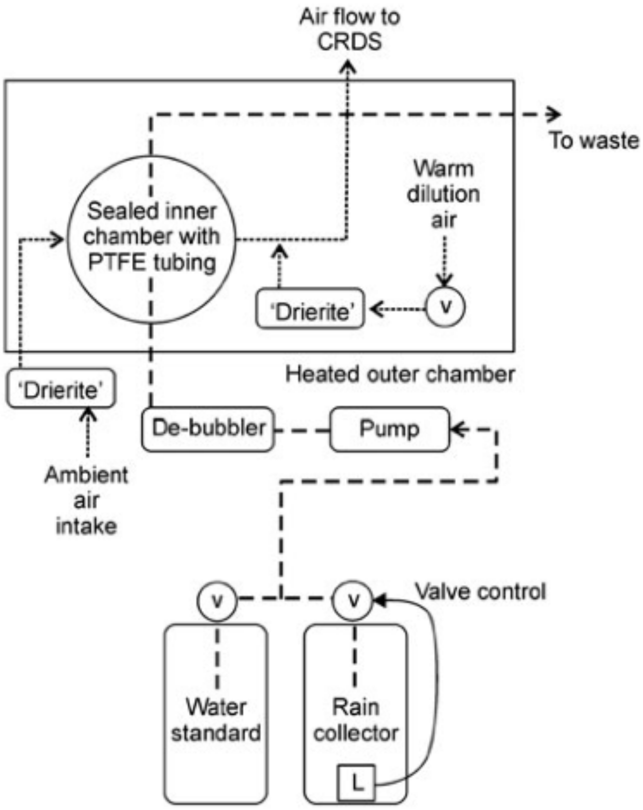

Figure 8. *Schematic of diffusion sampler set-up for continuous sampling of rainwater by CRDS. 'L' denotes level sensor; 'V' denotes valves (From Munksgaard, 2011).*

The data collected from these tests had accuracy and precision comparable with that of IRMS and CRDS using discreet injection of evaporated water samples. With two second sampling data integrated to 30 seconds the precision was found to be; $\delta^{18}O$ < 0.2 ‰; δD < 0.6 ‰ (1SD).

These field tests and additional laboratory tests indicated that factors normally affecting isotope readings whilst using CRDS, such as: temperature changes, water vapour concentration, water pumping rate and dissolved organic content were negligible, or manageable by the regular analysis of reference water. Memory effect between water of distinct isotopic signature was found to be negligible, at seven to eight minutes. This delay was determined to be due to the optical chamber of the CRDS rather than the diffusion cell.

These experiments demonstrated that simple, automated, fine time resolved monitoring of isotope data from liquid sources in the field is now possible using CRDS (Munksgaard, 2011).

2.5 Application of Instruments

The advances in isotope analysis technology discussed above are opening up new areas of research to scientists. Temporal and spatial resolution has increased dramatically and costs have been considerably reduced. The portability and robustness of instruments is facilitating their deployment outside the laboratory in previously inaccessible areas. How will these advances affect future research?

The ability to directly collect high resolution data from previously inaccessible or challenging locations such as rainforest catchments, mangroves and shallow river deltas will add to the understanding of the hydrological processes and mechanisms occurring in these areas. Multiple reach sections can be monitored simultaneously, automatically, in real time and compared for trends and relationships. Researchers can now monitor rainfall, groundwater and surface water simultaneously in real time leading to the possible identification of previously hidden short-term events.

In a paper published in September 2012 (a), Munksgaard et al. identified "extreme and rapidly changing $\delta^{18}O$ and δD values" in rainfall isotopes over short time intervals using high temporal resolution sampling on a field deployed DS-CRDS. This instrument recorded 5948 measurements over a period of 15 days. Highlighting the difference in resolution, the GNIP program had only recorded a total of 1532 monthly samples from seven Australian stations across Australia between 1962 and 2002. Munksgaard et al. concluded by suggesting that high resolution data collected by DS-CRDS could, not only be used for precipitation analysis, but also rapid processes occurring in terrestrial water systems that were previously hidden by the necessarily low resolution of previous instruments.

3. Site Characteristics & Risks

3.1 Location and Site Characteristics

Research for this experiment series was conducted at Thompson Creek, located at the Daintree Rainforest Observatory (DRO) research facility, near Cape Tribulation, Far-North Queensland (Figures 9, 10 & 11). This is a small creek located in undisturbed rainforest, within a steep, short, sub-catchment. Site characteristics for the Thompson Creek sub-catchment are described in Bass *et al.* (2011)(see Table 2).

Table 2. *Thompson Creek sub-catchment characteristics (from: Bass et al. 2011).*

Location	16°06'S, 145°27'E (within Daintree National Park)
Size of sub-catchment	1.7 km^2
Highest point	875 m
Height: research site	55 m
Distance from high point	2.3 km
Channel width	4 m
Channel depth (mean)	158 ±87 mm
Creek bed	Gravel, cobbles and large boulders (little sediment) Granitic and metamorphic
Vegetation	Complex mesophyll vine forest (Type 1a; Tracey 1982)
Dominant vegetation	*Cleistanthus myrianthus, Alstonia scholaris, Normambia normanbyi, Myristica insipida*
Mean annual rainfall	4900 mm (2006 – 2010: range 4518 – 7600 mm)
Wet season	December – April (74 % of annual rainfall)
Soil	Acidic, dystrophic, brown Dermasol (Isbell, 1996) Stone and cobble component: 20 – 50 % throughout

Coastal Far-North Queensland is located in the Wet Tropics region and is subject to heavy rains from summer monsoons and the occasional cyclone. The mean annual rainfall for the Daintree area is 4900 mm, and has been as high as 7600 mm (Bass et al. 2011), mostly falling during the relatively short ‘Wet Season’. This warm, wet climate supports a thriving tropical rainforest, which blankets the range of coastal mountains. Mt Sorrow, the peak that shadows the DRO, and supports the catchment, attains a height of 683 m above sea level. These conditions result in a very dynamic hydrological system. During a storm event the creek has been observed to rise over a metre within the space of one hour, with one of the bores becoming artesian and numerous springs occurring at break of slope and along the creek bank.

Thompson Creek was an ideal location to test the field deployment capability of the Picarro DS-CRDS, under challenging conditions, whilst simultaneously providing useful information on the ground/surface water interactions in an undisturbed, dynamic catchment.

Figure 9. *Satellite image of study area - Thompson Creek, Daintree Rainforest Observatory, Daintree National Park. (Google Earth, 2014, 16°06’S, 145°27’E)*

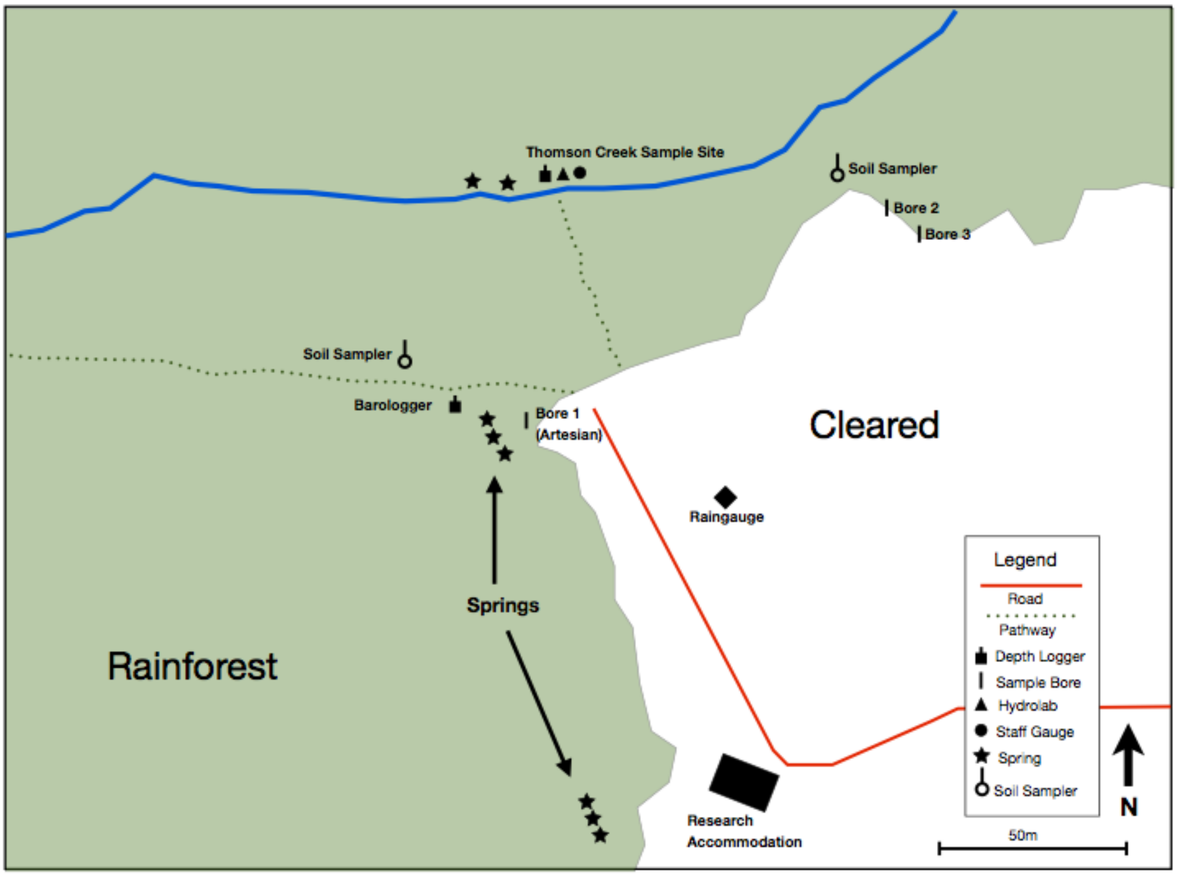

Figure 10. *Study area and instrument plan: Thompson Creek, Daintree Rainforest Observatory (DRO).*

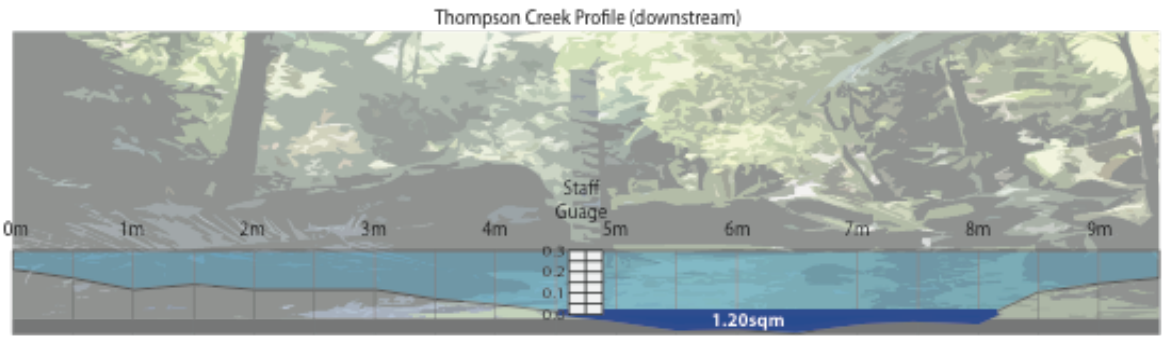

Figure 11. *Thompson Creek, profile at sampling site*

3.2 Risks

A number of potential risks to the success of the experiment were identified in the planning stage, these were:

- The risk of equipment damage due to strong storm flow and flooding. **Management** - ensure all equipment was adequately secured and out of possible flood zone.
- The experiments were rain event dependent.
  Management - ensure equipment was assembled and ready for deployment at short notice to take advantage of all possible opportunities.
- Equipment failure.
  Management - Ensure all equipment was checked and serviced regularly and that spare equipment and/or tools were available in case repairs were required in the field.
- Damage by white tailed rats.
  Management - cables and pipes should be large, and sturdy enough to prevent rat damage. Other equipment must be in rat proof containers.

The mitigation of risk factors, through strong initial planning and operational flexibility throughout the experiment was a key objective of this Masters by research.

4. Methods

4.1 Conventional Field Sampling Experiment

To collect as much supporting data as possible during the short, but intense storm events at the DRO, a suite of high temporal resolution loggers, conventional monitoring equipment, as well as the innovative Picarro DS-CRDSs were (Figure 12).

Although the foci of the experiments were the two Picarro CRDS: one recording rainwater isotope values, one the creeks, other instruments included:

- **Durridge, Rad-7** electronic radon detector. Measuring ^{222}Rn as a tracer is a good indicator of groundwater component.
- **Hydrolab MS5** multi-parameter sonde measuring pH, electrical conductivity (EC), depth, temperature, dissolved oxygen and turbidity in the creek water.
- **Solinst Levellogers,** with barrologer for calibration to atmospheric pressure, were located in the creek and sampling bores to measure water depth.
- Two **Hobo Raingauges** were located in the clearing.
- **Starflow (flow meter) ultrasonic doppler** instrument was located in the creek to measure discharge.
- A **Staff Gauge** was located in the creek to give a visual indication of water level and to allow calibration of levellogers.
- **ISCO autosamplers** were used to collect samples of creek, rain and overland flow.
- Two **suction cup lysimeters** were built and used to collect samples of soil water.
- Two **sampling bores** gave access to the groundwater.
- **Water Level Meter** and manual bailer for purging and measuring depth to water in the bores for calibration of levellogers.
- **EC/pH gauge** was used to manually record ground water and overland flow EC/pH

Chemical gauging (NaCl) was also conducted to provide discharge information, although a more thorough programme, run throughout the year, would be required to produce a useful discharge ratings curve.

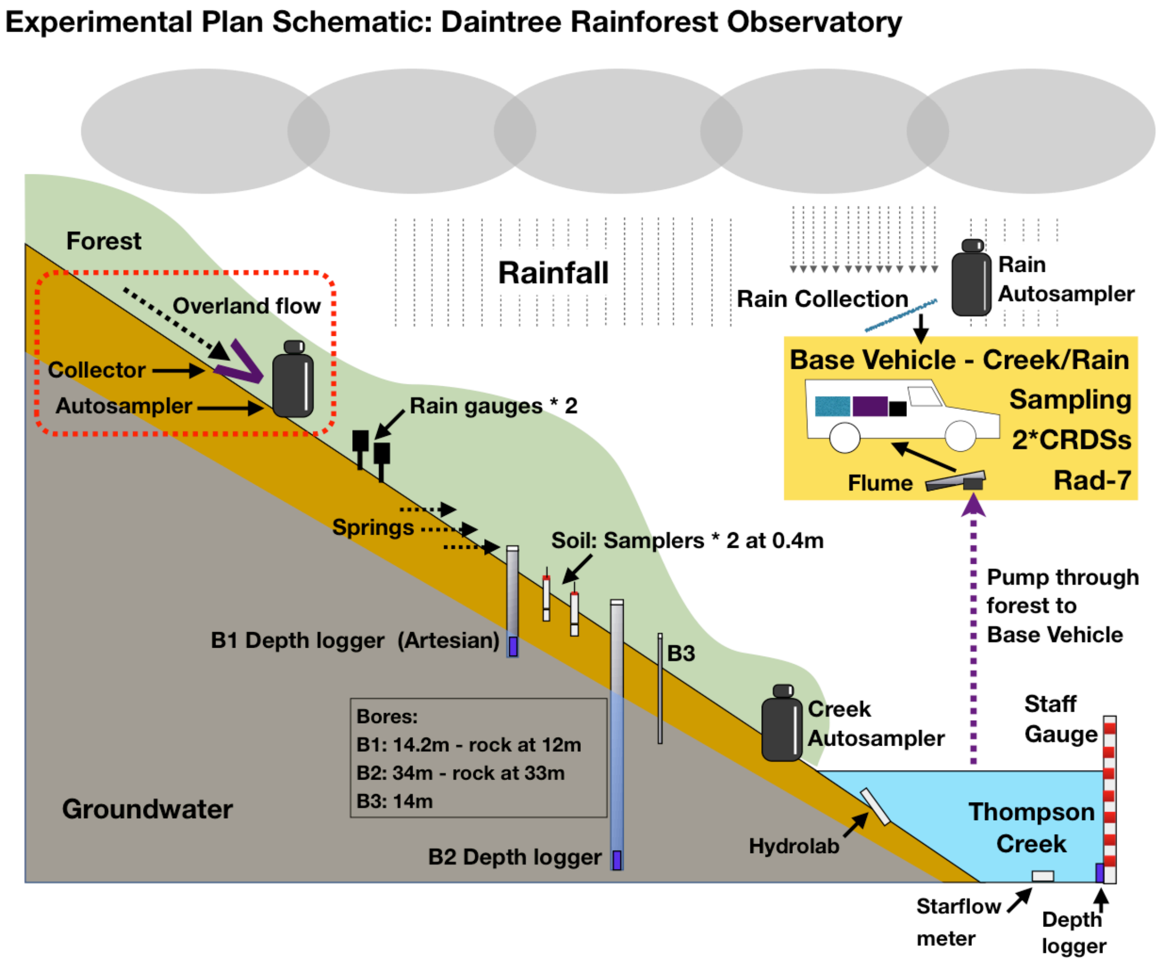

Figure 12. *Experimental plan schematic of Daintree Rainforest Observatory site (not to scale).*

Discreet sampling was conducted prior-to, during, and immediately after significant rain events. $\delta^{18}O$ and δD results were to be compared for: rainfall, soilwater, groundwater and creekwater. Isotope data was supplemented with information on: creek discharge and monitoring bore levels, rainfall volume and intensity, creek water chemistry/physical properties (pH, EC and turbidity) and creekwater radon concentration.

Rainwater

Precipitation volume and intensity was recorded using a Hobo tipping bucket data logging raingauge, located in an area clear of the canopy, adjacent-to the rainforest. Rainfall was monitored year round to identify patterns of high/low intensity over the two tropical seasons; wet and dry. The raingauge provided time/volume comparison data for the monitoring bore levels and storm hydrographs of creek discharge during rainfall events, allowing differentiation of the quikflow from the baseflow portions of the hydrograph. The time taken and the relative volume of water traveling through the system could help identify flow mechanisms and pathways. Records of weather systems were obtained (prevailing direction; type of system), from the Australian Bureau of Meteorology, to identify patterns in system origin relating to isotope composition of the resultant rainwater.

Soilwater

Samples of soilwater were collected from two suction cup lysimeters (Bajracharya & Homagain, 2006) that were constructed and installed in the rainforest (Figure 14). The lysimeters were installed at a depth of 40mm to collect water from the unsaturated zone. Samples were taken at six hourly intervals during the event. Air was pumped from the lysimeter tube using a hand pump, creating a partial vacuum, six hours prior-to sample collection. Over the 6-hour period soil water was sucked into the lysimeter through the water permeable ceramic cup.

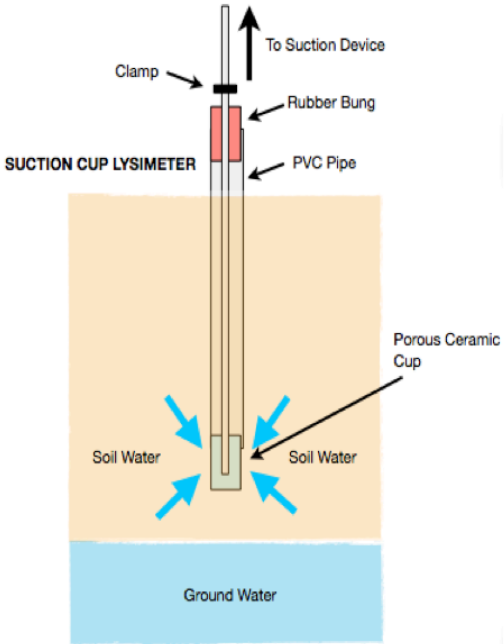

Figure 13*. Left: Soil sampler schematic and Right: Sampler installed at site with attached hand vacuum pump.*

Ground-water

Three monitoring bores are located at the DRO research site (Table 3):

Table 3. *Bore details (Ingham Drilling, drilling report, 2008).*

Details	Bore 1	Bore 2	Bore3
Depth	14.2 m	33.9 m	13.5 m
Bedrock	12.0 m	33.0 m	N/A
Slotted casing (1.2mm)	4.5 – 14.2 m	13.0 – 33.9 m	8.5 – 13.5 m
Bore diameter	125 mm	125 mm	54 mm
Location (relative to creek)	120 m S	160 m SE	170 m SE

Water levels were recorded and samples taken from each bore at six hourly intervals during the event. Prior-to removal of samples the bore was purged of stagnant water using a manual bailer, to ensure a representative groundwater sample was collected.

Creekwater

Figure 14. *Staff gauge at Thompson Creek sampling station.*

Water levels in the creek were read and recorded manually at 12-hour intervals from a staff gauge located at the creek sampling station (Fig.15). The staff gauge was used to calibrate depth loggers at the site. The depth of water was monitored continuously using a Solinst - 3001, 1.5 m pressure Levelloger (data-logger) located at the foot of the staff gauge; sampling at five minute intervals. A Solinst – 3001 Barrologer at the site was used to compensate the levellogers for variations in atmospheric pressure. A Starflow flow-meter and Hydrolab sonde instrument also recorded creek water depth, this could be used as ancillary data.

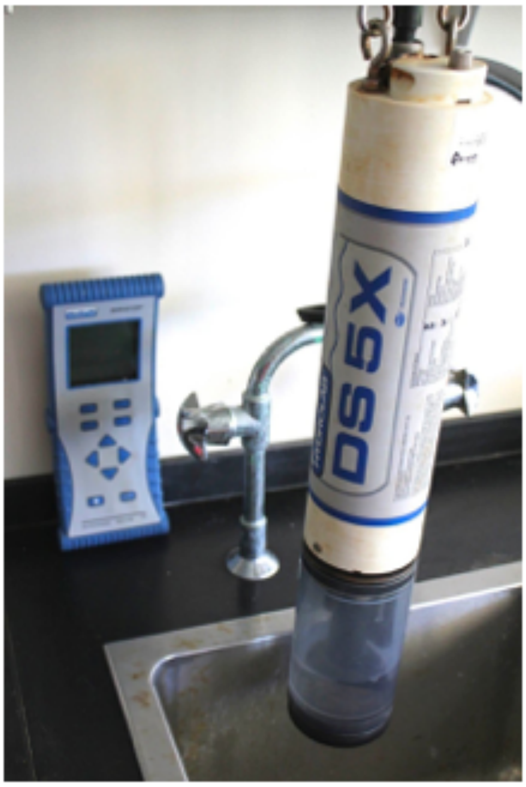

Figure 15. *Hydrolab DS-5 multi-parameter water quality monitor.*

During the event monitoring period a Hydrolab DS-5 multi-parameter water quality monitor (sonde) was used to record: depth, pH, EC, dissolved oxygen and turbidity at the creek site (Figure 16); sampling at five minute intervals. This data assisted in identifying the changes in creek water chemistry over the course of an event and, therefore could assist in identifying relative volumes of contributing water from the various sources: rain-water, soil-water and ground-water.

Figure 16. *A Unidata, Starflow Ultrasonic Doppler flow meter securely bolted to granite boulder.*

A Unidata, Starflow Ultrasonic Doppler flow meter was fixed to a secure point on the creek bed to measure creek water velocity (Figure 17). Recording interval for this unit was set at 10 seconds with power supplied by a 12 v battery nearby, on the creek bank. This instrument uses Doppler radar to measure the velocity of small bubbles and particles traveling in the water stream. These instruments are used extensively in hydraulic engineering situations to provide accurate discharge rates where a precise calculation of area cross section/depth can be entered into the software (e.g. pipes and concrete weirs/flumes) in the case of Thompson Creek such accurate information was unavailable, limiting the results from the Starflow to water velocity only.

Overland Flow

Overland flow was collected with an ISCO autosampler from a 500 ml container located at the terminus of an overland flow concentrator (Figure 18). Water was directed from a 2.5 m wide section of flat, gentle slope to the collection bottle, which was covered to prevent direct rain contamination of the sample. Each sample taken by the autosampler, at 30 min intervals, totally evacuated the container resulting in discrete, isolated samples. Overland flow water was analysed for EC, pH and isotopes. Samples were then transferred to collection bottles (Page 44)

Figure 17. *Overland flow concentrator and ISCO autosampler.*

Radon

^{222}Radon is a noble gas, which is radioactive (t½=3.8 days) and will, sparingly, dissolve in water. Radon can be a good tracer of groundwater (Hoehn & Von Gunter, 1989). Levels of radon are higher in groundwater due to the waters contact with various minerals over time. Radon is liberated from water when in contact with air; therefore surface waters will tend to have lower radon values. The pilot study had indicated that levels of radon in the groundwater at the DRO site were much higher than those from the creek.

Radon was analysed in the field using a Durridge Rad-7 Radon Detector with Rad-Aqua Water Accessory (Figures 19 & 20). Water was pumped from the creek flume to the Rad-Aqua using a small 'Whale' 12 V bilge pump. Discreet groundwater, overland flow and spring water samples were collected using the recommended collection protocols (with RAD-H_2O equipment) for earliest possible analysis, as the t½ of 3.8 days results in greater accuracy with earlier analysis.

Figure 18. *Rad-7 radon detector with partially activated 'Drierite', gas drying unit, operating from base vehicle*

Figure 19. *Rad-7 Aqua, radon detector water accessory is used to bring sample air radon concentration to equilibrium with that of the flow through creek water.*

Laboratory Analysis and Collection Protocols

Discreet samples for isotope analysis were stored in airtight high-density polyethylene bottles to prevent evaporative fractionation (Schulte, *et al.*, 2011). Bottles were filled to capacity to ensure no air remained in the bottle as evaporation space. All bottled samples were labeled and stored in a cool-box. Collected water was later analysed using a Picarro CRDS back at the James Cook University Hydrology Laboratory, with reference samples, used to calibrate the instrument, analysed by isotope-ratio mass spectrometry (IRMS) in the Analytical Laboratory at James Cook University.

4.2 Field deployment of CRDS

In this series of experiments, two CRDS with diffusion samplers were used to simultaneously analyse the water isotope values of both rain and creek water. To prevent contamination from ambient air moisture, mixing air was introduced through a Drierite medium (Anhydrous CaSO4), this ensure only sample water vapour was analysed by the instrument.

The two CRDSs were set up on the back tray of a Toyota, Land Cruiser utility vehicle, under a protective canopy. The vehicle was located in a clearing adjacent to the forest. Monitored water for each instrument was supplied from:

Creek - Water was pumped from the sampling station at Thompson Creek to a settlement flume. A precision peristaltic pump subsequently pumped the clean water to the diffusion sampler of the creek assigned Picarro via fine, sub - mm tubing, at a rate of 3 - 4 ml/min.

Rain - Rainwater was collected on a 0.62 m^2 corrugated plastic sheet and pumped directly to the diffusion sampler of the rain assigned Picarro. Rainwater was replaced with a tap water drift standard during breaks in rainfall, ensuring continuous flow to the Picarro and to facilitate compensation for instrument drift during processing.

Sea water (collected from Yorkies Knob yacht club) and Italian spring water (Santa Vittoria; Aqua Minerale, Traditional Mineral Water) were also used to calibrate the instruments and to adjust for any drift occurring in the creek monitoring CRDS. Calibration standards were of a known isotopic value determined by IRMS analysis at the Analytical Laboratory, James Cook University, Cairns.

Creek isotope data from the Picarro was supplemented with discreet water samples, collected with a 24-unit auto-sampler (ISCO 3700), every 15-minutes. These samples were analysed later in the laboratory.

4.3 CRDS data processing

Pre-Processing

The raw data was recorded as *.dat files within the instrument. The data was then downloaded and processed to produce a workable Excel file:

Creating an MS Excel spreadsheet

- Raw data was downloaded to USB from the Picarro USB port. The files covered 12-hour periods, or parts thereof.
- *.dat files files were changed to *csv.
- The csv files were then imported into Microsoft Excel in delineated, space/comma-separated columns.
- The raw data were recorded at 2-second intervals, this becomes RAM hungry when manipulating large time sections, slowing or freezing the computer. To reduce file data size a macro was run on the file, which averaged the values over 15-second intervals.
- Unused columns were deleted from the spreadsheet, leaving date, time, H_2O/dry air mix and both $\delta^{18}O$ and δD integrated to a 15-second average.
- The final step was to adjust date/time from GMT to local time using an Excel formula.

Instrument Drift Correction

Any drift error was adjusted using reference water standards. Sea water (high δ values), Italian spring water (low δ values) and tap water (medium δ values) standards were used to bracket each instrument run and, in the case of the rain monitoring Picarro, a tap water standard was analysed throughout the experiment whenever there was no rainfall. The mean value for each standard was recorded over the course of twenty readings (4min 20sec), the mean value between the standards was then used to quantify any drift throughout the experiment caused by fluctuations in ambient air temperature and heat build up within the instrument. A linear adjustment was then made to correct for such instrument drift prior to normalisation to VSMOW.

Normalisation to VSMOW

Both the Italian and the seawater were of a known VSMOW value, to allow normalisation of the data to the international reference standard.

4.4 Experimental trips

This section discusses the features of the individual trips taken to the DRO between March 2012 and May 2013.

Trip 1 - Pilot Study

The first field experiment at the DRO was conducted during a storm event, towards the end of the 2012 wet season, 16-21 March.

This was a pilot study for site investigation and to determine experiment feasibility, whilst collecting some preliminary data. At this stage the Picarro equipment had not been readied and there was no instrumentation on site. As rain gauges were not available sample volumes were recorded and later converted through regression analysis to depth in millimeters. Samples for later isotope analysis were collected from rainfall, creek, bores, soil samplers and overland flow.

Rainfall was collected in an open area, adjacent to the living quarters. A 5 l plastic bucket was used as the collection vessel. Water was collected every hour, total water volume recorded and two, sample rinsed, 120 ml bottles labeled and filled to capacity for later isotope analysis.

Creek water was pumped (Proactive, 12 v, 14 amps, Tornado Pump, 7.5 l/min) from the Thompson Creek sampling point in the rainforest, via standard 12 mm garden hose, approximately 80 m to a collection vessel in the clearing. The hose was cable tied to trees at approximately 1.5 m above ground, to reduce the chance of damage by the white tailed rats endemic to the area. The creek sample water discharged into a 25 l bucket that also contained the Hydrolab multi-parameter sonde (Hydrolab DS5-X). The bucket was covered to prevent contamination by rainwater and samples were collected every hour as per rainwater.

The two bores on site were sampled at 12 hr intervals. First bore level was measured, then the bore was purged prior to sampling, using a Tornado 12 v pump, to ensure the sample was representative of fresh groundwater, rather than stagnant water sitting in the bore. Samples were bottled as per rainwater.

Samples were collected from the on site soil water vacuum lysimeters. These required priming with a vacuum pump at least half an hour before sample collection to suck water through the ceramic cup collectors. The same vacuum pump was used to extract the water from the tube into a collection vessel, from where it was bottled for later analysis as per rainwater.

Trip 2 - The Short Flood

The first experiment for the 2012/13 wet season occurred 2 - 8 March 2013, when a monsoon trough descended over the northern region of Australia, generating heavy rains about the far-north Queensland coast (Figures 21 & 22). Two significant rain events occurred during this time: an intense downpour, during a thunderstorm, on the afternoon of 3/3/13 (Event 1) and a much less intense event, of longer duration, the following afternoon (Event 2). Results for these events are presented on Page 55. The two Picarro DS-CRDS (L2130-i) were deployed to simultaneously analyse rain and creek-water isotopes during these events.

The base vehicle was located in a topographically lower location, to facilitate flow from the more upstream sampling point in the creek. This position was chosen to improve efficiency of water transport to the flume and possibly result in syphoning of the water from the creek to the base vehicle. Piping was redirected through the forest but increase in flow or reduced power usage was negligible. Water was pumped from the creek using a Commercial Electric, 240 v, 750 w, dirty water, submersible pump that was powered by a Honda EU20i generator. Generator run-time was approximately 7 hr on a full tank of fuel (4.1 l). With two 20 l fuel containers we were able to run the generator for just over 3 days continuously before requiring more fuel. Extra fuel could be collected from the Diwan fuel station, 20 min south of the DRO.

Rainwater was collected on a sloping corrugated plastic collection sheet, from where it was pumped to the 'rain Picarro' on the tray of the base vehicle. When rain was not available to pump, an automatic switch changed the sample to a reference standard to ensure constant supply to the Picarro and allow later drift calibration. An ISCO autosampler was also engaged to sample excess rainwater from this collection sheet at regular intervals, to be analysed later in the laboratory, as a backup for the CRDS.

Power was supplied to the instruments from the DRO facility generator using extension leads running via an RCD, with cables supported above the ground on stakes. Connections were secured within IP44 safety chord locks.

During this extreme event discrete overland flow samples were collected manually when possible, although a more regimented, automatic collection, using an overland flow concentrator, would prove to be a more efficient method in subsequent experiments.

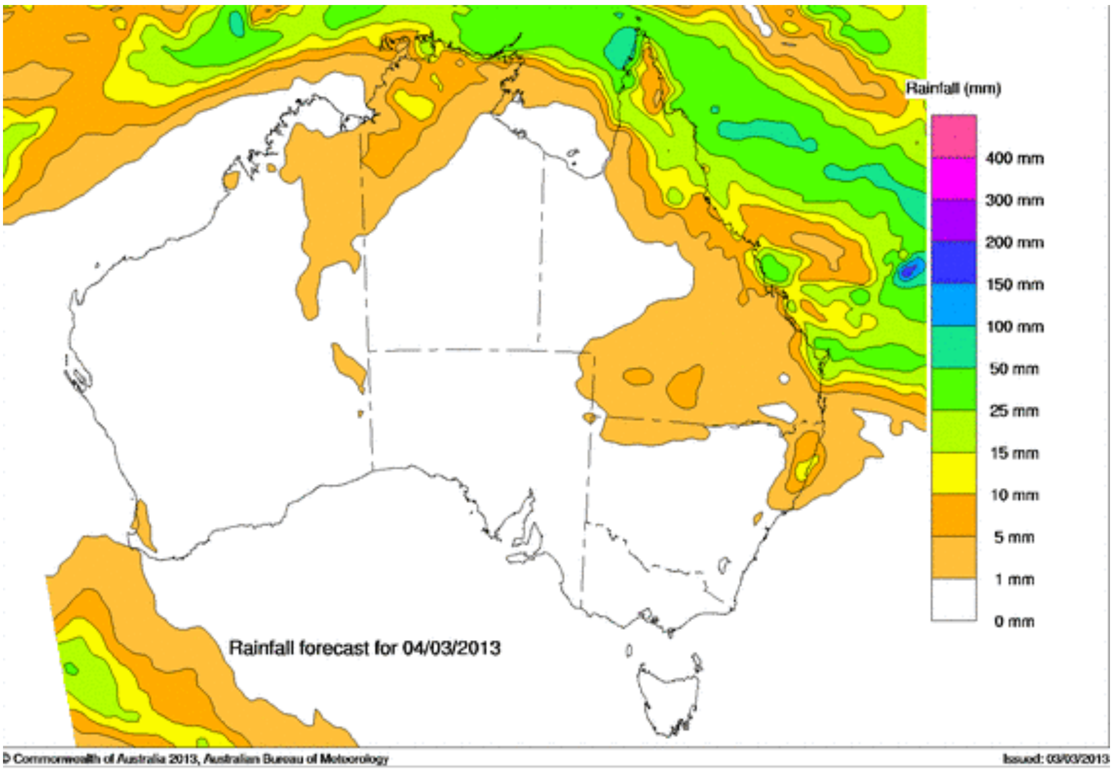

Figure 20. *Bureau of Meteorology rainfall forecast map for Australia showing southern encroachment of monsoon system producing heavy rain along the Queensland coast 03/03/2013 (Commonwealth of Australia, ABOM, 2013)*

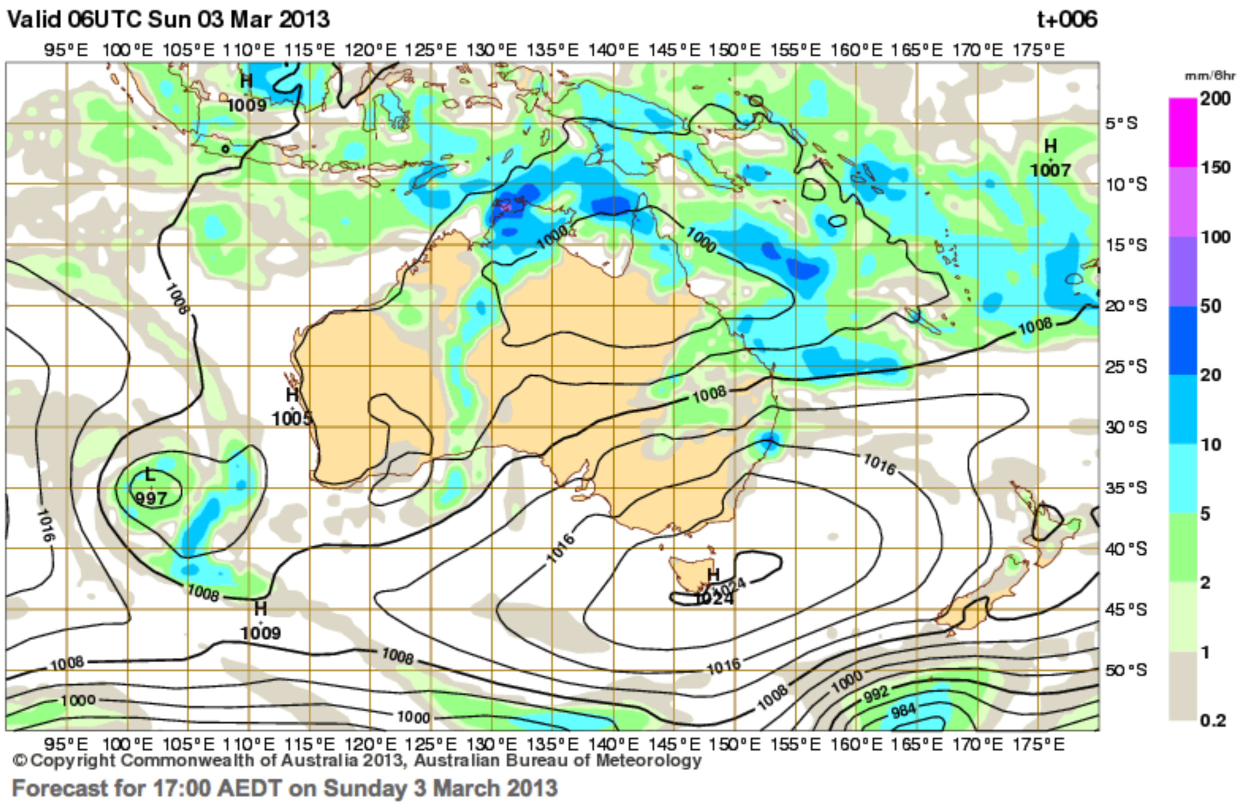

Figure 21. *Bureau of Meteorology, Mean sea level pressure analysis map. Event 1: 03/03/2013, showing southern encroachment of monsoon (Commonwealth of Australia, ABOM, 2013)*

Trip 3 - The Long Flood

The next field trip occurred from 7 to 13 of April, 2013. This was very late in the wet season for such an event to occur, with very heavy rain for the entire six days. This extended flood event was not ideal for monitoring the cycle of initial rise and eventual fall of water levels. Once again the goal was to record water isotope data for both rainwater and creek water simultaneously on two Picarro CRDSs. Due to the extended period, failure due to equipment stress, battery limitations (10 * 12 v batteries in operation with only 2 chargers available) and limited resources was a threat to the success of the experiment. As the 240 v pump was damaged during the main flood event of this trip (and a new 240 v failed within 10 min of starting) we reluctantly returned to using the power hungry Tornado 12 v pump to transfer water from the creek to the flume, this was later replaced by two, in-line Whale bilge pumps after failing.

Trip 4 - Cyclone Zane

The final experiment for the 2012/13 wet season occurred between 27 April, 2013 and 4 May, 2013. Tropical cyclone Zane formed in the Coral Sea, 700 km South-East of Port Moresby, Papua New Guinea on 27 April, 2013. The Cape York region was placed on cyclone alert as Zane reached Category 2 on 30 April. The cyclone then began to track North-West and dissipated rapidly. The cyclone provided no rain but still brought strong, gusty winds to the Daintree region.

Experimental set-up was essentially the same as the previous experiment, with some modifications. Pumping from the creek was still by the 12 v Whale bilge pump, in-line series, as we had not had the opportunity to source a new 240 v pump and auxiliary fuel tank for the generator.

The following table (Table 4) reports the samples collected or recorded during each of the five trips to the Thompson Creek research site.

Table 4. *Summary of sampling realised for each trip.*

Samples Collected/ Recorded	Manual Samples (autosampler or by hand)	Groundwater levels	Rain Picarro	Creek Picarro	Rainfall Amount	Temperature	Creek level
Pilot Study	Rainfall/ Overland Flow/ Ground Water	Yes	No	No	Yes	Ambient/ Creek	Yes
Trip 1	Rainfall/ Overland Flow/ Soil Water/ Ground Water	Yes	Instrument not available	yes	No Rain	Ambient/ Creek	Yes
Trip 2	Rainfall/ Overland Flow/ Soil Water/ Ground Water	Yes	Yes	Yes	yes	Ambient/ Creek	Yes
Trip 3	Rainfall/ Overland Flow/ Soil Water/ Ground Water	Yes	Yes	Deployed but failed due to flooding and duration of event	yes	Ambient/ Creek	Yes
Trip 4	Soil Water/ Ground Water	Yes	No Rain	Yes	No rain	Ambient/ Creek	Yes

5. Results

Most experienced field researchers are aware of the unforeseen challenges that can be encountered using sensitive instruments, under difficult conditions, in the field. In recent years there has been a shift from laboratory analysis of discreet samples, to automated field setups, with high-resolution instruments. The challenge of implementing a mixed multi-instrument array to record a field event is in planning to mitigate, or prevent, any unforeseen difficulties or instrument failures. New technologies prove a further challenge, as their capacity to operate successfully in the field may not have been thoroughly tested. Successful operation may require amendments to the standard laboratory procedures, and the best way to identify the optimal field procedure is for the instrument to be tested, under stress, in the field.

5.1 Trip 1 (16-21/03/2012) – Pilot Study

The site had experienced heavy rain for a number of days prior to our arrival, resulting in numerous active springs at the break of slope to the east of the site and along the creek itself. Water was flowing from the top of casing of bore #1 and Thompson Creek had an abundant discharge, with an approximate height, comparing photo to later installed staff gauge, of 0.8 m. Site observations indicated evidence of strong unidirectional surface flow around root structures tending downslope to the creek (Figure 23).

Lab analysis of samples using the Picarro CRDS (raw samples - not calibrated to SMOW) indicated significant variability in rainwater isotopes and a large drop in isotope values during the peak rain event. Soilwater samples were of a consistent lower value than both bores and the creek, with the creek at a slightly lower value than the bores.

Figure 22. *Asymmetrical erosion around tree roots indicate strongly directional overland flow.*

This pilot study was of assistance in the planning of future experiments at the site. Observations indicated that we would need to:

- Implement a systematic discharge-monitoring plan using chemical (NaCl) gauging, at various creek levels, to establish a rating curve.
- A gauge would be required to measure the height (head) of the artesian bore when flowing. This would involve plugging the bore and measuring the height variation using clear plastic hose.
- Wait for low creek levels to install the Starflow discharge logger securely to the creek bed. It could be temporarily installed on a heavy block of concrete, but this could still wash away in a large flood event

With the March event being the last significant rain of the 2011/12 wet season follow-up trips deployed infrastructure, such as: rain gauges, piping, soil water samplers, staff gauges and loggers. Samples of creek water and bore water were collected and levels recorded on each trip.

The following 2012/13 wet season was very late in arriving, with rainfall for the season being well below average (Figure 24).

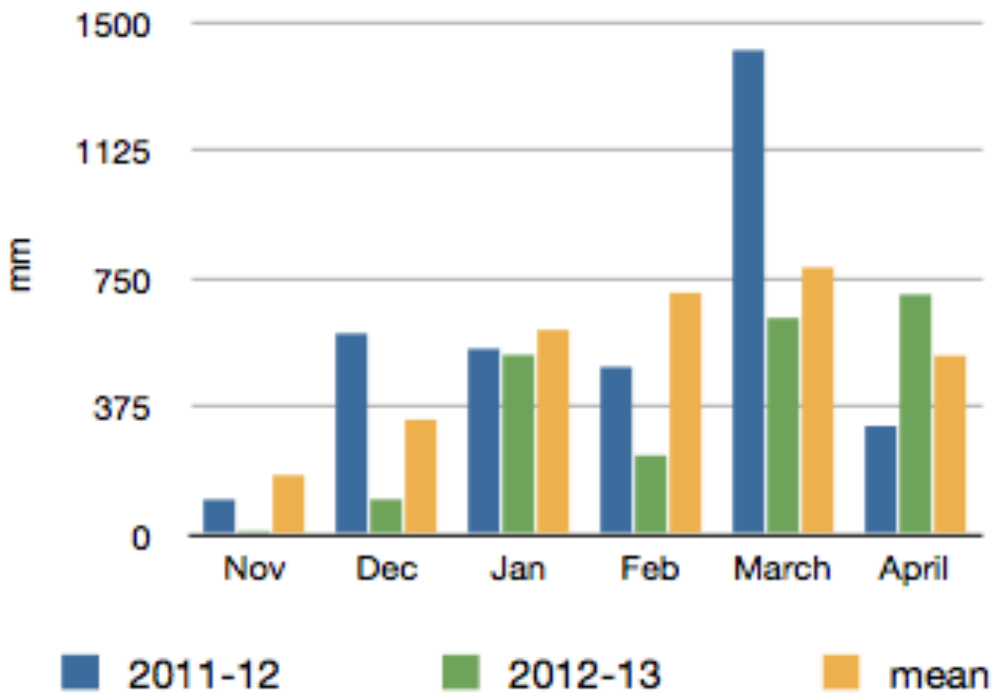

Figure 23. *Wet season rainfall, Daintree (BOM, 2013). 2012/13 season both lower and later than average.*

The first potential rain event was predicted to occur between 8-13 of February 2013. Only one Picarro was available, which was set to record creek water isotopes. A new rainwater collector was constructed for this trip, with an ISCO autosampler collecting the water. Unfortunately the rain event did not transpire, with only light rains occurring. The creek level remained at a very low level (0.17 m) throughout the experiment resulting in no useful event data. Despite this, improvements were made to the experimental set-up:

- White tailed rat damage had become evident, so the damaged garden hose was replaced with tough, PN-10 polyethylene (Blue Line), high-density tubing for water transfer through the forest
- The Tornado 12 V hydrology pump failed to operate due to a small crack in the casing. This was replaced with a Commercial Electric 240 v submersible pump, that

was powered by a Yamaha generator - EF2000iS, 2000 W inverter with 4.2 l capacity fuel tank.

- Refueling or battery change was a regular, ongoing issue, with trips through the forest during the night, often accompanied by intense rainfall and strong winds. Safety was of paramount importance in these situations as tree limb drop is a hazard in heavy wind and rain. At least two people were required for trips into the forest, with two-way radios in communication with the DRO office. On some occasions conditions made it foolhardy to enter the forest, resulting in pump failure and loss of data.

5.2 Trip 2 (2-8/03/2013) – Short Flood

Two significant events occurred during the monitored period of Trip 2: *Event 1* on the 3/3/2013 and *Event 2* on 4/3/2013.

Rainfall

Event 1 (Figure 25 & 26) (15:50-19:43 hr, 3/3/13) was a thunderstorm with intense rainfall (32.4mm total, 21.63 mm/hr). Overland flow rapidly formed rill and gully flow accompanied by a rapid rise in creek level.

Event 2 (Figure 26) (12:17-18:51 hr, 4/3/2013) was a much less intense event over a longer time period (5.8 mm total, 0.95 mm/hr). Mean ambient air temperatures fell by approximately 2 °C compared to the previous day (Figure 27). No overland flow was observed and creek level rise was small (Figure 27).

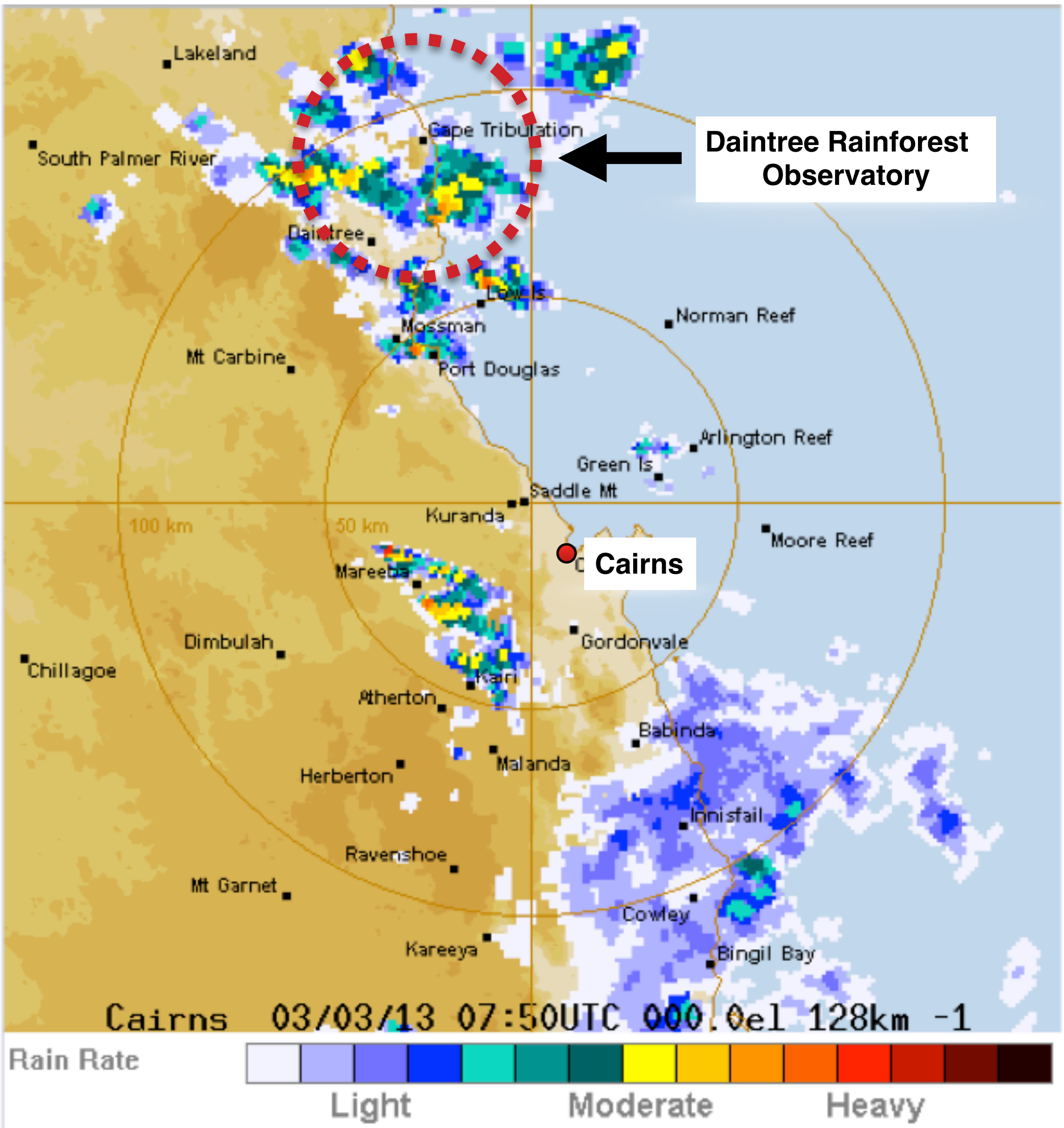

Figure 24. *Bureau of Meteorology, 128 km Cairns radar loop showing peak convective storm system over Daintree Rainforest Observatory. Event 1: 3/3/2013, (Commonwealth of Australia, ABOM, 2013)*

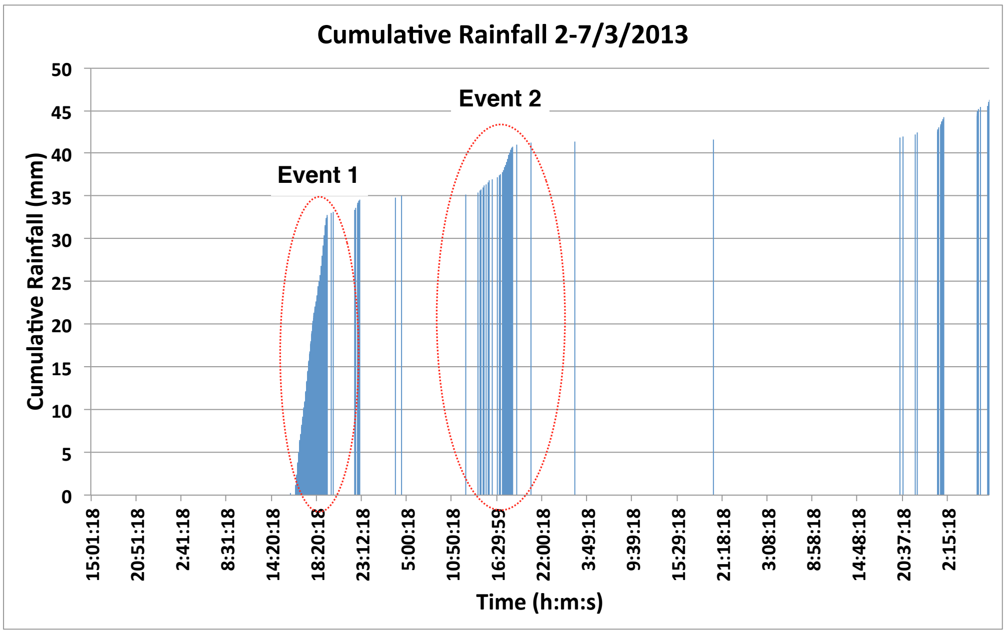

Figure 25. *Cumulative rainfall from 2-7/3/2013 showing: Event 1 on 3/3/2013 and Event 2 on 4/3/2013.*

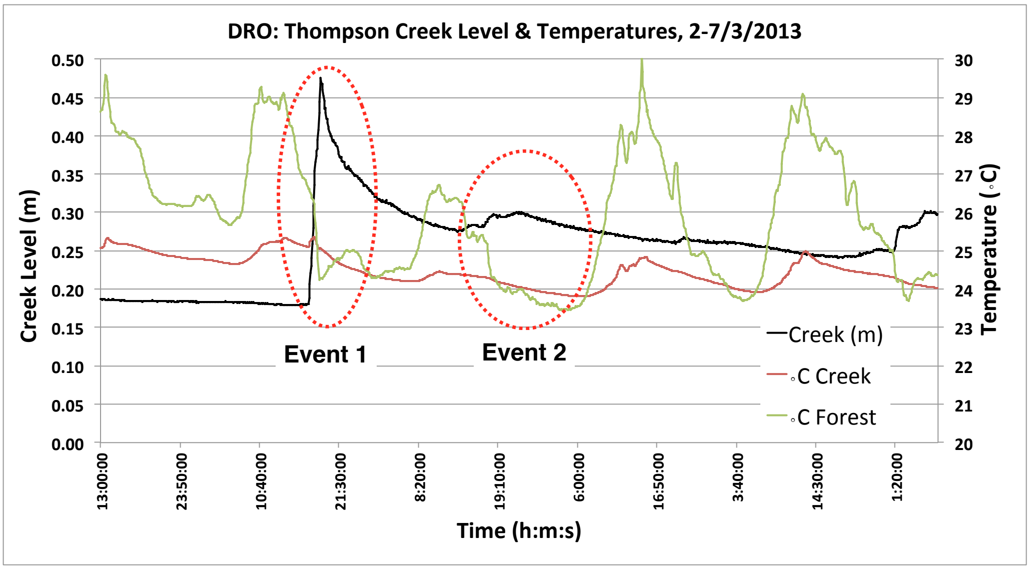

Figure 26*. Thompson Creek water level from 2-3/3/2013 with ambient air and creek water temperatures. Event 1 creek level rise of 0.3 m/2.5 hr was of greater magnitude and intensity than Event 2's creek level rise of 0.02 m/8 hrs corresponding to rainfall intensity. Mean ambient air temperature was approximately 2 ℃ lower at the start of the second event.*

Groundwater

There was a small spike (0.02 m over 90 min) in groundwater lever during Event 1, followed by a more attenuated rise (0.16 m over 4 days) over the following days (Figure 28).

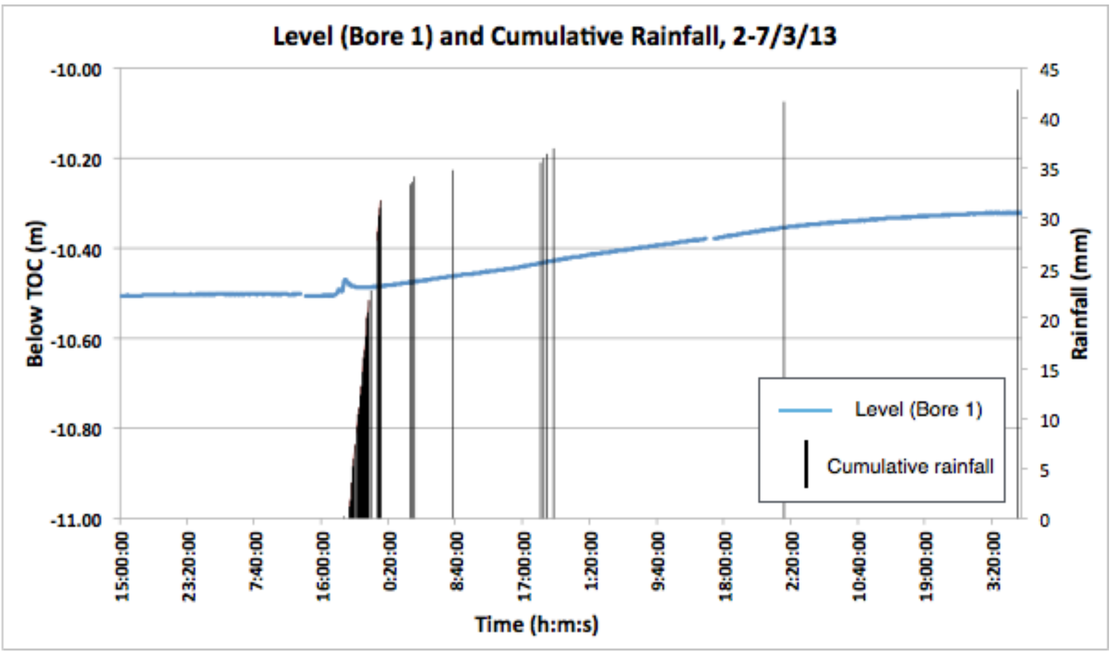

Figure 27. *Bore 1, water level below top of casing, showing small, sharp rise during the intense rain of Event 1 on 3/3/2013, followed by a gentle rise over the following four days.*

Isotopes

As explained in chapter one (Page 19) $\delta^{18}O$ and δD values tend to have a direct linear relationship, which can be expressed as the Global Meteoric Water Line (GMWL), with the equation $\delta D = 8.0 * \delta^{18}O + 10$ ‰ (Craig, 1961a). Variations about this line are useful in identifying moisture source areas and non-equilibrium evaporation. In this study the interest was in isotope variability over time, the identification of distinct end-members and any relationships between the isotope values of separate water compartments. With this in mind a decision was made to use $\delta^{18}O$ alone, as, for our purposes, this would act as a surrogate for δD. Figure 29, below, demonstrates the strong linear relationship corresponding to the GMWL of rain, ground and creekwater samples collected during the Daintree experiment.

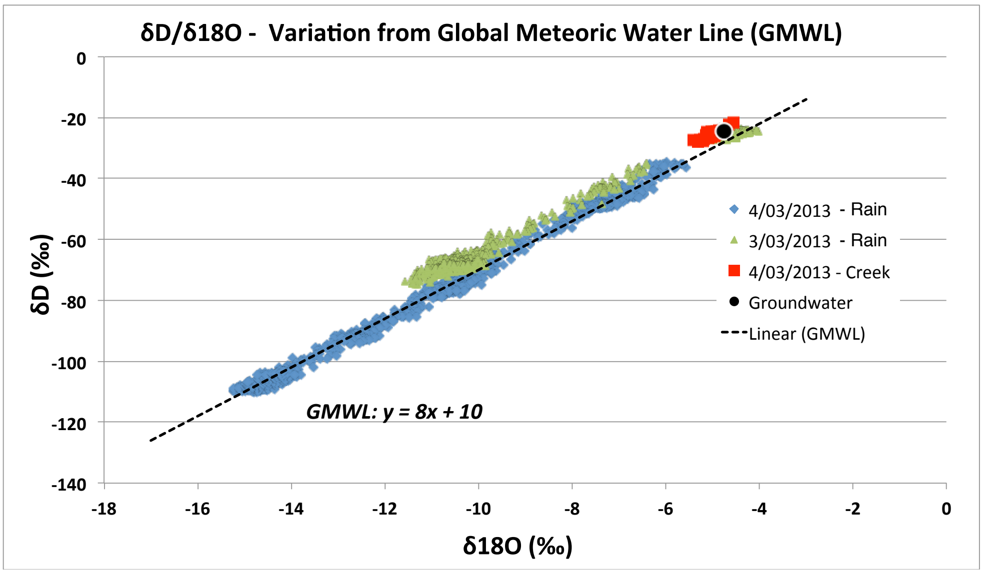

Figure 28. *$\delta^{18}O$ /δD relationship during events 1 & 2 (incorporating the Global Meteoric Water Line). Both events show a strong linear relationship having R2 values > 0.99. Isotope data precision at 15-second integration $\delta^{18}O$ = 0.16, $\delta 1D$=0.53 (1 SD)*

Descriptive Statistics

Rainwater Isotope results for the March field research show a large range of values, with $\delta^{18}O$ -15.24 ‰ to -0.11 ‰ (n = 31,309) (Figure 30). The table below (Table 4) shows comparative statistics between the two major events. Isotope values fell much more dramatically during the second, less intense event (Figure 30). The two events are described individually below.

Table 5. *Comparison of Event,1 Event 2 rainfall and Event 2 creek statistics.*

	EVENT 1 (3/3/2013)	EVENT 2 (4/3/2013)	Event 2 (Creek)
δ18O Mean	-8.53	-10.61	-4.93
δ18O Maximum	-4.02	-5.56	-4.17
δ18O Minimum	-11.57	-15.24	-5.77
δ18O 25th Percentile	-10.59	-12.70	-5.11
δ18O 50th Percentile	-10.09	-10.35	-4.93
δ18O 75th Percentile	-4.88	-7.69	-4.74
Event Time	15:50-19:43hr	12:17-18:51hr	11:30-24:00hr
Duration	3hr 53min	6hr 34min	12hr 30min
Rain Volume	32.4mm	5.8mm	
Sample Interval	13sec n=688	13sec n= 1560	15 sec n= 3,000
Rain Intenity	21.63mm/hr	0.95mm/hr	
Average °C Daily	26.57	24.97	
Minimum °C Daily	24.24	23.73	
Maximum °C Daily	29.26	26.72	

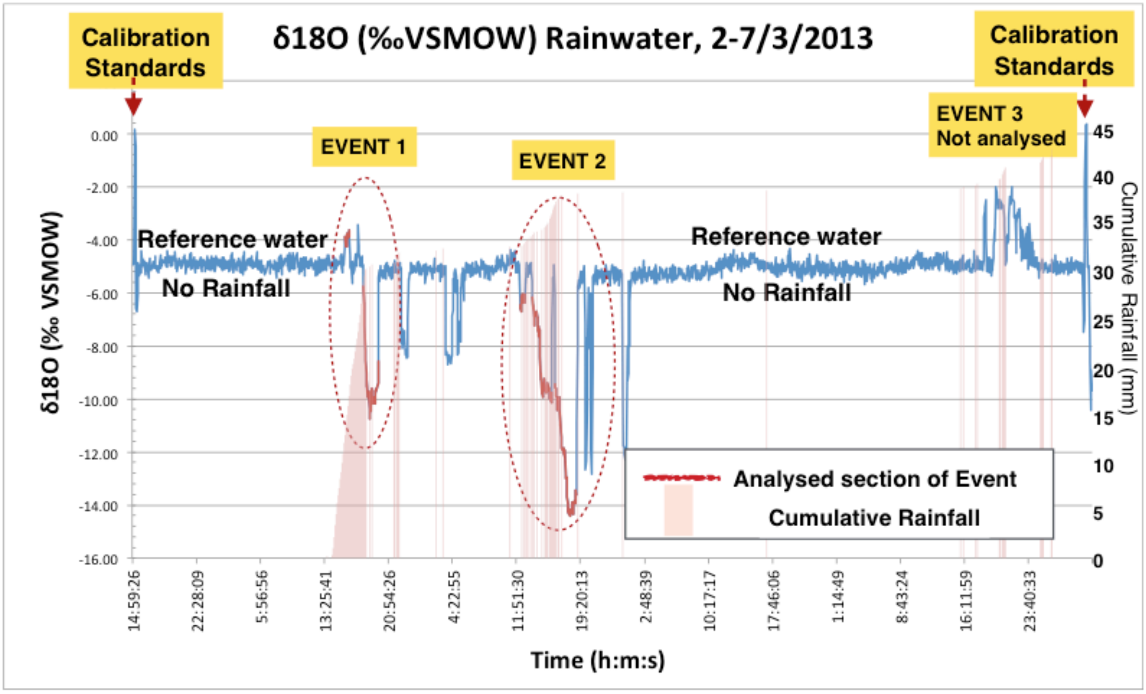

Figure 29. *δ¹⁸O (‰ VSMOW) rainwater, recorded using a Picarro DS-CRDS at the DRO over 6 days. Events 1 and 2 highlighted. Extreme bracketing values indicate sea water and Italian water normalising standards. δ18O value ≈ -5.5 corresponds to tap water drift referencing standard.*

Event 1: (Figure 31)

Initial isotope values during the event were relatively high compared with the tap water drift referencing standard, but began to fall dramatically as the storm progressed (from $\delta^{18}O$ = -4.02 ‰ to -11.57 ‰; mean -8.53, over 1 hr 18 min). Overland flow samples were collected within the forest and from gully flow during the event for later analysis (Mean $\delta^{18}O$ overland flow = -5.68 ‰, n = 3). Unfortunately turbidity resulted in blockages within the fine peristaltic tubing of the creek Picarro resulting in no useful data for the creek at the peak of this event.

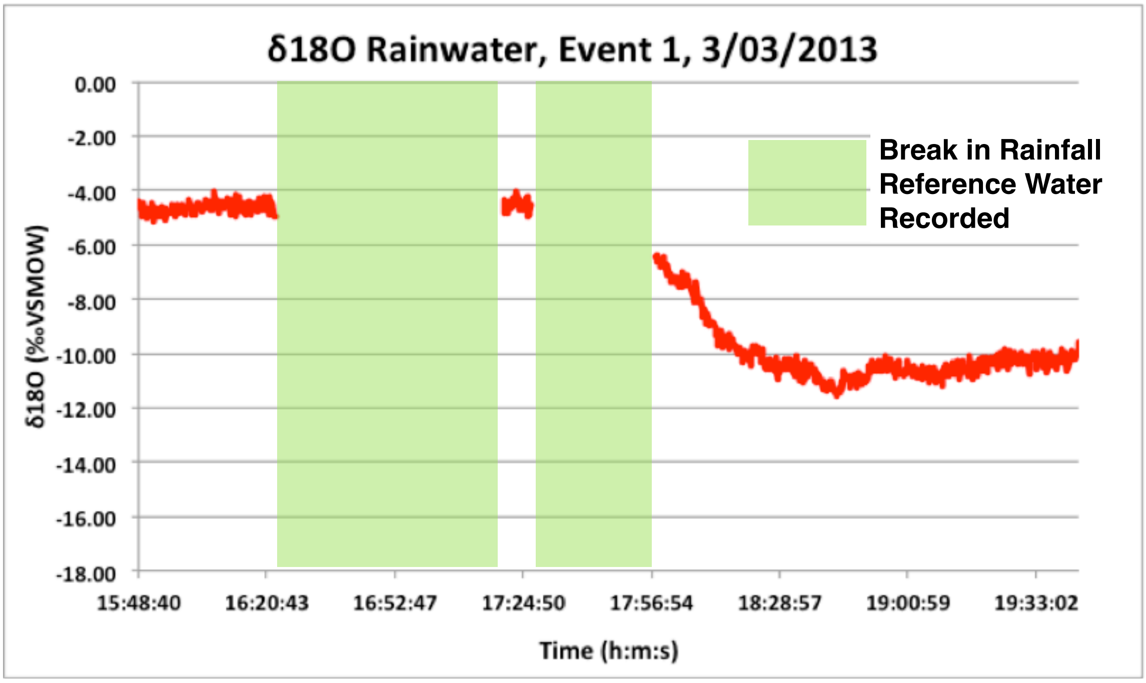

Figure 30. *Event 1: $\delta^{18}O$ (‰ VSMOW) recorded using a Picarro DS-CRDS at Daintree Rainforest Observatory during a rain event on 3/3/2013. Gaps indicate break in rainfall.*

Event 2: (Fig 32 and 33).

This event recorded lower isotope values than the first event (from $\delta^{18}O$ = -15.24 to -5.26; mean -10.61, over 7 hrs) (Figure 32). Overland flow was not evident with relatively gentle rain falling throughout. A much smaller rise in creek level was observed over a longer period (Event 1: 0.3 m/2.5 hr; Event 2: 0.02 m/8 hr [Figure 27]). With a corresponding lack of turbulence, the creek Picarro recorded the isotope values throughout this event. Discreet samples were collected by autosampler every 15-minutes from the creek to authenticate Picarro values (Figure 33).

The creek $\delta^{18}O$ values for Event 2 showed relatively little change throughout ($\delta^{18}O$ = -3.13 ‰ to -4.73 ‰) (Figure 33) although a slight depression in δ values is evident between 17:00 & 19:00hrs. This depression is also evident in discreet samples that were collected from the creek every 15-minutes during the event. Prior to any fall in values (11:30-14:50 hr) the average creek $\delta^{18}O$ = -4.75 matches groundwater contribution. A minimum value of $\delta^{18}O$ = -5.77 (19:40 hr) suggests contribution of event water. The depression in isotope values corresponds to peakflow subsequent to the rain event.

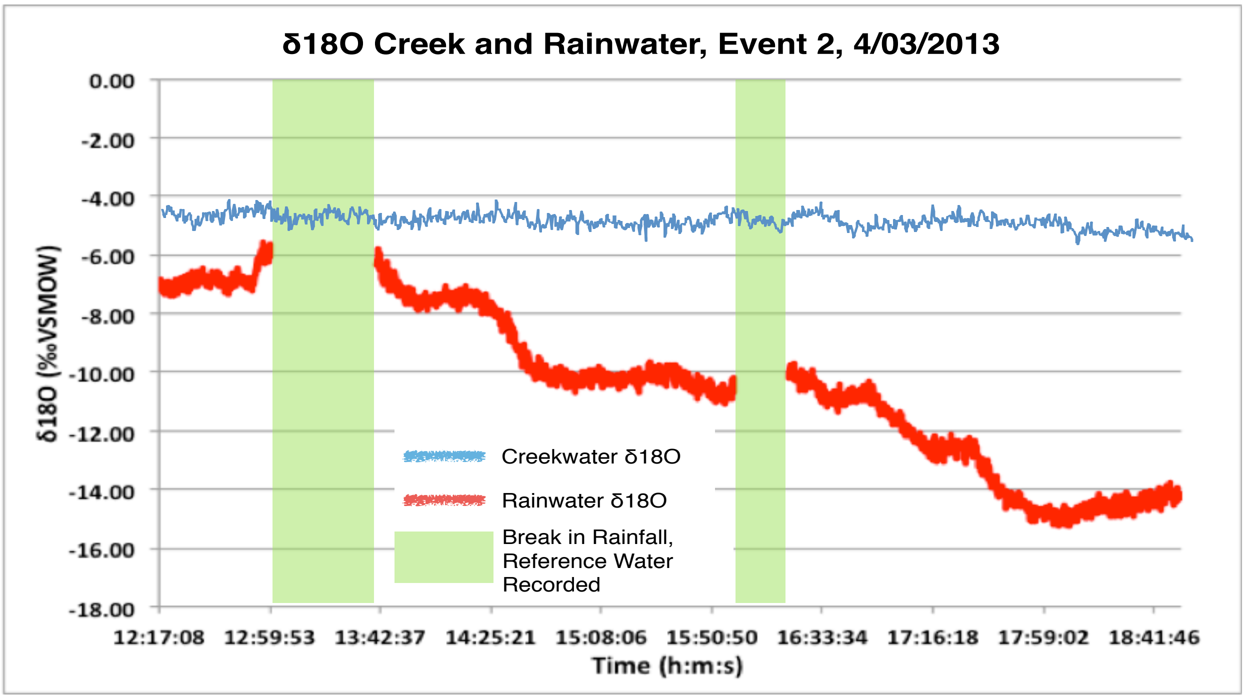

Figure 31 *Event 2: δ18O (‰ VSMOW) recorded using a Picarro DS-CRDS at Daintree Rainforest Observatory during a rain event on 4/3/2013. Gaps indicate break in rainfall. Corresponding creek and rainwater values indicated for comparison.*

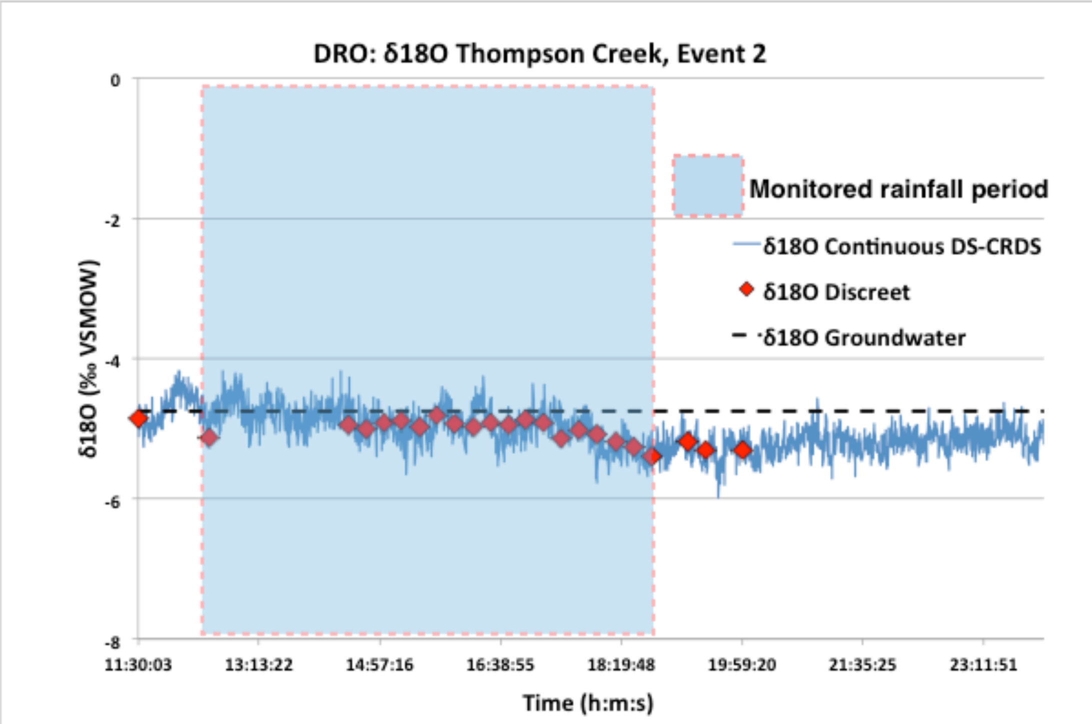

Figure 32. *Event 2: Thompson Creek $\delta^{18}O$ (‰ VSMOW) recorded using a Picarro DS-CRDS at Daintree Rainforest Observatory during a rain event on 4/3/2013. Discreet samples collected every 15-minutes to authenticate Picarro values. Continuous line indicates groundwater $\delta^{18}O$ = -4.75 ‰. A small fall in Isotope values is evident between 17:00 & 19:00 hr on both Picarro and matching discreet samples. A very fast response is suggested, with a slight fall in creek isotope values evident almost immediately subsequent to the start of the intense rain period, around 14:00 hr.*

Rainfall Intensity/ Temperature v $\delta^{18}O$ Values

Goller et al., (2005) observed no correlation between rainwater $\delta^{18}O$, temperature and rainfall amount in experiment in an Ecuadoran rainforest using oxygen isotopes to trace water pathways. Data from the March Daintree experiment supports these findings. During the two rain events there was found to be no correlation between rainfall intensity (mm/15 min) and rainfall isotope values: Event 1, R2 = 0.19 (Figure 35) and Event 2, R2 = 0.32 (Figure 37).

Daily temperature cycles result in falling temperatures each afternoon. As a rain event proceeds, rainout effect results in falling isotope values. If a rain event occurs in the afternoon the fall in values may be incorrectly linked to the fall in temperature. To compensate for these falling afternoon temperatures, and focus on temperature changes due to the storms transit, the difference from average temperature cycles for the six days of the experiment was used, any movement away from this average was then checked for correlation with isotope values.

A negative correlation was found between the difference from average temperature and isotope values for Event 1, R2 = 0.8 (Figure 38). This correlation is counter-intuitive, as a lower temperature should result in lower isotopic rainwater values due to the temperature at condensation. The correlation is best explained through the change in isotopic composition due to a rainout effect (Gat, 1996). No correlation was found over the longer, less intense, Event 2, R2 = 0 (Figure 39).

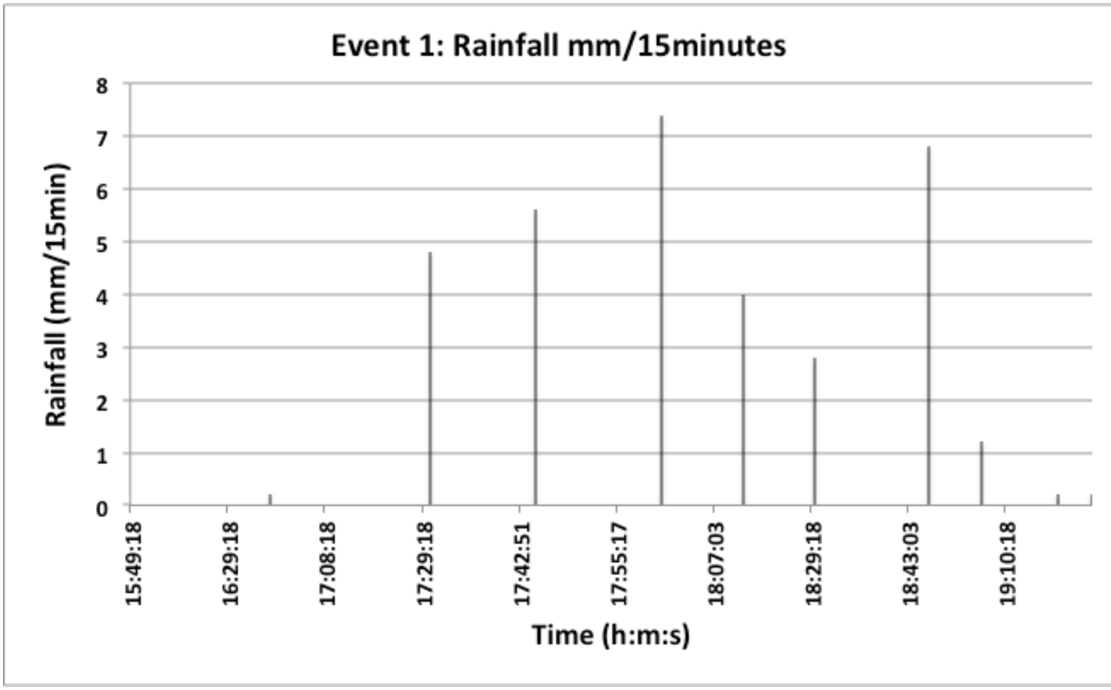

Figure 33. *15-minute rain intensity during Event 1*

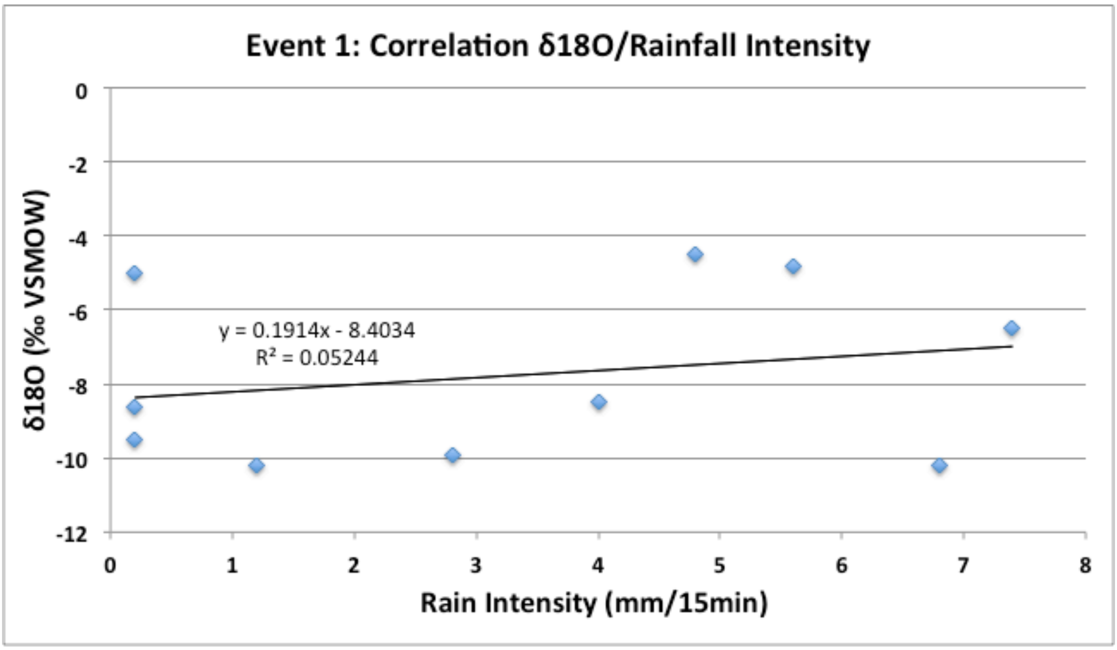

Figure 34. *Correlation between 15-minute rain intensity and rainwater $\delta^{18}O$ during Event 1.*

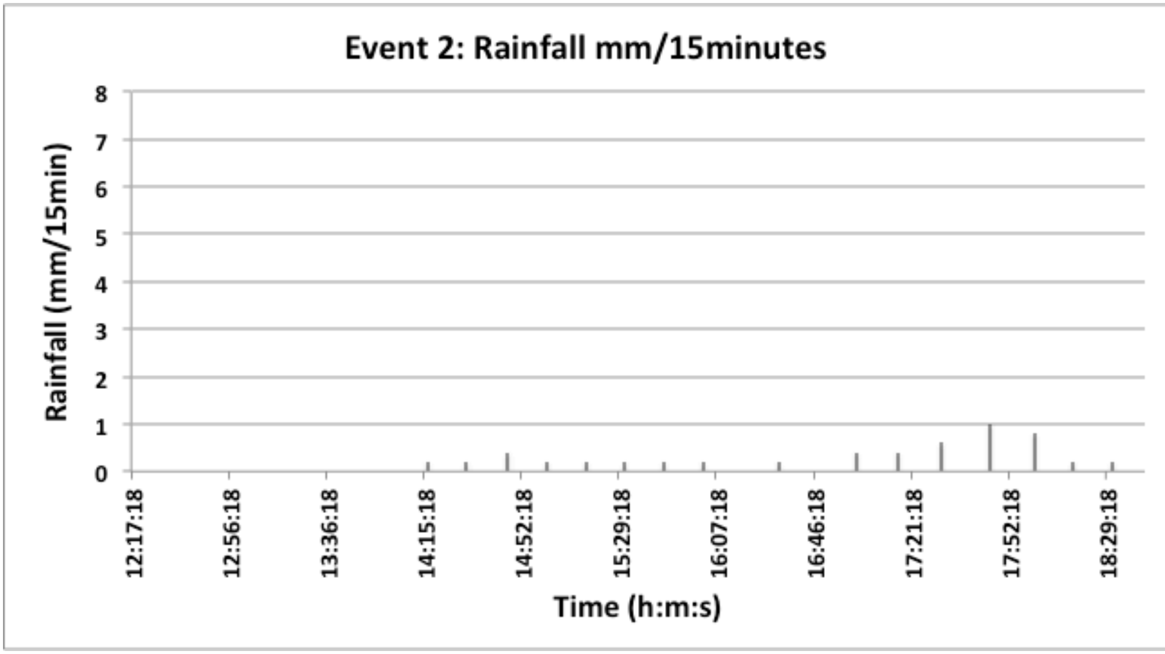

Figure 35. *15-minute rain intensity during Event 2*

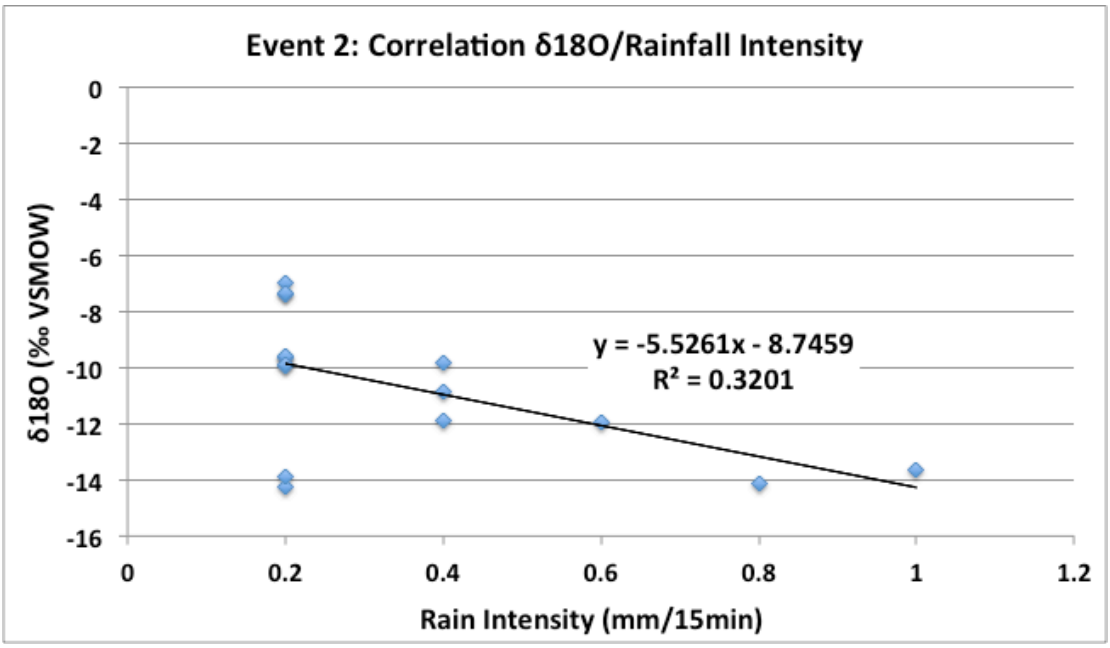

Figure 36. Correlation between 15-minute rain intensity and rainwater $\delta^{18}O$ during Event 2

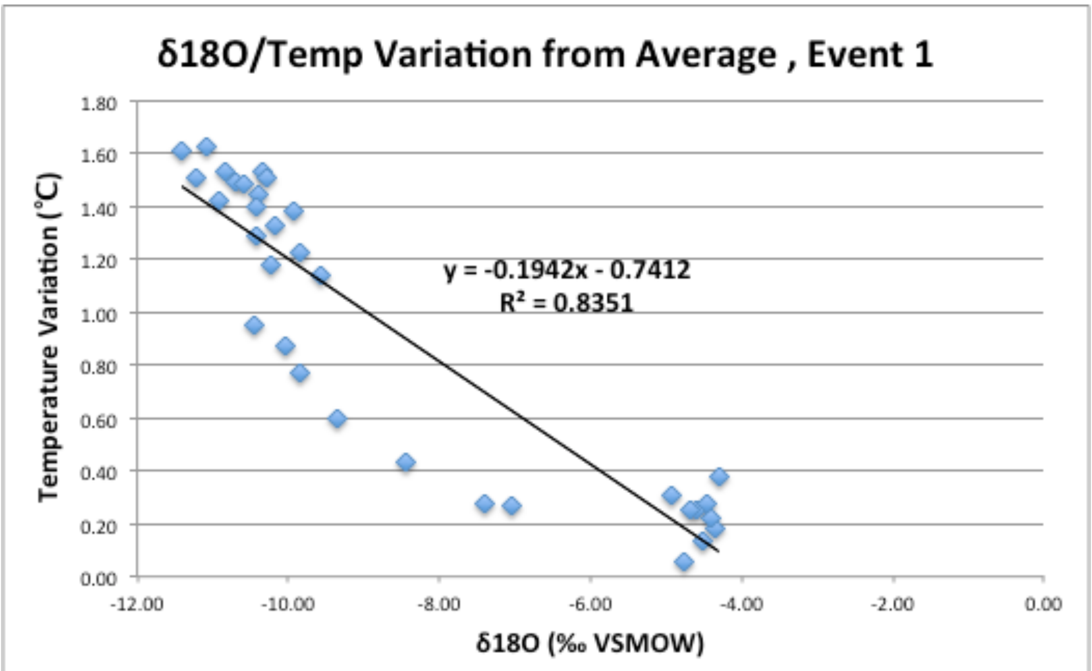

Figure 37. *Correlation between the difference from average of daily temperatures between 2-7/3/2013 and δ18O during Event 1.*

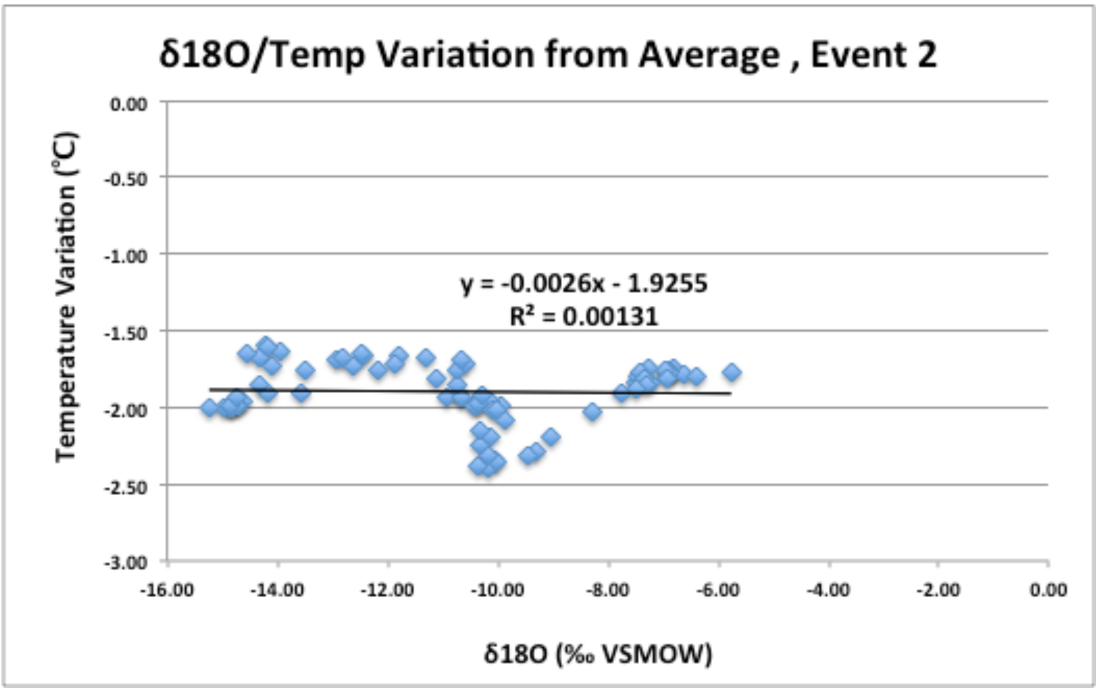

Figure 38. *Correlation between the difference from average of daily temperatures between 2-7/3/2013 and $\delta^{18}O$ during Event 2*

Modeling

A simple two-component hydrograph separation technique was used to determine relative contribution of event and pre-event water to streamflow. These results are not inclusive of temporal variation in transport between rainfall and creek or weighting for rain intensity. Synchronous changes are assumed for this study due to the fast response times suggested by results (Figure 32) and observations, but actual catchment response times and mechanisms require further investigation for more explicit results.

Using δ18O as the tracer with rainwater/event water as run-off and groundwater/pre-event water, proportional contributions to Thompson creek were calculated during Event 2 using the following equation:

$$X = \frac{C_s - C_p}{C_e - C_p}$$

Where X is contribution of event water to total discharge, C expresses $\delta^{18}O$ (‰) concentration, with subscripts s, p and e expressing creek water, pre-event water (groundwater), and event water (rainwater) $\delta^{18}O$ (‰) concentration respectively (Clark and Fritz, 1997). Application is subject to the following assumptions:

(1) Isotopic signature of the event-water is significantly different from that of pre-event water.

(2) Isotopic signature of event water is stable throughout.

(3) Isotopic value of groundwater is equivalent to that of soil water or soil water contribution is known to be negligible.

(4) There is minimal contribution from surface storage.

(Sklash & Farvolden, 1979)

In the case of Event 2, isotope values for the event-water are significantly different from those of pre-event water throughout the event. Event 1 would have been unsuitable for this modeling, as early event-water, at the commencement of the storm, had similar isotopic values to pre-event water. There could also be more than two distinct components contributing to streamflow, in this case the value and contribution of soil water and surface storage is unknown (Klaus & McDonnell, 2013; Kendall & McDonnell, 2012).

Variability in rain isotope values resulted in variation in calculated event water contribution over time. Actual contribution to discharge is temporally controlled by the efficacy of the runoff mechanisms providing event water to the creek. These mechanisms may be impacted by rain intensity, antecedent soil moisture and storm duration. For instance, at the beginning of a storm, after a dry period, water may infiltrate directly into the ground whereas towards the end of an intense rain event, with soil saturated, overland flow may be the dominant mechanism, causing rapid transit of rainwater to the creek. In the case of Thompson Creek, the catchment is relatively small and steep (Bass et al. 2011), therefore a fast response to intense rainfall can be expected. During Event 2 a small synchronous drop in creek isotope values at peakflow indicates that the system is fairly responsive. Although overland flow has been observed, infiltration rates are relatively fast in the rainforest and infiltration excess overland flow (Horton, 1933) can be discounted. Other fast transit mechanisms such as direct precipitation onto the creek, saturated excess overland flow (Hewlett & Hibbert, 1967) closer to the creek, or pipe/channel flow may be responsible for this fast response.

Calculations using constant mean $\delta^{18}O$ values for creek (-4.93 ‰) and groundwater (-4.75 ‰) with statistical mean and extremes for rainwater were used to determine percentage event water contribution to discharge:

Maximum:	rain value δ -5.56 ‰ = 22 %
Mean	rain value δ -10.91 ‰ = 0.03 %
Minimum	rain value δ -15.24 ‰ = 0.02 %

If the continuous (30-second integrated) rainwater isotope values are used, as rain values fall (down to -15.24 ‰) below those of fixed creek values (at -4.93‰), the calculated percentage contribution of event water to discharge is less (down to 0.02 %), as the event water's effect on creek value is not recorded (falling creek values in conjunction with falling event water values would indicate greater event water contribution). The following graph shows this percentage contribution of event water during Event 2, whilst also comparing this with modeling results derived from the 15-minute discreet samples, to address the fluctuations in creek isotopic values during the event. Apart from indicating a much higher initial contribution, using variable creek values also resolves smaller fluctuations, showing a modest peak in the second half of the event corresponding to a change in rain intensity (Figure 39).

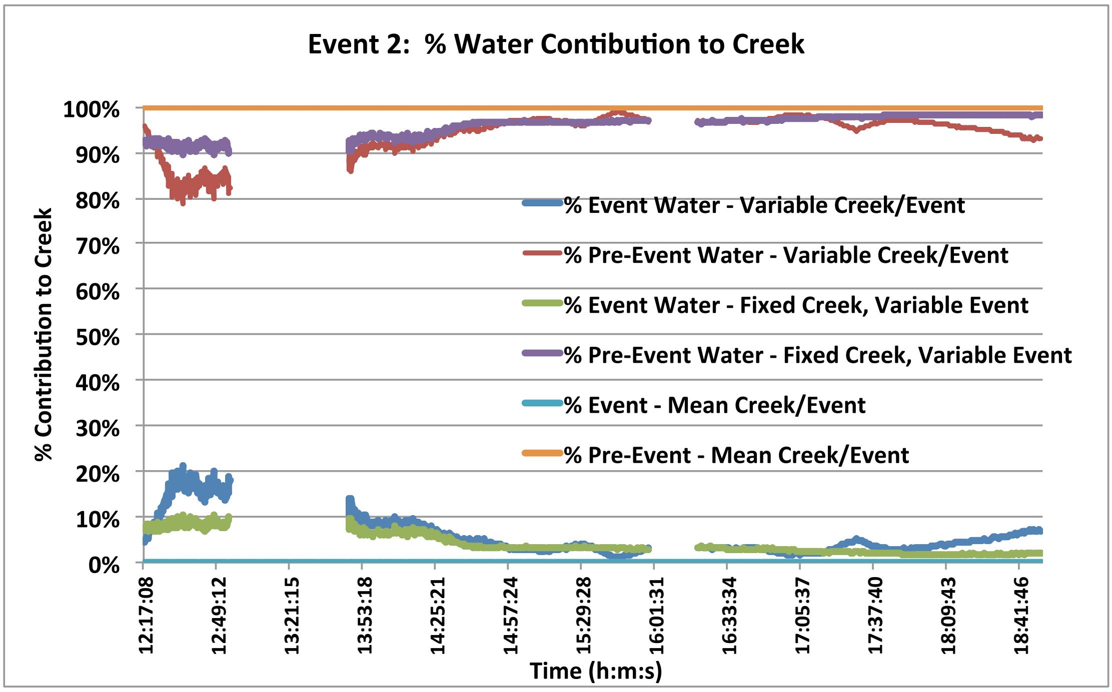

Figure 39. *Comparison of two component models of water contribution to discharge using (i) fixed values for ground and creek water and 30-second integrated values for rainwater (ii) fixed values for groundwater, 15-minute discreet samples for creek water and 30-second integrated values for rainwater, and (iii) fixed mean values for all contributors*

As mentioned previously (Page 69), using statistical mean values to calculate relative contribution of event water to discharge results in an input of 0.03 %. If we look at mean contribution values of real time analysis, the event water contributions are 3.88 %, using mean fixed value creek/groundwater and 5.53 % using mean 15-minute values for creekwater and fixed value groundwater.

5.3 Trip 3 (7-13/4/13) – Long Flood

The April event was a tropical low with heavy, intense rain, over an extended period and featured significant flooding. Both the length of the event and the extent of the flooding resulted in operational challenges, and ultimately in a lack of results for the trip. Despite this, the stress and challenge of this trip resulted in useful modifications to techniques and methodologies that could ensure the success of future experiments.

This flood cut off access to the 240 v pump and subsequently resulted in damage from the strong currents, debris and rocks washed down the creek. The location of the base vehicle was also flooded to approximately 40 cm depth. Although the flume was protected, using a temporary dam built from the vehicle toolbox held in place with steel star pickets, water flow to the flume was disrupted due to the pump damage. This resulted in loss of data during the critical period of this flood event, with consequent interruption of water supply to the creek Picarro and the Rad-7. The 240 v pump was replaced with two 12 v Whale bilge pumps connected in series, but this was too late to capture the main flood event. As the Picarro takes up to 20-minutes to settle down after a disruption in water supply and calibration standards need to be re-run to bracket the sampling set, much of the data was of little use.

Figure 40. *Thompson Creek at typical flow (Level ≈ 0.2 m)*

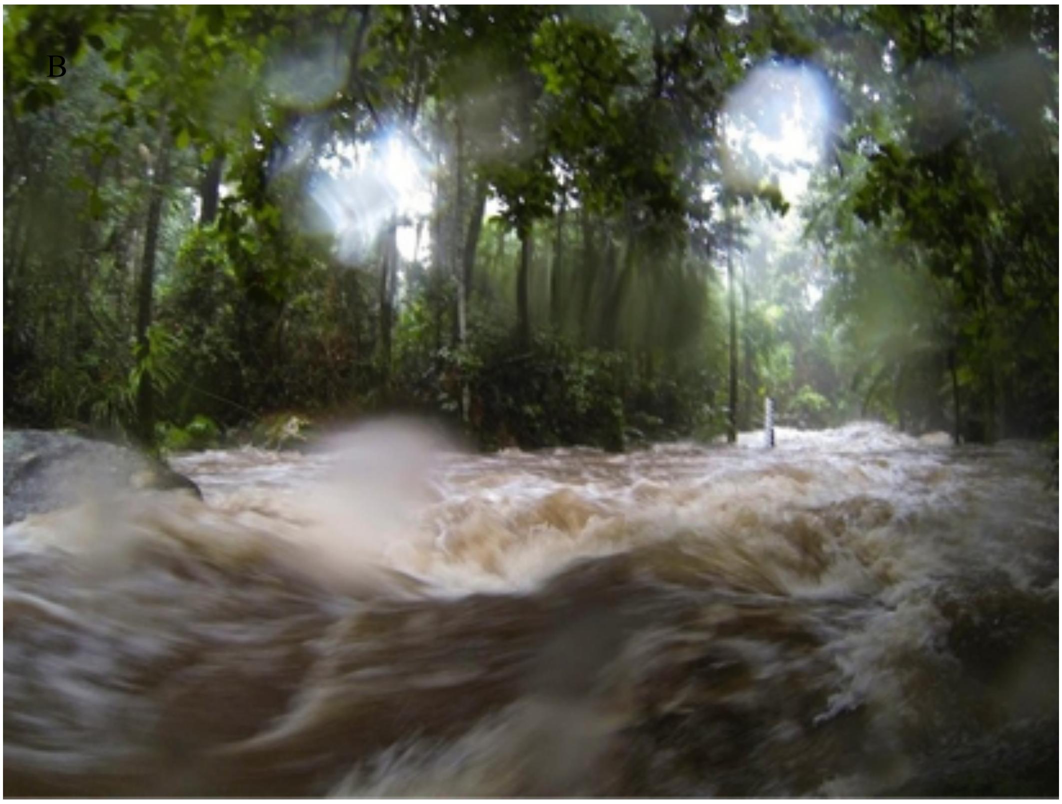

Figure 41. *Thompson Creek during th April 2013 flood (level 1.2 m)*

For this experiment we were using a new peristaltic pump (John Morris Scientific Masterflex, I/P® Precision Brushless Pump with Analog Remote and Easy-Load Pump Head, 115/230 VAC) to supply water to the DS-Cell of the Creek Picarro, as our regular pump was not available. This pump, with its associated tubing, had a much higher pumping capacity (0.1 – 8 l/min), which unfortunately produced excess pressure within the DS-Cell, causing a small rupture. Within a couple of hours of initiating the Picarro the gauge indicated very high water vapour content in the sampled air, which could not be rectified by increasing dry air flow. Eventually the level came down to within operational parameters but the instrument was behaving erratically, with a very slow response time. Later investigation back at James Cook University revealed the damage and the DS Cell tubing was replaced. The damage effectively rendered the instrument's data meaningless, as standards were not analysed correctly and fluctuations were not recorded with adequate resolution.

Another problem encountered during this, and the previous field trip, was what appeared to be air bubbles building up in the fine peristaltic pump tubing to the creek monitoring Picarro. This caused the pump to fail on a number of occasions and was initially thought to be caused by air bubbles transferred from the flume. On further investigation tiny silt particles were found in the tube, causing air bubbles to back up behind them. Due to the extreme turbidity of the creek during flood the flume was unable to settle out fine suspended silt particles. This problem was resolved by attaching a 1cm^3 sponge to the intake tube at the flume. The sponge was cleaned regularly to ensure no silt build up and good water flow. No re-occurrence of the blockages occurred during the rest of this, or subsequent experiments.

On checking the rain gauges we became aware of another problem; ants. Ants had nested in both rain gauges, which had interfered with the tipping buckets. This was easily remedied through regular inspection, cleaning and the application of insecticide and petroleum jelly (Vaseline) around the lower legs of the support structure. Unfortunately some rainfall data was lost for this event.

Although the creek Picarro was only working intermittently, the rainwater Picarro worked well, in spite or requiring re-booting four times before it would switch to recording mode. This is an unresolved issue and has been reported to the manufacturers who are aware of such problems.

The autosampler on the overland flow concentrator was also successful in collecting regular discreet samples. Samples from soil water and groundwater were collected for later analysis in the laboratory.

The auto samplers on both creek water and rainwater failed to collect water for 12 hrs during the event when the peristaltic tubing alarms were triggered. These are factory set for 10,000 cycles, when this is reached the instrument alarms and fails to operate. The tubing was found to be in good condition and the alarms on both instruments were reset.

One unusual feature of this trip was the activation of springs and the artesian bore towards the end of the event. The artesian was only activated briefly, but it gave us the opportunity to test the pressure gauge that was constructed to fit the head of the bore #1. At 10:55 am on 13/4/13 a height of 61 cm was measured above the casing of the bore in the 2.5 cm transparent tubing. Depending on the event a high sampling frequency (15-minute) may be required, as this episode indicated that the artesian flow can be quite transient. Unfortunately, due to other commitments during the flood a regular sampling regime was not implemented during this flood.

Towards the end of the experiment, maintaining battery power to the various instruments became difficult, with battery replacement frequency increasing rapidly in response to necessarily low charge times. The 12 V pump to the Rad-7 was taken off line so that water supply could be maintained to the flume for the creek Picarro (the focus of the experiment). To remedy these issues, during long events, more batteries or more chargers would be required. Using a 240 V pump with a generator and auxiliary fuel tank is a preferred option for creek water transfer and a 240 V to 12 V transformer would be the ideal solution for reliable power to the base vehicle instruments (to replace batteries to the two peristaltic pumps, 12 V Rad-7 bilge pump and rainwater collector valve control switch). Using this configuration only five small 12 V batteries would be required: one for each of the three autosamplers, one for the Starflow meter and one for the bore sampling pump. Eight batteries and two chargers and adequate fuel supply to the generator would sustain power indefinitely in the field.

On downloading data from the creek Starflow logger the alarm "No prompt from logger, check for embedded logger scheme" was displayed. Battery power to the instrument was sufficient and there was communication between the computer and the instrument. Unfortunately, although the Starflow Logger had worked well on previous occasions, no data could be collected for this trip. It was, on a later occasion, removed from the creek bed, when the water receded, and returned to the Hydrology Lab for investigation. Some rodent damage to the cable was found that might have caused a partial failure in communication or power to the instrument.

Both soil samplers tubing were found to have rodent damage, one being completely gnawed through. The tubing was replace and protective casings were built using PVC piping to remedy the issue.

On download of data from the Hydrolab sonde it was discovered that, although it had fresh batteries installed at the start of the experiment, it had only recorded for three days. The instruments sample rate was set at 5-minute intervals, which was not unusual, so it was determined that the problem may lie with the sealed battery unit. Service and maintenance would be required and testing back at the laboratory.

On the final day of the experiment the creek level decreased rapidly, dropping 50 cm over three hours in the early hours of the morning. Unfortunately this left the creek transfer pump dry, resulting in loss of water supply to the flume, and therefore to the creek Picarro, during this important part of the event. The creek autosampler also failed as its uptake line was above water level. Greater attention to repositioning creek instrument would be required to ensure this did not occur again. On subsequent trips the creek instruments and equipment, pump uptake lines for the flume and autosampler, along with the Hydrolab, were attached securely to removable three metre, steel star pickets, which were secured to nearby trees and wedged into rocks in the creek bed. This method proved effective in alleviating the problems encountered with rapid creek level changes causing limited access, equipment damage and pump failure.

As Drierite desiccant supply was running low and the regular University supply being unavailable, re-activated desiccant was used for this experiment. As anhydrous calcium sulfate desiccant absorbs moisture its colour changes from blue, when active, to pink, when exhausted. To reactivate the material it was placed in an oven at 230 C for two hours and then transferred to a sealed stainless steel vacuum flask for cooling, prevention of contact with fresh, moist air on cooling being essential to producing a fully activated product.

Although little useful data was collected from this trip the challenges provided by such an extended, intense event helped identify weaknesses and develop a more effective operational strategy for future trips.
In summation, operational changes were made to:

- Vehicle re-located to a less flood prone site
- 12 V Hydrology pump replaced with in line bilge pumps, proving more effective and using less power
- Modifications to the Picarro water sampling pump to prevent damage to DS-Cell from excess water pressure
- Application of sponge to sample water intake line to reduce silt contaminants to DS-Cell and Picarro.
- Preventative measures to reduce the chance of ants interfering with rain gauge operation.
- Inspected tubing and re-set Autosampler peristaltic tubing alarms. Suggest regular inspection and monitoring of tubing alarm schedule.
- Successful testing of artesian head gauge suggesting a dedicated monitoring routine would be of value during larger flood events.
- Suggested alterations to instrument/equipment power to improve reliability and reduce consumption of power resources.
- Identification of white tailed rat damage resulting in increased instrument protection measures.
- Attaching instruments/equipment to removable three-metre star pickets to increase accessibility and allow level adjustment.
- Methodology for the re-activation of air desiccant, in the field, reduces requirement for sourcing fresh desiccant during an extended rain event.

An increase in experiment personnel is also recommended (from two to four) on such a long experiment. This would increase instrument inspection/maintenance frequency, assist in monitoring and reduce overall workload, allowing me to get some sleep.

5.4 Trip 4 (27/4/13 to 4/5/13) – Cyclone Zane

The final trip of the 2013 wet season occurred at the end of April when Cyclone Zane approached the Far North Queensland coast. This was unexpected, as it was quite late in the season for major rain events and cyclones. Unfortunately the cyclone veered to the north, providing no rain but resulted in strong winds to the Daintree region.

The Creek Picarro continued to behave erratically, with very slow response times not sufficient for calibration or capturing transient events. As mentioned previously (Page 72), this was a result of a rupture to the expanded PTFE tubing within the diffusion cell causing water contamination inside the Picarro unit. This damage was discovered and rectified after this experiment but rendered creek isotope data for the Cyclone Zane experiment meaningless.

The Hydrolab continued to have problems with battery life. Although sample rate had been reduced from 5 minutes to 10 minutes, all contacts cleaned and seals checked. A fresh set of batteries only resulted in 48 hours recording time. A more thorough investigation of the power issue to this instrument would be required.

Over the course of the event, as wind-strength increase, modifications were made to the protective coverings to the base vehicle resulting in a low profile secure structure that could withstand the strong winds.

Although ground/surface water monitoring of isotopes was unsuccessful during this trip due to lack of rainfall, it provided the opportunity to test improvements that had been made to the operating procedures. Discreet sampling, recording of levels, pumps, power supply and the Rad-7 all worked successfully over the 5 days. Although there was no rainfall, the rainwater Picarro operated successfully on tap-water drift standard.

6. Discussion and Conclusion

The 2012/13 wet season series of experiments at the Daintree Research Observatory tested the Picarro, Cavity Ring-Down Spectrometers, under challenging conditions, over extended time periods. These instruments, along with a suite of conventional and high resolution monitoring instruments/methods have the capacity to identify fine temporal variability in catchment mechanisms. With new equipment/methods a testing phase is required to iron out problems, find weaknesses and find the best operating methods. This series of experiments has two sets of quite distinct results:

1. **Challenges and Solutions:** Modifications made to methodology and the high temporal resolution instruments suite so as to provide the optimal chance of a successful experiment under the challenging conditions faced and,

2. **Continuous, simultaneous creek/rainwater isotope monitoring**: The successful results of Trip 2, Event 2, where both creek and rainwater isotope values were monitored, at high temporal resolution, simultaneously.

6.1 Challenges and Solutions: Trips 1-4

Field experiments are notoriously tricky. Once outside the laboratory the world can become a scary place. Things do not always work out as planned, or even imagined. In an early version of 'Murphy's law' Alfred Holt, in 1877, wrote at a meeting of the Institute of Civil Engineers –

> *"It is found that anything that can go wrong at sea generally does go wrong sooner or later, so it is not to be wondered that owners prefer the safe to the scientific"*

When conducting experiments with novel instruments, in unusual configurations, in remote locations, under challenging conditions even with the best planning, things will go wrong. Failure under these conditions can be frustrating, but here lays the opportunity to learn, to implement changes that will result in more robust experimental methods.

In this series of experiments challenges included

- Working in a remote location within a tropical rainforest
- Intense rainfall, flood and wind over extended periods
- Instruments untested under such operative field conditions (Picarros)
- A complex instrument matrix and discrete sampling regimen requiring diligent monitoring and maintenance.

Over the course of the experimental series methods were developed and operational improvements made that optimised the chance of success:

- Development of protective casings for the soil samplers
- Successful field testing of the artesian pressure monitor and suggested monitoring frequency
- Implementation of sponge filter to remove fine silt fraction from creek Picarro supply water to prevent blockages
- Re-activation method established and tested for Drierite desiccant
- Suggested power supply modifications to ensure constant operation of equipment over extended period
- Suggested monitoring frequency for creek equipment and instruments during active events
- Checking and re-setting all autosampler peristaltic tubing alarms
- Optimal locations for base vehicle, instruments and equipment to: reduce chance of damage, improve access and enhance performance.
- Use of removable three metre steel pickets to allow access, adjustment and facilitate removal of equipment during flood
- Methods to reduce impact of ant colonies on rain-gauges
- Development of robust protective screening method for base vehicle to cater for strong winds

By the last trip the experimental set up and monitoring was running smoothly and efficiently.

Although the Picarros had suffered intermittent undiagnosed boot issues, both instruments performed well. Failures occurred due to disruption of sample water supply, caused by: pump failure, line blockages or excess pressure from the peristaltic pump causing the DS Cell rupture. Unfortunately the initial rupture in the DS Cell of one instrument had allowed some water, and subsequently evaporites to deposit, within the CRDSs analysing chamber, adversely affecting the instruments results. Once these issues were identified they were rectified and the instrument returned to recording realistic values. Generally the Picarros were found to be robust, accurate and capable of operating under the DROs challenging conditions for extended periods, with little overseeing or maintenance required. With instruments capable of recording real time isotope values, under such conditions, over extended periods, we have the opportunity to dramatically increase our understanding of the hydrological processes and mechanisms occurring in the catchment.

Recommendations/ Lessons Learnt

From the experience of the 2012/13 field season I would recommend that there be sufficient personnel to allow appropriate monitoring of all equipment and continuous sampling over the full 24 hours, for up to seven days. In the instance of the instruments deployed, and the set up at the DRO, I would recommend at least four personnel (only two personnel were on site during the reported series). Ideally a technician and assistant pair would be assigned to: **1**. Picarro instruments/Rad-7 and **2**. Discreet sampling, metrics and conventional instruments. This would reduce the large workload and provide backup when required. If less staff are available I suggest that the experiment focus on:

- Simultaneous isotope analysis of rain and creek water using CRDS
- Physical measurements of rain, creek and ground water
- Discreet sampling (autosampler where appropriate) of rain, groundwater, overland flow, soil and creek water

Other recommendations include: regular service/maintenance of equipment, having (numerous) alternative options for equipment failures, backup equipment available where possible and ensuring that equipment is ready for deployment at short notice.

6.2 Trip 2 – Continuous, simultaneous creek/rainwater isotope monitoring

Trip 2 resulted in the most useful data of the four trips, with Event 2 of Trip 2 achieving successful simultaneous creek/rainwater analyses of isotopes values throughout. There was large variability in isotope values both between and during the two studied events. The first event, an extreme, intense rainfall event, occurring over a short time period, demonstrated a $\delta^{18}O$ fall of > 7.55 ‰ VSMOW whereas during the second event $\delta^{18}O$ values fell by > 9.68 ‰ VSMOW, but over a longer period of less intense rainfall. Positive correlation between both rain intensity/ambient air temperature and δ values during both events was found not to be significant. This confirms the results of Goller et al., 2005, showing no direct and simple relationship between rain intensity or ambient air temperature and isotope values.

Isotope values of storm systems, and even individual clouds, are highly variable (Munksgaard et al., 2012) and are influenced by factors affecting fractionation. Moisture source areas and precipitation history (Dat & Daansgaard, 1972; Munksgaard, 2012) will determine the general isotopic signature of the system. Local factors, such as: convection, the temperature of condensation (Daansgaard, 1967; Hartlet, 1981), re-evaporation during rainfall (dependent on droplet size, distance travelled, temperature and relative humidity [greater towards centre of system]) may cause variation over smaller distances/times. Many factors are therefore involved in determining the isotopic composition of storm rainwater and these factors can cause high temporal and spatial variations within a system. In this case high intra-system variation is demonstrated by the rapidly falling isotope values of both Events 1 and 2.

The fidelity and temporal resolution of isotope data from this experiment allows us to identify extreme, short-term processes that may be occurring within the catchment. Munksgaard et al. (2012) identified high variability in rainwater isotope values using Picarro DS-CRDS at fine, 30 second integrated, resolution in far-north Queensland in 2012. The Daintree experiments confirm Munksgaard's results, with large variation over single rain events. Do these variations translate to short-term temporal variations in isotope values within Thompson Creek? Figure 33, Event 2, $\delta^{18}O$ ‰VSMOW continuous values indicates a small, but significant fall in isotope values corresponding to lower values in rainwater (Figure 32).

A simple two-component hydrograph separation model was used to determine the relative contribution of rainwater to the creek discharge.
Three methods were used:

- Using three rainfall values (min, max, mean) for event water, with mean values for pre-event and creek water. This method yields a range of possible values that could have been produced from collecting single individual discreet samples during the event.
- A graph using the real time values for event water and mean values for pre-event and creekwater.
- A graph using real time values for rainwater, 15-minute discreet samples for creek water and a mean value for pre-event water.

Using these three methods to identify any difference between individual discreet sampling and one/two component high temporal resolution sampling we can see how the higher resolution and the extra component can highlight subtle changes in relative contribution to the creek over time. If discreet samples are collected simultaneously and analysed comparatively they will represent what is occurring at that time, but if a number of samples are taken over the event, and statistical means are used for modeling, then the results could vary to an order of magnitude from actual contributions. Using real, high temporal resolution values also has the benefit of producing a graph of relative contribution over time that may highlight temporal changes in compartment contribution to the creek during a storm event. By using these methods, in combination with high resolution rain intensity data, a more accurate model of an event can be created leading to a greater understanding of the processes and mechanisms occurring in the studied catchment.

Additional time series analysis methods (e.g. correlative analysis) could be applied to this time series (Shumway & Stoffer, 2013). This would result in a more in-depth analysis, but was beyond the scope of this particular study.

Temporal resolution of isotopic analyses in the past has been fairly coarse due to the labour, cost and time involved in the collection and processing of discreet samples. With benefits of real time analysis, cost/time efficiency, technical simplicity, robustness, portability, low energy consumption and simple pre-processing of data the Picarro instruments are ideal for analysing continuous, simultaneous event/pre-event waters, under challenging field conditions.

Results from this experiment demonstrate that high temporal resolution modeling can identify rapid fluctuations in contribution to creek discharge from event and pre-event water that would be obscured by lower resolution discrete sampling. Contributions calculated using continuous values over the event, rather than a few discreet values, also produce more realistic overall results.

As our understanding of systems improves there is a requirement for higher precision, both spatial and temporal, to further define mechanisms and processes. Important processes occurring over short time intervals may be missed when samples are collected outside those intervals. Continuous sampling is ideal to ensure the most useful information is collected, and recent developments in instrumentation are making continuous, accurate sampling of water isotopes a reality.

The challenge for future researchers will be to deploy these instruments, within arrays to simultaneously monitor various components of the terrestrial water cycle in ‘real time’, so that a catchment’s hydraulic processes can be understood at a much higher temporal resolution than previously possible. Such high temporal resolution may reveal processes and mechanisms that were previously hidden. Identification of short-term processes within small, highly responsive catchments is important in understanding, and better managing: erosion, floods/droughts, pesticide/nutrient application to crops and possible contamination of waterways.

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