# Water Vapour Measurements in the Canadian High Arctic

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Physics University of Toronto

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#### Abstract

This thesis provides an evaluation of atmospheric H<sub>2</sub>O measurements at the high Arctic site in Eureka, Nunavut made using ground-based and satellite instruments. The focus is on measurements acquired using a solar absorption Fourier transform infrared spectrometer (the 125HR) located at the Polar Environment Atmospheric Research Laboratory (PEARL), as part of the MUSICA project.

Close agreement is observed between H<sub>2</sub>O total columns from seven PEARL instruments, with mean differences  $\leq 1.0 \frac{\text{kg}}{\text{m}^2}$  and correlation coefficients (R)  $\geq 0.98$ , except for a comparison between a microwave radiometer and a radiosonde product, which had a correlation coefficient of 0.92. Comparisons revealed a 6% wet bias in the 125HR MUSICA product. Atmospheric Emitted Radiance Interferometer measurements were shown to provide accurate H<sub>2</sub>O measurements, e.g. within 4% of radiosondes.

The PEARL 125HR and Eureka radiosondes were used to demonstrate that the Atmospheric Chemistry Experiment (ACE) satellite instruments, ACE-FTS and ACE-MAESTRO, produce accurate H<sub>2</sub>O profiles in the upper troposphere and lower stratosphere. ACE-FTS showed a wet bias of up to 6 ppmv (6 to 13%) of 125HR measurements between 6 and 14 km and was within 6 ppmv (12%) of radiosondes between 7 and 11 km. ACE-MAESTRO profiles showed a dry bias relative to the 125HR of between 7% and 12% between 6 and 14 km. ACE data showed closer agreement with the radiosondes and 125HR than did other satellite datasets, e.g. MIPAS, MLS, SCIAMACHY, and TES, except AIRS, which showed mean differences within 5%.

In addition, TCCON H<sub>2</sub>O and  $\delta$ D total column datasets, retrieved from near-infrared 125HR spectra, and not yet assessed in detail, were compared with the well-validated MUSICA products at Eureka and six other globally-distributed sites. The results showed TCCON measurements agree well with MUSICA, although the H<sub>2</sub>O product had a small dry bias (6%) and the  $\delta$ D had a high bias (40‰).

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## List of Acronyms

ACE Atmospheric Chemistry Experiment

ACE-FTS ACE-Fourier Transform Spectrometer

**ACE-MAESTRO** ACE-Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation

ACIA Arctic Climate Impact Assessment

AERI Atmospheric Emitted Radiance Interferometer

AIRS Atmospheric Infrared Sounder

AVK averaging kernel

CANDAC Canadian Network for the Detection of Atmospheric Change

CCSM3 Community Climate System Model 3

**CESM** Community Earth System Model

CFC chlorofluorocarbon

CFH cryogenic frostpoint hygrometer

CSA Canadian Space Agency

CST Community Solar Tracker

DOFS degrees of freedom for signal

DOY day of year

E-AERI Extended-range AERI

ECCC Environment and Climate Change Canada

ECMWF European Centre for Medium-Range Weather Forecasts

ECV Essential Climate Variable

ENVISAT European Environmental Satellite

ESA European Space Agency

**EWS** Eureka Weather Station

FPH frostpoint hygrometer

FOV field of view

**FTIR** Fourier transform infrared

**FTS** Fourier transform spectrometer

FWHM full width at half maximum

GCOS Global Climate Observing System

GEOSCCM Goddard Earth Observing System Chemistry Climate Model

GHG greenhouse gas

GPS Global Positioning System

**GRUAN** GCOS reference upper air network

GUI graphical user interface

HITRAN High-Resolution Transmission Database

IGRA Integrated Global Radiosonde Archive

**ILS** instrument line shape

IMK-IAA Institut für Meteorologie und Klimaforschung and Instituto de Astrofísica de Andalucía

IPCC Intergovernmental Panel on Climate Change

IUP Institut für Umweltphysik

JAWS Joint Arctic Weather Stations

JPL Jet Propulsion Laboratory

LMS lowermost stratosphere

MIPAS Michelson Interferometer for Passive Atmospheric Sounding

MIPAS-B MIPAS balloon-borne

MIR mid-infrared

MOPD maximum optical path difference

MOPITT Measurements of Pollution In The Troposphere

MLS Microwave Limb Sounder

**MUSICA** Multi-platform remote sensing of isotopologues for investigating the cycle of atmospheric water

MWR microwave radiometer

NASA National Aeronautics and Space Administration

NCAR National Center for Atmospheric Research

NCEP National Center for Environmental Prediction

NDACC Network for the Detection of Atmospheric Composition Change

NDSC Network for the Detection of Stratospheric Change

NIR near-infrared

NOAA National Oceanic and Atmospheric Administration

**OEM** Optimal Estimation Method

**0PAL** Zero-altitude PEARL Auxiliary Laboratory

OCO-2 Orbiting Carbon Observatory-2

**OPD** optical path difference

**OSIRIS** Optical Spectrograph and InfraRed Imaging System

P-AERI Polar-AERI

PARIS-IR Portable Atmospheric Research Interferometric Spectrometer for the Infrared

PC partial column

PEARL Polar Environment Atmospheric Research Laboratory

**PSC** polar stratospheric cloud

**RH** relative humidity

RL PEARL Ridge Laboratory

RMSD root-mean-squared difference

**RS** radiosonde

SAA solar azimuth angle

SAFIRE Surface and Atmospheric Flux, Irradiance, and Radiation Extension

SCIAMACHY Scanning Imaging Absorption Spectrometer for Atmospheric Chartography

SCISAT Scientific Satellite

**SEA** solar elevation angle

SNR signal-to-noise ratio

SPARC Stratosphere-troposphere Processes And their Role in Climate

SPM sun photometer

SZA solar zenith angle

TC total column

TCCON Total Carbon Column Observing Network

**TES** Tropospheric Emission Spectrometer

UTLMS upper-troposphere lowermost-stratosphere

UTLS upper-troposphere lower-stratosphere

UV ultraviolet

VMR volume mixing ratio

WAVAS Water Vapour Assessment

WCRP World Climate Research Program

WMO World Meteorological Organization

**ZPD** zero path difference

125HR Bruker IFS 125HR Fourier transform spectrometer

# 1 Introduction and motivation

# 1.1 Earth's changing atmosphere

Human civilization's impact on the Earth's environment is profound. Many scientists have started to refer to the current geological time period as the Anthropocene, reflecting the global significance of anthropogenic influences on the planet (Zalasiewicz et al., 2017). Changes to the composition of the atmosphere due to anthropogenic factors are among the key impacts used to quantify how and when humanity became one of the planet's dominant environmental forces (Crutzen, 2002; Ellis et al., 2016). Atmospheric composition changes are among the most concerning and consequential of humanity's environmental impacts.

The atmosphere is changing due to anthropogenic activity in many ways. For example, chlorofluorocarbons (CFCs) used in refrigerants and other products in the 20th century created large-scale depletion of the stratospheric ozone layer in the polar regions (Rowland, 1989). Recently, there have been signs of ozone layer recovery, but the chemical depletion of ozone caused by anthropogenically-emitted CFCs is expected to continue for decades (Strahan and Douglass, 2018). Emission of SO<sub>2</sub> from coal burning has acidified lakes, soils, and ecosystems in Ontario and elsewhere (Schindler, 1998). NOx, particulate matter, and other pollutants emitted from vehicles with internal combustion engines increase the risk of serious health impacts on humans (Chen et al., 2015; Health Canada, 2016). In addition, the emission of large quantities of greenhouse gases into the atmosphere from power plants, vehicles, and industrial activity, including the emission of 2.1 Tg of CO<sub>2</sub> between 1750 and 2012 (Le Quéré et al., 2014), has changed the atmospheric radiation budget (Hansen et al., 2005). This increase in atmospheric radiative forcing from anthropogenically-emitted greenhouse gases has led to a myriad of changes to the planet, including rising sea levels, warmer surface and tropospheric temperatures, shifts in precipitation and weather patterns (IPCC, 2013). There are few places on Earth, if any, left untouched by humanity's powerful presence.

Cognizant of the need to understand how changes to the atmosphere will affect the environment, the international scientific community has deployed instruments on land, in the air, and in orbit to take measurements of the atmosphere's constituents. This knowledge enables investigation into how the atmosphere works and how and why it is changing. This understanding will help humanity make informed decisions about its actions — individually and as a society.

The research presented in this thesis focuses on measurements of water vapour, one of the most important gases in the atmosphere. Water vapour plays major roles in the atmosphere chemically, dynamically, and radiatively. Climate-change-induced shifts to the global hydrological cycle affect atmospheric transport processes, creating and intensifying droughts and flooding (Trenberth et al., 2014). These changes will pressure and threaten ecosystems as well as resources used by human society.

### 1.2 Water vapour in the Earth's atmosphere

Water is common in the universe (Torres and Winter, 2018). However, it is often frozen (Moneti et al., 2001). The development of life, as we currently know it, requires the presence of liquid water. When astronomers created the concept of a "habitable zone" around a star to describe where life is likely to arise, the existence of conditions that allow for a liquid water was the most fundamental factor (e.g., Shapley, 1953; Kasting et al., 1993; Ramirez et al., 2017). On Earth, the ranges of pressures and temperatures allow water to exist as a solid, liquid, and gas.

The total amount of water near the surface of the Earth is estimated to be  $1.39 \times 10^{21}$  kg (Shiklomanov, 1993).<sup>1</sup> The oceans contain 96.5% of this water; ice caps, glaciers and permanent snow contain 1.7%. Freshwater in lakes and rivers, a crucial resource for humanity and land-based ecosystems, only amounts to  $9.3 \times 10^{16}$  kg, or 0.007% of the total water on Earth. The average amount of water in the atmosphere has been estimated to be  $1.27 \times 10^{16}$  kg (Trenberth et al., 2005), only about 0.0009% of the total water on the planet or 0.036% of the Earth's freshwater. The reservoirs containing Earth's water are illustrated in Figure 1.1. The small scale of the atmosphere's water relative to the overall amount of water on Earth and the size of the planet are illustrated in Figure 1.2.

<sup>&</sup>lt;sup>1</sup> There are large uncertainties regarding how much water is beneath the planet's crust. Some estimates of water stored in the mantle are enormous (e.g., Fei et al., 2017). For example, Schmandt et al. (2014) argued there is a large reservoir of  $H_2O$  in the mantle transition zone, approximately the same size as the oceans, within wadsleyite and ringwoodite minerals.



Figure 1.1: Reservoirs of Earth's near-surface water. The y-axis is the category of the quantity in the x-axis, e.g., freshwater reservoirs. Text labels the reservoir as well as the percent of the total water on Earth it contains. Two reservoirs in the "Other freshwater" line are not labelled due to space limitations, biowater (0.00008%), represented by the black line between soil and swamps, and rivers (0.00015%), represented in magenta between swamps and the atmosphere. Data are from Shiklomanov (1993).



Figure 1.2: Illustration of Earth's total amount of water and its partitioning between salt and fresh water (modified from U.S. Geological Survey).

Despite this small fraction of the total, atmospheric water vapour connects water reservoirs with each other through evaporation and precipitation, and plays key roles in the atmosphere. The amount of water in a particular time and place varies, but water vapour is the fourth most abundant atmospheric constituent (0.25%) overall, after nitrogen (78%), oxygen (20.95%), and argon (0.93%). The movement of water between its phases of matter and across the planet is called the hydrological (water) cycle.

The scale of the water cycle is extraordinary. Its movement of molecules is far larger than that of other biogeochemical cycles on Earth. Solar heating of the planet drives the evaporation of  $4.49 \times 10^{17} \pm 2.22 \times 10^{16} \frac{\text{kg H}_20}{\text{yr}}$  (Rodell et al., 2015). 87% of evaporation occurs from oceans (Oki and Kanae, 2006); the remainder occurs over land from evapotranspiration. This evaporation requires an enormous quantity of energy. Approximately 25% of solar energy reaching the planet leaves the surface through the evaporation of water (Trenberth et al., 2009). Since the intensity of sunlight reaching the planet depends on latitude, most evaporation occurs at tropical latitudes. The energy transported with the water is an important component of the global energy cycle (Hwang et al., 2010; L'Ecuyer et al., 2015).

Water vapour is moved around the planet through atmospheric currents. A greater amount of water is evaporated from the oceans than is returned directly through precipitation. There is a net flux of water from the oceans to land (e.g., estimates by Chahine, 1992 and Oki and Kanae, 2006). A summary of water's fluxes into and out of the atmosphere is illustrated in Figure 1.3.


#### Figure 1.3: Summary of water cycle fluxes from Oki and Kanae (2006).

Due to its global abundance and properties as a solvent, water is an important participant in biogeochemical cycles such as the carbon cycle.<sup>2</sup> Precipitation scavenges atmospheric gases and particles and deposits them to the ground and ocean. Liquid water flowing over surfaces also dissolves minerals and other substances. The water cycle is a vehicle that facilitates other constituents' movement through the planet's environment.

Exact pathways through which water travels are shaped by atmospheric and ocean circulation patterns, as well as surface features. Figure 1.4 illustrates the significant variability of atmospheric water vapour across the planet.

<sup>&</sup>lt;sup>2</sup> Atmospheric water dissolves atmospheric  $CO_2$  to form carbonic acid; this solution chemically weathers rocks when deposited on the ground through precipitation. Minerals such as calcium are brought to the oceans through this process, where they combine with carbonate to form sedimentary rock.





Once evaporated, water in the troposphere has a residence time of about one week in the atmosphere (Serreze et al., 2006). The maximum amount of water vapour that can be in the atmosphere before reaching saturation is exponentially dependent on temperature, as described by the Clausius-Clapeyron equation. This relationship is evident in Figure 1.5, which shows the atmospheric water vs. surface temperature at Eureka, Nunavut (80°N, 86°W). This figure also shows, through the colour-coding of the markers, the seasonality of surface temperatures, which reach a maximum of about 20°C in summer and minimum of about –50°C in winter.



Figure 1.5: (a) Total column of water vapour vs. surface temperature. (b) Surface mixing ratio of water vapour vs. surface temperature. Black line represents the maximum possible water vapour, e.g., 100% relative humidity, at a given temperature. Data are from Global Climate Observing System Reference Upper Air Network-processed Eureka radiosonde measurements taken between September 2008 and March 2017. Colours indicate the day of year of the measurement.

When humidity is transported into conditions with a lower saturation point, i.e. sufficiently low temperatures or pressures, it condenses out of the air as liquid or ice. Over long time scales, global evaporation equals global precipitation (Trenberth et al., 2009). Each year, the atmosphere recycles its water content dozens of times (Chahine, 1992).

The abundances of water vapour vary by multiple orders-of-magnitude throughout a single profile. Figure 1.6 shows an example of water vapour volume mixing ratio (VMR) in the troposphere and lower stratosphere measured by a radiosonde at Eureka as well as a nearly-simultaneous and nearly-co-located observation of water vapour in the upper troposphere, stratosphere, and mesosphere by the Atmospheric Chemistry Experiment (ACE)-Fourier Transform Spectrometer (ACE-FTS) satellite instrument. Combined, these two profiles illustrate that water vapour profile abundances vary by five orders-of-magnitude from the surface to 100 km.



Figure 1.6: Coincident water vapour profiles measured by a Eureka radiosonde and ACE-FTS showing that water vapour abundances range through multiple orders-of-magnitude. Distance between the measurements was calculated using the radiosonde launch location and the ACE-FTS 30-km tangent height. The tropopause height was calculated by the Global Climate Observing Network Reference Upper Air Network's processing, which uses the 2°C/km lapse rate definition.

Water vapour abundances also vary spatially from one location to another – particularly when separated by latitude, as shown in Figure 1.4. These variable abundances require dense sampling to capture short time and distance-scale processes. As shown in Figure 1.7, radiosonde humidity profiles recorded 12 hours apart can have quite different structure and abundances.



Figure 1.7: H<sub>2</sub>O profiles measured 12 hours apart on March 10, 2017 using radiosondes at Eureka, Nunavut.

## 1.2.1 Stratospheric water vapour

Very small amounts of water vapour are present in the stratosphere compared to the troposphere, as illustrated in Figure 1.6 for the case of Eureka, Nunavut. Indeed, measurements taken by the Microwave Limb Sounder (MLS) satellite instrument show that VMRs typically range between 4 and 10 ppmv throughout the stratosphere above Eureka, Nunavut. Figure 1.8 shows the timeseries of H<sub>2</sub>O VMR from MLS at 100 hPa ( $16 \pm 0.2$  km), which illustrates conditions in the lower stratosphere.

The primary mechanism transporting water vapour from the troposphere into the stratosphere is convection in the tropics and wave driving (Holton et al., 1995). Once in the lower stratosphere, water vapour moves slowly further into the stratosphere. The amount of water that reaches the

stratosphere is sensitive to the temperature of the tropical tropopause (Brewer, 1949). The tropical tropopause acts as a filter, limiting the amount of water vapour that can pass through it into the stratosphere. The temperature of the tropical tropopause is typically lower than at other latitudes, while its altitude is typically higher, as shown in Figure 1.9. Annual variation in the tropical tropopause temperature modulates the amount of water vapour entering the stratosphere. This produces a pattern of varying water vapour abundances being transported upwards by the Brewer-Dobson circulation called the atmospheric tape recorder (Mote et al., 1996).



Figure 1.8: Water vapour VMRs measured by MLS at 100 hPa altitude over Eureka, Nunavut. Colours are mapped to the H<sub>2</sub>O VMRs, i.e. the y-axis value, for enhanced readability.

The largest local source of stratospheric water vapour, aside from transport,<sup>3</sup> is methane oxidation, through reaction R1:

$$CH_4 + OH \rightarrow CH_3 + H_2O.$$

(R1)

 $<sup>^{3}</sup>$  H<sub>2</sub> provides another source of stratospheric H<sub>2</sub>O, but its contribution is small (Rohs et al., 2006).

Stratospheric sinks of water vapour include reactions with  $O(^{1}D)$ , which is generated by the photolysis of O<sub>3</sub> in both the troposphere and stratosphere (Jacob, 1999). Stratospheric water vapour can also be photolyzed by UV radiation to produce OH (Minschwaner et al., 2011):

$$H_2O + h\nu \rightarrow OH + H.$$

As a source of OH, water vapour is actively involved in atmospheric chemistry (Stenke and Grewe, 2005).



Figure 1.9: Average (a) tropopause temperatures and (b) tropopause heights at 274° longitude (corresponding to Eureka) in March 2017 from National Center for Environmental Prediction reanalysis.

(R2)

In the polar regions, the formation of Polar Stratospheric Clouds (PSCs), which can occur when temperatures reach below -78°C, is also a water vapour sink. This PSC dehydration has been observed, for example, by Vömel et al. (1997) and Khosrawi et al. (2017). PSC formation connects the water cycle to polar ozone depletion chemistry processes, i.e., by providing a surface for heterogenous chemistry that facilitates the conversion of chlorine reservoir species into active chlorine. Moreover, increased stratospheric water vapour may enhance PSC formation and the associated ozone depletion chemistry (Shindell, 2001).

Not only do PSCs facilitate ozone depletion chemistry directly, the impact of increased stratospheric water vapour on the radiative balance contributes a potential link between water vapour and ozone depletion processes as well. As stratospheric water vapour increases, its radiative impact is such that the troposphere becomes warmer while the stratosphere becomes cooler (Forster et al., 1999, 2002), pushing conditions towards the low temperatures favourable for PSC formation.

## 1.2.2 Radiative balance

Without an atmosphere, the Earth's mean surface temperature would be below the freezing point of water at the surface of the planet. This was first calculated and discussed by Fourier in 1824 (Burgess, 1836). The importance of the atmosphere in controlling the temperature at the surface of the planet began to be recognized in the late 18<sup>th</sup> and early 19<sup>th</sup> centuries.

### 1.2.2.1 Historical measurements

In 1774, Horace Benedict de Saussure showed, through measurements of the intensity of solar radiation at various altitudes reached by climbing mountains, that the atmosphere absorbs sunlight (Barry, 1978; Fleming, 1999). In the 1820s, Joseph Fourier argued that the Earth is warmer than it would be if it were simply warmed by the Sun. He postulated multiple possible explanations. One of those suggestions was that the atmosphere acted as an intermediary between the Earth and the heat arriving from the Sun, creating a warming effect. However, while Fourier recognized that the Earth's temperature "can be augmented by the interposition of the atmosphere," he also admitted it was, given the information available at the time, "difficult to know how far the atmosphere

influences the mean temperature of the globe" (Burgess, 1836).<sup>4</sup> Thirty-five years later, John Tyndall made the first quantitative measurements of atmospheric constituents' radiative absorption properties.

In 1859, Tyndall made measurements of the relative proportion of radiation absorbed and emitted by H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, and other gases (Tyndall, 1861). This apparatus is shown in Figure 1.10, a copy of a diagram included in a collection of Tyndall's lectures about heat (Tyndall, 1863).<sup>5</sup> These measurements showed that water vapour absorbed more radiation than other atmospheric constituents. Tyndall inferred that water vapour was the most consequential atmospheric constituent for atmospheric radiative balance and temperatures (Tyndall, 1861, 1863, 1873). He later stated that without the radiative influence of atmospheric water vapour, Earth would be "held fast in the iron grip of frost" (Tyndall, 1873). Tyndall's early measurements opened a new thread of inquiry into the atmosphere's radiative balance that continues to be a topic of research today.

Each molecule has absorption and emission spectra resulting from transitions between its vibrational, rotational, and electronic states. Figure 1.11 broadly illustrates absorption features from atmospheric gases at wavelengths in the range of solar and terrestrial radiation.

Water vapour has a complicated absorption spectrum. Sophisticated modern spectroscopic techniques have identified approximately 64,000 absorption lines between the microwave and infrared regions, corresponding to the transitions between rotational and vibrational states available to the water molecule (Gordon et al., 2007). Both absorption and emission spectral features can be used to obtain information about the abundances and distribution of water vapour and other gases in the atmosphere.

Due to its strong infrared absorption, water vapour has a dominant effect on climate and radiative forcing (Soden et al., 2002; Dessler et al., 2008). Kiehl and Trenberth (1997) estimated that water

<sup>&</sup>lt;sup>4</sup> Fourier's publication in 1824 was in French, in the *Annales de Chimie et de Physique* No. 27. The quote is from the English translation by Ebenezer Burgess, published in 1837 in the *American Journal of Science*.

<sup>&</sup>lt;sup>5</sup> It was fortunate that the U of T Thomas Fisher Rare Book Library had an original copy of Tyndall (1863) available for my use. Consulting with original works offered invaluable insight into early research. I regret, however, that despite my effort to handle the 155-year old book with great care, it fell into two pieces, of roughly equal size, while I read it. The library said that this is a normal part of their materials' use. I hope they repaired it.

vapour is responsible for 60% of the clear-sky natural greenhouse effect. Changes to water vapour abundances can thus lead to changes in atmospheric temperatures.

This effect is dependent on a variety of factors, including the altitude at which the change occurs. Energy absorption by many spectral lines is saturated at low altitudes. However, changes in the upper troposphere and lower stratosphere (UTLS) water vapour can cause changes to the atmosphere's radiative balance, and thus temperatures (Soden et al., 2008; Riese et al., 2012; Dessler et al., 2013). This has been observed experimentally. Solomon et al. (2010) showed that the 10% decrease in stratospheric water vapour between 2000 and 2009 reduced the surface warming trend by 25%. Trends in tropospheric and stratospheric water vapour, in the UTLS in particular, are thus of interest.



Figure 1.10: Tyndall's apparatus for measuring the absorptive properties of atmospheric gases in 1859. Figure from Tyndall (1863).



Figure 1.11: (a) Blackbody spectra representative of the Sun and Earth. (b) Spectrum of absorption at 11 km. (c) Spectrum of absorption at ground level. Figure from Wallace & Hobbs (2006), Fig 4.7.

#### 1.2.3 Trends and feedbacks

Increases in water vapour have been observed in recent decades. Tropospheric water vapour abundances are increasing at a rate of 1.2% per decade (Trenberth et al., 2005, 2007). Adding water vapour to the atmosphere directly has little impact on global climate because water will condense out of the atmosphere on relatively short timescales, e.g., several days. However, atmospheric temperature increases, e.g., those caused by increases in non-condensing greenhouse gases (GHGs), lead to increases in water vapour since there is an abundance of liquid water sources. This increase in water vapour abundances is sustained because increased temperatures reduce the amount of water vapour condensing out of the atmosphere. This increase in water vapour impacts the Earth atmosphere's radiative balance. This reinforcing cycle of increases to atmospheric temperatures and water vapour abundances is called the water vapour feedback effect. Atmospheric water vapour amplifies the radiative impact of GHGs such as CO<sub>2</sub> and CH<sub>4</sub>.

Stratospheric water vapour feedback has been estimated to be 0.3 W m<sup>-2</sup> for every 1 K temperature change at 500 hPa (Dessler et al., 2013).

Positive trends in upper stratospheric water vapour have been observed by multiple satellite records, from 1988 to 2010 (Hegglin et al., 2014). Aircraft, balloon, ground, and satellite observations between 1954 and 2000 show a +1% per year trend in stratospheric water vapour (Rosenlof et al., 2001). Frostpoint hygrometer (FPH) measurements at Boulder, Colorado have been made since 1980 and have shown an average trend in stratospheric water vapour between 16 and 26 km altitude of  $27 \pm 6\%$  between 1980 and 2010 (Hurst et al., 2011). Variation in the tropical tropopause temperature is likely the reason for part of the observed changes (Randel et al., 2004). Increases in methane oxidation due to anthropogenic methane emissions explain about a quarter of the observed stratospheric water vapour increase (Rohs et al., 2006; Hurst et al., 2011). Dessler et al. (2013) used model results from the Goddard Earth Observing System Chemistry Climate Model (GEOSCCM) to predict that lowermost stratospheric water vapour will continue to increase through the  $21^{st}$  century, mostly due to transport through the tropopause, which bypasses the tropical tropopause cold point. Trends in stratospheric water vapour are a topic of ongoing investigation.

# 1.3 Arctic atmospheric water vapour

Despite its remote location, the Arctic environment is significantly affected by anthropogenic activity. Observations of the Arctic region are particularly sparse and important for understanding how the planet's atmosphere is changing (ACIA, 2004). A prominent example is how the impacts of greenhouse gas emissions and global warming are amplified at polar latitudes.

Temperatures in the Arctic have increased more than elsewhere on the planet. Temperature records indicate the changes in Arctic surface air temperature are twice as large as the global average (Wendisch et al., 2017), as shown in Figure 1.12. This larger increase in temperatures at Arctic latitudes is known as Arctic amplification, an aspect of the climate system that is driven by multiple factors, including the decline in sea ice, increases in water vapour abundances, and changes to cloud cover (Serreze et al., 2011).



Figure 1.12: Temperature differences relative to historical mean (1951-1980) from Wendisch et al. (2017), showing the larger warming in the Arctic relative to other latitude regions. Near-surface air temperature data are from NASA Goddard Institute for Space Studies (GISS) Surface Temperature Analysis (GISTEMP).

At Eureka, Nunavut (80°N, 86°W), a research site in the Canadian high Arctic, surface temperatures increased by  $0.88 \pm 0.17$  °C per decade between 1972 and 2007 (Lesins et al., 2010). This observed Arctic warming trend is expected to continue (IPCC, 2013). Indeed, a 57year timeseries of near-surface temperatures from radiosondes show a clear warming in all months of the year at Eureka, Nunavut. Changes in these yearly averages between 1961 and 2017 are shown in Figure 1.13. These results differ from Lesins et al. (2010) in showing a smaller trend in the Eureka temperature increase, i.e., of 0.55 °C/decade. This difference is due to the differences in the time periods examined; the Lesins et al. analysis ended in 2007, where there is a maximum in the temperature timeseries. The following decade (2008-2017) showed a cooling trend, on average. In addition, the Lesins et al. analysis began in 1972, which had lower temperatures than the 1961 starting point used in Figure 1.13, contributing to the larger overall warming trend reported.



Figure 1.13: 1-year and 5-year running means of Eureka radiosonde temperatures at 10 m altitude from 1961 to 2017 (solid lines), with linear best fit lines (dashed lines).

The atmosphere of the polar regions has significantly less water vapour than elsewhere on the planet. Total columns of water vapour are typically a fraction of values found at equatorial latitudes (as seen in Figure 1.4). Overall, the Arctic contains about 1.6% of the total atmospheric water vapour or  $2.03 \times 10^{14}$  kg (Serreze et al., 2006).<sup>6</sup>

The source of atmospheric water vapour in the Arctic is transport from lower latitudes and local evaporation, e.g., from leads in the Arctic Ocean. One major transport process that brings water vapour into the Arctic is mixing due to the breaking of planetary waves. Transient eddies are also a large source of moisture transport for high latitudes (Jakobson et al., 2010). Atmospheric rivers, synoptic-scale filamentary structures that carry enhanced water vapour content out of the tropics, are also important contributors to high-latitude water vapour transport (Newman et al., 2012; Gimeno et al., 2014; Neff et al., 2014).

<sup>&</sup>lt;sup>6</sup> The Serreze et al. (2006) study reported the Arctic atmospheric water vapour as 203 km<sup>3</sup>, primarily using European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-40 reanalysis data from 1979-2001. The area covered included the Arctic Ocean and the land areas that drain into it.



# Figure 1.14: Water evaporating from leads into the Canadian Arctic atmosphere near Iqaluit, Nunavut. Photo taken February 12, 2017 at 3:11 PM near Baffin Island, Nunavut.

Since there is a small amount of humidity in the Arctic atmosphere, spectral windows in the infrared region of the spectrum that are usually saturated, i.e. no radiation can pass through the atmosphere at those frequencies without being absorbed, are not fully saturated in the Arctic. Consequently, increases in atmospheric water vapour can have a particularly acute effect on radiative balance of the Arctic atmosphere (Tobin et al., 1999; Turner et al., 2010).

Measurements at Eureka, Nunavut have shown evidence of a positive trend in atmospheric emitted radiances at 10 and 20 µm during winter and summer (Mariani, 2014). Since these atmospheric windows are sensitive to changes in water vapour and clouds, these trends indicate that changes are occurring in the energy budget of the atmosphere above Eureka. This motivates monitoring of changes to radiation and atmospheric water vapour.

Alongside the observed warming, the total column of water vapour at Eureka increased by  $10 \pm 3\%$  between 1961 and 2007, based on the analysis of Eureka radiosoundings (Lesins et al., 2010). Analysis of radiosonde water vapour below 500 hPa from 1979 to 2008 by Serreze et al. (2012) also showed statistically significant positive trends at Eureka, with the largest increases during summer. These observations of increasing water vapour columns aligns with the expectation that water vapour abundances will increase globally as temperatures increase (Soden et al., 2002). National Center for Atmospheric Research Community Climate System Model, version 3 (CCSM3) results also show an increase in water vapour in the Arctic due to increased local evaporation and increased flux convergence (Skific et al., 2013). This is an important feedback effect in the climate system.

# 1.4 Motivation and objectives

The Canadian Arctic is a vast area with scarce atmospheric measurements, despite its relevance to many current scientific topics. Motivated by the goal of better understanding atmospheric composition, processes, and chemistry in the high Arctic, the Polar Environment Atmospheric Research Laboratory (PEARL) was established in 2006. The datasets collected by PEARL instruments have been used in numerous studies and contribute to many international networks, as well as to validation of satellite measurements. Each winter since 2004, an intensive field campaign takes place at PEARL during February and March: the Canadian Arctic ACE/OSIRIS Validation Campaign. During this period, a team of scientists associated with the Canadian Network for the Detection of Atmospheric Change (CANDAC) operate instruments, perform maintenance, troubleshooting, and install upgrades. The measurements collected contribute to the validation of the Canadian ACE and Optical Spectrograph and InfraRed Imaging System (OSIRIS) satellite data products.

One of the permanently-installed PEARL instruments is a Fourier transform spectrometer (FTS), a Bruker-built IFS 125HR. The PEARL 125HR is able to measure a wide variety of atmospheric constituents. The instrument will be described in detail in Chapter 3. This thesis focuses on understanding the water vapour dataset produced from the PEARL 125HR measurements.

The scientific goal of this thesis is to investigate the accuracy of atmospheric water vapour measurements available at Eureka, with the following specific objectives:

- To assess the accuracy of the PEARL 125HR water vapour retrievals produced by the Multi-platform remote sensing of isotopologues for investigating the cycle of atmospheric water (MUSICA) technique, using comparisons to other water vapour datasets produced at Eureka.
- 2. To assess the accuracy and limitations of UTLS water vapour observations near Eureka produced by the ACE-FTS and ACE-MAESTRO satellite instruments, using the Eureka radiosondes and PEARL 125HR as a reference, as well as other satellite datasets.
- 3. To assess the global Total Carbon Column Observing Network (TCCON) Fourier transform infrared (FTIR) spectrometer water vapour retrieval products using

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comparisons with the well-validated MUSICA FTIR spectrometer water vapour product and radiosondes.

# 1.5 Outline

This thesis began in Chapter 1 with a brief overview of motivations for understanding the Earth's atmosphere, with particular attention on the significance of water vapour. The rest of the thesis is structured as follows: In Chapter 2, historical techniques used to measure water vapour as well as the radiosonde water vapour measurements acquired at Eureka are reviewed. Fourier transform spectroscopy is described in Chapter 3, as well as the retrieval technique used to obtain water vapour data from the PEARL 125HR measurements. In Chapter 4, new ground-based water vapour datasets in Eureka are compared, with emphasis on confirming the accuracy of the new 125HR retrieval technique developed by Schneider et al. (2016) at this high Arctic site. New PEARL Atmospheric Emitted Radiance Interferometer (AERI) measurements of water vapour are also assessed. Chapter 5 analyzes comparisons between water vapour profile measurements at Eureka. The geographic scope expands in Chapter 6, where comparisons are made between two ground-based networks of 125HR FTIR instruments to assess the utility of TCCON water vapour products and the comparability of the two measurement techniques. Finally, Chapter 7 summarizes the thesis and notes opportunities for future work.

# 1.6 Contributions

The 125HR at PEARL has been maintained and operated by several people since its installation in 2006. Between 2012 and 2015, I was responsible for acquiring mid-infrared (MIR) 125HR measurements. This involved being on-site to operate the instrument during Canadian Arctic ACE/OSIRIS Validation Campaigns in February and March of 2012, 2013, 2014, and 2015. During these campaigns, I also performed instrument maintenance and troubleshooting in collaboration with fellow U of T Ph.D. students Joseph Mendonca (2012-2014) and Sebastien Roche (2015), who were responsible for near-infrared (NIR) 125HR operations. During the 2014 PEARL campaign, I was also responsible for running the PARIS-IR FTIR instrument; however, I did not use the collected data. During the 2015 campaign, I acquired lunar absorption measurements, which had not previously been done using the PEARL 125HR. In 2014 and 2015, upgrades were made to enable 125HR measurements to be run on-site with significantly less operator time and to be run remotely through the internet, e.g. from U of T. In support of this effort, I created new code to operate the 125HR in MIR mode semi-automatically, minimizing the time needed to run the instrument. I also revised the 125HR's Standard Operating Procedures (SOP) document and created concise Quick Reference Guide documents summarizing key procedures to support CANDAC operators' operation of the 125HR.

In 2014 and 2015, I helped test a new 125HR sun-tracker instrument installed by Jim Drummond (CANDAC PI), Pierre Fogal (PEARL Site Manager), and Anthony Pugliese (U of T M.Sc. student) with software developed by Jonathan Franklin (Dalhousie University Ph.D. student).

In 2015, I set up, installed, and tested a new computer to run the PEARL 125HR. I worked with Joseph Mendonca, Jonathan Franklin, and Yan Tsehtik (CANDAC Data Manager) to set up and test remote access for the 125HR and sun-tracker computers. I used this remote access, the upgraded code, and the new sun-tracker to run MIR 125HR measurements from Toronto throughout the year in collaboration with Joseph Mendonca, CANDAC operator Mike Maurice, and Pierre Fogal.

This work involves the use of many datasets produced by the efforts of many people and groups. The MIR 125HR water vapour retrievals used extensively in this work were performed by Matthias Schneider and his team at the Karlsruhe Institute of Technology (KIT) through the MUSICA project. TCCON retrievals of water vapour were performed by TCCON members using the spectral fitting software GGG. The TCCON total column water vapour datasets used for analysis in Chapter 6 were extracted by Nicholas Deutscher. Retrievals of water vapour from the PEARL P-AERI and E-AERI were done by Penny Rowe at NorthWest Research Associates. Radiosonde measurements at Eureka were made by ECCC meteorological technicians at the Eureka Weather Station. The GRUAN processing of the Eureka radiosonde files used in Chapters 1, 4, 5, and 6 was done by Michael Sommer at the GRUAN Lead Centre. Satellite datasets used in the Chapter 5 comparisons were produced through the teams of scientists on each mission. NDACC and TCCON measurements at Kiruna, Sodankylä, Bremen, Karlsruhe, Izaña, Wollongong, and Lauder used in Chapter 7 were provided by Jesse Nusbaumer and David Noone.

# 2 Atmospheric water vapour measurements

The important role of atmospheric water vapour in the chemistry, dynamics, weather, and climate of the planet has motivated the development of techniques that can measure it accurately, with high horizontal and vertical resolution, and that can be deployed to obtain global coverage. However, our understanding of the abundance, variability, and transport of water vapour is incomplete (Stevens et al., 2013; Hegglin et al., 2014). More observations are needed to investigate these gaps in our understanding of the atmosphere (Trenberth et al., 2014). The work presented in this thesis contributes to ongoing efforts to improve atmospheric water vapour measurements.

This chapter begins with a short overview of historical water vapour measurements. Next, it describes the primary measurement site for the research presented. Lastly, it describes the radiosonde measurements taken at Eureka, which are used as a reference for comparisons presented in later chapters.

# 2.1 Historical measurements of atmospheric humidity

Observations of atmospheric water vapour have been made for hundreds of years. However, instruments invented and used during the 15<sup>th</sup> to 18<sup>th</sup> centuries had low resolution, accuracy, and precision. In addition to the high uncertainties of these measurements, these early instruments were rarely used in an organized, widespread, standardized manner (Camuffo et al., 2014).

Early instruments to measure humidity were often constructed to exploit the hygroscopic properties of materials, e.g., that could absorb and re-evaporate humidity from the surrounding environment. One of the earliest measurement techniques for measuring atmospheric water vapour was described in the mid-1400s by Cardinal Nicholas de Cusa (Frisinger, 1977). He proposed constructing an instrument for the measurement of atmospheric humidity by suspending a large quantity of wool on one side of a balance, with stones on the other side. This instrument would be calibrated by setting the weight of the stones equal to the weight of the wool in dry air. The proportionality between the absorption of water by the wool and its change in mass allowed relative humidity to be crudely inferred. In subsequent centuries, scientists such as Leonardo Da Vinci, Francesco Folli, and Robert Hooke worked on creating improved

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atmospheric water vapour measurements. It was Johann Lambert, in the late 1700s, who first used the term 'hygrometer' to refer to an instrument used for atmospheric humidity measurements (Frisinger, 1977).

Changes to the length, mass, or shape of hygroscopic materials formed the basis for many early humidity measurements. For example, Lambert (1769, 1774) described the design of a hygrometer that exploited the hygroscopic property of catgut. A length of catgut was attached to a needle. When the amount of humidity in the surrounding air changed, the catgut would coil or uncoil, turning the needle. This instrument was significant because Lambert used it, along with a thermometer, to make daily measurements of the humidity and temperature of the German cities Berlin, Sagan, and Wittenberg for more than a year – a rare dataset for the time period. The data revealed a strong seasonal pattern in temperature and humidity, as well as a strong correlation between them (Lambert, 1774). In 1771, Lambert advocated for the creation of a global atmospheric observation network (Frisinger, 1977).

One of the first long-term scientific datasets of atmospheric humidity was taken by Vincenzo Chiminello and his colleagues (Camuffo et al., 2014). Chiminello's observatory recorded multiple measurements of humidity each day at 7:00, 15:00, and 21:00, between 1794 and 1826 in Padua, Italy. One of the instruments they used was a hair hygrometer originally designed by Horace-Benedict de Saussure (de Saussure, 1783), which used humidity-dependent changes in the length of the hair to measure atmospheric humidity. Chiminello also designed his own hygrometer, which used goose quills filled with mercury (Chiminello, 1785). When the quill tube shrank or expanded due to its absorption/release of atmospheric humidity, the mercury level of the tube changed. An adjacent, identically sized thermometer produced measurements of mercury level changes due to temperature that were used to remove the temperature effect from the humidity measurement. Modern analysis of this early timeseries has concluded that the measurements had an overall uncertainty of approximately 10% (Camuffo et al., 2014). This early timeseries is exceptional. Until the late 1800s, atmospheric measurements were limited to the surface, and were geographically very sparse.

#### **Balloon-borne atmospheric measurements**

Scientists designed and flew a variety of balloon-based instruments for atmospheric measurements between the 1890s and 1920s, following the development of hot air ballooning in the 1800s. These measurements, e.g., taken using thermometers, barometers, and hygrometers, were limited by the materials available for constructing the balloons, the weight of available sensors, and the limited means of recording and transmitting data. Some balloon-based instruments required an operator to accompany them (Frisinger, 1977). Others used clock-driven pen-and-ink recording devices, however, these were often large, heavy, and costly, requiring a large balloon to lift the payload (DuBois, 2002).

In 1901, Richard Assmann was the first to launch a scientific payload into the atmosphere using sealed rubber balloons that expanded as they reached higher altitudes. This approach provided a significant advance in the ability to acquire measurements of the atmosphere above the surface, as they were less costly, could reach the stratosphere, and tended to ascend at a roughly constant rate. The first balloon payload that resembled modern instruments was flown on January 7, 1929 by Robert Bureau, who coined the term 'radiosonde' for balloon instruments that relayed measurements of the atmospheric temperature (using a bimetallic thermometer), pressure (using a Bourdon tube), and humidity (using a hair hygrometer) back to a ground station by radiowaves (DuBois, 2002). Three years later, Vilho Väisälä launched the first of his radiosonde designs in December 1931 (Vaisala, 2018). These instruments were able to reach the stratosphere. Väisälä founded a company to produce and sell the balloon instruments (Vaisala) that continues to play a leading role in radiosonde instrument design today. In 1938, the U.S. Weather Bureau began flying radiosondes and established a network of measurement sites (Ewen et al., 2008). An example of an early National Oceanic and Atmospheric Administration (NOAA) radiosonde is shown in Figure 2.1.

The number of meteorological stations launching radiosondes grew significantly from the 1940s to the 1970s. This growth included the Joint Arctic Weather Stations (JAWS), a project by the Canadian and U.S. governments to establish and operate meteorological observation sites across the North American Arctic (Heidt, 2011). In 1980, there were at least 1600 stations collecting radiosonde data worldwide. Figure 2.2 shows the growth in the number of radiosonde launch

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sites and the growth of the number of levels reported in the Integrated Radiosonde Archive (IGRA), an archive of homogenized long term radiosonde datasets (Durre et al., 2006).



Figure 2.1: Launch of a radiosonde on May 7, 1936 in Washington, DC, U.S., by the U.S. Bureau of Standards. Image from NOAA National Weather Service Collection (Image ID wea01108, available online at: http://www.photolib.noaa.gov/bigs/wea01108.jpg).



Figure 2.2: (a) Number of radiosonde stations contributing to the Integrated Radiosonde Archive. (b) Number of radiosonde profile levels reported. Figures from Durre et al. (2006).

Current radiosonde observation launch sites are shown in Figure 2.3. There are sites worldwide; however, observations are sparse in the polar regions and over oceans. The decline in the number of radiosonde sites, starting in the 1980s, coincides with the entry of atmospheric observations using satellite-based remote sounding instruments in low-Earth orbit, as well as the development of ground-based instruments such as LIDARs, radiometers, and Fourier transform spectrometers.



Figure 2.3: Global radiosonde launch sites. Figure from www.weather.gov/jetstream/radiosondes (last accessed July 12, 2018).

# 2.2 Modern observations of water vapour

Direct measurements of atmospheric composition have grown more sophisticated, however, such measurements are resource-intensive at a finely-resolved global scale. The WMO World Weather Watch collects surface observations of meteorological data, including relative humidity, from approximately 10,000 sites for weather prediction and modelling. However, these data are limited to the surface, have sparse coverage in the polar regions, and do not include information about the composition of the atmosphere, aside from humidity, since their focus is on meteorological parameters, e.g., temperature and pressure. Atmospheric remote sensing techniques developed in the 20<sup>th</sup> century offer a means of achieving the spatial and temporal coverage of observations needed to monitor and understand the composition of the atmosphere.

Remote sensing observations commonly involve the measurement of radiation that has been emitted and/or absorbed by atmospheric constituents. These observations can be collected by instruments located at ground-based observatories, on balloon-based platforms, on aircraft, or aboard satellites. The spectra acquired by remote sounding instruments can be used to infer the composition of the atmosphere and the vertical distribution of atmospheric constituents. Chapter 3 offers a description of one approach to these measurements, FTIR spectroscopy.

# 2.2.1 Ground-based measurements

In 1991, the Network for the Detection of Atmospheric Composition Change (NDACC), then known as the Network for the Detection of Stratospheric Change (NDSC), began producing global measurements of the atmosphere using a variety of instrumentation, e.g. lidars, microwave radiometers, and FTIR spectrometers (Kurylo, 1991; De Mazière et al., 2018). Initially, NDACC focused on atmospheric composition and chemistry in the stratosphere, but this mandate was later broadened to include tropospheric species. NDACC measurements are also used to validate satellite observations.

Currently, there are about 70 observing stations participating in NDACC; 25 of these contribute mid-infrared (MIR) FTIR spectrometer measurements. Canadian FTIR observations in Toronto, Ontario, and Eureka, Nunavut contribute to the NDACC. A subset of the NDACC FTIR spectrometer sites have participated in the MUSICA project, which retrieved water vapour and water vapour isotopologue total columns and profiles from NDACC spectra. This product is described in more detail in Chapter 3.

In 2004, a new network of FTIR spectrometers was established to study the carbon cycle using near-infrared (NIR) measurements, the Total Carbon Column Observing Network. TCCON uses the same standard instrumentation as most NDACC sites, the Bruker-made IFS 125HR spectrometer, but uses a different beamsplitter, detector, and measurement settings. Currently, 25 stations contribute FTIR spectrometer measurements to TCCON, including Canadian sites in East Trout Lake, Saskatchewan and Eureka, Nunavut.

### 2.2.2 Satellite-based measurements

Atmospheric measurements have been acquired by remote sensing satellite instruments since the 1960s. For example, the National Aeronautics and Space Administration (NASA)'s Nimbus satellites, launched between 1964 and 1978, observed the atmosphere using microwave and infrared radiometers. Despite the success of these mid-20<sup>th</sup> century satellite measurements, it wasn't until the 1980s and 1990s that high quality satellite measurements of water vapour became available (SPARC, 2000). In particular, the first long-term atmospheric water vapour measurements were acquired by the Stratospheric Aerosol and Gas Experiment II (SAGE II), aboard NASA's Earth Radiation Budget Satellite, from 1984 to 2005, and by the Upper Atmosphere Research Satellite (UARS) instruments, e.g., the Microwave Limb Sounder (UARS-MLS) and HALogen Occultation Experiment (HALOE). HALOE acquired measurements of stratospheric water vapour from 1991 to 2005, between 65°N and 65°S latitude. A more recent MLS instrument, aboard NASA's Aura spacecraft, continues to acquire atmospheric measurements, reaching between 82°S and 82°N, including much of the polar regions. There are many instruments currently acquiring satellite-based measurements of atmospheric water vapour. For example, Chapter 5 of this thesis discusses satellite measurements over the Canadian Arctic made by the ACE, Atmospheric Infrared Sounder (AIRS), Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), MLS, Tropospheric Emission Spectrometer (TES), and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY).

## 2.2.3 Assessments of atmospheric observation capabilities

Assessments of atmospheric observation capabilities for water vapour have been undertaken by several organizations. The results of these reports are highlighted below.

#### GEWEX

In the late 1980s, the World Climate Research Program (WCRP) organized a meeting to discuss the global water cycle. The conclusion of scientists participating was that the global water cycle was not well-understood, largely due to the lack of data. This led to the creation of one of the world's largest global change research projects, the Global Energy and Water Cycle Experiment (GEWEX) (Chahine and Vane, 1992). Its research efforts are ongoing. GEWEX recently published a detailed assessment of tropospheric water vapour measurements. It identified many

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challenges to attaining a global understanding of the water cycle, including large inconsistencies in long-term total column water vapour measurements in deserts, mountainous regions, and the polar regions (Schröder et al., 2016). The conclusions of the GEWEX review of the state of water cycle measurements reiterated the need to improve on satellite profiling capabilities, to diligently validate data products, and to acquire stable, bias-corrected total column and profile datasets. GEWEX recommends that the scientific community develop and deploy instruments with the ability to measure humidity globally with high quality, 10-km spatial resolution, and 3hour temporal resolution. Improving measurements of atmospheric water is key to mapping and understanding the water cycle and its role in related phenomena.

#### SPARC

In 1992, the WCRP created the Stratosphere Processes And their Role in Climate (SPARC) project (now called the Stratospheric-tropospheric Processes And their Role in Climate) to coordinate research into Earth system processes, aiming to promote understanding of atmospheric chemistry, physics, and climate. In addition to contributing to international assessments on topics such as ozone depletion and climate science, SPARC has assessed the state of observations for stratospheric water vapour. In 2000, SPARC released SPARC Report No. 2 (2000), also known as the Water Vapour Assessment report (WAVAS).

WAVAS concluded that the atmospheric science community's understanding of the variability and trends of water vapour in the UTLS and stratosphere was inadequate. Causes of long-term variability in the stratosphere, for example, were still being investigated, as observations had not yet been fully reconciled with known factors, such as methane oxidation and changes to tropopause temperatures. The assessment's recommendations began with the need for improved long-term monitoring, especially of upper tropospheric water vapour because of its important radiative impact. Moreover, it recommended the use of multiple instruments that produce complementary observations at a variety of latitudes. The long-term measurements of UTLS water vapour at Boulder, Colorado using FPHs were highlighted due to their valuable contribution to both trend analysis and satellite validation. The report recommended that other sites launch balloon-based instruments capable of acquiring UTLS water vapour measurements, and that future satellite missions use those datasets for validation. A second SPARC assessment of stratospheric water vapour measurements (WAVAS-II) is currently underway, with results published in an inter-journal special issue of ESSD/ACP/AMT. The contributed works so far indicate that while considerable progress has been made, e.g., in quantifying FPH measurement uncertainties (Vömel et al., 2016), validating satellite measurements (Hurst et al., 2016), and comparison of long-term satellite records of stratospheric and mesospheric water vapour (Khosrawi et al., 2018), many of the core observational needs noted by the WAVAS assessment (and others) are not yet met.

#### GCOS

In 2016, the WMO's Global Climate Observing System (GCOS) program assessed the needs of the global observing system. GCOS considers acquiring measurements of water vapour profiles to an accuracy of 5% essential for understanding the climate system (GCOS, 2016). The total column of atmospheric water vapour is considered an Essential Climate Variable (ECV). The GCOS requirement is for frequent (better than every 4 hours) water vapour total column measurements within 2% accuracy. However, the 2016 GCOS report recognizes that global measurements of water vapour are not yet acquired routinely at these accuracy levels. Instruments and measurement techniques are being developed to fill this observational need, and motivate the work in this thesis.

# 2.3 Measured quantities and unit conversions

Water vapour is commonly measured in terms of its abundances, both near the surface and as a vertical profile, and in terms of its total amount within a column of air. Typically, abundances are reported as VMR in parts per million by volume (ppmv). The total column of water vapour is reported in either molecules/m<sup>2</sup> or precipitable water vapour in mm. This section describes the calculation of these quantities from measurements.

## 2.3.1 Relative humidity to volume mixing ratio

Some instruments report relative humidity rather than VMR. Measuring relative humidity is equivalent to measuring the ratio of the partial pressure of water vapour relative to the saturation vapour pressure of water vapour, e.g.:

$$RH = \frac{P_{H_2O}}{e_s(T)} \times 100\%,$$
(2.1)

where  $P_{H_2O}$  denotes the partial pressure of water vapour,  $e_s$  denotes the saturation vapour pressure, and the resulting relative humidity value is in %. Note in the equation that it is dependent only on temperature. As temperature increases, the partial pressure of water vapour that can exist in the atmosphere increases as well, since  $e_s(T)$  increases.

The partial pressure of a gas  $(P_x)$  is related to the VMR  $(C_x)$  of the gas and the total atmospheric pressure (P):

$$P_x = C_x \cdot (P - P_x) \cong C_x \cdot P. \tag{2.2}$$

It is useful to note that this approximates mole fraction  $(\frac{P_x}{P})$  as VMR  $(\frac{P_x}{P-P_x})$ , which is reasonable when  $P_x$  is small.

Combining Equations 2.1 and 2.2 allows the VMR of water vapour to be calculated from radiosonde measurements of relative humidity, temperature, and pressure using:

$$C_{H_2O} = \frac{RH \cdot e_s(T)}{P},\tag{2.3}$$

where RH is relative humidity,  $e_s$  is the saturation vapour pressure, and P is total pressure.

Empirical equations describing the relationship between the saturation vapour pressure of water vapour ( $e_s$ ) and atmospheric temperature have been constructed through theoretical and experimental research. Many equations for  $e_s$  exist, such as those proposed by Goff (1957), Buck (1981), Hyland and Wexler (1983), and Murphy and Koop (2005).

#### 2.3.2 Atmospheric total columns

The total amount of an atmospheric constituent between the surface and the top of the atmosphere over an area is known as a 'total column'. Standard units for atmospheric total columns are molecules/m<sup>2</sup>, though molecules/cm<sup>2</sup> are also used, depending on the abundance of the gas being observed. A total column can be calculated by integrating the profile of a gas from the surface to the top of the atmosphere, e.g.:

$$Total \ column = \int_{surface}^{TOA} n_x(z) \ dz, \tag{2.4}$$

where  $n_x$  is the number density of gas x at an altitude (z), and TOA is the top of the atmosphere. Often, the number density of the desired constituent is not directly available. If a measurement produces a profile of an atmospheric gas in volume mixing ratio, the number density profile of the gas can be calculated using the number density profile of air, e.g.:

$$n_x(z) = C_x(z) \cdot n_{air}(z), \qquad (2.5)$$

where  $C_x(z)$  is the VMR of gas x at a particular altitude (z).

The number density of air can be calculated using profiles of pressure and temperature and the Ideal Gas Law, e.g.:

$$n_{air}(z) = \frac{N_A \cdot P(z)}{R \cdot T(z)},\tag{2.6}$$

where *P* is pressure in units of Pascals and *T* is temperature in units of Kelvin at a particular altitude (z). *R* is the gas constant ( $R = 8.31 \frac{J}{mol \cdot K}$ ). *N*<sub>A</sub> is Avogadro's number, 6.0221409 × 10<sup>23</sup>  $\frac{molecules}{mole}$ .

The total column of the gas is thus calculated from the mixing ratio by:

$$Total \ column = \int_{surface}^{TOA} C_x(z) \ n_{air}(z) \ dz, \tag{2.7}$$

or, combining with Equation 2.6:

$$Total \ column = \int_{surface}^{TOA} C_{x}(z) \frac{N_{Av} \cdot P(z)}{R \cdot T(z)} \ dz.$$

$$(2.8)$$

# 2.3.3 Precipitable water vapour units

Total columns of certain molecules are sometimes expressed in units particular to that species, such as the use of Dobson units for measuring total columns of ozone. In the case of water vapour, units of precipitable water vapour (PWV) are often used. PWV is the height of the layer of water which would result from the condensation of the entire total column to standard temperature and pressure. This concept is illustrated by Figure 2.4.



Figure 2.4: Illustration of precipitable water units from Munroe (2014).

Starting from a total column in molecules/m<sup>2</sup>, a total column of water can be converted to PWV by:

$$PWV = TC_{H_2O} \cdot \frac{MM_{H_2O}}{\rho_{H_2O} \cdot N_{Av}},$$
(2.9)

where  $MM_{H_2O}$  is the molar mass of water,  $\rho_{H_2O}$  is the density of liquid water, and  $TC_{H_2O}$  is total column of water vapour.

This can be seen and verified by dimensional analysis:

$$PWV \ [mm] = \ TC \ \left[\frac{molecules H_2O}{m^2}\right] \cdot MM_{H_2O} \left[\frac{g H_2O}{1 \, mol}\right] \cdot \frac{1}{N_{Av}} \left[\frac{1 \, mol}{molecules}\right] \cdot \frac{1}{\rho_{H_2O}} \left[\frac{1 \, m^3}{kg \, H_2O}\right] \cdot \frac{1 \, kg}{1000 \, g} \ ,$$

where variables are defined as above for Equation 2.9.

Equation 2.9 results in a value for PWV in units of meters. It is convenient to convert this to units of mm PWV for conditions on Earth, where atmospheric PWV typically ranges between 1 and 70 mm, as illustrated by Figure 1.4. Furthermore, it is useful to note that [mm PWV] are equivalent to  $\left[\frac{\text{kg}}{\text{m}^2}\right]$ . This conversion uses the density of water, and can be intuitively seen using dimensional analysis:

 $[mm PWV] = mm \cdot \frac{1}{10^{3}mm} \cdot \frac{10^{3}kg}{1} = [\frac{kg}{m^{2}}].$ 

PWV is also known as Integrated Water Vapour (IWV) and Total Water Column (TWC).

# 2.4 Eureka, Nunavut measurement site

Eureka, Nunavut is a small Canadian research outpost situated at 80°N in the remote polar climate of Ellesmere Island. Its location is shown in Figure 2.5. It primarily exists to support Environment and Climate Change Canada (ECCC)'s Eureka Weather Station (EWS), but also supports research programs led by universities, government agencies, and other organizations. The most significant of these is the Polar Environment Atmospheric Research Laboratory (PEARL), run by a group of Canadian universities through CANDAC. Until PEARL opened in 2006, the only information regularly gathered locally about atmospheric water vapour was obtained through the launch of radiosondes at the EWS. The suite of PEARL instruments has expanded the available information about the atmosphere above Eureka substantially. PEARL is strategically located for Arctic studies, as well as the validation of satellite measurements. Many polar-orbiting satellites have overpasses with Eureka. In addition, limb-viewing satellites commonly have coincidences with Eureka due to their measurement geometry. As a result, measurements taken at PEARL have contributed to many validation studies, e.g. of ACE (Griffin et al., 2017), Measurement of Pollution in The Troposphere (MOPITT) (Buchholz et al., 2017), Orbiting Carbon Observatory 2 (OCO-2) (Wunch et al., 2017), and OSIRIS (Adams et al., 2012).



Figure 2.5: (a) Ellesmere Island, showing permanently inhabited places. (b) Map of Canada, showing Eureka along with other locations, highlighting the typical flight path between Toronto and Eureka. Eureka is denoted by a red circle in both panels.

PEARL consists of multiple facilities. Instruments whose water vapour datasets are used for this study are located at the PEARL Ridge Laboratory (RL), the zero-altitude PEARL Auxiliary Laboratory (0PAL), and the EWS. These locations are shown on the image in Figure 2.6. The RL is located at 80.05°N, 86.42°W on top of a ridge at 610 m elevation, 15 km west of the EWS. 0PAL is located in Eureka at 79.59° N, 85.56° W, near sea level (10 m a.s.l.), approximately 250 m from the EWS radiosonde launch location. The Ridge Lab and 0PAL sites often experience different local weather conditions (Fogal et al., 2013).



Figure 2.6: Locations of measurement sites. Satellite image from Google Maps. Last accessed September 28, 2018.

Eureka is a challenging site for water vapour measurements. It is an extremely cold and dry environment. Between fall and spring, there are frequent temperature and humidity inversions in the lower troposphere. Figure 2.7 (a) shows an example of a wintertime low-altitude temperature inversion using radiosonde data, along with a typical summer temperature profile for comparison. The temperature inversion affects atmospheric mixing. For example, exhaust from the Eureka diesel generators can get "trapped" in the lowest couple of kilometers of altitude because of the negative lapse rate, as shown in Figure 2.7 (b).



Figure 2.7: (a) Examples of Eureka radiosonde temperature profiles. A wintertime lowaltitude temperature inversion is seen in blue; a typical example summer temperature profile is shown in green for comparison. The PEARL Ridge Lab altitude is noted with a red dotted line. (b) Exhaust from the diesel generators at the Eureka Weather Station collects in the atmosphere directly above the station and moves horizontally due to the strong temperature inversion. Image taken March 16, 2014 at 5:02 PM (local time).

Open water occurs regionally during summer, but during the rest of the year the region's fjords and sounds are frozen. The surrounding geography is mountainous and variable. Solar-viewing measurements are often made at large solar zenith angles, especially during spring and fall. The smallest solar zenith angle (SZA) at Eureka's 80°N latitude is 56.5°. It is not possible to use atmospheric measurement techniques that require sunlight during polar night, which lasts from mid-October until late-February at Eureka. The changing amount of sunlight hours per day at Eureka is shown in Figure 2.8. These conditions, along with the availability of several instruments located at two different altitudes, offers the opportunity to investigate the effectiveness of different measurement techniques.



Figure 2.8: Number of sunlight hours per day at Eureka, Nunavut. Colours illustrate the number of daily sunlight hours.

The Eureka radiosonde dataset has informed weather research for over fifty years, and offers useful information about water vapour abundances and variability near Eureka. Figure 2.9 shows radiosonde water vapour profiles recorded between January 2007 and December 2017, along with overall and seasonal mean profiles (Eureka radiosonde measurements are described in more detail in Section 2.3). The water vapour VMR profiles vary by an order of magnitude between winter and summer. The maximum VMR of water vapour in the atmosphere above Eureka is at the surface during summer months. During the rest of the year, water vapour abundances reach their maximum 1-2 km above the surface. This low-altitude inversion in the water vapour profile is apparent in the mean water vapour profiles shown in Figure 2.9 for all seasons except summer.



Figure 2.9: Water vapour VMR profiles acquired by Eureka radiosondes between January 2007 and December 2017. Individual profiles are shown in grey, seasonal means in colour, and overall mean in black.

When analysing the ability of different measurement techniques to capture information about water vapour, its vertical distribution should be considered. Figure 2.10 illustrates the portion of the total column typically found beneath a given altitude, using EWS radiosonde data from January 2007 to December 2015. 90% of the Eureka water vapour total column is found beneath an altitude of 4.40 km; 50% is found beneath an altitude of 1.60 km. Seasonal analysis gives similar results; however, there are differences in the vertical distribution of water vapour in the lowest few kilometers. The lowest altitudes contain more of the total column during the summer than during the winter. This may be due to the availability of local humidity sources during the summer, when there is open water in the neighbouring fjord. Ground-based and satellite instruments without sufficient sensitivity to the lowest altitudes may be seasonally biased, and underestimate total columns more in summer than in winter.


Figure 2.10: Vertical distribution of water vapour, based on Eureka radiosonde measurements between January 2007 and December 2015. (a) The portion of the total column beneath a given altitude. (b) The portion of the total column beneath 4 km in each season, showing change in the mean vertical distribution of the water vapour total column over the year.

# 2.5 Radiosondes

Radiosondes carrying payloads to measure atmospheric profiles of temperature, pressure, humidity, and sometimes other quantities (e.g., ozone) are used at sites around the world. Radiosonde measurements, particularly humidity measurements at Eureka, will be used throughout this thesis.

Eureka radiosonde measurements are made by an instrument payload lofted into the atmosphere by a hydrogen-filled balloon, launched twice daily (11:15 and 23:15 UT) from the EWS. Figure 2.11 (a) shows the launch of a radiosonde balloon. Occasionally, radiosondes are launched at other times of the day for campaign-related reasons. Typically, these balloons (and the measurements) reach the middle of the stratosphere (30 to 33 km). The Vaisala RS92 radiosonde model (Figure 2.11 (b)) currently used by the EWS has been subject to extensive testing and validation (e.g., Miloshevich et al., 2009). Humidity is measured using a thin-film hydrophilic polymer sensor that changes conductivity depending on how much water it has absorbed from (or lost to) the surrounding environment.



Figure 2.11: (a) Launch of radiosonde at the Eureka Weather Station on March 6, 2015 at 6:15 PM local time. (b) RS92 radiosonde sensor with inset image showing the temperature sensor and one of the humidity sensors. Photo from Dirksen et al. (2014).

The quantity derived from the radiosonde measurement is relative humidity. When Vaisala calibrates the response of the humidity sensor's capacitance to the amount of humidity in the surrounding environment, it uses the  $e_s$  formula of Hyland and Wexler (1983), which is:

$$e_{s} = exp(\frac{-0.58002206*10^{4}}{T} + 0.13914993 \times 10 - 0.48640239 \times 10^{-1} \times T + 0.41764768 \times 10^{-4} \times T^{2} - 0.14452093 \times 10^{-7} \times T^{3} + 0.65459673 \times 10 \times log(T)),$$

$$(2.10)$$

where  $e_s$  is the saturation vapour pressure in units of Pascals and *T* is the temperature in Kelvin. Consequently, Equation 2.10 must be used for  $e_s$  when converting RS92 radiosonde RH measurements to VMR, e.g., using Equation 2.3 (Miloshevich et al., 2006).

When total columns are calculated from Eureka radiosonde measurements, the PWV can be calculated from radiosonde measurements by combining Equations 2.3, 2.8, 2.9, and 2.10:

$$PWV = \left[\int_{surface}^{TOA} \frac{RH(z) * es(T)}{P(z)} \cdot \frac{N_A * P(z)}{R * T(z)} dz\right] \cdot \frac{MM_{H_2O}}{\rho_{H_2O}},$$
(2.11)

where  $e_s$  is from Equation 2.10.

Calculation of partial columns, e.g., above or below the RL altitude, follows the same procedure described for the total column calculation, except that the altitude limits of the integration change.

#### 2.5.1 Radiosonde biases

The widespread use of radiosondes for meteorology has made them a useful measurement for atmospheric science as well. However, radiosonde sensors have a variety of biases that affect the measurements. The Vaisala radiosonde humidity sensor has been shown to work well at cold temperatures (below  $-70^{\circ}$  C) and low abundances (below 5 ppmv), but its sensitivity to water vapour is limited at low pressures. For this reason, Miloshevich et al. (2009) recommend limiting radiosonde humidity measurements to altitudes with pressures greater than 100 hPa during daytime and 75 hPa at night. The mean altitude at which the atmosphere at Eureka has a pressure of 100 hPa is 16.01 km, based on radiosonde measurements taken between 1961 and 2017.

The RS92 is also known to have a dry bias due to solar heating of the sensor (Vömel et al., 2007b). Measurements taken by radiosondes during the AIRS Water Vapour Experiment (AWEX) campaign at the Atmospheric Radiation Measurement Southern Great Plains site in 2004 showed a daytime dry bias of 6-8% when compared with a co-located microwave radiometer (Miloshevich et al., 2009). This error depends on the solar radiation intensity, which is a function of the SZA and sensor orientation. The lack of a protective cover introduces a second error source, which partially offsets the radiative heating: forced cooling occurs as the sensor rises with the balloon. This effect depends strongly on pressure, and thus decreases with altitude. The dry bias caused by solar heating of the sensor is not significant in Eureka during winter due to the lack of sunlight; however, it can affect measurements during the sunlit portion of the year. Changes in sunlight at Eureka were illustrated in Figure 2.8.

RS92 humidity measurements are also known to be affected by low-temperature calibration error dry biases, as well as vertical resolution smoothing due to sensor response time lag (Vömel et al., 2007b; Miloshevich et al., 2009). The calibration error and time-lag error affect low-temperature measurements, and are relevant for Eureka conditions.

To correct for known biases in a consistent, transparent, and well-documented manner, Eureka radiosonde measurements have been processed with software developed by the GCOS Reference Upper Air Network (GRUAN). GRUAN's objective is to produce a set of traceable, homogeneous reference datasets for atmospheric research using radiosonde measurements from geographically distributed sites (Immler et al., 2010). Eureka is not a GRUAN-participating site; however, a subset of the Eureka radiosonde measurements has been processed by the GRUAN software for use in atmospheric research at PEARL.

#### 2.5.2 GRUAN-processed Eureka radiosonde dataset

Radiosondes are designed and launched to support operational meteorology. While radiosonde measurements are frequently used for scientific research, the datasets are not always ideally suitable because meteorological needs differ from those of climate and atmospheric science. For example, standard radiosonde data do not include uncertainty estimates. GRUAN data processing for RS92 radiosonde measurements corrects known biases, recovers GPS location information, and calculates uncertainties. This procedure is described by Dirksen et al. (2014),

and is briefly summarized here. Since it will be referenced repeatedly, Dirksen et al. (2014) will be referred to as D2014.

GRUAN processing does not use the pre-launch ground check reading of the humidity sensor measurement of a desiccant near 0% RH, as this can introduce a systematic bias in the humidity profile due to the degradation of the desiccant. This is particularly relevant to measurements performed at tropical sites due to the high ambient humidity; however, this desiccant drift is unlikely to have much impact at very dry polar sites such as Eureka.

The temperature-dependent bias of the humidity sensor, noted by Miloshevich et al. (2006) using data collected during the AWEX campaign and not due to the known radiative heating or timelag issues, is corrected using an empirical correction factor. This bias is attributed to inaccuracies in the Vaisala calibration of the humidity sensors (Miloshevich et al., 2006), and affects measurements taken between -20°C and -70°C. The reference points used for this correction are derived from comparisons between frostpoint hygrometer and RS92 measurements at Lindenberg and Yangjiang, and are similar to results by Vömel et al. (2007b).

The well-known radiative heating dry bias of the RS92 humidity measurements (Vomel et al., 2007b; Miloshevich et al., 2009) is corrected by multiplying the relative humidity by a correction factor (Equation 5 in D2014). This correction factor depends on the temperature, pressure, speed, and estimated actinic flux. The sensitivity of the RS92 humidity sensor to radiative heating depends on the production year because of changes made to the sensor in 2006 and 2009. Tests performed at Lindenberg derive the factors needed for D2014's Equation 5 for each of these time periods, which are listed in D2014 Table 4.

At +20°C, the RS92 humidity sensor responds quickly to changing conditions, i.e., less than 1 second. However, this response time slows at low temperatures. At -40°C, the response time is roughly 20 seconds, reducing the vertical resolution of the humidity profile to about 100 m. This introduces errors in the UTLS. D2014 describes an algorithm for correcting the time-lag, which improves upon an algorithm introduced by Miloshevich et al. (2004). The use of the GRUAN time-lag correction (i.e., described by D2014) is verified using coincident RS92 and FPH measurements in the tropical tropopause region, where there are temperatures below -50°C. The results show that the uncorrected RS92 loses vertical resolution seen by the FPH, which are recovered by the GRUAN processing technique.

The uncertainty reported by the GRUAN processing consists of many components, e.g., the difference between the two sensors during the ground check is used to calculate a calibration uncertainty (Equation 11 in D2014), uncertainties resulting from the corrections applied to address the temperature-dependent, radiative heating, and time-lag biases, and statistical uncertainties for each data point. These uncertainties are summarized in Table 5 and described in detail in Section 6.7 of D2014.

The result of the GRUAN RS92 humidity measurement corrections are profiles that have a typical uncertainty of 3-5%, and that are typically wetter (larger water vapour mixing ratios) than standard Vaisala values (see Figure 17 in D2014). The Eureka dataset is consistent with these general features; its uncertainties tend to be within this range and the GRUAN-processed profiles tend to be wetter than the standard Vaisala radiosonde product.

GRUAN processing requires the use of the raw radiosonde data files, which are in a format created by Vaisala (\*.dc3db). ECCC provided their archive of raw radiosonde files for Eureka. However, there are gaps, which results in a smaller number of GRUAN measurements than for the standard radiosonde product.<sup>7</sup> There were no raw radiosonde files available before September 2008, and there are months-long gaps in 2009, 2010, and 2013. These gaps can be seen, for example, in the timeseries of Eureka radiosonde precipitable water vapour shown in Figure 2.12.

<sup>&</sup>lt;sup>7</sup> Standard radiosonde data files, as output by Vaisala software, include a few files: \*.ptu files contain pressure, temperature, altitude, and relative humidity data. \*.wnd files contain wind data. \*.e files are a mystery to me – no one has been able to tell me what they are.



Figure 2.12: Radiosonde precipitable water vapour data available from the Eureka Weather Station, between 2006 and 2017.

In total, 5625 radiosonde profiles are available for Eureka that have been processed using GRUAN methodology. The first processing run of Eureka radiosondes files occurred in mid-2013; thus the dataset used for the Weaver et al. (2017) comparison of water vapour total columns, presented in Chapter 4 of this thesis, spans September 3, 2008 to March 18, 2013. A second processing run occurred in fall 2017. The GRUAN-processed radiosonde dataset at Eureka currently spans September 3, 2008 to October 7, 2017. Work presented in Chapter 5 and 6 of this thesis uses this longer dataset.

GRUAN-processed data show that in the troposphere (and sometimes parts of the lower stratosphere), the uncertainty of Eureka radiosonde water vapour VMR profiles is typically 3 to 5%. Uncertainty in the water vapour VMR, calculated by propagating uncertainties in the conversion between relative humidity and VMR by quadrature, is dominated by the relative humidity uncertainty. Temperature measurement uncertainties are typically a few tenths of a degree. Pressures have uncertainties on the order of tenths of a hPa. In the lower stratosphere, the

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water vapour profile reaches a point where the uncertainty increases rapidly and the measurement is no longer meaningful. This point changes from profile-to-profile.

The differences between the water vapour VMR profiles calculated from standard radiosonde relative humidity measurements and those calculated using the GRUAN-processed data show a small dry bias in the standard radiosonde humidity measurements. The magnitude of this dry bias varies seasonally, likely due to changing amounts and intensities of sunlight, between 3 and 8%. This result aligns with the literature, e.g. Vömel et al. (2007b). These comparison results are shown in Figure 2.13. Profiles with a maximum altitude below 15 km were filtered out, as were profiles with large gaps in the troposphere.



Figure 2.13: Seasonal differences between standard radiosonde (RS) and GRUANprocessed radiosonde profiles at Eureka between September 2008 and June 2017. Profiles not reaching a maximum altitude of 15 km altitude are filtered out. N is the number of profile pairs. (a) Seasonal mean profiles. (b) Differences are radiosonde – GRUANprocessed radiosonde. (c) Percent difference is the difference taking GRUAN as a reference, i.e.,  $\frac{RS-GRUAN}{GRUAN}$  ×100%.

GPS location information about radiosonde flights, recovered by the GRUAN processing, enables an analysis of typical flight paths and distances from Eureka. This is useful information to consider when using the radiosonde data for comparison with other measurements. The position of radiosondes during their flight can be estimated using wind data, but it is more accurate to examine the GPS data directly. Figure 2.14 shows the radiosondes' maximum distance from Eureka while the balloon is below 10 km, where the vast majority of the water vapour column is located, and throughout the entire flight.



Figure 2.14: (a) Maximum distance from EWS reached while radiosonde is beneath an altitude of 10 km. (b) The maximum distance from Eureka reached by the radiosonde during the entire flight (i.e., up to an altitude of 35 km). The dashed red lines in (a) and (b) illustrate the mean distance for each dataset. The colours are coded for the density of data points (N) within each hexagon.

Based on the available raw radiosonde files processed by GRUAN, radiosondes launched from the EWS typically stay close to Eureka. They reached a mean maximum (horizontal) distance from the Eureka launch point of 63.8 km ( $\sigma = 53.2$  km) and 84.5% of flights stayed within 100 km of the RL throughout their flight. Radiosondes had a mean distance of 20.8 km ( $\sigma = 11.7$  km) at 10 km and all flights stayed closer than 100 km from Eureka. 99.4% of the water column is beneath 10 km, on average. These results show that the radiosonde measurements, despite the balloon's ability to drift away from the EWS with the wind, are representative of the atmosphere above Eureka. However, during December to March, radiosondes are frequently found to travel hundreds of km away from Eureka.



# 3 Fourier transform spectroscopy

# 3.1 Introduction

Spectrometers are widely used to acquire measurements of atmospheric constituents. To do so, they exploit the nature of molecules' interaction with light. A molecule can only emit or absorb radiation at energies corresponding to transitions between its rotational, vibrational, and electronic states. The energy states of atoms and molecules have been studied in laboratory experiments to produce comprehensive line-lists such as the HITRAN database.<sup>8</sup> When light passes through a gas and the spectrum of that light is observed, absorption features can be observed at wavelengths corresponding to these lines. These lines can also be observed when a gas emits radiation. Observed spectral lines can be compared to spectral databases to determine which gases caused them. Water vapour, for example, is known to have more than 64,000 spectral lines, corresponding to energies between the microwave and visible regions of light (Gordon et al., 2007).

In infrared spectroscopy, it is often convenient to describe light using wavenumbers instead of wavelength or frequency because wavenumbers are proportional to light energy, i.e.:

$$E_{photon} = hc\tilde{\nu},\tag{3.1}$$

where *h* is Planck's constant and *c* is the speed of light, and  $\tilde{v}$  is wavenumber.

Wavenumbers represent the spatial frequency of light, and are related to wavelength,  $\lambda$ , by:

$$\tilde{\nu} = \frac{1}{\lambda}.$$
(3.2)

Since light reaching Earth from the Sun is well characterized, e.g., it is regularly measured by space-based instruments and it can be approximated by a 5800 K blackbody curve, measurements of sunlight reaching the surface can be used to infer the composition of the

<sup>&</sup>lt;sup>8</sup> See the HITRAN website: http://www.cfa.harvard.edu/hitran.

atmosphere. As sunlight passes through the atmosphere, gases absorb some of that light. The absorption of sunlight at a particular wavelength can be described using the Beer-Lambert Law:

$$I(\lambda) = I_{\odot}(\lambda) e^{\frac{-\tau(\lambda)}{\cos \theta_o}}, \qquad (3.3)$$

where *I* is the solar light intensity observed at the ground,  $I_{\odot}$  is the solar light intensity at the top of the atmosphere,  $\tau$  is the atmospheric optical depth, which is the total absorption of radiation from the solar beam at a given  $\lambda$  integrated over a column, and  $\theta_o$  is the SZA.

Figure 3.1 shows a general schematic of solar absorption measurements conducted at the PEARL Ridge Lab, which are used to infer information about the gases present along the solar beam.



Figure 3.1: General illustration of a ground-based solar absorption spectroscopy measurement at PEARL Ridge Lab. The position of the Sun is tracked by an instrument on the roof, which directs a steady beam of sunlight into the laboratory, where the light is measured and analyzed using a FTIR spectrometer.

Observing the state of the atmosphere using this type of technique relies on methods that record a spectrum. There are a variety of approaches that can be used to produce a solar absorption spectrum, including the use of prisms, diffraction gratings, and interferometers. There are advantages to using FTSs, which will be described in the rest of this chapter.

# 3.2 Michelson interferometer

The Michelson interferometer at the heart of FTS instruments was first developed by Albert A. Michelson to measure the impact of aether flow on the speed of light (Michelson et al., 1887). Following this experiment, Michelson adapted the instrument to acquire precise measurements of distance using observations of spectral lines (Michelson, 1892). An illustration of Michelson's interferometer for spectroscopic measurements, as well as a schematic of the interferometer used by modern FTSs, is shown in Figure 3.2.





A Michelson interferometer functions by splitting a collimated beam of light into two equal-amplitude beams using a specialized optical component called a beamsplitter. In this experiment, when light is incident on the beamsplitter at 45°, half the light is transmitted and half is reflected. One of the beams is sent to a mirror in a fixed position; the other beam is directed towards a mirror that can be moved such that its distance from the beamsplitter changes along an axis parallel to the beam, as shown in Figure 3.2 (b). The difference between these two paths creates an optical path difference (OPD) between the two beams:

$$OPD = 2(d_{m2} - d_{m1}), (3.4)$$

where  $d_{m2}$  is the distance between the beamsplitter and the moving mirror and  $d_{m1}$  is the distance between the beamsplitter and the fixed mirror.

After the light transits the two paths, the beams return to the beamsplitter, where the beams are re-combined. The intensity of the re-combined beam depends on the OPD, since the constructive and destructive interference that occurs between the beams depends on the phase differences created by the OPD.<sup>9</sup> The image created by the recombined beam on a detector is thus an interference pattern. Since the source light is typically an extended source, the interference pattern takes the form of Hädinger (circular) fringes.

If the source radiation is a monochromatic beam, e.g., of wavelength  $\lambda_0$ , the intensity of the signal recorded at a particular location on a detector will vary sinusoidally as a function of the moving mirror's distance (or the OPD).<sup>10</sup> When the moving mirror is positioned such that the OPD is zero, i.e., zero path difference (ZPD), the two beams are in phase and interfere constructively when recombined. This produces a maximum intensity at the detector. As the mirror distance increases, the phase difference between the beams produces partial destruction and the observed intensity diminishes. Once the moving mirror is positioned at an additional distance of  $\frac{1}{4} \lambda_0$ , the OPD is  $\frac{1}{2} \lambda_0$ , and the beams interfere destructively. This results in a minimum signal at the detector. The cycle of coherence, interference, and destruction repeats for every  $\lambda_0$  of OPD. Thus, if a single wavelength of light is input into the interferometer, and the resulting interference pattern's central intensity is recorded at a range of OPDs, the measured output is a sine wave that has a separation between its maxima equal to the wavelength of the input light.

Measurements of distances can thus be made very precisely using a Michelson interferometer by performing measurements of interference fringe intensities produced when observing a

<sup>&</sup>lt;sup>9</sup> It is sometimes conceptually easier to imagine that the starting position of the moving mirror is equal to the distance between the beamsplitter and the fixed mirror, e.g.,  $d_{m1}$ , but this is not always the case.

<sup>&</sup>lt;sup>10</sup> In Michelson's experiments, the intensity of the interference fringes was referred to as the visibility. However, it is notable that he was not able to measure the intensity (or power) precisely; he estimated its value with his eyes.

monochromatic source of a known wavelength. Indeed, Michelson established that interferometric measurements of known atomic emission lines can be used as standard distance measurements. In examining the interference patterns produced by candidate spectral lines, which were believed to be single lines, Michelson discovered fine structure that had not yet been observed by dispersive instruments. For example, the red H emission line at approximately 656.2 nm was shown to be a doublet, rather than a single line (Michelson, 1891, 1892). This result suggested that the instrument had the potential to conduct high-resolution spectroscopy.

Following Michelson's work, his interferometer was adapted to conduct high-resolution laboratory spectroscopy measurements of gas samples and the atmosphere. These instruments are called FTSs in recognition that the measurements they produce contain the information of a highresolution spectrum, but in the form of its Fourier transform. The next section highlights the principles and design of FTSs, closely following the textbook by Griffiths and de Haseth (2007).

## 3.3 Fourier transform spectrometers

When applied to atmospheric measurements, FTS instruments measure light composed of many wavelengths, e.g., radiation emitted by the atmosphere itself or sunlight that has passed through the atmosphere. An FTS measurement is conducted by directing the polychromatic light through a Michelson interferometer in a similar manner as was described for a monochromatic source: the beamsplitter divides the input solar beam in half, with one of the beams directed towards a mirror at a fixed position and the other beam directed towards a mirror that is positioned at a distance that changes over the measurement time. This mirror distance increases (or decreases) at a constant rate as the instrument conducts a scan through OPDs, e.g.:

$$d_{m2} = d_{m2_i} + Vt , (3.5)$$

where  $d_{m2_i}$  is the initial position of the moving mirror, V is the velocity of the mirror and t is the elapsed time of the scan.

After traversing their respective paths, the two beams are directed back to the beamsplitter, at which point components of the two beams have a phase difference resulting from the OPD. The beamsplitter recombines the two beams, and the resulting light is directed to a detector. The path followed by light in a modern FTS is shown in Figure 3.3.

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Figure 3.3: Diagram of a Bruker IFS 125HR, showing the path followed by light in yellow. Original figure by Martin Ferus, Czech Academy of Sciences, used with permission.

The detector records the intensity of light at the central fringe of the interference pattern. The resulting pattern is much more complicated when measuring sunlight (or another polychromatic source) compared to the monochromatic case, as it is the result of many combined sinusoidal interference patterns. The measured intensity as a function of OPD (or time) is called an interferogram. The intensity of the recombined beam can be described mathematically by (Griffiths & de Haseth, 2007):

$$I(x) = \int_0^\infty B(\tilde{\nu}) \cos(2\pi \tilde{\nu} x) \, d\tilde{\nu}, \qquad (3.6)$$

where I(x) is the radiation intensity at a given OPD distance *x*, and *B* is the spectral intensity at wavenumber  $\tilde{v}$ .

Applying the Fourier transform to the interferogram recorded by an FTS produces a spectrum, i.e. the intensity as a function of wavenumber, that can be described by:

$$B(\tilde{\nu}) = \int_0^\infty I(x) \cos(2\pi\tilde{\nu}x) \, dx. \tag{3.7}$$

#### 3.3.1 FTS advantages

Interferometers have compelling advantages over prism and grating instruments. The entire spectrum of the input light is measured by an FTS at all time elements of a scan (Fellgett, 1958). This reduces the time needed to acquire a measurement when compared to dispersive instruments that must scan through a small portion of an overall spectrum when recording data. This is particularly advantageous when a large range of wavelengths are of interest. This is called the multiplex (or Fellgett's) advantage.

Furthermore, the circular aperture of the FTS allows more light into the instrument, enabling high signal-to-noise ratios (SNRs). Dispersive instruments send light through a narrow slit, which limits the amount of light contributing to each element of a spectrum (Jacquinot, 1960). This is known as the FTS throughput (or Jacquinot) advantage.

Lastly, FTS measurements have high wavenumber precision because the interferogram sampling can be calibrated by using a monochromatic source, e.g., a laser beam, of known wavelength that is also sent through the interferometer. When the fringe pattern of the laser's interference pattern results in zero voltage signal, e.g. a 'zero crossing', the signal at the detector is sampled. This precise and consistent sampling at exact OPD interval enables the addition and subtraction of interferograms. This is known as the wavelength (or Connes') advantage (Griffiths and de Haseth., 2007).

The advantages of using interferometry for spectroscopic measurements were compelling in the 1950s. However, a decade after Fellgett and Jacquinot's work, there was limited use of FTSs. Hochheimer (1969) attributes much of this reluctance to the lack of commercial instruments, the abstract nature of the measurement, and the need to convert the measured interferogram to a spectrum. At the time, the conversion of interferograms to spectra involved large expensive computers. These drawbacks were eroded as computer technology advanced and Cooley & Tukey (1965) developed the fast Fourier transform algorithm. An early FTS design was tested and used at the Kitt Peak Observatory in the mid-1970s (Ridgway et al., 1974). In the late 1970s, an updated FTS was installed at Kitt Peak and used for astronomical observations (Hall et al., 1979). This instrument was used for early atmospheric water vapour measurements from 1978 to 1983 (Wallace et al., 1984). Bruker introduced its first FTIR spectrometer in 1974, the IFS 110 (Bruker, 2018). FTIR spectrometers became increasingly available in the 1980s. For

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example, Bomem introduced its DA2-series commercial FTS in 1978 and its DA3-series FTS in 1980 (Buijs, 2009). Not long after, in 1984, a homemade FTS based on a Michelson interferometer was installed at the Jungfraujoch observatory for atmospheric measurements (Mahieu et al., 1997).<sup>11</sup> By the 1990s, the use of FTIR spectrometers for atmospheric observations had become widespread.

#### 3.3.2 Spectral resolution

The transformation of the interferogram described by Equation 3.6 to the spectrum described by Equation 3.7 assumes an infinite OPD, e.g., the integration limits are from zero to infinity. An infinitely long interferometer is not possible, thus the spectral information contained by the measurement is limited by the maximum OPD (MOPD) of the scan. In practice, FTS atmospheric observations are taken at MOPDs that range between a few centimeters and a few meters. The resolution of an FTS can be approximately defined as:

$$\Delta \tilde{\nu}_{max} = \frac{1}{L},\tag{3.8}$$

where *L* is the MOPD, and  $\Delta \tilde{v}_{max}$  is the maximum resolution since two sine waves with a wavelength difference of  $\Delta \tilde{v}$  cycle through constructive and destructive interference once at an OPD of  $(\Delta \tilde{v})^{-1}$  when passed through the interferometer. The resolution of the interferometer can be increased if a longer OPD is used.

The effect of having a limited OPD is equivalent to multiplying the interferogram by a boxcar function that is equal to one between ZPD and the MOPD and equal to zero everywhere else:

$$Boxcar(x) = \begin{cases} 1 & if -L \le x \le L \\ 0 & if x > |L| \end{cases},$$
(3.9)

where L is the MOPD and x is the position of the moving mirror.

<sup>&</sup>lt;sup>11</sup> Prior to 1984, multiple spectrometers had been installed at the Jungfraujoch observatory, located in the Swiss Alps (Delbouille et al., 1995). The first infrared solar spectroscopy measurements began in 1950, with a prism-grating spectrometer (Delbouille et al., 1960). However, these measurements had limited spectral resolution.

The result of transforming the boxcar function from *x* space to  $\tilde{\nu}$  space, e.g., by taking the Fourier transform, is the sinc function:

$$\operatorname{sinc}(\tilde{v}, L) = 2L \frac{\sin(2\pi\tilde{v}L)}{2\pi\tilde{v}L}.$$
(3.10)

An example of a boxcar function, as well as its Fourier transform, the sinc function, is illustrated in Figure 3.4.



Figure 3.4: (a) Boxcar function and (b) its Fourier transform, a sinc function. Units for signal in both panels are arbitrary.

The Fourier transform of an ideal, but OPD-limited, interferogram is a spectrum that is the convolution of Equation 3.6 with Equation 3.9. Thus, the instrument broadens spectral lines. The influence of FTS instrumental characteristics on the spectra it produces is called the Instrument Line Shape (ILS), which must be considered when analyzing FTS measurements.

The spectral resolution of the instrument can be calculated by using the distance between the two zero points on either side of the central maximum of the sinc function. This result is identical to Equation 3.8 (Griffiths and de Haseth, 2007). However, while this threshold specifies the condition for which adjacent lines are completely resolved, the practical resolution is higher than this amount since spectral features do not need to be completely resolved to be analyzed. For example, following its manufacturer's convention, the PEARL 125HR spectral resolution is calculated by (Batchelor et al., 2009):

$$\Delta \tilde{\nu}_{max} = \frac{0.9}{L}.$$
(3.11)

The ILS of a real FTS is not exactly a sinc function. Other aspects of FTS instruments affect the spectra they produce, such as their apertures' field-of-view (FOV), which is calculated by:

$$FOV = \frac{D}{2f},\tag{3.12}$$

where *D* is the diameter of the field stop placed at the focus of the collimating mirror and *f* is the focal length of the collimator.<sup>12</sup>

When the beam of light from the Sun fills the entire aperture, light entering the instrument diverges from the parallel. This angle,  $\alpha$ , is related to the distance between the optical axis, d, and the focal length of the collimator by:

$$\alpha = \frac{d}{f}.$$
(3.13)

Off-axis rays shift the measured wavenumbers by a factor of  $\tilde{v}(1-\frac{1}{2}\alpha^2)$ . Since this shift is linearly proportional to  $\tilde{v}$ , this effect can be compensated for in software processing (Griffiths and de Haseth, 2007).

The ILS of FTS instruments can be monitored to ensure the optics are optimally aligned, and to account for instrumental effects when analyzing the produced spectra. This is discussed in more detail in Section 3.4.3.

 $<sup>^{12}</sup>$  The equation would be slightly simpler, i.e. it would not need the factor of  $\frac{1}{2}$  if it used the radius; however, the use of the diameter is convenient because this is the aperture value that is easiest to measure and that is used by the FTS software in practice.

### 3.4 PEARL 125HR

A Bruker-made IFS 125HR FTS was installed at the PEARL Ridge Lab in July 2006. It joined NDACC shortly thereafter (Batchelor et al., 2009). The PEARL 125HR, as it will be referred to in this work, records high-resolution infrared solar absorption spectra during clear-sky conditions. A frequency-stabilized 1 mW helium-neon metrology laser with a wavelength of 633 nm is used to determine the precise location of the instrument's scanning mirror, which can reach a MOPD of 372 cm, as well as the detector sampling times. The interferometer arms of the 125HR use cube-corner retro-reflectors rather than the flat mirrors that are shown in Figure 3.2. The instrument is operated under vacuum at pressures less than 0.5 hPa.<sup>13</sup> The near-vacuum pressure of the instrument is maintained using a Duniway ISP-250B dry scroll pump. Spectra collected using the PEARL 125HR have been used to measure the atmospheric concentrations of many trace gases, including stratospheric ozone chemistry species (Lindenmaier et al., 2012), biomass burning products (Viatte et al., 2015), and water vapour (Schneider et al., 2012). PEARL 125HR measurements have also been used to validate satellite measurements, e.g., by ACE (Griffin et al., 2017), MOPITT (Buchholz et al., 2017), OCO-2 (Wunch et al., 2017), GOSAT (Holl et al., 2016), and OSIRIS (Adams et al., 2012).

As illustrated in Figure 3.1, a sun-tracking instrument on the PEARL Ridge Lab roof sends a beam of sunlight into the lab, where a 45° mirror directs the solar beam into the PEARL 125HR. The current arrangement of the PEARL 125HR within the Ridge Lab's IR Laboratory is shown in Figure 3.5.<sup>14</sup> The solar beam captured for use in the PEARL 125HR has sometimes been shared with other FTS instruments, e.g., with the Portable Atmospheric Research Interferometric Spectrometer for the Infrared (PARIS-IR) during annual ACE/OSIRIS satellite validation campaigns. Beam sharing between the PEARL 125HR and PARIS-IR can be seen in Figure 3.5.<sup>15</sup>

<sup>&</sup>lt;sup>13</sup> The Bruker OPUS software will not allow the 125HR to perform measurements if the pressure is above 1 hPa. However, PEARL 125HR standard operating procedures set a lower pressure threshold of 0.5 hPa for measurements. The preferred pressure for measurements is less than 0.1 hPa, which is typically achieved.

<sup>&</sup>lt;sup>14</sup> A description of the arrangement of the PEARL 125HR within the Ridge Lab IR Laboratory prior to 2010 is available in Lindenmaier (2012).

<sup>&</sup>lt;sup>15</sup> Side-by-side FTS measurements were also made with the PEARL 125HR and ECCC's Bomem-built DA8, which acquired MIR solar absorption measurements at the PEARL Ridge Lab between 1993 and 2008 on a seasonal/campaign basis.



Figure 3.5: The PEARL 125HR installed in the Ridge Lab IR Laboratory. Photo taken on March 2, 2015. The cube-shaped instrument in the middle-background is PARIS-IR.

The PEARL 125HR is used in multiple measurement configurations. It was initially configured to observe solar absorption spectra in the MIR at a resolution of 0.0035 cm<sup>-1</sup> (a MOPD of 257 cm) using a KBr beamsplitter, liquid nitrogen-cooled HgCdTe (MCT) and InSb detectors, and seven standard NDACC narrow bandpass filters.<sup>16</sup> The filters limit the wavenumber range of the spectra, increasing the SNR. The spectral ranges of the filters are listed in Table 3.1. The MCT detector is sensitive to radiation between 600 and 6000 cm<sup>-1</sup>; the InSb detector is sensitive to radiation between 1850 and 10 000 cm<sup>-1</sup>. The internal diagram of the 125HR in Figure 3.3 closely resembles the PEARL instrument in its MIR configuration. The main difference is that the PEARL 125HR has input optics for a solar beam in addition to the internal sources shown in the figure. A PEARL 125HR MIR measurement involves two consecutive scans that are co-added to produce each

<sup>&</sup>lt;sup>16</sup> NDACC has an eighth filter, covering  $1000 - 1400 \text{ cm}^{-1}$ ; however, it is not used for routine PEARL 125HR measurements.

spectrum.<sup>17</sup> Each of these two measurements are single-sided forward-backward scans, meaning there is a small OPD on one side of the ZPD (nearest to the beamsplitter), and then a much longer OPD on the other side of ZPD.

NDACC filter number	r Wavenumber range [cm <sup>-1</sup> ]	Wavelength range [µm]
1	3950 - 4300	2.32 - 2.53
2	2700 - 3500	2.85 - 3.70
3	2420 - 3080	3.25 - 4.13
4	1950 - 2700	3.70 - 5.13
5	1800 - 2200	4.55 - 5.55
6	700 - 1350	7.40 - 14.28
7	700 - 1000	10.00 - 14.28

Table 3.1: NDACC narrow bandpass filters used with the PEARL 125HR.

In 2010, the PEARL 125HR measurement capabilities were extended through the installation of an InGaAs detector and the acquisition of a CaF<sub>2</sub> beamsplitter. These components enable the 125HR to acquire NIR solar absorption measurements, which are taken at a resolution of 0.02 cm<sup>-1</sup> (a MOPD of 45 cm), and contribute to TCCON. The use of PEARL 125HR NIR measurements for participation in TCCON is detailed in Mendonca (2017). The spectral ranges of key PEARL 125HR MIR and NIR components are illustrated in Figure 3.6.

<sup>&</sup>lt;sup>17</sup> Four scans were taken and co-added from July 2006 to March 2009 (Lindenmaier, 2012); this was reduced to two to reduce measurement time and increase the number of measurements, as the signal-to-noise was sufficiently high with two scans.



Figure 3.6: Spectral ranges of PEARL 125HR detectors, beamsplitters, and NDACC filters.

Switching between MIR and NIR configurations requires manually changing the beamsplitter, as only one can be installed at a time. Changing the beamsplitter requires approximately 30 minutes because the instrument must first be brought back up to atmospheric pressure, and then re-evacuated to near-vacuum pressure before measurements can be resumed.

#### 3.4.1 PEARL FTS sun-tracker

The PEARL 125HR relies on a sun-tracking instrument on the roof of the PEARL Ridge Lab to supply a stable beam of sunlight into the instrument. Between 1992 and July 2013, the sun-tracker available for PEARL Ridge Lab FTSs relied heavily on an operator. This sun-tracker was installed by ECCC and is shown in Figure 3.7. To start sun-tracking operations, an operator had to unlock and remove a rooftop enclosure covering the mirror and motor system (which was susceptible to icing when closed during winter), align the primary mirror's starting position with the Sun so that light reached the tracking sensors inside the IR laboratory, and adjust the gain settings for the quadpole photodiode that provided active tracking. The photodiodes measured the intensity of the solar

light that was directed into the tracking sensors (inside the long narrow tube shown in Figure 3.7 (a)). The sensors then sent signals to motors on the roof that adjusted the tracking mirror to ensure the mirror was centered on the Sun. Gain and polarization settings of the tracking system needed frequent adjustment to ensure the photodiodes received sunlight within its operating thresholds.



(a)

(b)

Figure 3.7: Original ECCC sun-tracker for the PEARL Ridge Lab FTSs. (a) A small portion of the solar beam is directed towards a quad-pole diode which provides tracking. (b) The original rooftop solar-tracking mirror.

In July 2013, the original ECCC PEARL FTS sun-tracker was removed and a new (custom-built) solar tracker was installed, called the Community Solar Tracker (CST) (Franklin, 2015). The CST, whose Robodome-enclosed mirrors on the roof of the PEARL Ridge Lab are shown in Figure 3.8 (a), offered significant improvements over the original sun-tracker. The CST can operate in passive and active modes. In passive mode, it calculates the location of the Sun based on the location of the instrument and time. In active mode, it begins by positioning the mirrors according to the calculated position of the Sun, and then actively refines the tracking based on a small beam of the collected solar light that is directed into the tracker's video camera. The tracker's camera can be seen in Figure 3.8 (b), to the side and below the PEARL 125HR's input mirror. A neutral density filter sits above the position of the tracker camera in the path of the incoming light to ensure the intensity of sunlight does not damage the camera's sensor. The amount of sunlight reaching the camera sensor is also modified using an internal iris, which can be adjusted manually or automatically by the CST software.

The CST software, written in python, fits the image of the Sun in the camera to an ellipse, and uses this to monitor the position of the Sun. The CST software sends commands to the motors controlling the rooftop mirrors to maintain precise alignment of the tracking system on the center of the Sun. If there is a loss of active tracking, e.g., the camera does not have sufficient light to fit an image of the Sun due to clouds, the CST continues to move the tracking mirrors based on the theoretically calculated position of the Sun, i.e., it resorts to passive tracking. An operator interacts with the CST software, e.g., to open or close the Robodome hatch, change the tracking mode, or adjust calibration values, using a graphical user interface (GUI) developed by Jonathan Franklin. The precision and accuracy of the CST exceeds that of the previous sun-tracking system, and is described in detail by Franklin (2015).



Figure 3.8: The Community Solar Tracker, installed at the PEARL Ridge Lab to support FTS measurements. (a) The rooftop Robodome protecting the mirrors that track the Sun and direct sunlight downwards, into the IR Laboratory. Photo taken March 7, 2014. (b) The light reaching the IR Laboratory; some of the light is directed into the PEARL 125HR using a 45° mirror, some is directed into the camera used for tracking (located underneath the main table supporting the mirror), and some of the light is directed towards the PARIS-IR (pick-off mirror in the upper center, PARIS-IR is out-of-field). Photo taken March 2, 2015.

Experiments at PEARL showed that the CST can successfully track the full and gibbous Moon. Since the intensity of moonlight is much lower than sunlight, the neutral density filter installed in front of the tracker camera must be removed for active lunar tracking. This enables the PEARL 125HR to collect lunar absorption spectra, e.g., during Polar Night when solar absorption measurements are not possible. PEARL 125HR lunar absorption spectra were first collected in March 2015 and have been collected irregularly since then.

The CST control software enables the sun-tracker to be controlled remotely, e.g., through remote access to the PEARL 125HR sun-tracker computer. However, an on-site operator is needed to monitor weather. The CST system has no ability to sense if high winds, precipitation, or other potentially damaging weather occur, which would require that the Robodome hatch be closed to avoid damaging the tracking system.

### 3.4.2 PEARL 125HR operations

The PEARL 125HR is operated using Bruker's OPUS software.<sup>18</sup> Measurements can be run individually by setting parameters in the OPUS software, e.g., aperture size, filter, and gain. For greater efficiency, macro codes can be used to run sequences of measurements. These codes are written in the OPUS language by PEARL 125HR team members. Between 2006 and 2013, PEARL 125HR macros simply took a set sequence of measurements, and lasted for either one or two hours. In 2014, new macro codes were developed to run measurements semi-automatically. Once started, the MIR macro cycles through each NDACC filter and takes measurements continuously until there is not enough signal to acquire spectra in any of the filters for a sustained period of time.<sup>19</sup> Thus, measurements are automatically ended when the Sun sets or clouds come into the field-of-view.

<sup>&</sup>lt;sup>18</sup> Currently, the PEARL 125HR computer runs OPUS software version 7.2.

<sup>&</sup>lt;sup>19</sup> Because the filters cover different spectral ranges, available light sometimes allows measurements to be performed for some filters but not others. Filters 3 and 6 are the most readily acquired.

The use of this semi-automation macro code increases the number of PEARL 125HR measurements that can be acquired by minimizing the time between measurements, since the instrument moves immediately from one filter to the next. In addition, this code has the practical benefit of minimizing the time and effort needed from on-site or remote operators. On-site PEARL operators often have several instruments competing for their attention and may not be able to re-start macros immediately after they finish. In addition, while remote access to the PEARL 125HR computer enables remote control of measurements, the limited bandwidth of the PEARL internet connection creates lags in response time. Minimizing the time needed for a remote user to interact with the OPUS software maximizes measurement time. Another useful feature of the macro is that it tracks the number of spectra acquired in each filter since it was launched by the user. This information is displayed in a window, which helps operators monitor measurement acquisition.

The number of measurements acquired by the PEARL 125HR have varied over time. Figure 3.9 (a) shows the number of spectra acquired each year the instrument has been in operation. One factor influencing the measurement counts has been the improvements to the macro codes. Another factor has been the availability of on-site operators, whose involvement is still required despite upgrades to the instrument (e.g., the new tracker in 2013 and a new computer in 2015). MIR measurements require an on-site operator to fill the MCT and InSb detectors with liquid nitrogen, monitor weather conditions, start and end measurement macros, and perform maintenance and troubleshooting. The limited number of measurements in 2012 and 2013 are due to the absence of on-site support at PEARL caused by funding limitations.

After 2010, measurement time is split between MIR and NIR configurations. However, as can be seen in Figure 3.6, the CaF<sub>2</sub> beamsplitter used for NIR measurements also permits some MIR measurements; however, its spectral range only extends to NDACC filters 1 through 5, excluding filter 6, which is used to measure several key NDACC species. A macro is available to alternate between NIR and MIR measurements with the CaF<sub>2</sub> beamsplitter installed. Nonetheless, the use of a single instrument for the acquisition of two types of measurements, contributing to two different international networks, creates otherwise-avoidable gaps in the atmospheric monitoring produced by the instrument. The number of days when PEARL 125HR MIR, NIR, or MIR and NIR measurements were taken is shown in Figure 3.9 (b).

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The overall number of spectra acquired is broken down by month in Figure 3.9 (c). The seasonality of available sunlight hours, shown in Figure 2.8, is clearly evident. Relatively few measurements have been acquired during September, which has a similar number of sunlight hours as March, but tends to have considerable cloud cover. Weather, e.g., clouds, may be a limiting factor. The relatively large number of measurements in March can be partially attributed to the dedicated support by on-site personnel participating in the annual Canadian Arctic ACE/OSIRIS Validation Campaign at PEARL that occurs in February and March. The lack of NIR measurements in February is due to the TCCON requirement for a SZA less than 82°. Lastly, the upgrading of the solar tracker in summer 2013 enhanced the ability to acquire more PEARL 125HR spectra by decreasing the time and effort needed to operate the tracker, and enabling it to be run remotely.<sup>20</sup>

<sup>&</sup>lt;sup>20</sup> The PEARL 125HR and sun-tracker computers could technically be accessed from anywhere with an internet connection; however, in practice, remote operation of the instruments has been done from the Eureka Weather Station and Toronto. The sun-tracker was occasionally run from Halifax by Jonathan Franklin between 2014 and 2015, as he developed the CST software and helped troubleshoot its use at PEARL.



Figure 3.9: (a) Number of spectra acquired with the PEARL 125HR between August 2006 and December 2017. (b) Number of days each year when the PEARL 125HR acquired MIR and/or NIR spectra. (c) Number of spectra acquired by the PEARL 125HR each month summed from 2006 to 2017.

### 3.4.3 PEARL 125HR diagnostic tests

The optical alignment of the PEARL 125HR is assessed using regular measurements of lowpressure gas cells with known quantities of gases. These tests enable the calculation of the instrument's ILS, modulation efficiency, and phase error (Hase et al., 1999). To analyze MIR instrument performance, a 2 cm x 2.5 cm gas cell (length x diameter) with sapphire windows filled with approximately 200 Pa of HBr is used.<sup>21</sup> These HBr gas cells are produced in a homogenous manner for harmonized tracking of FTIR instrument alignment across NDACC sites (Coffey et al., 1998). The cell used in the PEARL 125HR is NDACC cell #30. To perform the cell test, it must be inserted into the PEARL 125HR's sample chamber, as shown in Figure 3.10. NIR gas cell tests are also conducted using a permanently-installed HCl cell; these NIR cell tests are described by Mendonca (2017).



Figure 3.10: HBr cell (NDACC cell #30) installed in the PEARL 125HR sample compartment. Photo taken on March 14, 2015 at 1:47 PM.

 $<sup>^{21}</sup>$  Recently, N<sub>2</sub>O cell tests have been performed with the PEARL 125HR; however, they are omitted here because this began after I ended direct involvement in instrument operations.

HBr cell tests involve two measurements taken at the same resolution as MIR solar absorption measurements, 0.0035 cm<sup>-1</sup>, using NDACC filter 3. 50 scans are co-added for each measurement. The first measurement is taken of the 125HR's internal MIR light source, an electrically heated Globar (a silicon carbide rod), which provides a background spectrum. A second measurement is taken with the MIR source light while the HBr gas cell is installed in the 125HR sample compartment. The HBr gas absorbs light at well-understood wavenumbers, creating spectral features in the observed spectrum. The ratio of the two spectra is calculated. This is done to remove systematic instrumental effects. An example of the resulting absorption spectrum is shown in Figure 3.11 (a).

PEARL 125HR HBr cell measurements are analyzed using software called LINEFIT, which is described by Hase et al. (1999) and Hase (2012). LINEFIT uses information about HBr line parameters as well as the 125HR temperature at the time of the measurement, to calculate a synthetic spectrum. This theoretical spectrum is convolved with the ideal ILS based on the FOV of the instrument. The ILS, modulation efficiency (ME), and phase error (PE) are varied until the LINEFIT algorithm converges on a solution that matches the measured HBr spectral features. LINEFIT calculates the ME and PE at 20 equidistant OPD positions between ZPD and the maximum OPD, e.g., 257 cm for the PEARL 125HR. The amount of HBr in the cell is also retrieved. The results shown and discussed here have been produced using LINEFIT version 9.<sup>22</sup> An example of an HBr absorption line from a PEARL 125HR cell test, as well as the LINEFIT version 9 model spectrum fit to it is shown in Figure 3.11 (b); the residuals from the fit are shown in Figure 3.111 (c).

<sup>&</sup>lt;sup>22</sup> Currently, the PEARL 125HR cell tests are analyzed using LINEFIT 14. However, that change occurred after I passed on responsibility for MIR measurements.



Figure 3.11: HBr cell test measurement results, acquired on February 27, 2014. Analysis performed using LINEFIT version 9. (a) Measured HBr absorption spectrum. (b) Example of an HBr spectral microwindow and absorption feature and the LINEFIT-calculated spectrum. (c) The residual of the spectral fit shown in (b).

The HBr cell is permanently sealed; however, the gas can decay due to chemical reaction with contaminants in the cell walls. It may also slowly leak out. The amount of HBr in the cell since the PEARL 125HR's installation, retrieved by the LINEFIT version 9 analysis, is shown in Figure 3.12. There has been a diminishing amount of HBr in the cell; however, it has remained relatively stable since about 2012.



Figure 3.12: Retrieval of the total amount of HBr in the PEARL 125HR cell (NDACC #30). Colours illustrate the y-axis HBr total column value.

The ILS of the PEARL 125HR has remained symmetric since its installation, indicating good alignment of the optics. An example of the PEARL 125HR ILS is shown in Figure 3.13. Its shape closely resembles a sinc function, which is the ideal ILS.



Figure 3.13: PEARL 125HR instrument line shape from an HBr cell test on February 27, 2014.
If the 125HR is imperfectly aligned, the ME deviates from unity and the PE deviates from zero (Hase, 2012). The value of the ME is normalized to the value at ZPD, so it always begins at a value of one in an OPD vs. ME plot. A non-unity ME broadens the ILS; a non-zero PE results in an asymmetric ILS. A non-ideal ILS causes inaccuracies in the measurements derived from spectra.

Modulation loss can occur, for example, due to divergence in the beam as it travels through the interferometer arm. Off-axis rays will have a different OPD than on-axis rays, or can be lost from the modulated beam entirely. The 125HR's use of cube corners instead of flat mirrors avoids off-axis rays caused by mirror tilt; however, lateral displacements of cube corners can produce a shear misalignment that affects the ILS (Kauppinen et al., 1992; Griffiths and de Haseth, 2007). A shear misalignment between the moving and fixed cube corner causes an apparent increase of modulation amplitude as function of OPD (Hase, 2012). A small increase of the ME is observed as a function of OPD in the PEARL 125HR LINEFIT results, e.g., of approximately 2% in the results shown in Figure 3.14.

Phase errors can be produced from imperfections in optical components, such as filters and beamsplitters. In addition, divergence and misalignment of the metrology laser can cause phase errors due to distorted sampling positions. If phase errors are present in the measurement, spectral information is lost when the interferogram is Fourier transformed into a spectrum.

An example of LINEFIT version 9 ME and PE results for a PEARL 125HR HBr cell test is shown in Figure 3.14. Between its installation in July 2006 and March 2016, the PEARL 125HR's modulation efficiency has stayed close to one, i.e. within 0.98 to 1.04 except one outlier (the strict requirements of TCCON are to maintain an ME within 0.95 and 1.05), and its phase error has remained near zero at all OPD values. Figure 3.15 shows the timeseries of ME and PE values at two key OPD values from 2006 to 2016, 257 cm, the maximum path difference of standard NDACC measurements, and 54.11 cm, which is approximately where the maximum phase errors typically occur in the PEARL 125HR.



Figure 3.14: Modulation efficiency and phase error of the PEARL 125HR, as calculated by LINEFIT version 9 from the HBr cell test performed March 14, 2015.



Figure 3.15: PEARL 125HR (a) modulation efficiency and (b) phase error for two OPDs (257 and 54 cm) between February 2007 and March 2016, as retrieved using LINEFIT version 9.

# 3.5 MUSICA water vapour

Information about water vapour total columns and profiles has been extracted from PEARL 125HR spectra using a retrieval technique developed by Matthias Schneider at the Karlsruhe Institute of Technology, as part of the Multi-platform remote sensing of isotopologues for investigating the cycle of atmospheric water (MUSICA) project. MUSICA retrievals were performed on spectra collected at 12 participating NDACC FTIR spectrometer sites, shown in Figure 3.16, by Schneider and his team.<sup>23</sup> This section provides a brief overview of the retrieval technique, which is described in detail in a series of papers by Schneider et al. (2006a, 2006b, 2010b, 2012, 2015, 2016), and summarized by Barthlott et al. (2017).



Figure 3.16: Map of ground-based FTIR spectrometer sites participating in MUSICA.

<sup>&</sup>lt;sup>23</sup> The MUSICA project ended in July 2016 with the completion of funding. 2014 is currently the final year for which data have been processed for all participating sites. There has been discussion of extending the datasets recently, but new processing has not yet been done.

#### 3.5.1 Water vapour isotopologues

The MUSICA retrieval produces information about the main isotopologue of water vapour, H<sub>2</sub><sup>16</sup>O, as well as the minor isotopologues, H<sub>2</sub><sup>18</sup>O and HDO. The acquisition of water vapour isotopologue data is a unique contribution to PEARL measurements. Transport and other processes, e.g., changes of state, preferentially remove heavier isotopologues. This is commonly referred to as "depletion", in reference to the relative diminishment of the minor isotopologue. Thus, this ratio can act as a tracer for physical processes (e.g., Dansgaard, 1964; Noone, 2012). Although measurements and analysis of water isotopologue ratios using ice cores, ground water, and precipitation have been done for decades, the remote sensing of atmospheric isotopologues has only recently been achieved.

Isotopologue ratios are typically expressed using  $\delta$ -notation. The ratio between HDO and H<sub>2</sub><sup>16</sup>O is expressed as  $\delta D$ , which is calculated using:

$$\delta D = \left(\frac{\frac{HDO}{H_2O}}{R_s} - 1\right) \times 1000 \,\%_0,\tag{3.14}$$

where *HDO* and *H<sub>2</sub>O* represent the abundances of HDO and H<sub>2</sub><sup>16</sup>O, and *R<sub>s</sub>* is a standard reference value for  $\frac{HDO}{H_2O}$ , representing the isotopic ratio composition of ocean water. The ocean water reference used by MUSICA is the Vienna Standard Mean Ocean Water (VSMOW), whose abundances of common water isotopologues are listed in Table 3.2.

lastonologua	VSMOW		
isotopologue	abundance		
$H_2^{16}O$	0.997317		
$H_2^{18}O$	0.00199983		
$H_2^{17}O$	0.000372		
HD <sup>16</sup> O	0.00031069		

 Table 3.2: The fractional abundances of the four most abundant isotopologues of water in the Vienna Standard Mean Ocean Water (Coplen, 1994).

A  $\delta D$  value equal to one represents an atmospheric ratio of isotopologues equal to that of standard samples of ocean water. Since the abundances of HDO and other isotopologues are orders-of-magnitude smaller than the abundances of H<sub>2</sub><sup>16</sup>O, ratios are expressed in units of per mille, ‰.

The ratio of H<sub>2</sub><sup>18</sup>O to H<sub>2</sub><sup>16</sup>O, referred to as  $\delta^{18}$ O, is calculated in the same manner, but with H<sub>2</sub><sup>18</sup>O abundances in place of HDO abundances. In addition,  $\delta$ D and  $\delta^{18}$ O allow the calculation of d-excess, using Equation 3.15, which carries information about the original evaporative conditions of the water, allowing potential identification of source regions (Dansgaard, 1964; Merlivat et al., 1967; Rokotyan et al., 2014):

$$d\text{-}excess = \delta D - 8\delta^{18}O. \tag{3.15}$$

### 3.5.2 MUSICA retrieval

The MUSICA retrieval analyzes water vapour spectral features in nine microwindows of NDACC filter 3 spectra: four contain H<sub>2</sub><sup>16</sup>O lines, three contain HDO lines, and two contain H<sub>2</sub><sup>18</sup>O lines. An example of a PEARL 125HR spectrum used for these retrievals is shown in Figure 3.17, along with the H<sub>2</sub><sup>16</sup>O microwindows. These microwindows have been chosen because they cover a range of strong and weak absorption lines that are not saturated when water vapour abundances are large, contain relatively well-isolated water vapour lines, and are small enough to be computationally efficient when analyzed without sacrificing information in the 'wings' of the spectral line shape, where there is information about the vertical profile.



Figure 3.17: (top) Example of a PEARL 125HR MIR spectrum recorded on March 14, 2014. (bottom) (a) through (d) show the microwindows used by the MUSICA retrieval to produce a  $H_2^{16}O$  total column and profile. The units are arbitrary units of signal used by the Bruker OPUS software. If it were calibrated, the units would be of radiance (W/m<sup>2</sup>/sr/cm<sup>-1</sup>).

The retrieval algorithm uses a model, called the forward model, F, to calculate a synthetic spectrum that represents what is theoretically expected to be measured by the instrument, given initial assumptions about the state of the atmosphere and the physics of the measurement. This modelled atmosphere includes the quantity of interest, x, e.g., the water vapour profile. The forward model also includes parameters, p, such as temperature and the ILS. These quantities are related to the measurement, y, by:

$$\mathbf{y} = \mathbf{F}(\mathbf{x}, \mathbf{p}) + \boldsymbol{\epsilon}, \tag{3.16}$$

where  $\epsilon$  is the error in the measurement.

The synthetic spectrum is compared to the measured spectrum and the forward model iteratively adjusts the a priori profile until it reproduces the measurement to an accepted threshold of accuracy (or until a maximum number of iterations is reached and the retrieval fails). In the case of the MUSICA retrieval, this process is implemented using the PROFFIT software, which uses a line-by-line radiative transfer model to describe how sunlight passes through the modelled atmosphere (Hase et al., 2004).

In practice, there are many atmospheric conditions that can generate a synthetic spectrum that matches a measured spectrum. The MUSICA retrieval uses the Optimal Estimation Method (OEM), described in detail by Rodgers (2000), to combine the measurement with a priori information about the atmosphere, e.g. a typical water vapour profile,  $x_a$ , to limit the possibilities and calculate the most probable atmospheric state.

Changes to the calculated spectrum using this method are made using a linearization around the a priori reference state,  $x_a$ , e.g.:

$$y - F(x_a) = \frac{\partial F(x)}{\partial x} (x - x_a) + \epsilon = K(x - x_a) + \epsilon, \qquad (3.17)$$

where **K** is called the weighting function matrix, i.e.,  $K_{ij} = \partial F_i(\mathbf{x}) / \partial x_j$ . **K** is also called the Jacobian, since it is a matrix of derivatives, or the sensitivity kernel because it describes how the forward model changes due to changes in the atmosphere.

The optimum solution, or the most likely state of the atmosphere, is found by minimizing the cost function, which is described by:

$$[y - F(x, p)]^T S_{\epsilon}^{-1} [y - F(x, p)] + [x - x_a]^T S_a^{-1} [x - x_a], \qquad (3.18)$$

where  $S_{\epsilon}$  is the measurement noise covariance, and  $S_a$  is the a priori covariance and is a constraint on the possible atmospheric states.

The first term of this expression represents the difference between the measured spectrum and the simulated spectrum for a given atmospheric state. The second term constrains the solution, the atmospheric state, x, by the a priori profile,  $x_a$ , and the  $S_a$ . In the case of the MUSICA retrieval, the  $S_a$  matrix takes into account the known variability of water vapour abundances, as well as the ratio between the abundances of the isotopologues.

The equations involved in the forward model's atmospheric radiative transfer are non-linear, so the cost function is minimized by a Gauss-Newton iteration method. The solution for the (i + 1)<sup>th</sup> iteration is:

$$x_{i+1} = x_a + S_a K_i^T (K_i S_a K_i^T + S_{\epsilon})^{-1} [y - F(x_i) + K_i (x_i - x_a)].$$
(3.19)

For this type of analysis, it is ideal to choose microwindows that contain only the species of interest, e.g., H2<sup>16</sup>O. However, this is not always possible. Gases that are not the target of the retrieval are called interfering species, and their abundances must also be adjusted by the model to fit the simulated spectrum to the observed spectrum. This makes the process of solving the cost function more computationally expensive and introduces additional sources of error. The MUSICA microwindows contain spectroscopic features of CH4, CO2, HCl, N2O, and O3, which are all fitted simultaneously along with the water vapour spectral lines. Figure 3.18 shows an example of all nine MUSICA microwindows, with the simulated spectrum and the residuals of the fit, from a retrieval performed on a spectrum acquired at the Karlsruhe observatory in Germany. The simulated spectrum is essentially identical to the observed spectrum, making them difficult to distinguish in the plot. However, this indicates a successful retrieval.



Figure 3.18: MUSICA microwindows from a measurement taken in Karlsruhe, Germany. The measured spectrum is a black line, but is hidden behind the red line, which is the nearly-identical simulated spectrum. The blue line is the difference between the two spectra, e.g., the residual of the fit. Figure from Barthlott et al. (2017).

The information content of the retrieval solution is usefully represented by the averaging kernel matrix, A, which is calculated by:

$$\boldsymbol{A} = \boldsymbol{G}\boldsymbol{K},\tag{3.20}$$

where G is the gain matrix, which describes the contribution of the measurement to the solution and is calculated by:

$$\boldsymbol{G} = (\boldsymbol{K}^T \boldsymbol{S}_{\epsilon}^{-1} \boldsymbol{K} + \boldsymbol{S}_{a}^{-1})^{-1} \boldsymbol{K}^T \boldsymbol{S}_{\epsilon}^{-1} = \boldsymbol{S}_{a} \boldsymbol{K}^T (\boldsymbol{K} \boldsymbol{S}_{a} \boldsymbol{K}^T + \boldsymbol{S}_{\epsilon})^{-1}.$$
(3.21)

An averaging kernel representing a measurement that completely describes the state of the atmosphere would be an identity matrix. In practice, however, information for a particular altitude is derived from a range of altitudes. The trace of A describes the number of independent pieces of information, referred to as the degrees of freedom for signal (DOFS). The sum of the rows of A represents the proportion of the solution that was derived from the measurement. This is referred to as the sensitivity, e.g., the sensitivity of the measurement to the state of the atmosphere. A sensitivity equal to 1 indicates that 100% of the information at a particular altitude was derived from the measurement. A sensitivity equal to zero indicates the retrieval has reproduced the a priori profile. An example of an averaging kernel from a MUSICA retrieval of H2<sup>16</sup>O using a PEARL 125HR spectrum is shown in Figure 3.19. PEARL 125HR MUSICA retrievals typically have DOFS of 2.9, and a sensitivity to water vapour primarily at tropospheric altitudes.



Figure 3.19: (a) Example of a typical MUSICA averaging kernel for a PEARL 125HR measurement, taken on August 3, 2006. Five altitudes are highlighted in colour to illustrate the measurement's ability to distinguish between different parts of the troposphere. (b) The retrieval's sensitivity, i.e. the sum of the row kernels, with two thresholds for measurement information noted by dashed lines. The highest altitude where sensitivity is above 0.9 (8.0 km) and 0.5 (12.0 km) is shown using black and red dashed lines, respectively.

#### 3.5.3 Distinctive features of the MUSICA retrieval

OEM-based retrievals are standard in the atmospheric research community, and are routinely run by the NDACC. The MUSICA retrieval has a few distinctive features. It is performed on a natural logarithmic scale, e.g., the atmospheric profiles, the Jacobians, a priori covariance matrix, etc. are all transferred to a logarithmic basis. This is necessary because the regularization of the cost function requires that the probability of possible states, e.g., the water vapour concentrations, are normally distributed. However, water vapour concentrations are log-normally distributed. In addition, the use of a log scale has been shown to improve the vertical resolution of the water vapour retrieval and reduce the correlation lengths between altitudes (Schneider et al., 2006b).

One of the challenges to isotopologue measurements is that there is a strong correlation between their abundances. As discussed in Schneider et al. (2006b), the  $S_a$  can be defined with a constraint on the variability between the isotopologue states. Schneider et al. (2012) describe how the ln[H<sub>2</sub>O] and ln[HDO] states are retrieved and  $\delta D$  is calculated by using  $\frac{\ln[H_2O] + \ln[HDO]}{2}$  and ln[HDO] -ln[H<sub>2</sub>O] as proxies for H<sub>2</sub><sup>16</sup>O and  $\delta D$ . Schneider et al. (2015) describe updates to the MUSICA retrieval, e.g., the removal of two of the original eleven microwindows because they sometimes saturate at wet sites. The updated retrieval is referred to as v2015 to distinguish it from the earlier retrieval, referred to as v2012. The v2015 also differs from v2012 in using a single a priori profile for all sites, rather than latitude-specific a priori profiles used in v2012. Schneider et al. (2016) further explain how d-excess can be retrieved in addition to H<sub>2</sub>O and  $\delta D$  following a procedure similar to that described by Schneider et al. (2012), but which uses a cross-constraint and proxy state that also includes H<sub>2</sub><sup>18</sup>O.

Lastly, Schneider et al. (2012, 2015) show that an a posteriori correction can be applied to the retrieval results, such that the H<sub>2</sub>O and  $\delta$ D values retrieved from each measurement have minimal cross-dependence. This ensures that the averaging kernels from both quantities are the same; however, this requires a downgrading of the H<sub>2</sub><sup>16</sup>O vertical profile information. Ensuring these quantities are independent is valuable because analysis of an H<sub>2</sub>O vs.  $\delta$ D plot can be used to investigate the transport of air parcels and the history of the sampled water vapour's changes of states (e.g., González et al., 2016; Noone, 2012). These products are referred to as the 'type 2'

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MUSICA product, whereas the products with maximum DOFS are referred to as 'type 1'. This thesis uses type 1 products.

### 3.5.4 Results for PEARL 125HR

The H<sub>2</sub><sup>16</sup>O dataset derived using the MUSICA retrieval with PEARL 125HR spectra is shown as a function of the day of year in Figure 3.20. This illustrates the lack of measurements during polar night and the seasonal cycle of water vapour abundances. In addition, Figure 3.20 shows the impact of the standard MUSICA quality control filtering, which removes measurements taken with a solar zenith angle greater than 78.5° because errors increase with SZA, as shown in Figure 3.21.

Since PEARL is located at a high latitude, this SZA filtering removes all measurements during the first and last month of solar absorption measurements. These are particularly valuable measurement time periods at PEARL because of the large changes to the atmosphere as a result of the return of sunlight. In addition, this is the time period when there is intense activity at PEARL related to satellite validation, which results in an increased number of measurements and scientific activity. The SZA and solar azimuth angle (SAA) at PEARL's location are illustrated in Figure 3.22.

The accuracy of the PEARL MUSICA  $H_2^{16}O$  dataset, as well as the implications of relaxing its SZA filtering is discussed in Chapter 4. The dataset with relaxed SZA filtering has been used to study the physical processes related to surface ozone depletion by Zhao et al. (2017).



Figure 3.20: PEARL 125HR H<sub>2</sub><sup>16</sup>O total column type 1 MUSICA v2015 dataset for August 2006 – October 2014, colour-coded by measurement solar zenith angle thresholds. Note that some red and green points are hidden by blue points.



Figure 3.21: Eureka MUSICA v2015 type 1 water vapour error vs. SZA for data between August 2006 and October 2014. The dashed magenta line denotes the 78.5° SZA criterion that is part of the standard MUSICA quality control. The dashed cyan line denotes the 85° SZA threshold, after which uncertainties increase noticeably. (a) The total error. (b) The statistical and systematic errors. The MUSICA extended dataset includes data filtered out by MUSICA's quality control criteria.



Figure 3.22: Position of the Sun from the location of the PEARL Ridge Lab for sample days of the year. Solar elevation angle (SEA), given on the left y-axis, is 90° – SZA.



# 4 Intercomparison of water vapour total columns at Eureka, Nunavut

Water vapour plays a significant role in the Earth's atmosphere, including a dominant effect on climate and radiative forcing (Soden et al., 2002; Dessler et al., 2008). Expanding and improving water vapour measurements is a priority of the atmospheric science community. The total column of water vapour is considered an ECV by the WMO. The objective set out by GCOS is to acquire global measurements with 2% measurement uncertainty with at least four-hour frequency. Observation techniques that meet and exceed these measurement goals are being actively developed.

This chapter examines the agreement between available total column water vapour datasets at Eureka. The accuracy of the new PEARL 125HR dataset produced by the MUSICA retrieval technique, described in Chapter 3, and a new retrieval using an emission FTIR is assessed. This chapter adapts results published in Weaver et al. (2017).

# 4.1 PEARL water vapour measurements

Several PEARL instruments make water vapour observations. Chapters 2 and 3 described measurements by the Eureka radiosondes and PEARL 125HR, respectively, in detail. The type 1 125HR MUSICA product is examined in this study. Other PEARL instruments also measure water vapour. Figure 4.1 illustrates the atmospheric water vapour time series from each PEARL and EWS instrument. In addition to the 125HR, the PEARL Ridge Lab has hosted a Sun photometer (SPM). 0PAL hosts another SPM and a microwave radiometer (MWR). During the time period examined in this study, there were also emission FTIR instruments that observe downwelling longwave radiation installed at the Ridge Lab and at 0PAL, the Polar-Atmospheric Emitted Radiance Interferometer (P-AERI) and the Extended-range Atmospheric Emitted Radiance Interferometer, their water vapour measurement techniques, and uncertainties.



Figure 4.1: Total column PWV at Eureka, measured by: (a) 125HR (the extended time series has removed the MUSICA SZA quality control criterion), (b) P-AERI and E-AERI (noting the location of the E-AERI), (c) Ridge Lab SPM, (d) 0PAL SPM, (e) 0PAL MWR, and (f) Eureka Weather Station radiosondes (standard and GRUAN data products).

			Measurement			Precipitable water vapour dataset (mm)			
Site	Instrument	Period	Duration	Frequency	Number	Mean	$\sigma$	Min	Max
Ridge Lab (610 m a.s.l.)	125HR MUSICA extended	Aug 2006– Oct 2014	5 min	0–12 day <sup>–1</sup> between late Feb and mid-Oct	3364 (2713 with SZA<85°)	6.9	3.5	0.9	17.9
	125HR MUSICA standard	Aug 2006– Aug 2014	5 min	1–12 day <sup>-1</sup> ; late Mar to mid-Sept	1889	5.4	3.8	0.4	19.1
	Sun pho- tometer	Mar 2007– Sept 2015	1 min	continuously when sunlight and clear skies available	89867	6.7	3	0.6	19.2
	E-AERI	Oct 2008– Sept 2009	7 min	continuously	6596	3.5	3.3	0.7	15.5
0PAL (10 m a.s.l.)	Sun pho- tometer	Apr 2007– Sept 2013	1 min	continuously when sunlight and clear skies available	63 010	10.3	3.5	1.7	21.1
	Microwave radiometer	Aug 2006– Jun 2010	5 min averages	continuously	368 706	5.1	4.1	0.1	26.8
	P-AERI	Mar 2006– Apr 2009	1 min	continuously	397 273	4.1	3.7	0.6	25.3
	E-AERI	Feb 2011– July 2013	7 min	continuously	24 395	4.3	4.4	0.6	17.7
Eureka Weather Station (10 m a.s.l.)	Radiosonde	Aug 2006– Dec 2015	120 min (60 min tropo- sphere)	twice per day	6852	5.5	4.6	0.4	27.1
	Radiosonde GRUAN	Sept 2008–Mar 2013	120 min (60 min tropo- sphere)	twice per day, but with gaps	2374	5.3	4.8	0.4	23.6

 Table 4.1: Eureka water vapour datasets used in this study.

#### 4.1.1 Emission FTIR

Two FTIR instruments that observe atmospheric emission at PEARL have been used to produce water vapour datasets: the E-AERI and the P-AERI. The P-AERI was installed at 0PAL in March 2006. The E-AERI was installed at the PEARL Ridge Lab in October 2008 (Mariani et al., 2012). After a seven-month overlap period with the E-AERI, the P-AERI was removed. Due to damage incurred to its detectors, the E-AERI did not take measurements between September 2009 and February 2011. Once repaired, the E-AERI was installed at 0PAL, where it remains.

The ABB Inc.-built AERI instruments (Knuteson et al., 2004b, 2004a) measure the downwelling radiation emitted by the atmosphere directly above Eureka continuously, weather permitting, at  $1.0 \text{ cm}^{-1}$  resolution. The spectral range of the E-AERI is 400 to 3000 cm<sup>-1</sup>, and that of the P-AERI is 500 to 3000 cm<sup>-1</sup>. E-AERI measurements were sampled every ~7 minutes. P-AERI measurements were sampled every 0.6 to 2 minutes. E-AERI measurements were calibrated using the standard processing software provided by ABB Inc., while the P-AERI measurements included additional processing (Rowe et al., 2011).

The sensitivity of downwelling infrared radiance to water vapour is greatest at low altitudes, where water vapour is most abundant. AERI measurements have been used to retrieve water vapour profiles (e.g., Feltz et al., 2003); however, retrievals of water vapour using PEARL AERI measurements are currently limited to total column amounts. The details of this retrieval are described in the appendix of Weaver et al. (2017). Uncertainties in retrieved PWV are 3% to 11% for summer to winter cases.

This work will refer to the combined dataset as the AERI; however, its three components will be examined: the P-AERI dataset at 0PAL, the E-AERI dataset at 0PAL, and the E-AERI dataset while installed at the RL. Distinguishing between the two measurement locations is important because of the difference in elevation and because water vapour is most abundant at low altitudes.

#### 4.1.2 Sun photometer

The PEARL Ridge Lab and 0PAL have both hosted a Cimel SPM. These measurements show the higher total columns measured at 0PAL, due to its lower altitude. SPMs measure solar radiation in eight spectral channels between 340 and 1640 nm. These automated sun-viewing radiometers are part of the global Aerosol Robotic Network (AERONET), and contribute data to a global aerosol optical depth (AOD) database (Holben et al., 1998). In this work, the AERONET Level 2.0 data

product is used, which has been cloud-screened and quality assured according to Smirnov et al. (2000). The Eureka SPMs are calibrated annually during polar night and are re-installed in the spring.

SPM data are used to produce total column aerosol optical depth measurements from inversions of spectral direct-sun and sky radiances. For water vapour measurements, a modified Langley plot technique described by Holben et al. (1998) is applied to observations of a spectral window at 940 nm. The AERONET water vapour retrieval is described by Smirnov et al. (2004). SPMs make measurements approximately every 3 minutes but are limited to clear sky conditions. The RL and 0PAL AERONET water vapour datasets do not have measurement uncertainties in the posted data files. Validation studies of the AERONET Cimel SPMs have shown that their data underestimates the water vapour total column by 10% (Alexandrov et al., 2009) and 5% (Pérez-Ramírez et al., 2014).

#### 4.1.3 Microwave radiometer

The MWR at 0PAL, a Radiometrics WVQ-1500, was installed in March 2006 in collaboration with NOAA. The MWR records microwave emissions in five channels between 22-30 GHz with a beam width of 5°. Two of the channels are used to statistically derive the PWV from zenith-pointing measurements (see Liljegren et al. (1996) and Westwater et al. (2001)). The measurements and retrieval technique are applied a few times per minute. This technique enables the MWR to observe water vapour all day and night in most conditions (e.g., during non-precipitating clouds), and to capture short-term variability. 5-minute averages have been calculated for use in this study. As of 2017, there has not been maintenance and calibration of the MWR, on account of its remote location, since a 2008 visit.<sup>24</sup> Only data up to June 30, 2010 has been plotted in Figure 4.1.

<sup>&</sup>lt;sup>24</sup> The MWR was removed, returned to the manufacturer for maintenance and calibration, and re-installed in summer 2018. Data acquired after re-installation has not yet been assessed.

## 4.1.4 Summary of PEARL PWV datasets

This section has presented the water vapour datasets from several ground-based PEARL instruments. The altitude of an instrument has a significant impact on the water vapour total columns observed; therefore, analysis of the datasets distinguishes between the instruments located at the 0PAL and RL sites. Table 4.1 summarized these datasets and noted how often measurements were taken, at which location and altitude the instrument is located, and whether total column or profile information is produced. Information about each dataset's mean, standard deviation (σ), minimum and maximum recorded PWV values are included. These dataset characteristics are influenced by sampling limitations, particularly in the case of instruments that are dependent on sunlight. Nonetheless, the datasets presented in this study indicate the total column of water vapour at Eureka can vary substantially, with values as small as 0.4 mm PWV and as large as 27 mm PWV recorded by the radiosondes. Figure 4.1 shows that water vapour columns at Eureka rarely exceed 20 mm PWV during summer and columns are frequently below 2 mm PWV during winter. In contrast, near the equator, PWV values can be as large as 70 mm, as shown in Figure 1.3. Table 4.2 summarizes estimated accuracies for the water vapour products, based on information available for each.

Instrument	Accuracy	Reference
125HR (MUSICA extended)	1.80% ( $\sigma = 0.61\%$ )	Calculated from the combined uncertainties of each datapoint
125HR (MUSICA standard)	~1%	Schneider et al. (2012)
Sun photometer	5-10 %	Pérez-Ramírez (2014) and Alexandrov et al. (2009)
Microwave radiometer	$\sim$ 20 %	Westwater et al. (2001)
Radiosonde	$\sim$ 15 %	Miloshevich et al. (2009)
GRUAN	5.70%	Calculated
	$(\sigma = 1.6 \%)$	
E-AERI	3-11 % varies monthly	Rowe et al. (2008)
P-AERI	3–11 % varies monthly	Rowe et al. (2008)

Table 4.2: Estimat	ed accuracies of	f water vapour	column	retrievals	for Eure	eka instrumer	its.
		1					

# 4.2 Comparison of water vapour measurements

In this study, water vapour total columns are compared using units of mm PWV, which is equivalent to  $\frac{\text{kg}}{\text{m}^2}$ .

### 4.2.1 Method

Coincident total column measurements have been compared using difference and correlation plots. No instrument is used as a common reference. A full accounting of the differences between every combination of instruments is presented to show how each dataset relates to the others.

When comparing radiosonde and 125HR measurements, the differences in vertical sensitivity have been accounted for. To do so, radiosonde profiles were smoothed by the 125HR averaging kernel and then integrated to calculate the total column. The procedure for smoothing followed Rodgers and Connor (2003), using Equation 4.1. Before smoothing, the 125HR a priori profile was used to fill any gaps in the comparison profile (i.e., altitudes above the upper limit of radiosonde measurements). After smoothing, altitudes for which there were no original data were removed. This has negligible effect on the resulting total column, as very little water vapour exists in the stratosphere relative to the troposphere.

$$x_{smoothed} = Ax - Ax_a + x_a = x_a + A(x - x_a),$$
(4.1)

where  $x_a$  is the a priori profile, A is the averaging kernel, and x is the comparison profile.

When comparing the radiosondes to measurements taken by instruments located at the RL, the radiosonde profile above 610 m has been used. Comparing RL instruments with the radiosonde partial column above 610 m ensures the results are fair despite the altitude difference between the RL and the radiosonde launch point.

In this study, measurements are compared using absolute and percent differences. These are calculated using:

$$difference = X - Y, \tag{4.2}$$

and

% difference = 
$$\frac{(X-Y)}{\frac{1}{2}(X+Y)} \times 100\%$$
. (4.3)

Percent differences (PD) are calculated with respect to the average of the two measurements to avoid taking one of them as a reference.

When reporting the comparison results in the text, the standard error in the mean (SEM) is used to quantify the expected accuracy of the mean difference. i.e., a difference will be quoted as  $A \pm B$ , where A is the mean difference ( $\Delta$ ) and B is the SEM. The figures showing differences use the mean difference as well as the one standard deviation of the differences ( $\sigma$ ) to characterize the spread of the values. The tables summarizing the results also include the root-mean-squared differences (RMSD) and the total number of matches found between the comparison instruments (*N*).

## 4.2.2 Coincidence criteria

A two-hour temporal coincidence criterion was applied for all instrument comparisons. If multiple coincident measurements were found within this interval, only the closest pair was kept. Each matched pair is thus independent of others contributing to the overall assessment of different measurement techniques. This method often results in a substantially smaller time difference between coincident measurements than is otherwise permitted by the criterion. For example, the mean time difference between measurements used in the comparison between the 125HR and SPMs was 5.4 minutes. All comparisons were also performed using all possible pairs of coincidences within this criterion (not shown). While significantly increasing the number of matches, the observed agreement between instruments was very similar.

The wide time criterion was chosen to ensure sufficient matches were found for reasonable statistics, especially for comparisons involving the radiosondes. Radiosondes are launched twice a day at 6:15 and 18:15 local time. This generally does not align with measurements that require sunlight (i.e., SPMs, 125HR), especially during spring and fall. Figure 4.2 illustrates the trade-off between the mean percent difference (and scatter, the mean standard deviation) between the 125HR and SPM measurements. The scatter shows how consistently different the instruments are at each temporal coincidence criterion.



Figure 4.2: The variation in mean percent difference and scatter (1  $\sigma$ ) between the water vapour total column of the 125HR and SPM at the Ridge Lab as a function of the temporal coincidence criterion. The resulting number of coincidences is labelled next to each data pair.

Other instruments show similar patterns, with an initial increase in the number of coincident pairs levelling off for a larger temporal coincidence criterion. Since only the closest pair is kept, the benefit of a larger temporal criterion is much less when the comparison instrument offers a high temporal density of data (e.g., the 125HR and SPM (RL)). The mean time difference of coincident measurements was less than 10 minutes in all cases except those involving the radiosonde datasets. The majority of coincident measurements involving the radiosonde datasets are within 30 minutes, except the 125HR vs. radiosonde comparison (where the mean time difference was 55.0 minutes and 43% of coincident measurement pairs were within 30 minutes).

## 4.3 Results

#### 4.3.1 Radiosondes

The accuracy of the Eureka radiosonde dataset is usefully characterized by comparison to the 2371 radiosonde measurements processed by GRUAN. The radiosonde (RS) and GRUAN total columns agree closely, with a mean difference (RS – GRUAN) of  $-3.7 \pm 0.0\%$  (R = 1.00). Differences reveal that the Eureka radiosonde standard water vapour total columns have a small systematic dry bias relative to GRUAN. The magnitude of this underestimation of water vapour varies seasonally, with radiosonde columns dry biased by up to around 1 mm PWV during the summer (0.6 mm PWV or 5.0% on average). During winter, agreement is very close; the differences in the columns are 0.1 mm PWV (or 4.2%) on average. This is seen clearly in the profile differences, which were shown in Figure 2.13.

## 4.3.2 125HR

The PEARL RL's 125HR water vapour measurements show good agreement with those of other RL instruments. The percent differences between the 125HR and instruments located at the RL or with sufficient profile information to create a total column from the altitude of the RL (610 m) are illustrated in Figure 4.3.

The SPM at the RL shares the same location and the same solar-viewing measurement geometry as the 125HR. Despite measuring the same airmass at the same time (the mean difference in measurement time between the 125HR and SPM (RL) is 5.3 minutes), Figure 4.3 (a) shows that SPM (RL) measurements are consistently smaller than those of the 125HR. The MUSICA product is consistently wet biased (measures more water vapour) with respect to the SPM. The difference between the instruments varies seasonally, and is largest in the summer. Seasonal variations in the difference between FTIR and sun-photometer/radiometers have also been reported by Schneider et al. (2010) for a subtropical site.

During the period of time when the E-AERI was installed at the RL, its measurements compared favourably with the 125HR. This is shown in Figure 4.3 (b). The mean percent difference (E-AERI – 125HR) in coincident measurements was  $-0.4 \pm 0.0$  mm PWV ( $-6.5 \pm 0.3\%$ ). This is the closest agreement of all comparisons with the 125HR in this study. It is consistent with the

result of the GRUAN comparison, with both showing a similarly-sized small overestimation (wet bias) in the Eureka MUSICA product.

When comparing the 125HR and radiosondes, radiosonde profiles were smoothed with the 125HR averaging kernels and the total column calculated down to the PEARL Ridge Lab altitude of 610 m. Only 65 coincidences were found. As shown in Figure 4.3 (c), the mean difference (125HR - RS) was  $0.78 \pm 0.1$  mm  $(12.2 \pm 1.1\%)$ , with no clear seasonality. This difference is larger than the expected accuracy of the measurements. The MUSICA product overestimates the water vapour column with respect to the radiosondes, beyond the small dry bias of the radiosondes.

Comparisons with the GRUAN radiosonde products are limited to only 10 coincident measurements. The mean percent difference, shown in Figure 4.3 (d), was  $0.4 \pm 0.2$  mm (-5.2 ± 3.4%). Extending the coincidence criterion to allow for measurements within 3 hours instead of 2 hours produces 93 coincidences. In this case, the difference (125HR – GRUAN) is  $0.3 \pm 0.0$  mm (9.0 ± 1.1%). (If the radiosonde comparison's criterion was also extended to 3 hours, the agreement (125HR – RS) would become  $0.6 \pm 0.0$  mm (12.8 ± 0.0%) using 279 matches, which is consistent with the 2-hour coincidence criterion result.) This comparison shows that the MUSICA product (v2015) is likely wet biased, given the differences relative to both the GRUAN and radiosonde product.

Table 4.3 shows that these comparisons (shown in Figure 4.3), made with the extended MUSICA dataset with a relaxed 85° SZA limit applied, are consistent with the agreement that would be found with other Eureka instruments if the standard MUSICA dataset was used.



Figure 4.3: Comparisons of the 125HR water vapour with PEARL Ridge Lab and Eureka Weather Station instruments. (In Equation 4.3, X is 125HR and Y is the comparison instrument). The red lines denote the mean difference, while blues lines denote 1 standard deviation above and below the mean differences. The number of comparison pairs and the mean percent difference and standard deviation are noted for each comparison. Standard deviation is shown and reported to characterize the spread in the values.

	125HR MUSICA				
	(78.5° SZA limit)	(85° SZA limit)	(no SZA limit)		
GRUAN (EWS, RL pc)	N = 6 R = 0.97 m = 0.92 $\Delta = 0.69 \text{ mm}$ $\sigma = 0.66 \text{ mm}$ SEM = 0.27  mm RMSD = 0.92  mm PD = 9.77 % $\sigma = 7.11 \%$ SEM = 2.90 % RMSD = 11.73 %	N = 10 R = 0.99 m = 0.89 $\Delta = 0.44 \text{ mm}$ $\sigma = 0.61 \text{ mm}$ RMSD = 0.72  mm PD = 5.15 % $\sigma = 10.69 \%$ SEM = 3.38 % RMSD = 11.38 %	N = 19 R = 0.99 m = 0.88 $\Delta = 0.16 \text{ mm}$ $\sigma = 0.54 \text{ mm}$ RMSD = 0.12  mm RMSD = 0.55  mm PD = -1.74 % $\sigma = 14.27 \%$ SEM = 3.27 % RMSD = 14.00 %		
RS (EWS, RL pc)	N = 55	N = 65	N = 85		
	R = 0.96	R = 0.98	R = 0.98		
	m = 0.90	m = 0.89	m = 0.88		
	$\Delta = 0.88 \text{ mm}$	$\Delta = 0.78 \text{ mm}$	$\Delta = 0.58 \text{ mm}$		
	$\sigma = 0.74 \text{ mm}$	$\sigma = 0.73 \text{ mm}$	$\sigma = 0.74 \text{ mm}$		
	SEM = 0.10 mm	SEM = 0.09 mm	SEM = 0.08 mm		
	RMSD = 1.15 mm	RMSD = 1.06 mm	RMSD = 0.93 mm		
	PD = 12.65 %	PD = 12.19 %	PD = 8.44 %		
	$\sigma = 8.52 \%$	$\sigma = 8.90 \%$	$\sigma = 12.19 \%$		
	SEM = 1.15 %	SEM = 1.10 %	SEM = 1.32 %		
	RMSD = 15.21 %	RMSD = 15.05 %	RMSD = 14.77 %		
E-AERI (RL)	N = 168	N = 191	N = 210		
	R = 0.99	R = 1.00	R = 1.00		
	m = 0.93	m = 0.93	m = 0.93		
	$\Delta = 0.51 \text{ mm}$	$\Delta = 0.46 \text{ mm}$	$\Delta = 0.41 \text{ mm}$		
	$\sigma = 0.42 \text{ mm}$	$\sigma = 0.42 \text{ mm}$	$\sigma = 0.43 \text{ mm}$		
	SEM = 0.03  mm	SEM = 0.03 mm	SEM = 0.03 mm		
	RMSD = 0.66  mm	RMSD = 0.62 mm	RMSD = 0.59 mm		
	PD = 6.85%	PD = 6.49 %	PD = 5.15 %		
	$\sigma = 4.30\%$	$\sigma = 4.29 \%$	$\sigma = 6.39 \%$		
	SEM = 0.33%	SEM = 0.31 %	SEM = 0.44 %		
	RMSD = 8.08%	RMSD = 7.78 %	RMSD = 8.20 %		
RL SPM	N = 1280	N = 1304	N = 1386		
	R = 0.99	R = 0.99	R = 0.99		
	m = 0.84	m = 0.84	m = 0.83		
	$\Delta = 1.05 \text{ mm}$	$\Delta = 1.04 \text{ mm}$	$\Delta = 1.06 \text{ mm}$		
	$\sigma = 0.65 \text{ mm}$	$\sigma = 0.65 \text{ mm}$	$\sigma = 0.71 \text{ mm}$		
	SEM = 0.02 mm	SEM = 0.02 mm	SEM = 0.02 mm		
	RMSD = 1.23 mm	RMSD = 1.23 mm	RMSD = 1.28 mm		
	PD = 15.08 %	PD = 15.10 %	PD = 15.22 %		
	$\sigma = 6.50 \%$	$\sigma = 6.48 \%$	$\sigma = 7.03 \%$		
	SEM = 0.18 %	SEM = 0.18 %	SEM = 0.19 %		
	RMSD = 16.42 %	RMSD = 16.43 %	RMSD = 16.77 %		

## 4.3.3 AERI

Comparisons between the E-AERI while it was located at 0PAL and other 0PAL instruments show close agreement, as illustrated by Figure 4.4. Since AERI measurements occur throughout the day and night, and during polar night, many coincidences are found with radiosondes and the MWR. Comparisons with the E-AERI showed agreement of  $3.2 \pm 0.2\%$  (N = 475) with radiosondes,  $1.0 \pm 0.3\%$  (N = 300) with GRUAN, and  $3.3 \pm 0.1\%$  (N = 1685) with the SPM (0PAL) (where E-AERI is used as X in Equation 4.3). Because MWR measurements were limited to the time period before July 1, 2010, before the E-AERI was installed at 0PAL, there were no coincidences between the E-AERI and MWR. The P-AERI (X in Equation 4.3) showed agreement of  $1.7 \pm 0.2\%$  (N = 639) with the radiosondes,  $0.5 \pm 0.4\%$  (N = 108) with GRUAN,  $2.2 \pm 0.0\%$  (N = 2662) with the SPM (0PAL), and  $-1.5 \pm 0.1\%$  (N = 46,054) with the MWR.

Comparisons between the E-AERI while it was installed at the PEARL Ridge Lab and Ridge Lab instruments show similar agreement. Observed agreement (where E-AERI is X in Equation 4.3) was  $-6.5 \pm 0.3\%$  (N = 191) with the 125HR and  $5.6 \pm 0.2\%$  (N = 898). This is illustrated in Figure 4.5.



Figure 4.4: Same as Figure 4.3 but for 0PAL-based AERI percent difference comparisons with 0PAL and Eureka instruments. (Percent differences calculated using Equation 4.3 where X is P-AERI or 0PAL E-AERI.)



Figure 4.5: Same as Figure 4.3 but for Ridge Lab-based comparisons between the E-AERI and the 125HR, SPM, RS, and GRUAN. Note that the RS and GRUAN datasets are columns calculated starting at the RL altitude (610 m). (Percent differences calculated using Equation 4 where X is E-AERI and Y is the comparison instrument.)

# 4.4 Differences vs. day of year and SZA

Summary statistics do not typically describe a dataset completely. Examination of the time series is often informative, revealing outliers and other features.<sup>25</sup> Patterns in the data often represent physical aspects of the system under study.

Differences were examined to see if they varied with day of year. Generally, the day of the year tracks closely with temperature, which largely predicts water vapour abundances. This was shown in Figure 1.4. Changes in the SZA also vary on an annual scale, as illustrated in Figure 3.20.

When examining the agreement vs. SZA, no clear pattern was observed in most comparison results. Figure 4.6, for example, illustrates the differences between the 125HR and the E-AERI at the RL. This comparison is highlighted because of the similarity between the instruments, e.g., they are both FTIR spectrometers, and because the E-AERI does not depend on sunlight and its measurement geometry is zenith-viewing. As noted earlier, MUSICA retrievals are typically limited to 78.5° SZA. Differences with other instruments up to 85° SZA show no clear trend. Some of the datasets are filtered by SZA as part of their quality control (e.g., AERONET SPM products are limited to SZA less than 79°).

<sup>&</sup>lt;sup>25</sup> This concept is nicely illustrated by the Datasaurus Dozen, a dataset and illustration described by Matejka and Fitzmaurice (2017), which builds on the well-known Anscombe's Quartet. It can be used to illustrate how a dataset can be substantially modified while retaining identical summary statistics. The gif illustration is available online at: https://www.autodeskresearch.com/publications/samestats (last accessed: September 28, 2018).



Figure 4.6: Differences between the 125HR and E-AERI (RL) vs. SZA. The red dashed line indicates the mean of the differences; the blue dashed lines show the mean plus or minus one standard deviation.

## 4.5 0PAL to Ridge Lab partial column comparisons

Radiosonde profiles below 610 m were used to calculate and examine the partial column between the two measurement sites. Radiosonde measurements show the PWV of the partial column between the measurement sites remains below 5 mm; between January and March this partial column has values less than 0.1 mm.

As shown in Figure 4.7 (b), approximately 20% of the Eureka water vapour column is found in the 600 m altitude range between 0PAL and the Ridge Lab. Measurements of this partial column have been calculated using the standard and GRUAN-processed radiosonde profiles.

In addition, 37,476 near-simultaneous SPM measurements at both sites were used to calculate a partial column, i.e. by subtracting the RL total column measurement from the 0PAL total column.

Results show the radiosonde and GRUAN partial columns below the RL altitude compare very similarly to their total columns (i.e., a mean difference of 3.9% and 3.7%, respectively, where X = GRUAN and Y = RS in Equation 4.3). However, agreement between the partial column calculated from the SPM measurements and those from the radiosonde datasets is relatively poor. The mean difference between the SPM and RS partial columns was  $13.7 \pm 1.1\%$  ( $\sigma = 25.3\%$ ); the mean difference between the SPM and GRUAN partial columns was  $20.7 \pm 1.6\%$  ( $\sigma = 22.5\%$ ). The larger variability observed between the partial columns and the total column comparisons may be due to the larger variability of water vapour near the surface. Table 4.4 summarizes the comparisons between the partial column datasets. Correlation plots between the partial column datasets are shown in Figure 4.8.



Figure 4.7: (a) Total column of water vapour and the partial column of water vapour between the 0PAL and RL altitudes, calculated using Eureka radiosonde profiles. (b) The percent of the total column of water vapour found beneath the altitude of the RL, as measured by the radiosondes.


Figure 4.8: Comparisons between the partial columns of water vapour from 0PAL to the RL, using data from the SPMs and radiosondes.

Table 4.4: Results of intercomparison of PWV measurements of partial columns between 0PAL and the RL. Variables are the same as those defined for Table 4.3. Instruments along the x axis (top) are X while instruments along the y axis (side) are Y in Equations 4.2 and 4.3.

	RS (below 610 m)	SPM (0PAL-RS)
GRUAN (below	N = 2371	N = 203
610 m)	R = 1.00	R = 0.84
	m = 1.02	m = 0.65
	$\Delta = -0.03 \mathrm{mm}$	$\Delta = 0.57 \mathrm{mm}$
	$\sigma = 0.03 \mathrm{mm}$	$\sigma = 0.63 \mathrm{mm}$
	SEM = 0.00  mm	SEM = 0.04  mm
	RMSD = 0.04 mm	RMSD = 0.85 mm
	PD = -3.93 %	PD = 20.74 %
	$\sigma = 1.70\%$	$\sigma = 22.46\%$
	SEM = 0.03 %	SEM = 1.58 %
	RMSD = 4.28 %	RMSD = 30.53 %
RS (below		N = 502
610 m)		R = 0.79
		m = 0.62
		$\Delta = 0.39 \mathrm{mm}$
		$\sigma = 0.62 \mathrm{mm}$
		SEM = 0.03  mm
		RMSD = 0.73 mm
		PD = 13.68 %
		$\sigma = 25.33\%$
		SEM = 1.13 %
		RMSD = 28.76 %

# 4.6 Summary of PWV comparisons

Comparisons were conducted between all combinations of the instruments at each site. Not every combination of instruments was shown in detail; this section focused on comparisons between the new FTIR datasets (125HR and AERIs) and co-located instruments. A complete set of correlation plots for available instrument dataset combination at the RL is given in Figure 4.9. Similarly, 0PAL correlation plots are given in Figure 4.10. Each row and column of the correlation plots in Figure 4.9 and Figure 4.10 illustrate how well a specific instrument agrees with the other instruments. Presenting all combinations of instruments in this manner allows the differences between the instruments to be observed as they relate to one-another, and potential biases to be revealed (e.g., the 125HR is consistently shown to overestimate the water vapour column with respect to other instruments). Comparisons between the SPMs, RS, and GRUAN partial columns between 0PAL and RL altitudes were summarized in correlation plots in Figure 4.8.

RL results are summarized in Table 4.5. 0PAL results are summarized in Table 4.6. Comparisons between measurements of the partial column between the sites are summarized in Table 4.7. These tables include the number of coincidences found, mean differences, correlation coefficients, standard error of the mean, root-mean-squared differences, and correlation plot slopes.



Figure 4.9: Water vapour total column (mm PWV) correlations between instruments at the RL. Data used for the radiosonde and GRUAN comparisons with the 125HR have been smoothed with the MUSICA averaging kernels.



Figure 4.10: Water vapour total column (mm PWV) correlations between instruments at 0PAL.

	125HR (RL)	GRUAN (EWS, RL pc)	RS (EWS, RL pc)	E-AERI (RL)	SPM (RL)
125HR (RL)		N = 10 R = 0.99 m = 1.10 $\Delta = -0.44 \text{ mm}$ $\sigma = 0.61 \text{ mm}$ SEM = 0.19  mm RMSD = 0.72  mm PD = -5.15% $\sigma = 10.69\%$ SEM = 3.38% RMSD = 11.38%	N = 65 R = 0.98 m = 1.07 $\Delta = -0.78$ mm $\sigma = 0.73$ mm SEM = 0.09 mm RMSD = 1.06 mm PD = -12.19 % $\sigma = 8.90 \%$ SEM = 1.10 % RMSD = 15.05 %	N = 191 R = 1.00 m = 1.06 $\Delta = -0.46 \text{ mm}$ $\sigma = 0.42 \text{ mm}$ SEM = 0.03 mm RMSD = 0.62 mm PD = -6.49 % $\sigma = 4.29 \%$ SEM = 0.31 % RMSD = 7.78 %	N = 1304 R = 0.99 m = 1.16 $\Delta = -1.04 \text{ mm}$ $\sigma = 0.65 \text{ mm}$ SEM = 0.02 mm RMSD = 1.23 mm PD = -15.10 % $\sigma = 6.48 \%$ SEM = 0.18 % RMSD = 16.43 %
GRUAN (EWS, RL pc)	N = 10 R = 0.99 m = 0.89 $\Delta = 0.44 \text{ mm}$ $\sigma = 0.61 \text{ mm}$ SEM = 0.19  mm RMSD = 0.72  mm PD = 5.15 % $\sigma = 10.69 \%$ SEM = 3.38 % RMSD = 11.38 %		N = 2371 R = 1.00 m = 1.03 $\Delta = -0.15 \text{ mm}$ $\sigma = 0.13 \text{ mm}$ SEM = 0.00 mm RMSD = 0.20 mm PD = -3.98 % $\sigma = 1.29 \%$ SEM = 0.03 % RMSD = 4.18 %	N = 68 R = 1.00 m = 1.02 $\Delta = 0.00 \text{ mm}$ $\sigma = 0.09 \text{ mm}$ SEM = 0.01 mm RMSD = 0.09 mm PD = 0.60 % $\sigma = 4.18 \%$ SEM = 0.51 % RMSD = 4.19 %	N = 250 R = 0.99 m = 1.09 $\Delta = -0.62 \text{ mm}$ $\sigma = 0.63 \text{ mm}$ SEM = 0.04 mm RMSD = 0.89 mm PD = -7.85 % $\sigma = 7.00 \%$ SEM = 0.44 % RMSD = 10.51 %
RS (EWS, RL pc)	N = 65 R = 0.98 m = 0.89 $\Delta = 0.78$ mm $\sigma = 0.73$ mm SEM = 0.09 mm RMSD = 1.06 mm PD = 12.19 % $\sigma = 8.90 \%$ SEM = 1.10 % RMSD = 15.05 %	N = 2371 R = 1.00 m = 0.97 $\Delta = 0.15 \text{ mm}$ $\sigma = 0.13 \text{ mm}$ SEM = 0.00 mm RMSD = 0.20 mm PD = 3.98 % $\sigma = 1.29 \%$ SEM = 0.03 % RMSD = 4.18 %		N = 124 R = 1.00 m = 0.97 $\Delta = 0.14 \text{ mm}$ $\sigma = 0.31 \text{ mm}$ SEM = 0.03 mm RMSD = 0.34 mm PD = 5.30 % $\sigma = 6.03 \%$ SEM = 0.54 % RMSD = 8.01 %	N = 1038 R = 0.99 m = 1.08 $\Delta = -0.39$ mm $\sigma = 0.60$ mm SEM = 0.02 mm RMSD = 0.72 mm PD = -4.31 % $\sigma = 7.50 \%$ SEM = 0.23 % RMSD = 8.64 %
E-AERI (RL)	N = 191 R = 1.00 m = 0.93 $\Delta = 0.46 \text{ mm}$ $\sigma = 0.42 \text{ mm}$ SEM = 0.03 mm RMSD = 0.62 mm PD = 6.49 % $\sigma = 4.29 \%$ SEM = 0.31 % RMSD = 7.78 %	N = 68 R = 1.00 m = 0.97 $\Delta = 0.00 \text{ mm}$ SEM = 0.01  mm RMSD = 0.09  mm PD = -0.60 % $\sigma = 4.18 \%$ SEM = 0.51 % RMSD = 4.19 %	N = 124 R = 1.00 m = 1.02 $\Delta = -0.14 \text{ mm}$ $\sigma = 0.31 \text{ mm}$ SEM = 0.03 mm RMSD = 0.34 mm PD = -5.30 % $\sigma = 6.03 \%$ SEM = 0.54 % RMSD = 8.01 %		N = 898 R = 0.99 m = 1.12 $\Delta = -0.47 \text{ mm}$ $\sigma = 0.49 \text{ mm}$ SEM = 0.02 mm RMSD = 0.68 mm PD = -5.61 % $\sigma = 4.62 \%$ SEM = 0.15 % RMSD = 7.27 %
RL SPM	N = 1304 R = 0.99 m = 0.84 $\Delta = 1.04 \text{ mm}$ $\sigma = 0.65 \text{ mm}$ SEM = 0.02  mm RMSD = 1.23  mm PD = 15.10% $\sigma = 6.48\%$ SEM = 0.18% RMSD = 16.43%	N = 250 R = 0.99 m = 0.90 $\Delta = 0.62$ mm $\sigma = 0.63$ mm SEM = 0.04 mm RMSD = 0.89 mm PD = 7.85 % $\sigma = 7.00 \%$ SEM = 0.44 % RMSD = 10.51 %	N = 1038 R = 0.99 m = 0.90 $\Delta = 0.39$ mm $\sigma = 0.60$ mm SEM = 0.02 mm RMSD = 0.72 mm PD = 4.31 % $\sigma = 7.50 \%$ SEM = 0.23 % RMSD = 8.64 %	N = 898 R = 0.99 m = 0.88 $\Delta = 0.47 \text{ mm}$ $\sigma = 0.49 \text{ mm}$ SEM = 0.02 mm RMSD = 0.68 mm PD = 5.61 % $\sigma = 4.62 \%$ SEM = 0.15 % RMSD = 7.27 %	

Table 4.5: Results of intercomparison of PWV measurements at the RL. Variables are the same as those defined for Table 4.3. Instruments along the x axis (top) are X while instruments along the y axis (side) are Y in Equations. 4.2 and 4.3.

# Table 4.6: Results of intercomparison of PWV measurements at 0PAL Variables are the same as those defined for Table 4.3. Instruments along the x axis (top) are X while instruments along the y axis (side) are Y in Equations 4.2 and 4.3.

	E-AERI (0PAL)	P-AERI (0PAL)	MWR (0PAL)	GRUAN (EWS)	RS (EWS)	SPM (0PAL)
E-AERI (0PAL)		<i>N</i> = 0	<i>N</i> = 0	$\begin{split} N &= 300 \\ R &= 1.00 \\ m &= 0.97 \\ \Delta &= 0.11 \text{ mm} \\ \sigma &= 0.28 \text{ mm} \\ \text{SEM} &= 0.02 \text{ mm} \\ \text{RMSD} &= 0.30 \text{ mm} \\ \text{PD} &= 0.98 \% \\ \sigma &= 4.55 \% \\ \text{SEM} &= 0.26 \% \\ \text{RMSD} &= 4.65 \% \end{split}$	$\begin{split} N &= 475 \\ R &= 1.00 \\ m &= 1.01 \\ \Delta &= -0.10 \text{ mm} \\ \sigma &= 0.26 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.28 \text{ mm} \\ \text{PD} &= -3.20 \% \\ \sigma &= 4.27 \% \\ \text{SEM} &= 0.20 \% \\ \text{RMSD} &= 5.34 \% \end{split}$	$\begin{split} N &= 1685 \\ R &= 0.98 \\ m &= 1.05 \\ \Delta &= -0.43 \text{ mm} \\ \sigma &= 0.55 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.70 \text{ mm} \\ \text{PD} &= -3.27 \% \\ \sigma &= 4.32 \% \\ \text{SEM} &= 0.11 \% \\ \text{RMSD} &= 5.42 \% \end{split}$
P-AERI (0PAL)	N = 0		$\begin{split} N &= 46,054 \\ R &= 0.99 \\ m &= 1.09 \\ \Delta &= -0.14 \text{ mm} \\ \sigma &= 0.52 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.54 \text{ mm} \\ \text{PD} &= 1.48 \% \\ \sigma &= 16.23\% \\ \text{SEM} &= 0.08 \% \\ \text{RMSD} &= 16.30 \% \end{split}$	$\begin{split} N &= 108 \\ R &= 1.00 \\ m &= 0.93 \\ \Delta &= 0.02 \text{ mm} \\ \sigma &= 0.14 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.14 \text{ mm} \\ \text{PD} &= -0.47 \% \\ \sigma &= 4.21 \% \\ \text{SEM} &= 0.41 \% \\ \text{RMSD} &= 4.22 \% \end{split}$	$\begin{split} N &= 639 \\ R &= 1.00 \\ m &= 0.97 \\ \Delta &= 0.00 \text{ mm} \\ \sigma &= 0.29 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.29 \text{ mm} \\ \text{PD} &= -1.72 \% \\ \sigma &= 5.74 \% \\ \text{SEM} &= 0.23 \% \\ \text{RMSD} &= 5.99 \% \end{split}$	$\begin{split} N &= 7248 \\ R &= 0.99 \\ m &= 1.02 \\ \Delta &= -0.23 \text{ mm} \\ \sigma &= 0.42 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.48 \text{ mm} \\ \text{PD} &= -2.19 \% \\ \sigma &= 4.13 \% \\ \text{SEM} &= 0.05 \% \\ \text{RMSD} &= 4.67 \% \end{split}$
MWR (0PAL)	<i>N</i> = 0	$\begin{split} N &= 46054 \\ R &= 0.99 \\ m &= 0.91 \\ \Delta &= 0.14 \text{ mm} \\ \sigma &= 0.52 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.54 \text{ mm} \\ \text{PD} &= -1.48 \% \\ \sigma &= 16.23 \% \\ \text{SEM} &= 0.08 \% \\ \text{RMSD} &= 16.30 \% \end{split}$		$\begin{split} N &= 693 \\ R &= 0.92 \\ m &= 0.86 \\ \Delta &= 0.13 \text{ mm} \\ \sigma &= 1.21 \text{ mm} \\ \text{SEM} &= 0.05 \text{ mm} \\ \text{RMSD} &= 1.21 \text{ mm} \\ \text{PD} &= -2.20 \% \\ \sigma &= 20.47 \% \\ \text{SEM} &= 0.78 \% \\ \text{RMSD} &= 20.57 \% \end{split}$	$\begin{split} N &= 2527 \\ R &= 0.98 \\ m &= 0.90 \\ \Delta &= 0.19 \text{ mm} \\ \sigma &= 0.88 \text{ mm} \\ \text{SEM} &= 0.02 \text{ mm} \\ \text{RMSD} &= 0.90 \text{ mm} \\ \text{PD} &= -1.88 \\ \sigma &= 17.33  \% \\ \text{SEM} &= 0.34  \% \\ \text{RMSD} &= 17.43  \% \end{split}$	$\begin{split} N &= 20396 \\ R &= 0.98 \\ m &= 0.98 \\ \Delta &= 0.56\mathrm{mm} \\ \sigma &= 0.59\mathrm{mm} \\ \mathrm{SEM} &= 0.00\mathrm{mm} \\ \mathrm{RMSD} &= 0.82\mathrm{mm} \\ \mathrm{PD} &= 6.87\% \\ \sigma &= 7.76\% \\ \mathrm{SEM} &= 0.05\% \\ \mathrm{RMSD} &= 10.37\% \end{split}$
GRUAN (EWS)	$\begin{split} N &= 300 \\ R &= 1.00 \\ m &= 1.02 \\ \Delta &= -0.11 \text{ mm} \\ \sigma &= 0.28 \text{ mm} \\ \text{SEM} &= 0.02 \text{ mm} \\ \text{RMSD} &= 0.30 \text{ mm} \\ \text{PD} &= -0.98 \% \\ \sigma &= 4.55 \% \\ \text{SEM} &= 0.26 \% \\ \text{RMSD} &= 4.65 \% \end{split}$	$\begin{split} N &= 108 \\ R &= 1.00 \\ m &= 1.07 \\ \Delta &= -0.02 \text{ mm} \\ \sigma &= 0.14 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.14 \text{ mm} \\ \text{PD} &= 0.47 \% \\ \sigma &= 4.21 \% \\ \text{SEM} &= 0.41 \% \\ \text{RMSD} &= 4.22 \% \end{split}$	$\begin{split} N &= 693 \\ R &= 0.92 \\ m &= 0.99 \\ \Delta &= -0.13 \text{ mm} \\ \sigma &= 1.21 \text{ mm} \\ \text{SEM} &= 0.05 \text{ mm} \\ \text{RMSD} &= 1.21 \text{ mm} \\ \text{PD} &= 2.20 \% \\ \sigma &= 20.47 \% \\ \text{SEM} &= 0.78 \% \\ \text{RMSD} &= 20.57 \% \end{split}$		$\begin{split} N &= 2371 \\ R &= 1.00 \\ m &= 1.03 \\ \Delta &= -0.19 \text{ mm} \\ \sigma &= 0.16 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.25 \text{ mm} \\ \text{PD} &= -3.72 \% \\ \sigma &= 1.96 \% \\ \text{SEM} &= 0.04 \% \\ \text{RMSD} &= 4.20 \% \end{split}$	$\begin{split} N &= 264 \\ R &= 0.99 \\ m &= 1.05 \\ \Delta &= -0.20 \text{ mm} \\ \sigma &= 0.61 \text{ mm} \\ \text{SEM} &= 0.04 \text{ mm} \\ \text{RMSD} &= 0.64 \text{ mm} \\ \text{PD} &= -0.72 \% \\ \sigma &= 5.83 \% \\ \text{SEM} &= 0.36 \% \\ \text{RMSD} &= 5.86 \% \end{split}$
RS (EWS)	$\begin{split} N &= 475 \\ R &= 1.00 \\ m &= 0.99 \\ \Delta &= 0.10 \text{ mm} \\ \sigma &= 0.26 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.28 \text{ mm} \\ \text{PD} &= 3.20 \% \\ \sigma &= 4.27 \% \\ \text{SEM} &= 0.20 \% \\ \text{RMSD} &= 5.34 \% \end{split}$	N = 639 R = 1.00 m = 1.02 $\Delta = 0.00 \text{ mm}$ $\sigma = 0.29 \text{ mm}$ SEM = 0.01 mm RMSD = 0.29 mm PD = 1.72 % $\sigma = 5.74 \%$ SEM = 0.23 % RMSD = 5.99 %	$\begin{split} N &= 2527 \\ R &= 0.98 \\ m &= 1.07 \\ \Delta &= -0.19 \text{ mm} \\ \sigma &= 0.88 \text{ mm} \\ \text{SEM} &= 0.02 \text{ mm} \\ \text{RMSD} &= 0.90 \text{ mm} \\ \text{PD} &= 1.88 \% \\ \sigma &= 17.33 \% \\ \text{SEM} &= 0.34 \% \\ \text{RMSD} &= 17.43 \% \end{split}$	N = 2371 R = 1.00 m = 0.97 $\Delta = 0.19 \text{ mm}$ $\sigma = 0.16 \text{ mm}$ SEM = 0.00  mm RMSD = 0.25  mm PD = 3.72% $\sigma = 1.96\%$ SEM = 0.04% RMSD = 4.20%		$N = 692  R = 0.99  m = 1.05  \Delta = -0.07 mm  SEM = 0.03 mm  RMSD = 0.67 mm  PD = 0.40 %  \sigma = 6.63 %  SEM = 0.25 %  RMSD = 6.64 %$
SPM (0PAL)	$\begin{split} N &= 1685 \\ R &= 0.98 \\ m &= 0.92 \\ \Delta &= 0.43 \text{ mm} \\ \sigma &= 0.55 \text{ mm} \\ \text{SEM} &= 0.01 \text{ mm} \\ \text{RMSD} &= 0.70 \text{ mm} \\ \text{PD} &= 3.27 \% \\ \sigma &= 4.32 \% \\ \text{SEM} &= 0.11 \% \\ \text{RMSD} &= 5.42 \% \end{split}$	$\begin{split} N &= 7248 \\ R &= 0.99 \\ m &= 0.96 \\ \Delta &= 0.23 \text{ mm} \\ \sigma &= 0.42 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.48 \text{ mm} \\ \text{PD} &= 2.19 \% \\ \sigma &= 4.13 \% \\ \text{SEM} &= 0.05 \% \\ \text{RMSD} &= 4.67 \% \end{split}$	$\begin{split} N &= 20396 \\ R &= 0.98 \\ m &= 0.98 \\ \Delta &= -0.56 \text{ mm} \\ \sigma &= 0.59 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.82 \text{ mm} \\ \text{PD} &= -6.87 \% \\ \sigma &= 7.76 \% \\ \text{SEM} &= 0.05 \% \\ \text{RMSD} &= 10.37 \% \end{split}$	$\begin{split} N &= 264 \\ R &= 0.99 \\ m &= 0.93 \\ \Delta &= 0.20 \text{ mm} \\ \sigma &= 0.61 \text{ mm} \\ \text{SEM} &= 0.04 \text{ mm} \\ \text{RMSD} &= 0.64 \text{ mm} \\ \text{PD} &= 0.72 \% \\ \sigma &= 5.83 \% \\ \text{SEM} &= 0.36 \% \\ \text{RMSD} &= 5.86 \% \end{split}$	$\begin{split} N &= 692 \\ R &= 0.99 \\ m &= 0.93 \\ \Delta &= 0.67 \text{ mm} \\ \sigma &= 0.67 \text{ mm} \\ \text{SEM} &= 0.03 \text{ mm} \\ \text{RMSD} &= 0.67 \text{ mm} \\ \text{PD} &= -0.40 \% \\ \sigma &= 6.63 \% \\ \text{SEM} &= 0.25 \% \\ \text{RMSD} &= 6.64 \% \end{split}$	

# 4.7 Discussion

Total column comparisons between Eureka water vapour datasets exhibited good overall agreement. All comparisons showed *R* values of 0.98 or greater, indicating excellent correlation between Eureka water vapour measurements taken by several different instruments. The exception to this is the MWR and GRUAN comparison, for which R = 0.92. Instruments that sample different air masses because of their line-of-sight, location, measurement timing and length, or sensitivity will show differences because water vapour has high variability over short timespans, altitudes, and distances (Steinke et al., 2015).

The 600 m altitude difference between the two measurement sites was examined by comparing the partial columns available from the radiosondes, GRUAN, and SPM data. The magnitude and variability of the difference between measurements using the radiosondes and the SPMs, at the two sites a short distance away (15 km), demonstrates the significant influence of altitude and meteorological variability on water vapour measurements. This provides useful context for other comparisons of instruments at the RL and 0PAL sites. Due to the observed magnitude and variability in the partial columns, comparisons between instruments located at different altitudes have not been shown.

# 4.7.1 125HR

The 125HR agreement with other instruments' measured water vapour total columns shows high correlation ( $R \ge 0.98$ ) and a small overestimation of the water vapour column. Due to the consistency of the observed difference, particularly with trusted datasets such as the GRUAN measurements, the Eureka MUSICA product appears to have a wet bias. The agreement between the 125HR and (smoothed) Eureka radiosondes, for example, has a larger difference than expected from the accuracy of the instruments. Given that the radiosondes appear to have a small dry bias of approximately 4% based on GRUAN comparisons, the radiosonde measurements suggest the 125HR has a wet bias of around 6%. Furthermore, comparisons between the 125HR and other instruments support this wet bias observation. Agreement between the 125HR and the E-AERI (while co-located at the RL) shows the 125HR overestimates water vapour to a similar magnitude. Differences between the 125HR and the SPM (RL) (125HR – SPM) are larger than other comparisons (i.e., 15%); however, this result is consistent with other comparisons in the context of SPMs' known underestimation of water vapour by up to 10%. Differences between the 125HR

and SPM (RL) are informative since the instruments share a solar-viewing measurement geometry, are co-located (within meters), and have closely coincident measurement times.

The previous MUSICA retrievals (v2012, type 1) for the Eureka 125HR showed closer agreement with the other instruments than does the current MUSICA retrieval version (v2015, type 1) used in this study. Agreement between the Eureka v2012 MUSICA retrieval (X in Equation 4.3) and GRUAN ( $0.6 \pm 3.3\%$ , N = 10), E-AERI (RL) ( $0.6 \pm 0.3\%$ , N = 191), and SPM (RL) ( $8.7 \pm 0.2\%$ , N = 1109) are within expected instrument accuracies and biases (e.g., the dry bias of the radiosondes and SPMs). Moreover, the v2012 comparison results are consistent with previous MUSICA intercomparison studies (e.g., Schneider et al., 2010). Table 4.7 summarizes the water vapour comparisons using the MUSICA v2012 retrieval and a subset of MUSICA v2015 data using the same measurements as the v2012 product.

Two major changes in the v2015 MUSICA retrieval, aimed at improving the network-wide consistency of the MUSICA FTIR products from sites around the world, are likely to have contributed to this change in observed agreement with other high Arctic measurements. First, the a priori profile used for v2015 retrievals was a global average of water vapour, replacing v2012's a priori profiles based on latitude-specific radiosonde measurements. For Eureka retrievals, this meant the v2015 a priori profile had more water vapour than is present at Eureka except during summer. (Seasonal mean water vapour profiles measured by Eureka radiosondes were shown in Figure 2.9.) The MUSICA v2015 and v2012 a priori profiles are shown in Figure 4.11, along with radiosonde profiles measured from 2007 to 2017. (The mean of the Eureka radiosonde profiles does not align exactly with the v2012 a priori because a combination of Arctic radiosondes were used to derive a the profile shape for use at high latitude MUSICA sites.) Second, the v2015 retrieval replaced two of v2012's spectral windows containing strong absorption features (which had saturated at high-humidity sites such as Wollongong, Australia), with one spectral window having weaker absorption lines (Barthlott et al., 2017). It is unlikely that the strong absorption features used in v2012 saturate in high Arctic spectra, and likely that they contributed useful information to the retrieval. While MUSICA's change in spectral lines enables consistency across FTIRs located at sites with very different humidity conditions worldwide, the v2015 spectral windows and global a priori might not be ideal for high-latitude, low-humidity conditions. Nevertheless, an Arctic bias of a few percent is still a good value for a dataset that is optimised for global consistency.



Figure 4.11: MUSICA v2012 and v2015 a priori profiles, with Eureka radiosonde profiles measured from 2007 to 2017.

The difference between the v2015 and v2012 Eureka MUSICA products is  $5.6 \pm 0.0\%$  overall (v2015 – v2012). Differences are greatest during summer and follow a seasonal pattern, as shown in Figure 4.12. Figure 4.13, a correlation plot for both datasets, shows that the difference increases linearly as humidity increases. This difference is very similar in magnitude to the observed bias relative to other Eureka instruments, and suggests changes to the MUSICA retrieval (the selected spectral windows and the usage of a global uniform a priori profile) decreased the accuracy at the high Arctic site of Eureka. In addition, the  $\delta D$  products from the two retrievals show a difference that also increases linearly as  $\delta D$  increases (also shown in Figure 4.13).

Table 4.7: Results of comparisons between RL instruments and coincident MUSICA v2012 and v2015 datasets, including number of coincidences (N), correlation coefficient (R), slope of the correlation best fit line (m), mean difference ( $\Delta$ ), standard deviation of difference ( $\sigma$ ), standard error of the mean (SEM), and root- mean-square difference (RMSD) in mm and %. Instruments along the x axis (top) are X while instruments along the y axis (side) are Y in Equations 4.2 and 4.3.

	MUSICA v2012 (coincident with v2015)	MUSICA v2015 (coincident with v2012)
MUSICA v2015	$\begin{split} N &= 2046 \\ R &= 1.00 \\ m &= 1.05 \\ \Delta &= -0.31 \text{ mm} \\ \sigma &= 0.19 \text{ mm} \\ \text{SEM} &= 0.00 \text{ mm} \\ \text{RMSD} &= 0.37 \text{ mm} \\ \text{PD} &= -5.63 \% \\ \sigma &= 0.96 \% \\ \text{SEM} &= 0.02 \% \\ \text{RMSD} &= 5.71 \% \end{split}$	
GRUAN (EWS, RL pc)	$\begin{split} N &= 10 \\ R &= 0.99 \\ m &= 0.94 \\ \Delta &= 0.17 \text{ mm} \\ \sigma &= 0.41 \text{ mm} \\ \text{SEM} &= 0.13 \text{ mm} \\ \text{RMSD} &= 0.43 \text{ mm} \\ \text{PD} &= 0.65 \% \\ \sigma &= 10.44 \% \\ \text{SEM} &= 3.30 \% \\ \text{RMSD} &= 9.92 \% \end{split}$	$N = 10  R = 0.99  m = 0.89  \Delta = 0.44 mm  \sigma = 0.61 mm  RMSD = 0.72 mm  PD = 5.15 %  \sigma = 10.69 %  SEM = 3.38 %  RMSD = 11.38 %$
RS (EWS, RL pc)	$\begin{split} N &= 35 \\ R &= 0.98 \\ m &= 0.90 \\ \Delta &= 0.52 \text{ mm} \\ \sigma &= 0.62 \text{ mm} \\ \text{SEM} &= 0.10 \text{ mm} \\ \text{RMSD} &= 0.80 \text{ mm} \\ \text{PD} &= 8.00 \% \\ \sigma &= 8.13 \% \\ \text{SEM} &= 1.37 \% \\ \text{RMSD} &= 11.37 \% \end{split}$	N = 35 R = 0.99 m = 0.87 $\Delta = 0.78 \text{ mm}$ $\sigma = 0.65 \text{ mm}$ SEM = 0.11  mm PD = 12.11% $\sigma = 7.71\%$ SEM = 1.30% RMSD = 14.30%
E-AERI (RL)	$\begin{split} N &= 191 \\ R &= 1.00 \\ m &= 0.98 \\ \Delta &= 0.06 \text{ mm} \\ \sigma &= 0.33 \text{ mm} \\ \text{SEM} &= 0.02 \text{ mm} \\ \text{RMSD} &= 0.34 \text{ mm} \\ \text{PD} &= 0.58 \% \\ \sigma &= 4.13 \% \\ \text{SEM} &= 0.30 \% \\ \text{RMSD} &= 4.16 \% \end{split}$	N = 191 R = 1.00 m = 0.93 $\Delta = 0.46 \text{ mm}$ $\sigma = 0.42 \text{ mm}$ SEM = 0.03  mm RMSD = 0.62  mm PD = 6.49% $\sigma = 4.29\%$ SEM = 0.31% RMSD = 7.78%
RL SPM	$N = 1109 R = 0.99 m = 0.89 \Delta = 0.60 \text{ mm}$ $\sigma = 0.51 \text{ mm}$ SEM = 0.02 mm RMSD = 0.79 mm PD = 8.67 % \sigma = 5.85 % SEM = 0.18 % RMSD = 10.46 %	$N = 1109 R = 0.99 m = 0.85 \Delta = 1.00 mm \sigma = 0.63 mm SEM = 0.02 mm RMSD = 1.18 mm PD = 14.60 \% \sigma = 5.71 \% SEM = 0.17 \% RMSD = 15.68 \%$



Figure 4.12: Difference between MUSICA v2015 and v2012 type 1 H<sub>2</sub>O total columns, i.e., v2015 – v2012, using measurements acquired between August 2006 and October 2011 without SZA filtering.



Figure 4.13: MUSICA v2015 vs. MUSICA v2012 type 1  $\rm H_2O$  and  $\delta D$  total columns at Eureka.

#### 4.7.2 AERI instruments

Close agreement with measurements taken by other co-located Eureka instruments confirms the accuracy of the new AERI water vapour datasets. The P-AERI (located at 0PAL) showed agreement with the co-located SPM of  $2.2 \pm 0.0\%$ , with the RS of  $1.7 \pm 0.2\%$ , with GRUAN of  $0.5 \pm 0.4\%$ , and with the MWR of  $-1.5 \pm 0.1\%$  (where X in Equation 4.3 is P-AERI). The small overestimation of water vapour observed with respect to the SPM and RS may be due to the dry bias of those instruments. The E-AERI showed similar results in comparisons to these datasets and those at the RL. These results, particularly the close agreement observed with GRUAN, support the value and use of the new AERI water vapour measurements.

#### 4.7.3 Microwave radiometer

The MWR observes water vapour year-round; thus it has many matches with P-AERI (N = 46,054) and RS (N = 2527) measurements. The agreement between the MWR and those instruments, whose measurements are not dependent on sunlight, is close:  $1.5 \pm 0.1\%$  and  $1.9 \pm 0.3\%$ , respectively (where MWR is X in Equation 4.3). However, the MWR's agreement with co-located datasets has the largest scatter ( $\sigma$ ) of all comparisons and the largest root-mean-squared differences. While this study used 5-minute averages of the MWR measurements to better align with the measurements of comparison instruments, comparisons were also done using 30-minute averages. The results were similar. In addition, comparisons were conducted using a longer time series (August 2006 to August 2013) than was shown in the main results.

Agreement between the radiosondes and the MWR worsens dramatically after mid-2010. Prior to July 2010, the MWR agreement was consistent with the small known RS dry bias. Starting in fall 2010 and continuing through August 2013, the agreement diminished to  $-37.4 \pm 17.0\%$  ( $\sigma = 754.8\%$ ), with extreme difference outliers on the order of 1000% (the large relative values are also a consequence of the small PWV values during Arctic winter). The differences between these time periods of MWR measurements with respect to radiosondes is shown in Figure 4.14. Indeed, after the winter of 2010-2011, MWR water vapour total columns regularly report negative values in low-humidity conditions. Comparisons with other instruments, e.g., E-AERI and GRUAN, show the same difference characteristics.



Figure 4.14: Comparisons between the MWR and radiosondes. Data used in this study are in purple; data that are available but not used due to calibration and quality concerns are in grey. The change in agreement from fall 2010 onwards is clearly evident. The plot scale cuts off extreme outliers. As with other figures, the reported values are the mean  $\pm \sigma$ , where the standard deviation is used to characterize the spread in the values.

The accuracy problem of the MWR dataset is likely caused by the limited calibration and maintenance the instrument has received since installation. Poor agreement with the MWR after mid-2010 is interpreted to indicate a problem with the MWR data, rather than of other instruments. For example, the P-AERI shows close agreement with the MWR; however, it was only installed at 0PAL from 2006 to 2009. This study limited its use of MWR data to the end of June 2010 because of the observed calibration problem revealed by the comparisons. This result demonstrates the value of regularly conducting validation and comparison studies with co-located measurements. Partly as a result of the analysis presented here, NOAA recently removed the MWR for calibration. The instrument was re-installed in the summer of 2018.

#### 4.7.4 Radiosondes

Comparisons to the GRUAN radiosonde product shows that the standard radiosonde dataset has a small dry bias, particularly in the Eureka summer. This is consistent with other radiosonde studies (e.g., Miloshevich et al., 2009; Vömel et al., 2007). This dry bias helps explain why the radiosonde and GRUAN measurements don't show identical agreement with other instruments. Further, comparison results between the radiosondes and GRUAN are consistent across measurements of the total column, partial column above the RL, and partial column below the RL.

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#### 4.7.5 Sun photometers

Nearly all comparisons between PEARL SPMs and co-located instruments show an underestimation of water vapour by the SPMs, suggesting that they have a dry bias. This aligns with the existing SPM validation literature (e.g., Pérez-Ramírez et al., 2014). Results of comparisons between SPM measurements and co-located instruments at the RL show greater underestimation of the water vapour column than results using the same instruments at 0PAL (e.g., relative to the RS, GRUAN, and E-AERI).

# 4.7.6 Comparison of results to other studies

Other intercomparison studies have examined water vapour measurement techniques. However, parallels with this study are limited because other studies have been conducted within a different environment, have compared measurements to instruments not available at Eureka (e.g., global positioning system (GPS), FPH), and sometimes a different technique has been used to derive water vapour information from the same type of measurement (e.g., FTIR retrievals).

Buehler et al. (2012), who compared water vapour measurements at Kiruna, Sweden, also used an FTIR, radiosondes, and MWR. However, they do not explicitly give the results of any comparisons using the same combination of instruments used in this study. Their FTIR results showed a dry bias at low PWV and a wet bias at high PWV with respect to the GPS. They report that this result is 'roughly similar' to the radiosonde comparison with the GPS, but it is not clear how comparable this is to this study's direct FTIR (i.e., 125HR) vs. radiosonde results. They find an FTIR dry bias with respect to their MWR; however, we did not directly compare the FTIR and MWR at PEARL because they are at different altitudes. The observation of an FTIR dry bias at Kiruna differs from the observed wet bias seen in this study's examination of the Eureka FTIR MUSICA water vapour retrieval. However, the different FTIR retrieval details may be the source of the difference. They used the PROFFIT retrieval software, which is the same software used for MUSICA retrievals, and used a mix of strong and weak water vapour lines; however, the exact retrieval strategy is not described and is not harmonized with the MUSICA approach. Overall, Buehler et al. (2012) note that their instruments agree within  $\pm 1$  mm PWV. This is comparable to this study, for which the largest observed difference was 1.0 mm (125HR vs. SPM).

Palm et al. (2010) conducted a water vapour intercomparison at an Arctic site, Ny Ålesund. Many of the measurements they examined were satellite-based. Ground-based FTIR and MWR

measurements were compared to radiosoundings. Their results showed that both the FTIR and MWR measured systematically smaller water vapour columns than the radiosondes. This differs from the results shown in our study. However, their FTIR retrieval differs from the MUSICA retrieval used in the current study and their MWR instrument measures at different frequencies (142 GHz), as it is designed and optimized for measuring stratospheric and mesospheric ozone. Nonetheless, both studies showed high correlation between these instruments and the radiosondes (i.e., greater than R = 0.95).

The water vapour intercomparison study at Izaña by Schneider et al. (2010a) examined measurements taken by ground-based FTIR, SPM, GPS, and radiosonde instruments. While their sub-tropical island mountain location is very different from Eureka, the instrumentation used has parallels that in our study. In addition, the Izaña study used a similar FTIR retrieval technique to the MUSICA v2012 discussed here. The Izaña results find the SPM to systematically underestimate the PWV, which is similar to the results of this study. The FTIR comparison to the RS shows close agreement, with a mean difference of 0.06 mm or -3.3% (RS – FTIR). This is better agreement than observed at Eureka with either MUSICA retrieval version.

The current study adds to existing water vapour intercomparison studies. It offers a comparison of measurements taken at a unique location in the Canadian high Arctic. Moreover, the current study includes results from an extensive set of ground-based instruments and datasets. However, GPS measurements of the water vapour total column are notably common in other studies and measurement sites but are not available for Eureka. It would be useful to add this capability to PEARL's instrument suite, as it would provide an additional water vapour dataset and would enable another avenue for relating results at Eureka to those elsewhere.

# 4.8 Conclusions

This chapter compared high Arctic water vapour measurements taken by seven different instruments located at Eureka, Nunavut. This large site-wide intercomparison has confirmed the value and reliability of new measurements (i.e., the PEARL 125HR MUSICA and AERI products), and provided a detailed accounting of the comparability of measurements from a variety of commonly-used atmospheric monitoring instruments.

The accuracy of the MUSICA dataset derived from PEARL 125HR spectra is supported by comparisons with coincident measurements taken at Eureka. The MUSICA v2015 product shows

close agreement with other instruments; however, it has a small wet bias, which was not observed in comparisons using the previous MUSICA v2012 retrieval. Changes to the MUSICA retrieval intended to balance the needs of globally distributed FTIR sites created a small wet bias at this extremely dry high-latitude site. This underscores the challenge in assuring consistency across global observation networks as well as the performance of measurement techniques operating across a wide range of conditions.

This result affirms the conclusions of previous intercomparison studies at other MUSICA sites that 125HR measurements can yield reliable and precise information about atmospheric water vapour total columns. Moreover, these results also support the use of 125HR measurements taken beyond MUSICA's standard 78.5° SZA limit. Comparisons in this study included SZAs up to 85° without sacrificing the consistency with other instruments' measurements. Relaxing this constraint is useful for polar sites. Observed differences between the 125HR and other instruments are consistent with well-understood measurement technique biases and differences in observation geometry.

The moderate number of coincident measurements with radiosondes presented in this study suggests that the 125HR offers accurate information about water vapour abundances in the troposphere. The assertion of Schneider et al. (2016) that MUSICA retrievals offer approximately 10% accuracy is affirmed; however, a small wet bias of 5 to 6% is observed at Eureka.

The new AERI datasets presented in this study showed close agreement with other Eureka instruments (e.g., agreement better than 4% relative to GRUAN). AERI measurements thus offer reliable continuous observations of atmospheric water vapour total columns without reliance on sunlight. Adding this capability to existing water vapour observations is especially valuable at Eureka because there is no sunlight between mid-October and late-February, and for parts of the day during spring and fall. 125HR and AERI retrievals thus offer a reliable, accurate, and frequent source of information about atmospheric water vapour at Eureka. Application of the Eureka AERI water vapour retrieval algorithm to other Arctic AERI sites (e.g. Barrow, Alaska and Summit, Greenland) would be a useful next step. A standardized AERI water vapour dataset across the Arctic region would be a valuable addition to existing water vapour measurements and enable a comparison between Eureka and other Arctic AERI water vapour measurements.

The WMO GCOS has set out goals for the accurate measurement of essential climate variables, including water vapour. The GCOS goal for water vapour total columns is measurement accuracy

within 1 kg/m<sup>2</sup> (equivalent to 1 mm PWV) (WMO, 2018) and within 2% (GCOS, 2016). The comparisons shown in this work between the 125HR and AERI datasets and those of other instruments at Eureka show mean differences less than 1 mm PWV. The P-AERI shows mean agreement within 2% of other instruments. Measurements from other instruments do not show agreement within this threshold. This result motivates continued work on FTIR retrievals to attain accurate measurements of water vapour total columns for use by the climate and atmospheric community.

Radiosonde measurements are often used as a reference because of their reliable and wellunderstood character, as well as their high vertical resolution. The GRUAN-processed radiosonde product resulting from recent processing of the raw data reveals that the Eureka radiosonde measurements are affected by a small dry bias (approximately 4%), which is largest in the summer. This should be taken into account when using radiosondes as a reference for climatological and atmospheric investigations. Further, the additional information and accuracy offered by the GRUAN processing offers clear benefits to observations at Eureka. Participation in the GRUAN network would be advantageous for the site.

The NOAA MWR at PEARL showed reasonable correlations and agreement with other datasets in the period to mid-2010; however, under low-PWV conditions MWR measurements after fall 2010 show significant disagreement with other co-located instruments. The comparisons conducted in this work demonstrate the need to continuously validate data, especially data resulting from experiments in remote locations where maintenance and calibration opportunities are difficult and infrequent.

No single instrument is capable of capturing complete information about atmospheric water vapour at all times. There are limits to all measurement techniques. Moreover, most instruments have down-time due to technical challenges, particularly when operating in a harsh environment such as the high Arctic. The widespread agreement across the suite of Eureka instruments with different observation strengths offers a valuable capability to collectively measure water vapour abundances and variability in the Canadian high Arctic. The agreement seen between total column measurements suggest that a unified water vapour product at Eureka could be explored. This appears especially promising with a reliable AERI product available to fill in the polar night measurement gap left by the SPMs and 125HR, as well as the large temporal gaps (i.e., 12 hours) between radiosonde measurements.

# 5 Comparison of ground-based and satellite measurements of water vapour vertical profiles over Ellesmere Island, Nunavut

# 5.1 Introduction

Satellite-based instruments complement ground-based observations by producing frequent global measurements of atmospheric constituents. More than a dozen satellites are currently (or have been recently) making measurements of water vapour. There is interest in assessing the accuracy and quality of these datasets. For example, a SPARC activity is currently conducting a comprehensive overview of water vapour satellite measurements between the upper troposphere and lower mesosphere, called WAVAS-II, which intercompares the available satellite measurements to understand the differences between datasets, measurement uncertainties, and the trends in stratospheric and lower mesospheric and lower mesospheric water vapour.

Developing highly accurate and vertically-resolved UTLS water vapour profile measurements from satellite instruments is a priority of the atmospheric observing community (Müller et al., 2016). Changes to water vapour abundances in the upper troposphere and lower stratosphere are particularly consequential for radiative balance (Soden et al., 2008). Water vapour abundances are expected to increase the most in the lowermost stratosphere (LMS) (Dessler et al, 2013), i.e., altitudes above the tropopause and beneath the tropical tropopause (approximately 17 km), where the radiative impact of additional water vapour is maximum (Solomon et al., 2010). However, obtaining sensitivity to the troposphere and producing high vertical resolution profiles is challenging for many satellite instruments. Comparisons to ground-based observations offer an opportunity to assess the accuracy of satellite measurements.

The objective of the study presented in this chapter is to assess the Arctic water vapour vertical profiles retrieved from ACE satellite observations using comparisons to coincident measurements taken at a Canadian high Arctic observatory in Eureka, Nunavut. In addition, other satellite instruments with Eureka-coincident water vapour profile measurements are compared to put the ACE results in the context of the broader effort to measure water vapour from satellites. The importance of the upper troposphere and lowermost stratosphere (UTLMS) for understanding the atmosphere's radiative balance, and the sensitivity of the available Eureka

reference measurements, the focus of this work is on UTLMS altitudes, e.g., between 5 and 15 km. This study adds to earlier work that has compared ground-based FTIR measurements to ACE v3.5/3.6 (e.g., Griffin et al., 2017) and studies comparing ACE measurements to those of other satellites (e.g., Sheese et al., 2017). It has been submitted for publication in *Atmospheric Measurement Techniques* (Weaver et al., 2018).

This chapter is structured as follows. Section 5.2 describes the instruments and datasets used in the study. Section 5.3 compares the satellite and ground-based measurements, noting the methods used to match observations and account for different vertical sensitivities. Section 5.4 discusses the results of the comparisons. Section 5.5 offers conclusions about the ability of the ACE and other satellite datasets to contribute to our knowledge of high Arctic water vapour.

# 5.2 Instruments

This section presents the water vapour datasets from Eureka ground-based instruments and Eureka-coincident satellite instruments that are used in this study. Table 5.1 summarizes the available datasets, notes the technique, retrieval version, and how often measurements are taken. Figure 5.1 illustrates the temporal availability of atmospheric water vapour measurement from each instrument. Figure 5.2 illustrates the vertical ranges of the datasets.

Туре	Satellite/ Location	Instrument	Instrument type	Measurement geometry	Retrieval version	Time range used	Number of measurements within 500 km of Eureka (Aug. 2006 onwards)	Valid altitude range
Satellite	SCISAT	ACE-FTS	Fourier transform spectrometer	limb	v3.6	Aug. 2006 - Mar. 2017	551	mid-troposphere to mesosphere
		ACE- MAESTRO	grating spectrometer	limb	v30	Aug. 2006 - Sept. 2016	388	mid-troposphere to lower stratosphere
	AURA	TES	Fourier transform spectrometer	nadir	v6	Aug. 2006 - July 2011	5,630	P > 100 hPa
		MLS	radiometer	limb	v4.20-v4.22	Aug. 2006 - Dec. 2015	108,072	P <= 316 hPa
	ENVISAT	MIPAS	Fourier transform spectrometer	limb	IMK v5 & v7	Aug. 2006 - Apr. 2012	v5: 10428; v7: 10712	12 - 50 km recommended; profiles retrieved as low as 4.5 km
		SCIAMACHY	imaging spectrometer	limb	v3.01 & v4.2	Aug. 2006 - March 2012	v3.01: 1638; v4.2: 14530	11 - 25 km
	Aqua	AIRS	grating spectrometer	nadir	v6	Aug. 2006 - Dec. 2016	1,892,348	P >= 100 hPa
Ground-based	PEARL Ridge Lab	125HR	Fourier transform spectrometer	sun-viewing	MUSICA v2015	Aug. 2006 - Sept. 2014 (excluding Polar Night)	1889 (standard); 2713 (no SZA filter)	surface to 14 km (upper altitude varies)
	Eureka Weather Station	Radiosondes	capacitance sensor	balloon-borne in situ	Bias corrected and reprocessed	Sept. 2008 - Sept. 2017	5515	surface to 8 - 15 km (upper altitude varies)

Table 5.1: Summary of water vapour datasets used in this study.



Figure 5.1: Temporal range of datasets used in this study. *N* is the number of measurements.



Figure 5.2: Vertical range of datasets used in this study. The colour range shows the number of profiles (N) at each altitude level over the temporal range shown in Fig. 5.1.

# 5.2.1 Radiosondes

Radiosondes launched by the EWS were described in Chapter 2. For the study presented in this chapter, particular attention is needed to determine the altitude range over which measurements are valid. As the balloon rises through the atmosphere, there comes a point where the humidity sensor can no longer report a meaningful value. Limiting the radiosonde humidity measurements to below the tropopause height (TPH) or a typical tropopause value usually ensures that only physically meaningful observations are used; however, this potentially removes valid and useful information in the UTLS.

Eureka radiosonde humidity profiles often have clear structure and information about water vapour above the tropopause, which is typically between 8 and 12 km. Miloshevich et al. (2009) found that the tropopause is not a limiting factor for Vaisala RS92 humidity measurements, and reported close agreement between bias-corrected radiosonde and FPH profiles at temperatures below  $-70^{\circ}$ C and mixing ratios below 5 ppmv. They recommended limiting radiosondes to

pressures greater than 100 hPa during daytime and 75 hPa at night. The mean altitude at which the atmosphere above Eureka has a pressure of 100 hPa is 16.01 km ( $\sigma = 0.47$  km), based on radiosonde measurements between 1961 and 2017. Radiosonde humidity measurements have been limited to altitudes below 15 km for this study as a quality control measure. To correct for known biases in a consistent, transparent, and well-documented manner, the Eureka radiosonde measurements processed with GRUAN software have been used for this study. All references to radiosondes in this chapter refer to the GRUAN-processed radiosonde dataset. In total, this includes 5515 radiosonde profiles acquired between September 3, 2008 and October 7, 2017.

In the troposphere (and sometimes in parts of the lower stratosphere), the uncertainty of Eureka radiosonde water vapour mixing ratio profiles is typically 3 to 5%. Uncertainty in the water vapour mixing ratio, which is calculated from the measured RH, temperature, and pressure values using Equation 2.3, is dominated by the relative humidity uncertainty. Temperature measurement uncertainties are typically a few tenths of a degree. Pressures similarly have uncertainties on the order of tenths of a hPa. There are occasionally thin dry layers in the middle troposphere that have larger humidity uncertainty. These profile elements are kept. If there are sections of the profile larger than 500 m in the troposphere with high uncertainty values, the entire profile is filtered out.

In the lower stratosphere, the radiosonde water vapour profile reaches a point where the uncertainty increases rapidly. This point changes from profile-to-profile. Each individual water vapour profile has been limited to the altitude where this rapid increase in uncertainty occurs by finding where the uncertainty first reaches 20%. This is typically a few kilometers above the tropopause. Thus, each radiosonde profile has a different altitude range, depending on the height reached by the balloon and the uncertainty of the measurements. An example of a profile, showing the impact of the filtering, is shown in Figure 5.3. The mean altitude reached by the filtered profiles is 11.3 km ( $\sigma = 4.4$  km).

Once launched, radiosonde balloons drift away from the site due to winds. The radiosondes used in this study stayed within a mean distance of 29.8 km ( $\sigma = 16.5$  km) from Eureka while under 15 km altitude. The typical distance radiosonde balloons drift from Eureka was shown in Figure 2.14. The mean time to reach 15 km altitude was 54.4 minutes ( $\sigma = 6.2$  minutes).

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Figure 5.3: Eureka radiosonde data taken October 17, 2012, and processed by the GRUAN software, showing the impact of filtering based on a 20% uncertainty threshold. (a) Water vapour mixing ratio in ppmv. (b) Uncertainty in the water vapour mixing ratio. (c) Relative humidity, in units of % relative humidity. (d) Uncertainty in relative humidity in the same units as relative humidity, %. The dashed magenta line shows the height of the tropopause.

#### 5.2.2 PEARL 125HR

The PEARL 125HR water vapour dataset used in this chapter (v2015, type 1) was produced using the MUSICA retrieval technique summarized in Barthlott et al. (2017) and briefly described in Chapter 3. The accuracy of the MUSICA water vapour profiles is about 10% (Schneider et al., 2016). The sensitivity of the retrieval to the atmosphere varies seasonally due to its dependence on the SZA. The retrieval is typically sensitive throughout the troposphere (i.e., sensitivity above 0.9) and there is some sensitivity the lower stratosphere (e.g., sensitivity above 0.5). The MUSICA retrieval's sensitivity to the lower stratosphere is a maximum during March, which is also when ACE coincidences occur with Eureka.

Standard MUSICA quality control filtering excludes measurements recorded at SZAs greater than 78.5°. Due to Eureka's high-latitude location, this filter removes all measurements between February and the end of March, as well as between September and mid-October, which are exactly when there are ACE coincidences with Eureka. This filter has been removed for this study. A study of the MUSICA water vapour total column dataset derived from the PEARL 125HR showed that the SZA limit was likely unnecessarily strict, as agreement did not change between the 125HR and other instruments when the SZA limit was relaxed (Weaver et al., 2017). This was shown in Chapter 4. Standard quality control of the MUSICA dataset, which was applied to the data used here, is described in detail by Barthlott et al. (2017).

#### 5.2.3 ACE on SCISAT

The Canadian Space Agency's (CSA's) SCISAT was launched into a high-inclination (74°) 650-km altitude Earth orbit on August 12, 2003. This orbit enables limb-viewing measurements over the polar regions, as well as other latitudes. A description of the ACE mission is available in Bernath et al. (2005). There are two primary ACE instruments aboard SCISAT: ACE-FTS and ACE-Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (ACE-MAESTRO). They share a sun-tracker. ACE solar occultation limb-viewing observations involve keeping the sun-tracker pointed at the sun as the satellite approaches a sunrise or sunset during its orbit and recording sequences of atmospheric and exo-atmospheric absorption spectra.

Coincidences between ACE and Eureka, e.g. ACE measurements whose 30-km tangent point is within 500 km of Eureka, occur during the months of February, March, September, and October.

348 out of 551 coincidences from ACE and Eureka between August 2006 to March 2017 occurred during February and March.

#### ACE-FTS

ACE-FTS is an FTIR spectrometer built by ABB Inc. It acquires spectra between 750 and  $4400 \text{ cm}^{-1}$  at a resolution of 0.02 cm<sup>-1</sup>. This series of solar occultation measurements, taken every 2 seconds, is used to retrieve trace gas profiles between the mid-troposphere and 150 km with a vertical resolution ranging between 3 and 4 km (Boone et al., 2005, 2013). This technique has a horizontal resolution of ~300 km (Bernath, 2017).

This study uses ACE-FTS v3.6 data, provided on the 1-km altitude grid in water vapour mixing ratio. Measurements with quality control flags identifying outliers, high percent errors, or instrument/processing errors were filtered out, following recommendations in Sheese et al. (2015). The water vapour retrieval is limited to altitudes between 5 and 100 km.

The validation of an earlier version (v2.2) of ACE-FTS (and to a limited extent, ACE-MAESTRO) water vapour retrievals was performed by Carleer et al. (2008). They concluded that ACE-FTS measurements provide accurate H<sub>2</sub>O measurements in the stratosphere (better than 5% from 15-70 km) but expressed no firm conclusions about its water vapour measurements in the upper troposphere. Comparisons to FPH measurements showed a possible small dry bias in ACE-FTS measurements at altitudes near 10 km.

Sheese et al. (2017) examined the current ACE-FTS v3.6 H<sub>2</sub>O product (as well as other molecules) by comparing it with co-located MIPAS and MLS measurements by hemisphere. Correlations between ACE-FTS and MLS were observed to be greater than between ACE-FTS and MIPAS. Their analysis examined stratospheric altitudes, where a mean relative difference in the ACE-FTS water vapour product was observed above 16 km ranging from -12 to 2%. In addition, tight coincidence criteria of 15 minutes and 25 km were applied to examine agreement near the hygropause. A mean dry bias of 20% was observed in ACE-FTS profiles relative to MIPAS v5 and MLS v3.3/3.4 at 13 km altitude.

#### ACE-MAESTRO

ACE-MAESTRO is a dual spectrometer with a wavelength range of 285 to 1015 nm and a resolution of 1.5 to 2.5 nm (McElroy et al., 2007). The ACE-MAESTRO water vapour retrieval algorithm produces profiles with an approximate vertical resolution of 1 km, and is described by Sioris et al. (2010) with updates described in Sioris et al. (2016). Water vapour profiles are retrieved from ACE-MAESTRO optical depth spectra. The tangent height registration of the optical depth spectra relies on matching simulated O<sub>2</sub> slant columns obtained from air density profiles, based on ACE-FTS temperature and pressure, with slant columns observed by ACE-MAESTRO using the O<sub>2</sub> A band. The water vapour profiles are retrieved on an altitude grid that matches the vertical sampling. Within 500 km of Eureka, ACE-MAESTRO water vapour profiles include altitudes ranging between 4 and 25 km.

The ACE-MAESTRO water vapour dataset is sparser than the ACE-FTS dataset for two main reasons. ACE-MAESTRO pointing determination requires the existence of ACE-FTS data, so the available ACE-MAESTRO occultation events are a subset of the ACE-FTS occultations. In addition, ACE-MAESTRO ozone is a necessary input to the water vapour retrieval. The ozone retrieval fails occasionally; this is the cause of most of the measurements missing from the ACE-MAESTRO water vapour product relative to ACE-FTS product.

#### 5.2.4 Aqua

NASA launched the Aqua satellite into a near-polar sun-synchronous 705 km altitude orbit on May 4, 2002. Aqua's orbit has a 1:30 PM equatorial crossing time and an inclination of 98.2°. It is part of the A-Train constellation of Earth-observing satellites. The primary mission of Aqua instruments is to study the atmospheric component of the global water cycle (Parkinson, 2003).

#### AIRS

The AIRS instrument is a hyperspectral thermal infrared grating spectrometer on board Aqua. Its detector observes Earth-emitted radiance from a nadir orientation using 2378 channels between 3.7 and 15.7 µm. AIRS acquires an enormous number of measurements, collecting about three million spectra per day (Chahine et al., 2006).

AIRS water vapour retrievals have been used to study processes such as the water vapour feedback (Dessler et al., 2008), to evaluate climate models (Pierce et al., 2006), and to improve

numerical weather forecasting (Chahine et al., 2006). AIRS aims to produce dense global measurements of temperature and humidity at an accuracy comparable to radiosondes. This study uses level 2 AIRS v6 data, described in detail by Susskind et al. (2003, 2014). The standard temperature product is provided on 28 pressure levels, while the standard water vapour product has 15 pressure levels from 1100 to 50 hPa (e.g., between the surface and approximately 20 km in altitude near Eureka).

Only altitudes that meet the "best" level of quality are used for this study, following the guidelines in the AIRS v6 user guide (Olsen et al., 2017). The altitude range for which AIRS profiles are available varies significantly, with fewer passing the quality control filter at low-tropospheric altitudes. The AIRS retrieval is insensitive to water vapour layers with less than 0.01 mm of integrated water vapour. This approximately translates to water vapour abundances less than 15 ppmv (Olsen et al., 2017), typically affecting profile elements above 15 km near Eureka. AIRS is also limited to altitudes with pressures greater than 100 hPa, and has diminishing sensitivity at altitudes with pressures less than 300 hPa (approximately 9 km near Eureka). As mentioned in the discussion of the radiosondes' altitude range, 100 hPa occurs at approximately 16 km in altitude above Eureka. The relative abundance of AIRS profiles ensures measurements are nonetheless available for comparisons.

# 5.2.5 Aura

NASA's Aura satellite was launched into a near-polar sun-synchronous 705 km orbit on July 15, 2004. It is part of the A-train constellation of Earth-observing satellites, orbiting 15 minutes behind Aqua. Aura's orbit has a 98.2° inclination and an equatorial crossing time near 1:45 PM local solar time. Instruments aboard Aura, such as MLS and TES, study atmospheric chemistry and dynamics.

#### MLS

MLS measures radiation emitted from the atmosphere from a limb-viewing geometry. The atmosphere is scanned twice each minute as the satellite progresses through an orbit that offers a nearly global coverage, between 82°N and 82°S. MLS measurements have been used to assess data from ACE as well as other satellite measurements, e.g., Hegglin et al. (2013) and Sheese et al. (2017). This study uses MLS v4.2 data, described by Livesey et al. (2017).

MLS water vapour profiles are vertically resolved at pressures less than 383 hPa, with a vertical resolution ranging between 1.3 and 3.6 km from 316 to 0.22 hPa (Livesey et al., 2017). At Eureka, MLS's lower altitude limit of 316 hPa corresponds to altitudes near 8 km. MLS water vapour profiles agree within 1% of FPH measurements in the stratosphere, i.e. at P < 100 hPa (Hurst et al., 2014). Hurst et al. (2016) showed that agreement between MLS v4.2 and the FPH measurements began to diverge in 2010 at a rate of approximately 1% per year. At 215 hPa and 316 hPa, MLS v1.5 was observed to have a dry bias of 11 to 23% relative to 10 geographically dispersed FPH measurement sites (Vömel et al., 2007b).

#### TES

TES is an FTS aboard Aura that observes emitted infrared radiance between 650 and 3050 cm<sup>-1</sup> spectral resolution of 0.10 cm<sup>-1</sup> when observing in nadir mode and 0.025 cm<sup>-1</sup> limb-viewing mode (Beer et al., 2001). Limb-scanning measurements were performed only until May 2005. The TES water vapour retrieval uses nadir observations, which have a footprint of 5 km by 8 km. Routine measurements involve a series of observations continuously for 16 orbits (26 hours).

Measurements are only available near Eureka's high Arctic latitude until September 2008. The latitudinal range of TES measurements was limited to latitudes between 50° S and 70° N in summer 2008 to conserve instrument life (Herman et al., 2014). Measurements were further limited to between 30° S and 50° N in spring 2010. However, high-latitude measurements were recorded in July 2011 as part of a special observation set.

TES retrieval v6 is used for this study. It is based on an optimal estimation non-linear leastsquares approach described by Bowman et al. (2006). The vertical information content of TES profiles varies; retrievals with less than 3 DOFS are filtered out. In the subset of measurements examined in this study, TES DOFS range between 3.0 and 5.2.

Comparisons between TES v5 water vapour and global radiosonde measurements have shown a wet bias of 15% in the middle troposphere (Herman et al., 2014). Shephard et al. (2008) compared TES water vapour v3 with radiosondes, finding a wet bias in TES retrievals of between 5% in the lower troposphere and 15% in the upper troposphere.

#### 5.2.6 EnviSat

The European Space Agency (ESA)'s Environmental Satellite (EnviSat) was a large platform for Earth observation instruments. Launched into a polar orbit on March 1, 2002, with an inclination of 98.5° and an equatorial crossing time of 10:00 AM mean local solar time. Observations from its ten instruments ended in April 2012. On board were three atmospheric limb sounders: GOMOS, MIPAS, and SCIAMACHY. Water vapour datasets produced by the latter two instruments are used in this chapter. The decade of measurements taken by MIPAS and SCIAMACHY have been widely used to study atmospheric composition, and are often used in comparisons to other limb sounders.

#### MIPAS

MIPAS is an FTIR spectrometer that observes mid-infrared atmospheric emission from a limbviewing geometry (Fischer et al., 2008). The spectral resolution of MIPAS was reduced from 0.025 cm<sup>-1</sup> to 0.0625 cm<sup>-1</sup> in 2004 due to technical problems. The timeframe examined in this study, 2006 onwards, is entirely during the reduced spectral resolution period. This measurement mode has improved spatial resolution. In polar regions, the nominal tangent altitude spacing is 1.5 km in the UTLS region.

This study uses MIPAS retrieval v5 and v7 from the Institute of Meteorology and Climate Research (IMK). Both retrieval versions cover the same temporal range. This retrieval technique is described by von Clarmann et al. (2009) and uses Tikhonov regularization. In the UTLS, the profiles are provided on a 1-km grid. At 10 km, the vertical resolution (v5) is 3.3 km and the horizontal resolution is estimated to be 206 km (Von Clarmann et al., 2009). Quality control filtering is applied according to recommended values. MIPAS water vapour data are recommended for use only above 12 km altitude. However, in this study all available altitudes provided in the official data release are used. MIPAS water vapour profile retrievals reach altitudes as low as 5 km.

Stiller et al. (2012) compared an earlier version of the MIPAS IMK retrieval (v4) with cryogenic frostpoint hygrometer (CFH) measurements of water vapour profiles during the Measurements of Humidity in the Atmosphere and Validation Experiments (MOHAVE) campaign at the Jet Propulsion Laboratory (JPL) Table Mountain Facility near Wrightwood, California in

October 2009. Above 12 km, MIPAS showed agreement within 10%. Results suggest MIPAS v4 water vapour might be 20-40% wet biased around 10 km.

#### SCIAMACHY

SCIAMACHY is an imaging spectrometer that has limb, nadir, and occultation viewing modes (Bovensmann et al., 1999). Limb measurements of scattered sunlight are the basis for the Institut für Umweltphysik (IUP) v3.01 and v4.2 water vapour retrievals used in this study. Both retrieval versions cover the same temporal range. It is based on the optimal-estimation approach described by Rodgers (2000) using a first-order Tikhonov constraint. The vertical resolution is approximately 3 km. The retrieval calculates a scaling factor for the tropospheric water vapour profile; altitudes below 10 km are not recommended for use and are not used here. The details of this retrieval are described in Weigel et al. (2016) for v3.01. For v4.2, several changes were implemented to improve the aerosol correction and the vertical resolution. Additionally, version v4.2 uses all appropriate SCIAMACHY measurements, while v3.01 only uses a subset. One issue for limb sensing is the need for cloud-free scenes. This is limited by the sampling approach, which was constrained by the data rate available on EnviSat.

Weigel et al. (2016) compared MIPAS v3.01 to MIPAS v5, MLS v3.3, and other satellite datasets, in 30° latitudinal bands. Results showed SCIAMACHY limb measurements between 10 and 25 km in altitude were reliable between 11 and 23 km, and accurate to about 10% between 14 and 20 km. Below 14 km, differences with other datasets increase to up to 50%, showing a possible SCIAMACHY v3.01 wet bias, which is most pronounced in the tropics and least in the polar latitudes.

# 5.3 Comparison of water vapour measurements

Water vapour profiles from ACE-FTS, ACE-MAESTRO, AIRS, MIPAS, MLS, SCIAMACHY, and TES were compared with Eureka radiosonde and PEARL 125HR measurements following the methodology described below.

#### 5.3.1 Method

Coincident profile measurements have been compared using difference and correlation plots. Absolute differences and percent relative differences were calculated using:

$$difference = X - Y, \tag{5.1}$$

$$\% difference = \frac{(X-Y)}{Y} \times 100\%, \tag{5.2}$$

where X is the satellite measurement and Y is the reference measurement, e.g. the 125HR or radiosondes.

To show the overall agreement observed between the measurements, the means of coincident profile differences were calculated. Altitude ranges for which there are measurements available vary for each contributing matched pair of profiles, resulting in a variable number of profiles contributing to comparisons at each altitude. The number of contributing matches at each altitude level is reported in the comparison figures.

In addition to showing profile comparisons, comparisons at specific representative altitudes are presented. These illustrate the extent of the variability in the overall mean agreement between the datasets.

A minimum number of 15 coincidences ( $N \ge 15$ ) is chosen for results to be reported and shown in the tables and figures. This aimed to balance the reality that there are limited numbers of coincidences available and the need to ensure there are a meaningful number of comparison results available at each altitude.

#### 5.3.2 Coincidence criteria

A three-hour temporal coincidence criterion was used for all comparisons and applied in two ways. Firstly, if multiple coincidences were found within this interval, only the closest pair was kept. Each pair of coincident measurements is thus independent of others. The comparisons were also performed using all possible coincidences within this criterion. While increasing the number of matches, in some cases significantly, the observed agreement between instruments was similar to that for the first method, which is summarized in Tables 5.2 and 5.3, later in this chapter. Results using the first method are discussed below. Results of comparisons where all possible coincidence pairs are used are available in Supplementary Tables 1 and 2 of Weaver et al. (2018).

A 500 km spatial coincidence criterion was also applied. The spatial criterion is similar in scale to the horizontal area covered by a limb-viewing satellite measurement. When calculating the distance between PEARL and an ACE observation, the 30 km (calculated geometrically) tangent height of the ACE measurement was used as the satellite measurement's position. This approach has previously been used for ACE validation, e.g., Fraser et al. (2008).

The difference in measurement geometries, and the long path of a limb-viewing measurement in particular, can result in ACE-FTS measuring a different airmass than the 125HR and radiosondes. Figure 5.4 illustrates the variation of water vapour abundances in the region around Eureka using AIRS measurements at 400 hPa (corresponding to altitudes between 6.1 and 7.5 km, with a mean altitude of 6.7 km and a standard deviation of 0.2 km) for two sample months, March and July, in a representative year (2015). Variability in the water vapour abundances in the region around Eureka is seen to be larger in the summer than in the winter. October resembles the results shown for March.

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Figure 5.4: AIRS water vapour abundances at 400 hPa near Eureka (indicated by red star), in March and July, 2015.

# 5.3.3 Smoothing

When comparing satellite profiles with the PEARL 125HR, the comparison instrument's profile was smoothed by the MUSICA averaging kernel of the 125HR measurement to account for the vertical resolution differences between the instruments. The procedure for smoothing followed Rodgers and Connor (2003):

$$\boldsymbol{x_{smoothed}} = \boldsymbol{A}(\boldsymbol{x} - \boldsymbol{x_a}) + \boldsymbol{x_a}, \tag{5.3}$$

where  $x_a$  is the MUSICA a priori profile, x is the comparison instrument profile, and A is the averaging kernel matrix. Since the MUSICA water vapour retrievals are performed on a logarithmic scale, the smoothed profile was calculated using:

$$\boldsymbol{x_{smoothed}} = e^{A(x-x_a)+x_a},\tag{5.4}$$

where  $x, x_a$ , and A are in log<sub>e</sub> space.

Before smoothing, the satellite profile was interpolated to the MUSICA retrieval grid and the MUSICA a priori profile was used to fill gaps in the comparison profile (e.g., altitudes beneath

the lower limit of satellite measurements). After smoothing, altitudes for which there were no original data were removed.

When comparing satellite measurements to the radiosonde profiles, radiosonde profiles were smoothed using the satellite's averaging kernels where possible, i.e., for SCIAMACHY and TES, following the same procedure described for the 125HR. MIPAS retrievals do not use an a priori profile, so the smoothed radiosonde profile is calculated using:

$$\boldsymbol{x_{smoothed}} = e^{A\boldsymbol{x}}.$$

In the cases of ACE-FTS, ACE-MAESTRO, AIRS, and MLS, the radiosonde profiles have been smoothed using Gaussian weighting functions with a full-width half-maximum (FWHM) that approximates the vertical resolution of the satellite measurement. This procedure is used because ACE retrievals do not have averaging kernels. MLS has an averaging kernel for the polar regions; however, the user's guide states that the use of the water vapour averaging kernel at the lowest valid altitude levels (i.e., lower stratosphere at 316 hPa and 262 hPa) is not recommended (Livesey et al., 2017). Since these altitudes are of particular interest to this study, the MLS averaging kernels are not suitable. AIRS also has averaging kernels, distributed in supplementary data files; however, the AIRS averaging kernels only capture the information added during the final physical retrieval, but not information extracted from the AIRS radiances during the neural network step. The width of the AIRS weighting functions is used to estimate a Gaussian smoothing function that generally overestimates the amount of smoothing. Thus, weighting functions are used in these cases as a reasonable approximate method of smoothing the vertical resolution of these profiles.

To create weighting functions, first, Gaussian functions are calculated using:

$$GF(z) = \left(\sqrt{2\pi} \cdot \frac{FWHM}{2\sqrt{2ln2}}\right)^{-1} \cdot \exp\left(\frac{-(z-z_0)^2}{2(\frac{FWHM}{2\sqrt{2ln2}})^2}\right),\tag{5.6}$$

where FWHM is the full-width half-maximum, z is the new low-resolution grid point,  $z_o$  are the original altitude levels.

Weighting functions were calculated by sampling the GF at the original radiosonde measurement altitude levels and normalizing the GF so that the total weight assigned to all profile elements is equal to one. The weighting functions are different for each pair of coincident profiles because the vertical sampling of each radiosonde profile varies. Lastly, smoothed profiles were calculated by convolving the water vapour VMR profile of the radiosonde with the weighting functions (*wf*):

$$x_{smoothed}(z_i) = \sum_{i=1}^{N} w f_i \cdot \text{VMR}(z).$$
(5.7)

An example of weighting functions used to align the radiosonde measurement with the approximate vertical resolution of ACE-FTS is shown in Figure 5.5 (a). Figure 5.5 (b) shows an example of a radiosonde profile before and after smoothing. Weighting functions with a FWHM equal to 3.0 km have been used to approximate the vertical resolution of ACE-FTS, while comparisons to ACE-MAESTRO, AIRS, and MLS used weighting functions with a FWHM of 1.0 km.



Figure 5.5: (a) An example of the weighting functions used to smooth the radiosonde profiles to ACE-FTS vertical resolution. (b) The corresponding radiosonde profile, both as measured (blue line) and after smoothing (maroon line) with the weighting function shown in (a).
# 5.4 Comparison results

Results between the satellites and the 125HR at 6.4 km are highlighted because the 125HR has very good sensitivity at that altitude, and this is near the lowermost altitude reached by the ACE measurements. Comparison results between the satellites and the radiosondes are highlighted at 10 km because radiosondes have sensitivity at that altitude and this is the lowermost altitude of other comparison studies, e.g., Sheese et al. (2017), and it is near the lower limit of many satellite datasets.

Some combinations of instruments did not have significant overlap in time, location, or vertical sensitivity. MIPAS and the radiosondes had no coincidences due to a mismatch in the time of day of the measurements as well as the quality control filtering. The temporal ranges of the TES and radiosonde datasets did not overlap. SCIAMACHY did not have any coincidences with the radiosondes, unless the coincidence criterion was expanded to 6 hours. Even then, only eight matches were found. SCIAMACHY and the 125HR had 201 coincidences; however, SCIAMACHY is limited to altitudes above 10 km, where the 125HR has limited sensitivity.

### 5.4.1 Ground-based reference measurements

As illustrated in Figure 5.6, comparison between the 125HR and 137 coincident (GRUANprocessed) radiosonde profiles smoothed by 125HR averaging kernels shows agreement within 5% between 8 and 14 km; the 125HR has a wet bias relative to the radiosonde profiles below 8 km of approximately 8% (with closer agreement below 2 km). This is similar to the 6% wet bias in the PEARL 125HR total columns relative to the Eureka radiosondes reported by Weaver et al. (2017) and shown in Chapter 4. If all possible coincident pairs are used, rather than limiting comparisons to unique pairs, the number of contributing matches increases to 270 and the agreement is very similar.



Figure 5.6: Comparison between Eureka (GRUAN-processed) radiosonde and PEARL 125HR water vapour VMR. (a) Mean profiles (solid lines)  $\pm$  the standard deviation (dashed lines). (b) Mean VMR difference (where X = radiosonde and Y = 125HR), using Equation 5.1. (c) Mean percent difference, using Equation 5.2. Grey dotted lines show  $\pm 10\%$ . In (b) and (c), the colour shading shows the number (N) of differences in each hexagon. (d) Number of coincident profile pairs at each altitude level.

### 5.4.2 ACE-FTS

76 pairs of coincident ACE-FTS and PEARL 125HR measurements show close agreement. Between 6 and 9 km, agreement is within 11 ppmv and 13%; between 8 and 14 km, agreement was within 1.4 ppmv and 10%. Full profile comparisons are shown in Figure 5.7. The mean difference of 18 coincident profiles at 6.4 km was  $-6.3 \pm 8.4$  ppmv ( $0.2 \pm 6.8\%$ ); the time series of differences at 6.4 km are shown in Figure 5.8. At 8.0 km, 46 coincident measurements agreed to within  $1.4 \pm 2.6$  ppmv ( $7.2 \pm 6.6\%$ ). Correlation plots at 6.4 km, 8.0 km, and 9.8 km are presented in Figure 5.9. Between 6 and 14 km, correlation coefficients (*R*) are between 0.48 and 0.80. Expanding the time criterion to 6 hours nearly doubles the number of coincidences but results in similar agreement. Overall, relative to the 125HR, ACE-FTS shows a wet bias between 8 and 14 km of 7 to 10% and small differences of approximately 10 ppmv (2%) near 6 km (Figure 5.7).



Figure 5.7: Summary of differences between satellite measurements (X) and PEARL 125HR (Y). (a) The mean of profiles used in the comparison. (b) The mean VMR difference between the satellite profiles and the 125HR profiles, using Equation 5.1. (c) The mean percent difference between the satellite profiles and the 125HR profiles, using Equation 5.2. (d) The number of coincident profile pairs contributing to the comparison at each altitude level. Grey dotted lines in (b) and (c) show  $\pm 10$  ppmv and  $\pm 10\%$ , respectively.



Figure 5.8: Time series of percent differences between satellite and 125HR water vapour measurements at 6.4 km altitude for (a) ACE-FTS and ACE-MAESTRO, (b) AIRS, (c) MIPAS and TES. In each case, the differences follow Equation 5.2, where the satellite is X and the PEARL 125HR is Y.



Figure 5.9: Correlation plots for the ACE-FTS, ACE-MAESTRO, and AIRS satellite measurements vs. 125HR at three altitudes. The number of points in a given hexagon is colour-coded to show the density of the points. The scale at the end of a row shows the colour map used for that row. Solid black lines are 1:1 reference lines, i.e., slope = 1; green dashed lines are lines of linear best fit. N is the number of coincident measurements for comparisons between the instruments at that altitude. R is the correlation coefficient. m is the slope of the best fit line.

108 coincident measurements were found between ACE-FTS and Eureka radiosondes. Profile differences are shown in Figure 5.10. Figure 5.11 shows these results along with results from other satellite comparisons with the radiosondes. Between 7 and 11 km, differences are within 6 ppmv (12%). At 6 km, ACE-FTS and radiosonde profiles mean differences are  $-13.3 \pm 12.1$  ppmv (22.8  $\pm$  9.2%). Differences at 10 km,  $-5.4 \pm 2.0$  ppmv ( $-9.1 \pm 6.9$ %), are shown in Figure 5.12 (a). Correlation plots at 6.4 km, 8.0 km, and 9.8 km are shown in Figure 5.13. Correlation coefficients between 6 and 12 km range between 0.52 and 0.94.



Figure 5.10: Summary of differences between ACE satellite measurements (X) and Eureka radiosondes (Y). (a) The mean of profiles used in the comparisons. (b) The mean VMR difference between the ACE profiles and the radiosonde profiles, using Equation 5.1. (c) The mean percent difference between the ACE profiles and the radiosonde profiles, using Equation 5.2. (d) The number of coincident profiles contributing to the comparison at each altitude level. Grey dotted lines in (b) and (c) show  $\pm 10$  ppmv and  $\pm 10\%$ , respectively.



Figure 5.11: Summary of differences between satellite measurements (X) and Eureka radiosondes (Y). (a) The mean of profiles used in the comparison. (b) The mean VMR difference between the satellite profiles and the radiosonde profiles, using Equation 5.1. (c) The mean percent difference between the satellite profiles and the radiosonde profiles, using Equation 5.2. (d) The number of coincident profiles contributing to the comparison at each altitude level. Grey dotted lines in (b) and (c) show  $\pm 10$  ppmv and  $\pm 10\%$ , respectively.



Figure 5.12: Percent differences between satellite measurements and the Eureka radiosondes at 10 km altitude, for (a) ACE-FTS and ACE-MAESTRO, (b) AIRS, (c) MLS. In each case, the differences follow Equation 5.2, where the satellite is *X* and the Eureka radiosondes are *Y*.



Figure 5.13: Correlation plots for the ACE-FTS, ACE-MAESTRO, and AIRS satellite measurements vs. Eureka radiosondes at three altitudes. The number of points in a given hexagon is colour-coded to show the density of the points. The scale at the end of a row shows the colour map used for that row. Solid black lines are 1:1 reference lines, i.e., slope = 1; green dashed lines are lines of linear best fit. N is the number of coincident measurements for comparisons between the instruments at that altitude. R is the correlation coefficient. m is the slope of the best fit line.

In addition, comparisons have been done between the ACE-FTS and AIRS, using AIRS as the reference (i.e., *Y* in Equations 5.1 and 5.2) to provide additional comparisons with a relatively large number of coincidences. Differences at 10 km were  $-1.5 \pm 0.3$  ppmv ( $-6.1 \pm 1.7\%$ ), increasing at lower altitudes to  $-17.0 \pm 3.7$  ppmv ( $39.6 \pm 4.3\%$ ) at 6 km. Correlation coefficients for altitudes between 6 and 12 km were between 0.62 and 0.81. Correlation plots of ACE-FTS vs. AIRS at 6, 8, and 10 km are shown in Figure 5.14.



Figure 5.14: Correlation plots for ACE-FTS and ACE-MAESTRO vs. AIRS satellite measurements at three altitudes. The number of points in a given hexagon is colour-coded to show the density of the points. The scale at the end of a row shows the colour map used for that row. Solid black lines are 1:1 reference lines, i.e., slope = 1; green dashed lines are lines of linear best fit. N is the number of coincident measurements for comparisons between the instruments at that altitude. R is the correlation coefficient. m is the slope of the best fit line.

### 5.4.3 ACE-MAESTRO

27 coincident measurements found between ACE-MAESTRO and the PEARL 125HR show agreement within 12 ppmv (7%) between 6 and 8 km and within 3 ppmv (12%) between 9 and 14 km. Overall, between 6 km and 14 km, ACE-MAESTRO shows a dry bias of approximately 10% relative to the 125HR (Figure 5.7). Examining the agreement at specific altitudes in the middle and upper troposphere shows scatter around the zero line, illustrated in Figure 5.8.

103 coincident ACE-MAESTRO and radiosonde profiles were found with overlap between 5 and 11 km. Mean differences were large at 5 km, e.g.,  $-84.0 \pm 121.1$  ppmv ( $123.4 \pm 71.1\%$ ). Percent differences oscillate around -10% between 7 and 10 km. At 8 km, ACE-MAESTRO had 90 coincidences with the radiosondes, with differences of  $-16.3 \pm 8.7$  ppmv and  $-7.6 \pm 9.4\%$ . At 10 km, absolute and relative mean differences were  $-2.6 \pm 3.2$  ppmv and  $-5.9 \pm 10.9\%$ , respectively, shown in Figure 5.12.

In addition, comparisons have been done between ACE-MAESTRO and AIRS, using AIRS as the reference. Differences at 10 km were  $-0.7 \pm 0.9$  ppmv ( $-10.5 \pm 3.7\%$ ), decreasing at lower altitudes to  $-13.7 \pm 7.5$  ppmv ( $69.9 \pm 13.5\%$ ) at 6 km. Correlation coefficients for altitudes between 6 and 12 km were about 0.45. Correlation plots of ACE-MAESTRO vs. AIRS at 6, 8, and 10 km are presented in Figure 5.14.

# 5.4.4 Other satellite measurements vs. the 125HR and radiosondes AIRS

Close agreement was observed between 3189 coincident AIRS and 125HR measurements and between 2489 coincident AIRS and radiosonde profiles. AIRS profiles agree with the 125HR within 5% between 1 km and 14 km, as shown in Figure 5.7. A mean agreement of  $-9.7 \pm 3.5$  ppmv ( $-1.6 \pm 1.5\%$ ) was observed between AIRS and 125HR measurements at 6.4 km, where both instruments have good sensitivity. This is shown in Figure 5.8 (b). In the midtroposphere, agreement is within 4%, e.g., at 3.0 km, the mean difference is  $-3.8 \pm 1.6\%$  ( $\sigma = 32.7$ ). Correlation coefficients at all altitudes are above 0.84. Correlation plots for AIRS vs. 125HR at 6.4, 8.0, and 9.8 km are shown in Figure 5.9.

Mean agreement within 5% is observed between AIRS and the radiosondes between 1 and 7 km, as shown in Figure 5.11. Differences as large as 13% are observed between 8 km and 14 km.

Differences at 10 km are shown in Figure 5.12 (b), where scatter around zero is seen. As well, the time series of differences shows a potential seasonality to the agreement, with a low (dry) bias maximum in summer. Tightening the coincidence criteria to 2 hours and 25 km significantly reduces the number of matches, with 45 contributing to comparisons at 1 km and 1255 contributing to comparisons at 8 km. Results from these tighter matches show differences of less than 4% between 2 and 7 km, with slightly larger differences at 1 km, a mean difference of  $7.5 \pm 0.8\%$  ( $\sigma = 30.4$ ). Differences remained similar between 8 and 14 km with these stricter coincidence criteria.

### MIPAS

MIPAS v5 and v7 comparisons with the PEARL 125HR show a dry bias of approximately 15% in the upper troposphere. At 6.4 km, the lowest altitude available for comparisons with a reasonable number of coincident measurements (N = 64), mean differences using MIPAS v5 were  $-38.2 \pm 11.9$  ppmv ( $-22.4 \pm 7.8\%$ ). MIPAS v7 showed differences similar to v5 with respect to the 125HR at 6.4 km, i.e.  $-46.9 \pm 11.2$  ppmv ( $-25.3 \pm 5.9\%$ ). The time series of differences between the 125HR and MIPAS datasets at 6.4 km is illustrated in Figure 5.7 (c), showing large scatter around the zero line. Correlation at 6.4 km was moderate (R = 0.50). Between 7 and 14 km a good correlation was observed for both retrieval versions (R > 0.81). Agreement improves between 7 and 10 km. MIPAS v5 reaches a mean difference of  $-3.6 \pm 0.4$  ppmv ( $-10.1 \pm 1.1\%$ ) at 9.8 km. Above 10 km, differences are small, better than 2 ppmv and 7%.

No MIPAS measurements were coincident with radiosondes, due to the partial overlap of the datasets (September 2008 to April 2012), and also because MIPAS only had Eureka coincidences during mid-day and mid-night, resulting in no matches within 3 hours of radiosonde launches.

If AIRS is used as a reference, MIPAS v5 and v7 have hundreds or thousands of matches for comparison at each altitude level. The results show that MIPAS has a dry bias relative to AIRS of approximately 15% between 6 and 10 km, comparable to the 125HR results.

### MLS

Relative to the 125HR, an MLS dry bias is observed in the UTLS, where mean differences range from  $-8.8 \pm 0.4$  ppmv ( $-18.6 \pm 0.8\%$ ) at 8.8 km to  $-0.0 \pm 0.0$  ppmv ( $-42.8 \pm 17.8$  ppbv;  $-0.3 \pm 0.4\%$ ) at 13.6 km. This can be seen in Figure 5.7. At 9.8 km, mean differences between 2443 coincidences were  $-4.8 \pm 0.2$  ppmv ( $-12.5 \pm 0.6\%$ ); at 12.0 km, mean differences between 2445 coincidences were  $-0.4 \pm 0.0$  ppmv ( $-4.6 \pm 0.5\%$ ).

MLS comparisons with the radiosondes have overlap only between 9 and 13 km; comparisons are shown in Figure 5.11. At altitudes between 9 and 12 km the matched measurements are highly correlated, with *R* values between 0.83 and 0.92. Comparisons between MLS and radiosondes showed a dry bias at altitudes between 8 and 12 km. At 10 km, MLS had 447 coincidences with radiosonde measurements, with a mean differences of  $-5.1 \pm 1.2$  ppmv ( $-25.6 \pm 1.4\%$ ). The time series of differences between MLS and the radiosondes at 10 km is shown in Figure 5.12 (c).

### SCIAMACHY

SCIAMACHY could be compared only with the 125HR, as its measurements did not have coincidences with the radiosonde dataset used in this study. 201 SCIAMACHY v3.01 and 1506 SCIAMACHY v4.2 profiles had coincidences with the 125HR; however, these are limited to altitudes above 10 km. Profile comparison results are shown in Figure 5.7. For both retrieval versions, a small dry bias is seen with respect to the 125HR at 10.8 and 12.0 km, i.e. 5% for v3.01 and 10% for v4.2. At 13.6 km, mean differences were about 1%.

### TES

TES shows moderate agreement with the PEARL 125HR, but TES had only a single coincidence with the Eureka radiosonde dataset. The latter is largely because TES had no coincidences with Eureka after September 2008, except for a few during mid-July 2011 (Figure 5.1). As seen in Figure 5.7, 361 TES measurements showed a dry bias relative to the 125HR of approximately 10% in the lower troposphere, a small dry bias to a small wet bias in the mid-troposphere, and a wet bias (e.g. 20-25%) in the UTLS. The time series of differences at 6.4 km is shown in Figure 5.8 (c), where large scatter around the zero line is seen, e.g.,  $\sigma = 75.1\%$ .

### 5.4.5 Summary of profile comparisons

A summary of comparisons between the satellites and the PEARL 125HR is presented in Table 5.2. Table 5.3 provides a summary of the comparisons between the satellites and the Eureka radiosondes. In addition to the number of measurements, means, standard deviations, and SEMs at each altitude, these tables also include the medians of the differences. If the distance criterion was reduced to 350 km, similar differences were observed, but with a much smaller number of coincident measurements in some cases. There is no apparent temporal trend in the differences between satellite datasets and the Eureka-based reference measurements.

In a few of the comparisons, the reported means of the absolute differences and percent differences had different signs, e.g., the mean of the absolute differences was negative while the mean of the percent differences was positive, e.g., the comparison between AIRS and the radiosondes at 12 km. This is the result of reporting the mean of individual comparisons, rather than comparing the mean profiles of each instrument. The latter would ensure that the sign is always the same in both cases. The medians of the absolute differences and percent differences were always of the same sign. Figure 5.15 shows an example of the differences histogram for the AIRS vs. radiosondes comparison at 6.0 km. The distribution is approximately Gaussian, but there is a small skewness that differs between the absolute differences are of opposite signs, the medians are the same sign. Histograms were plotted for the differences between each instrument comparison at each altitude discussed in this study. These results indicated that the differences are typically distributed in a nearly Gaussian manner, justifying the use of the mean, SEM, and standard deviation to characterize the results.



Figure 5.15: Histogram of (a) absolute differences and (b) percent differences between AIRS and the Eureka GRUAN-processed radiosondes (AIRS – radiosondes) at 6.0 km altitude. Red dashed lines are the mean of the differences, blue dashed lines are the means  $\pm \sigma$ , and the tan solid lines show the median of the differences.

Instrument	Altitudo		Mean	σ [ppmv]	Median	Mean	σ [%]	Median
(retrieval		N	difference $\pm$		difference	difference $\pm$		difference
version)	[ĸm]		SEM [ppmv]		[ppmv]	SEM [%]		[%]
ACE-FTS	6.4	18	$-6.3 \pm 8.4$	35.7	-2.0	$+0.2 \pm 6.8$	28.9	-4.0
(v3.6)	8.0	46	$+1.4 \pm 2.6$	17.6	-1.4	$+7.2 \pm 6.6$	44.8	-1.4
	9.8	65	$\pm 0.5 \pm 0.4$	3.3	-0.1	$+6.1 \pm 3.9$	31.8	-1.4
	12.0	74	$+0.4\pm0.1$	0.9	+0.3	$+9.7\pm2.8$	23.8	+7.7
ACE-MAESTRO	6.4	18	$-11.9\pm16.7$	71.0	-20.9	$-6.7 \pm 19.2$	81.5	-30.0
(v30)	8.0	23	$-5.6\pm6.5$	31.4	-9.0	$-6.1 \pm 18.7$	89.6	-29.5
	9.8	25	$-2.0 \pm 1.5$	7.3	-3.4	$-10.8\pm14.7$	73.6	-28.8
	12.0	26	$-0.6\pm0.3$	1.7	-0.8	$-11.4 \pm 9.5$	48.5	-22.3
AIRS	3.0	434	$-92.8\pm17.0$	354.2	-61.4	$-3.8\pm1.6$	32.7	-9.2
(v6)	6.4	881	$-9.7\pm3.5$	105.1	-15.5	$-1.6 \pm 1.5$	75.9	-10.5
	8.0	1448	$-11.1 \pm 1.5$	56.6	-6.8	$-2.9\pm1.0$	38.8	-8.7
	9.8	2517	$-2.7\pm0.2$	11.4	-1.6	$-3.5\pm0.6$	31.5	-8.6
	12.0	2798	$-0.1\pm0.0$	1.8	-0.0	$\pm 1.8 \pm 0.4$	23.4	-0.8
MIPAS	6.4	24	$-38.2 \pm 11.9$	58.3	-24.4	$-22.4 \pm 7.8$	38.1	-25.5
(IMK v5)	8.0	93	$-15.8\pm3.0$	29.2	-9.3	$-18.7 \pm 3.2$	30.4	-22.0
	9.8	604	$-3.6\pm0.4$	9.5	-2.3	$-10.1 \pm 1.1$	27.7	-14.2
	12.0	897	$-0.3\pm0.0$	1.7	-0.2	$-1.4 \pm 0.7$	21.9	-4.2
MIPAS	6.4	32	$-46.9 \pm 11.2$	63.4	-25.3	$-25.3 \pm 5.9$	33.5	-24.4
(IMK v7)	8.0	96	$-17.0 \pm 3.1$	30.0	-9.8	$-20.1 \pm 3.1$	29.7	-22.5
	9.8	634	$-3.8\pm0.4$	9.7	-2.3	$-10.3 \pm 1.1$	27.5	-13.9
	12.0	902	$-0.3\pm0.0$	1.8	-0.2	$-1.4 \pm 0.7$	22.0	-4.0
MLS	8.0	13	$-15.9 \pm 2.8$	10.2	-12.4	$-33.1 \pm 3.6$	12.9	-34.2
(v4.2)	9.8	2443	$-4.8\pm0.2$	11.9	-3.2	$-12.5 \pm 0.6$	29.7	-17.1
	12.0	2445	$-0.4\pm0.0$	1.9	-0.4	$-4.6 \pm 0.5$	23.0	-7.7
SCIAMACHY (IUP v3.01)	12.0	201	$-0.1 \pm 0.1$	1.9	-0.4	$-1.8 \pm 1.9$	26.7	-7.8
SCIAMACHY (IUP v4.2)	12.0	1506	$-0.4\pm0.0$	1.5	-0.4	$-5.7\pm0.5$	21.2	-7.5
TES	3.0	361	$-168.2 \pm 45.2$	859.6	-112.6	$-1.0 \pm 2.3$	43.4	-9.0
(v6)	6.4	361	$+66.9\pm15.6$	296.7	+19.5	$+23.8\pm3.9$	75.1	+6.6
	8.0	361	$+30.2\pm5.8$	110.8	+13.0	$+27.6 \pm 4.0$	76.2	+11.9
	9.8	361	$+6.4 \pm 1.0$	19.4	+4.6	$+26.0 \pm 3.2$	60.4	+16.2
	12.0	361	$+1.5 \pm 0.2$	3.0	+1.3	$+23.5 \pm 2.1$	39.2	+19.7

Table 5.2: Summary of satellite vs. 125HR comparison results. Differences are satellite – 125HR.

Instrument (retrieval version)	Altitude [km]	Ν	Mean difference ± SEM [ppmv]	σ [ppmv]	Median difference [ppmv]	Mean difference ± SEM [%]	σ [%]	Median difference [%]
ACE-FTS	6.0	57	$-13.3 \pm 12.1$	91.5	+13.6	$+22.7\pm9.2$	69.1	+10.3
(v3.6)	8.0	92	$-1.8 \pm 3.6$	34.7	1.8	$-1.8 \pm 7.2$	69.5	+4.7
	10.0	51	$-5.4\pm2.0$	14.0	-0.4	$-9.1\pm6.9$	49.4	-3.2
	12.0	19	$+1.2\pm0.4$	1.6	+1.7	$+32.0\pm6.6$	28.6	+36.2
ACE-MAESTRO	6.0	54	$-62.4\pm36.8$	270.7	-29.3	$+27.0\pm24.8$	181.9	-25.6
(v30)	8.0	90	$-16.3 \pm 8.7$	82.3	-11.7	$-7.6\pm9.4$	89.5	-34.4
	10.0	41	$-2.6 \pm 3.2$	20.3	-1.2	$-5.9\pm10.9$	89.5	-12.8
	12.0	12	$-1.3\pm0.6$	2.0	-2.0	$-35.8\pm10.6$	36.9	-45.8
AIRS	3.0	584	$-27.5 \pm 16.8$	407.0	-38.3	$+5.4 \pm 1.9$	46.2	-4.8
(v6)	6.0	1423	$-15.6 \pm 2.5$	93.7	-3.7	$+3.0 \pm 1.0$	39.0	-3.4
	8.0	2127	$+3.1\pm0.9$	42.3	+3.8	$+12.7\pm0.7$	34.2	+8.4
	10.0	868	$-11.2 \pm 0.6$	18.6	-4.2	$-12.4\pm0.9$	27.5	-14.0
	12.0	50	$-2.0 \pm 1.2$	8.3	+0.4	$+5.2 \pm 4.1$	28.8	+8.9
MLS	8.0	12	$-34.1 \pm 28.3$	98.2	-6.6	$-25.6 \pm 14.8$	51.1	-35.6
(v4.2)	10.0	447	$-5.1 \pm 1.2$	25.0	-3.5	$-25.6 \pm 1.4$	29.4	-28.0
	12.0	42	$-2.4 \pm 1.2$	7.7	+0.0	$-4.9 \pm 4.0$	26.1	+0.1

Table 5.3: Summary of satellites vs. radiosonde comparison results. Differences are satellite – radiosondes.

# 5.5 Discussion

This study's moderately tight temporal criterion, 3 hours, aimed to minimize the impact of water vapour's variability on the observed agreement between measurements by different instruments. The variability of water vapour over the 500 km distance criterion likely contributes to the differences observed between measurements. This is especially true for lower-tropospheric measurements, given the variability of surface terrain in the region around Eureka. The seasonally-changing TPH also introduces a source of variability, particularly for altitudes between 8 and 10 km. In the summer, the TPH is often above 8 km at Eureka, and sometimes is above 10 km. The TPH can be as low as 6 km. H<sub>2</sub>O abundances and variability are typically larger at altitudes below the TPH. However, no seasonal pattern in the differences were observed, or pattern with respect to the TPH.

Measurement techniques also result in differences in the air sampled. While radiosondes measure air close to Eureka throughout their profile, the 125HR's solar-viewing geometry primarily samples air south of Eureka due to the large SZA of high-latitude measurements. The limbsounding satellite measurement techniques of ACE-FTS, ACE-MAESTRO, MIPAS, MLS, and SCIAMACHY yield vertical profiles by observing across long horizontal stretches of atmosphere. While this technique enables the retrievals to resolve vertical structure, this horizontal path results in profiles containing information about the atmosphere across an extended area. Thus, exact agreement between the satellite and ground-based measurements is not expected. It is worth noting that all of the instruments' measurement techniques observe the atmosphere only in cloud-free conditions, except the Eureka radiosondes.

Since ACE coincidences with Eureka are limited to periods of time when water vapour abundances are relatively similar across the region, the distance criterion is expected to have less impact on the observed agreement than if year-round measurements were compared. Typical March and July water vapour abundances in the area around Eureka at a specific altitude were shown in Figure 5.4.

Agreement between both ACE instruments and the Eureka reference measurements was closer than that observed in global comparisons conducted by Carleer et al. (2008), which examined an earlier version of these water vapour datasets (ACE-FTS v2.2 and ACE-MAESTRO v1.0) and reported differences on the order of 40% at altitudes lower than 15 km and a possible dry bias at

around 10 km altitude. Sheese et al. (2017) reported an ACE-FTS negative bias ranging between 3 and 20% relative to MLS and MIPAS at around 14 km; however, the Sheese et al. analysis involves measurements taken over a broad range of global geographic locations and did not discuss altitudes below 13 km.

The ACE-FTS comparisons presented here show a positive (wet) bias of between 7 and 10% relative to the 125HR in the 8 to 14 km altitude range. Relative to the Eureka radiosondes, ACE-FTS shows close agreement (within 4% or 6 ppmv) in the upper troposphere (7 to 9 km). At altitudes above 10 km, a positive (wet) bias relative to the radiosondes is observed, ranging between 12 and 32%, although this corresponds to very small mean differences, i.e. of about 1 ppmv. If AIRS is taken as a reference, a larger number of coincidences is found and similar results are observed, although with closer agreement around 10 km.

ACE-MAESTRO profiles show a dry bias relative to the 125HR of approximately 10% down to 7 km. Comparisons to the radiosondes also showed a dry bias, ranging from -3% at 7 km to -21% at 11 km. At 6 km and below, differences between ACE-MAESTRO and the radiosonde profiles are large, as was the case in the 125HR comparison; however, in both cases there are too few coincidences for firm conclusions. Using AIRS as a reference results in hundreds of coincidences and similar results, e.g. similar magnitudes with an increasingly large difference at altitudes below 7 km.

ACE-MAESTRO shows weak correlations with the Eureka 125HR and radiosonde datasets in Figures 5.7 and 5.10. However, this is likely due to the combination of water vapour's variability, seen in the Figure 5.9 and 5.13 correlation plots involving AIRS, and the relatively small number of coincidences found. As shown in Figure 5.14, the number of coincidences and the correlations between ACE-MAESTRO and AIRS are much larger, e.g. N = 233 and R = 0.64 at 10 km, while the differences are similar to other comparisons, e.g., there were large differences at 6 km. In addition, the correlation and best-fit line are impacted by outlier points at low altitudes (e.g., at 6.4 km in the comparison with the 125HR) that influence the overall statistics because of the relatively small number of coincidences at those altitudes. ACE-FTS correlation plots are also affected by outliers.

For both ACE-FTS and ACE-MAESTRO, measurements at altitudes below approximately 5 km are often not possible because ACE's sun-tracker is unable to lock onto the Sun reliably due to cloud effects and refraction (Boone et al., 2005). This issue may contribute to the larger

differences observed at low altitudes. This is especially the case with ACE-MAESTRO, whose retrieval produces profiles extending as low as 4 km with tangent heights determined by extrapolation based on the vertical sampling above 5 km.

AIRS and TES are the only satellite instruments in this study whose measurements are performed in nadir-viewing modes and whose retrieval products reach the lower troposphere. Humidity inversions typically occur near Eureka between 500 m and 2 km in altitude. Sometimes, major structure is seen in the water vapour profile between 2 and 4 km as well. Individual profile-to-profile comparisons with the Eureka radiosondes shows that AIRS retrievals do not fully capture structure in the humidity inversion feature, explaining much of the individual profile differences at the lowest altitude levels. This is expected because the vertical resolution of AIRS is not always sufficient to resolve these vertical structures (Susskind et al., 2014). The AIRS user guide warns of occasional 'strange results' in proximity to near-surface humidity inversions, however, the AIRS profiles coincident with Eureka showed no features that were oddly shaped or clearly erroneous. The magnitude of the inversion was often inaccurate or the inversion was not seen in the AIRS profile. This could also be in part due to a geographic or temporal mismatch between the measurements.

Similarly, individual profile-to-profile comparisons with the nearest radiosonde profile show that TES profiles often capture the general shape of the lower tropospheric humidity profiles structure; however, the smoothing operation is not enough to bring the measurements into agreement. Where radiosondes from earlier or later in the day reveal a humidity profile with less fine vertical structure, agreement between TES and the 125HR was much closer.

# 5.6 Conclusions

This study compared high Arctic water vapour vertical profile measurements taken by seven satellite-based instruments with measurements acquired by the Eureka radiosondes and the PEARL 125HR. The primary focus of the work was to assess the UTLMS water vapour retrieved from ACE-FTS and ACE-MAESTRO measurements. The ACE instruments' ability to observe UTLS water vapour is a valuable contribution to global atmospheric monitoring, as its profiles extend to lower altitudes than many other satellite-based measurements, particularly those retrieved from limb-viewing observations.

ACE-FTS and ACE-MAESTRO showed good agreement with both the radiosondes and the 125HR in the UTLMS. No obvious temporal trend is apparent in the differences. ACE-FTS showed a wet bias of approximately 7 to 10% relative to the 125HR. An ACE-FTS dry bias of 2 to 9% was observed relative to the radiosondes between 8 and 10 km. While agreement is observed in the upper troposphere, the observed agreement did not reach the 5% accuracy goal set by the WMO GCOS. ACE-MAESTRO profiles at altitudes below 7 km had large differences relative to both the radiosondes and the 125HR; between 8 and 10 km, a dry bias between 6 and 18% is observed relative to both the radiosondes and the 125HR. Nonetheless, ACE water vapour measurements showed closer agreement overall with the Eureka reference measurements in the UTLS than did the other satellite datasets examined in this study, with the exception of AIRS.

AIRS water vapour profiles showed close agreement with both the 125HR and radiosonde measurements, i.e. within the 5% GCOS target. The observed accuracy of the AIRS measurements suggests they can be used for analysis of humidity conditions near Eureka. Given the high density and frequency of AIRS measurements, it would be worthwhile to use AIRS measurements to create climatologies of water vapour conditions near the site, and also to examine patterns of water vapour abundances in the region. AIRS data may also be useful for validation studies in cases where radiosonde and 125HR measurements do not offer sufficient numbers of coincident measurements. In addition, global UTLS comparisons between AIRS and ACE water vapour measurements could also be examined to better understand the accuracy of the ACE-FTS and ACE-MAESTRO water vapour datasets.

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MIPAS and SCIAMACHY comparisons at altitudes where the data are recommended (i.e., above 10 km) showed agreement within 6% of the 125HR. Coincidences with the radiosondes were not available. At upper tropospheric altitudes where the MIPAS data are not recommended for use, but are included in the publicly available data product, large differences and variability were observed. This supports the recommendation to limit the use of MIPAS v5 and v7 water vapour profiles to 12 km and above. MIPAS v5 and v7 and SCIAMACHY v3.01 and v4.2 comparison results were very similar.

MLS comparisons with the radiosondes and 125HR between 8 and 12 km showed a dry bias. This aligns with UTLS-region MLS dry biases observed by Hurst et al. (2016) and Vömel et al. (2007b) using FPH measurements.

FPH water vapour measurements at Eureka would enhance the ongoing satellite validation work there and enable a valuable reference for PEARL water vapour measurements. FPH measurements would offer improved accuracy as well as better coverage throughout the UTLS altitudes relative to the radiosondes and 125HR. FPH measurements have been used for the validation of other missions such as MLS (Hurst et al. 2016) and MIPAS (Stiller et al., 2012, using the MOHAVE measurements). Adding FPH measurements would be a useful next step for the comparison and validation of water vapour profiles at Eureka.

# 6 Comparison of network-wide TCCON and MUSICA water vapour measurements

# 6.1 Introduction

Water vapour measurements are highly valued, and new techniques to acquire them are being actively developed, as discussed in earlier chapters. Chapter 4 assessed the accuracy of the MUSICA H<sub>2</sub>O retrieval produced from the PEARL 125HR using comparisons with H<sub>2</sub>O measurements from several other PEARL instruments. The MUSICA product was shown to be highly accurate, which aligned with the results of validation studies at other sites. However, MUSICA was a time-limited project. Future extension of the MUSICA water vapour datasets is unclear; currently, they end in 2014. The limited time span and geographic coverage of the MUSICA datasets motivate the assessment of the water vapour data produced by TCCON, a long-term FTIR spectrometer measurement network of about 25 sites, which could be used for ongoing studies of the water cycle and for satellite validation. Past, current, and future TCCON sites are shown in Figure 6.1.



Figure 6.1: Map of the TCCON stations. Original figure from tccondata.org, retrieved September 28, 2018.

TCCON's priority is to produce highly accurate and precise long-time-scale records of CO<sub>2</sub> and CH<sub>4</sub> to study the carbon cycle and to support the validation of satellite datasets, e.g., measurements acquired by the Greenhouse Gases Observing Satellite (GOSAT) and OCO-2 (Wunch et al., 2011). TCCON also produces retrievals of N<sub>2</sub>O, HF, CO, H<sub>2</sub>O, and HDO total columns. The TCCON H<sub>2</sub>O dataset has been used in the validation of GOSAT H<sub>2</sub>O retrievals, e.g., by Dupuy et al. (2016) and Ohyama et al. (2017). In addition,  $\delta$ D calculated from TCCON H<sub>2</sub>O and HDO products has been used to validate GOSAT  $\delta$ D total columns (Boesch et al., 2013; Frankenberg et al., 2013) and SCIAMACHY  $\delta$ D (Scheepmaker et al., 2015) total columns. However, despite their use in satellite validation studies, there has not yet been a detailed and systemic comparison of the TCCON water vapour measurements with reference datasets, except a small number of comparisons to radiosondes at the Tsukuba, Darwin, Lamont, and Lauder sites (Wunch et al., 2010, 2015).

Some TCCON sites also have MUSICA data derived from co-located NDACC measurements. This offers an opportunity to use the well-validated MUSICA H<sub>2</sub>O and  $\delta$ D datasets to assess the TCCON water vapour products. This chapter presents a comparison of the TCCON water vapour products with the MUSICA datasets at several sites, as well as comparisons between TCCON and radiosonde H<sub>2</sub>O measurements.

# 6.2 Measurement sites

Water vapour measurements retrieved from FTIR spectra using the TCCON and MUSICA retrieval techniques, as well as measurements acquired by radiosondes, are compared in this study. Radiosonde measurements were described in Chapter 2. The MUSICA water vapour retrieval was described in Chapter 3.<sup>26</sup> The Eureka MUSICA  $\delta D$  timeseries is shown in Figure 6.2, illustrating that the MUSICA  $\delta D$  retrieval captures a large variability of values with a seasonal cycle. Since this chapter discusses measurements taken at multiple sites around the world, the PEARL 125HR dataset will be referred to as the Eureka dataset to be consistent with other sites, which are named for their location.

 $<sup>^{26}</sup>$  MUSICA H<sub>2</sub>O total columns are precise to about 1%; MUSICA  $\delta D$  is precise to about 30 ‰ (Schneider et al., 2012).

Eight TCCON sites have co-located (or relatively nearby) NDACC measurements: Eureka, Ny Ålesund, Sodankylä, Bremen, Karlsruhe, Izaña, Wollongong, and Lauder. Sodankylä does not have NDACC measurements; however, there is an NDACC station in Kiruna, located 258 km east of Sodankylä. This distance is not ideal for water vapour comparisons, as water vapour has large spatial as well as temporal variability. However, this distance is within the spatial coincidence criterion often used for satellite validation studies, e.g., Scheepmaker et al. (2015). The Sodankylä-Kiruna comparison has been included in the study with the expectation that a larger variability in observed agreement may be observed due to the distance between the sites. Ny Ålesund data have not been used in this study because when TCCON datasets were collected for analysis, it had not yet archived the retrieval version used by the other sites. Thus, data from seven sites are used. Of these, radiosonde data were available for five sites: Eureka, Sodankylä, Bremen, Izaña, and Lauder.<sup>27</sup>



Figure 6.2: Eureka MUSICA &D. Data points are colour-coded to the H2O total column.

<sup>&</sup>lt;sup>27</sup> Radiosonde data have been difficult to acquire in some cases. While there is, for example, IGRA data for sites near Karlsruhe and Wollongong, the humidity data archived in IGRA files is vertically sparse, even compared to levels archived for pressure and temperature. Inquiries about this went unanswered. The University of Wyoming has a portal for accessing radiosonde data (http://weather.uwyo.edu/upperair/sounding.html); however, it is not designed for the download of more than one sounding at a time. I contacted them to acquire data files for the sites in this study that were missing radiosonde data; however, the data provided were incomplete.

The location of the seven sites used in this study are listed in Table 6.1, along with the temporal overlap of TCCON and MUSICA measurements. These seven sites acquire measurements at a variety of latitudes, altitudes, and climates. The location of launch sites for radiosonde (RS) datasets used in this study are listed in Table 6.2, along with the distance to the FTIR spectrometer location, and the temporal overlap with the corresponding MUSICA and TCCON datasets.

To account for the impact of the altitude difference between FTIR and radiosonde measurements, radiosonde total columns have been calculated by integrating the radiosonde profile down to the altitude of the FTIR instrument, i.e., using Equations 2.8 and 2.9.

Sito	Latituda	Longitudo	Altitudo	Time range of	
Site	Latitude	Longitude	Altitude	TCCON & MUSICA overlap	
Eureka	80.05°N	86.42°W	610 m	Jul. 2010 – Sept. 2014	
Sodankylä (Kiruna)	67.37°N (67.84°N)	26.37°E (20.41°E)	188 m (419 m)	Jun. 2009 – Oct. 2014	
Bremen	53.10°N	8.85°E	27 m	Jan 2007 – Sept. 2014	
Karlsruhe	49.10°N	8.44°E	12 m	Apr. 2010 – Dec. 2014	
Izaña	28.30°N	16.50°W	2370 m	May 2007 – Aug. 2014	
Wollongong	34.41°S	150.88°E	30 m	Jul. 2008 – Sept. 2014	
Lauder	45.04°S	169.68°E	370 m	Aug. 2004 – Aug. 2014	

### Table 6.1: FTIR sites with TCCON and MUSICA measurements.

### Table 6.2: Radiosonde launch sites near FTIR locations.

FTIR site	Radiosonde – FTIR	Radiosc	onde site loc	ation	Temporal overlap range		
	distance [km]	Latitude	Longitude	Altitude	TCCON & RS	MUSICA & RS	
Eureka	12.24	79.98°N	85.93°W	10 m	Aug. 2010 – Aug. 2015	Aug. 2006 – Sept. 2014	
Sodankylä	53.41	67.37°N	26.63°E	179 m	May 2009 – Oct. 2012	Feb. 2009 – Oct. 2012	
Bremen	78.75	52.82°N	9.93°E	70 m	Jan. 2007 – Nov. 2014	Aug. 2004 – Sept. 2014	
Izaña	11.96	28.32°N	16.38°W	105 m	May 2007 – Nov. 2013	Jan. 2007 – Dec. 2013	
Lauder	0	45.04°S	169.68°E	370 m	Jun. 2004 – Dec. 2014	Jan. 2004 – Aug. 2014	

# 6.3 TCCON datasets

TCCON uses the same FTIR spectrometers used by NDACC, the Bruker IFS 125HR, described in Chapter 3. TCCON instruments record NIR solar absorption spectra at a maximum optical path difference of 45 cm, which corresponds to a spectral resolution of 0.02 cm<sup>-1</sup>. This instrument configuration uses an InGaAs detector and a CaF<sub>2</sub> beamsplitter. The spectral ranges of these components were shown in Figure 3.6 along with the components used for MIR NDACC measurements.

TCCON retrievals are produced using a software package called GGG and are described by Wunch et al. (2011, 2015). The data used in this study were produced using version GGG2014. The retrieval algorithm used by GGG to fit atmospheric spectra is called GFIT, which scales an a priori VMR profile to create a calculated spectrum that matches the measured spectrum. The H<sub>2</sub>O retrieval uses 15 spectral windows; the HDO retrieval uses six spectral windows. The H<sub>2</sub>O and HDO averaging kernels are very similar; they show nearly constant sensitivity throughout the atmosphere. TCCON a priori profiles and total columns are calculated for each measurement day. The H<sub>2</sub>O a priori VMR profiles are derived from National Center for Environmental Prediction (NCEP) reanalyses. The HDO a priori profile is inferred from the H<sub>2</sub>O a priori profile, assuming an H<sub>2</sub>O-dependent fractionation. This retrieval technique produces only a total column product.

Standard TCCON products are column-averaged dry-air mole fractions (DMFs), denoted as  $X_{gas}$ . This quantity is calculated using a retrieved column of O<sub>2</sub>:

$$X_{gas} = 0.2095 \frac{Column \, gas}{Column \, O_2} \,. \tag{6.1}$$

This approach improves measurement precision because errors common to both retrievals cancel. Thus, the standard TCCON water vapour products are  $X_{H_2O}$  and  $X_{HDO}$ . The accuracy of the H<sub>2</sub>O total columns has been estimated at 5% (Wunch et al., 2010).

For this study, H<sub>2</sub>O and HDO total columns were calculated using the O<sub>2</sub> columns to align the units with those of typical atmospheric water vapour measurements, such as the MUSICA datasets, e.g.,  $\frac{\text{kg}}{\text{m}^2}$  or mm PWV. TCCON  $\delta$ D was calculated from H<sub>2</sub>O and HDO total columns

using Equation 3.14. The timeseries of TCCON  $H_2O$  and  $\delta D$  at the seven sites used in this study are shown in Figure 6.3 and Figure 6.4, respectively.



Figure 6.3: TCCON H<sub>2</sub>O total columns at: (a) Eureka, (b) Sodankylä, (c) Bremen, (d) Karlsruhe, (e) Izana, (f) Wollongong, and (g) Lauder.



Figure 6.4: Same as Figure 6.3 but for TCCON δD total columns.

### 6.4 Comparisons

### 6.4.1 Method

In this study, measurements are compared using absolute and percent differences. These are calculated using:

$$difference = FTIR - X, \tag{6.2}$$

and

$$\% \, difference = \frac{(FTIR-X)}{X} \times 100\% \,, \tag{6.3}$$

where *FTIR* is either TCCON or MUSICA, and X is the reference, either MUSICA or radiosonde measurements.

As was the case in earlier chapters, comparison results reported in the text will use the standard error in the mean to quantify the accuracy of the mean difference. i.e., a difference will be quoted as  $A \pm B$ , where A is the mean difference ( $\Delta$ ) and B is the SEM, unless  $\sigma$  is explicitly reported. The figures showing differences show the mean difference as well as the one standard deviation of the differences to characterize the spread of the values ( $\sigma$ ). Results reported also include the total number of matches found between the instruments (N), the correlation coefficient (R), and the slope of the linear fit line (m).

A two-hour temporal coincidence criterion was applied for all instrument comparisons. If multiple coincident measurements were found within this interval, only the closest pair was kept. Actual time differences between coincident measurements are often less than 2 hours. For example, at Eureka, where the same 125HR instrument is used for TCCON and NDACC measurements, the mean time difference between coincident measurements was 53.0 minutes. At Lauder, there are dedicated 125HRs for TCCON and NDACC measurements, so the mean time difference of coincident measurements, 13.9 minutes.

Coincident measurements from MUSICA and TCCON H<sub>2</sub>O measurements are shown in Figure 6.5. Coincident  $\delta D$  measurements are shown in Figure 6.6.



Figure 6.5: Coincident TCCON and MUSICA H<sub>2</sub>O total column measurements at: (a) Eureka, (b) Sodankylä/Kiruna, (c) Bremen, (d) Karlsruhe, (e) Izaña, (f) Wollongong, (g) Lauder.



Figure 6.6: Same as Figure 6.5 but for coincident TCCON and MUSICA δD data.

# 6.5 Results

### 6.5.1 TCCON vs. MUSICA

The mean difference between TCCON and MUSICA H<sub>2</sub>O measurements is  $-1.00 \pm 0.02$  mm PWV ( $-7.52 \pm 0.15$  %) using data from all seven sites. This apparent TCCON dry bias is seen in the results at all sites in this study, except Sodankylä/Kiruna. The absolute differences at each site are shown in Figure 6.7; percent differences are shown in Figure 6.8. The Sodankylä/Kiruna data show mean differences of  $0.82 \pm 0.17$  mm PWV ( $11.28 \pm 1.47$  %), an opposite bias from all other site comparisons, as well as a greater scatter, i.e., the largest  $\sigma$ . Results at Karlsruhe show a seasonal pattern in the absolute differences, with a dry bias of up to 3 mm PWV in the summer, although a seasonal pattern is not seen in the percent differences. Lauder differences show less variability and fewer outliers starting in 2011, when the site's instrument was changed from a Bruker 120HR to a 125HR. All sites show very good correlations between TCCON and MUSICA measurements, i.e., with *R* values above 0.88. Correlation plots for TCCON and MUSICA H<sub>2</sub>O are shown in Figure 6.9.

The overall network-wide correlation between the TCCON and MUSICA H<sub>2</sub>O datasets was 0.98. If the Sodankylä/Kiruna comparison is excluded, this correlation increases to 0.99, the scatter decreases from  $\sigma$  of 14.00 to 11.16, and the mean difference slightly worsens to  $-1.13 \pm 0.02$  mm PWV ( $-7.52 \pm 0.18$  %). A correlation plot for H<sub>2</sub>O data from all sites is shown in Figure 6.10 (a). In addition, if the natural logarithm of the datasets is plotted, reflecting the distribution of water vapour's variability and the scale used for the MUSICA retrieval, the slope of the best fit line improves from 1.06 to 0.99. This is shown in Figure 6.10 (b).

Differences between TCCON and MUSICA  $\delta D$  show an overall mean difference of  $39.95 \pm 0.27$  ‰. Differences at each site are similar to this overall TCCON high  $\delta D$  bias. The largest difference, largest scatter, and weakest correlation is again observed at Sodankylä/Kiruna. Differences at Karlsruhe again show a seasonal pattern. The  $\delta D$  differences at each site are shown in Figure 6.11. Correlation plots for each site are shown in Figure 6.12, and a network-wide correlation plot is shown in Figure 6.13, where a correlation of 0.96 is observed. Removing the Sodankylä/Kiruna comparison slightly increases the correlation coefficient to 0.97; however, the mean difference, SEM, and  $\sigma$  do not change significantly.



Figure 6.7: Absolute differences between coincident TCCON and MUSICA H<sub>2</sub>O measurements at (a) Eureka, (b) Sodankylä/Kiruna, (c) Bremen, (d) Karlsruhe, (e) Izaña, (f) Wollongong, and (f) Lauder, calculated using Equation 6.2, where X is MUSICA. Dashed green lines show the mean difference. Dotted blue lines show the mean  $\pm \sigma$ .



Figure 6.8: Same as Figure 6.7 but for percent differences between TCCON and MUSICA H<sub>2</sub>O.



Figure 6.9: TCCON vs. MUSICA H<sub>2</sub>O correlation plots. Hexagon colour is coded to the density of data points. N is the number of measurements in the comparison, R is the correlation coefficient, m is the slope of the linear best fit line, and b is the intercept of the linear best fit line. The black line is the reference for slope = 1 and the dashed green line is the linear best fit line.


Figure 6.10: Network-wide correlation plot for TCCON vs. MUSICA H<sub>2</sub>O on: (a) linear scale, and (b) natural log basis (i.e.,  $ln(H_2O)$  of each dataset is plotted). Axis ticks are given on a linear scale in (b) for easier interpretation. Variables as defined for Figure 6.9.



Figure 6.11: Same as Figure 6.7 but for δD.



Figure 6.12: Same as Figure 6.9 but for MUSICA vs. TCCON δD correlation plots.



Figure 6.13: Network-wide TCCON vs. MUSICA δD correlation plot. Variables as defined for Figure 6.9.

#### 6.5.2 Radiosonde comparisons

MUSICA and TCCON H<sub>2</sub>O datasets have been compared to radiosondes at five sites. Overall agreement between MUSICA and radiosondes shows a mean difference, i.e. MUSICA – RS, of  $0.74 \pm 0.06$  mm PWV (19.22 ± 0.99 %) and a correlation coefficient of 0.91. The Sodankylä /Kiruna comparison is the only site that differs notably from the overall agreement, showing a mean difference of  $-0.98 \pm 0.23$  ( $-6.15 \pm 2.11$  %). The Lauder mean differences were smaller than at other sites; however, the correlation was weaker, i.e., it had a coefficient of 0.74. A network-wide correlation plot for MUSICA vs. radiosondes is shown in Figure 6.14 (a), with the correlation plot shown in a log-scale in Figure 6.15 (a). If the MUSICA Kiruna comparison (to the Sodankylä radiosondes) is removed, the overall agreement changes only slightly, e.g., the correlation improves to 0.915 from 0.907, and the slope of the best fit line changes from 0.92 to 0.94.

TCCON and radiosonde H<sub>2</sub>O are in close agreement, with a mean difference of  $-0.13 \pm 0.07$  mm PWV (4.50 ± 0.62 %) and a correlation coefficient of 0.88. Individual site comparisons are generally consistent with this overall result, with most showing a small TCCON wet bias. However, Lauder results are only moderately well correlated (R = 0.55) and show a small TCCON dry bias of  $-0.96 \pm 0.15$  ( $-0.99 \pm 1.24$  %), while other sites show a TCCON wet bias relative to the radiosondes and very good correlation, e.g., R > 0.95. Izaña shows a small mean difference,  $0.65 \pm 0.05$  mm PWV, but a relatively large percent difference,  $24.21 \pm 2.30$  %. Izaña also has the smallest mean TCCON H<sub>2</sub>O value (5.0 mm PWV) and the lowest recorded TCCON H<sub>2</sub>O value (0.6 mm PWV) of all the datasets. Removing the Sodankylä/Kiruna comparison does not have a significant impact on the overall results. A network-wide correlation plot for the TCCON vs. radiosondes is shown in Figure 6.14 (b), with the correlation plot shown on a log-scale in Figure 6.15 (b).

Site-by-site correlation plots for both MUSICA and TCCON vs. radiosondes are shown in Figure 6.16. Agreement at each site is better between TCCON and radiosondes than between MUSICA and radiosondes, except Lauder, where TCCON agrees more closely with MUSICA than with radiosondes.



Figure 6.14: (a) Network-wide MUSICA vs. radiosonde H<sub>2</sub>O correlation plot, (b) Networkwide TCCON vs. radiosonde H<sub>2</sub>O correlation plot. Variables as defined for Figure 6.9.



Figure 6.15: Same as Figure 6.14, but on log-scale.



Figure 6.16: Same as Figure 6.9 but for TCCON vs. MUSICA and radiosonde H<sub>2</sub>O correlation plots.

# 6.5.3 Summary of comparison results

Results of the comparisons presented in this study between the TCCON and MUSICA and radiosonde datasets are summarized in four tables. Tables 6.3 and 6.4 present comparison results for the TCCON vs. MUSICA H<sub>2</sub>O and  $\delta$ D datasets, respectively. Tables 6.5 and 6.6 provide comparison results for MUSICA vs. radiosonde and TCCON vs. radiosonde, respectively.

Table 6.3: Results of TCCON vs. MUSICA H<sub>2</sub>O total column comparisons. Differences are TCCON – MUSICA, and are calculated following Equations 6.2 and 6.3. N is the number of measurements,  $\Delta$  is the difference, SEM is the standard error in the mean,  $\sigma$  is the standard deviation, R is the correlation coefficient, and slope is the slope of the linear best fit line of the correlation plot.

Site	N	mean ∆ [mm PWV]	SEM [mm PWV]	σ [mm PWV]	mean ∆ [%]	SEM [%]	σ [%]	R	slope
Eureka	164	-0.69	0.04	0.55	-9.36	0.39	5.03	0.992	0.91
Sodankylä/Kiruna	401	+0.82	0.17	3.47	+11.28	1.47	29.36	0.877	0.99
Bremen	200	-1.25	0.06	0.89	-8.43	0.28	3.92	0.996	0.92
Karlsruhe	1590	-1.13	0.02	0.61	-6.28	0.06	2.29	0.999	0.94
Izaña	1265	-0.42	0.02	0.62	-7.01	0.36	12.91	0.982	0.91
Wollongong	1349	-2.03	0.05	1.95	-10.39	0.30	11.02	0.974	0.89
Lauder	1001	-0.88	0.06	2.00	-5.83	0.53	16.92	0.889	0.83
All	5970	-1.00	0.02	1.76	-6.26	0.18	14.00	0.980	0.91
All (no Sodankylä/Kiruna)	5569	-1.13	0.02	1.48	-7.52	0.15	11.16	0.987	0.91

Table 6.4: Same as Table 6.3 but for TCCON vs. MUSICA δD.

Site	N	mean ∆ [‰]	SEM [‰]	σ [‰]	R	slope
Eureka	164	40.00	0.96	12.27	0.99	1.11
Sodankylä/Kiruna	401	47.44	1.58	31.65	0.77	0.87
Bremen	200	37.20	0.85	12.03	0.98	1.13
Karlsruhe	1590	34.36	0.35	14.14	0.98	1.22
Izaña	1265	37.88	0.78	27.78	0.94	1.01
Wollongong	1349	43.51	0.42	15.27	0.90	1.11
Lauder	1001	44.20	0.65	20.59	0.79	0.86
All	5970	39.95	0.27	20.87	0.96	1.03
All (no Sodankylä/Kiruna)	5569	39.41	0.26	19.76	0.97	1.04

Site	N	mean ∆ [mm PWV]	SEM [mm PWV]	σ [mm PWV]	mean ∆ [%]	SEM [%]	σ [%]	R	slope
Eureka	55	0.69	0.09	0.70	11.06	1.32	9.80	0.966	1.01
Sodankylä/Kiruna	119	-0.98	0.23	2.50	-6.15	2.11	23.03	0.895	0.72
Bremen	138	1.75	0.23	2.65	15.39	1.63	19.18	0.936	1.05
Izaña	563	1.10	0.04	0.85	35.96	1.70	40.30	0.970	1.06
Lauder	487	0.46	0.15	3.24	8.10	1.44	31.81	0.736	0.76
All	1362	0.74	0.06	2.40	19.22	0.99	36.60	0.907	0.92
All (no Sodankylä/Kiruna)	1243	0.90	0.07	2.33	21.67	1.04	36.74	0.915	0.94

Table 6.5: Same as Table 6.3 but for MUSICA vs. radiosonde H<sub>2</sub>O total columns. MUSICA data from Kiruna are compared with radiosondes from Sodankylä.

Table 6.6: Same as Table 6.3 but for TCCON vs. radiosondes H<sub>2</sub>O total columns.

Site	N	mean ∆ [mm PWV]	SEM [mm PWV]	σ [mm PWV]	mean ∆ [%]	SEM [%]	σ [%]	R	slope
Eureka	72	-0.07	0.05	0.44	0.55	0.79	6.74	0.993	0.95
Sodankylä	398	0.19	0.04	0.84	2.97	0.54	10.82	0.992	0.99
Bremen	538	0.61	0.09	2.03	5.79	0.64	14.86	0.955	0.98
Izaña	250	0.65	0.05	0.84	24.21	2.30	36.39	0.965	0.96
Lauder	862	-0.96	0.15	4.28	-0.99	1.24	36.27	0.549	0.46
All	2120	-0.13	0.07	3.04	4.50	0.62	28.80	0.879	0.86
All (no Sodankylä)	1722	-0.20	0.08	3.34	4.85	0.76	31.52	0.845	0.82

### 6.5.4 Comparisons to GRUAN radiosondes

The known biases of the radiosondes, in particular the dry bias, may contribute to the observed FTIR wet biases. To check this potential impact on the comparison results, comparisons were also conducted between the FTIR data and the GRUAN radiosonde products available at Eureka, Sodankylä, Izaña, and Lauder.<sup>28</sup> Figures 6.17, 6.18, and 6.19 show comparisons between the FTIR networks and the GRUAN radiosonde products, equivalent to Figures 6.14, 6.15, and 6.16 that showed the comparisons with the standard radiosonde datasets. The number of coincidences is smaller in all cases. However, the results of these comparisons are consistent with the results of the comparisons with the standard radiosonde products. In many comparisons, correlation coefficients and/or slopes show an improved agreement. However, there are still biases evident, i.e., TCCON still appears to have a dry bias, although it is smaller than when the standard radiosonde product is used. There is also less scatter in the results, which may be the result of better quality control in the GRUAN products.

<sup>&</sup>lt;sup>28</sup> As noted in Chapter 2, Eureka is not a GRUAN site; however, GRUAN software has been used to produce a biascorrected dataset using Eureka radiosonde raw files. Ny Ålesund has GRUAN-processed radiosondes; however, as noted earlier, the Ny Ålesund TCCON data were not available in an up-to-date retrieval when this analysis was done.



Figure 6.17: Same as Fig. 6.14 but using the GRUAN radiosondes.



Figure 6.18: Same as Fig. 6.15 but using GRUAN radiosondes.



Figure 6.19: Same as Fig. 6.16 but using GRUAN radiosondes.

### 6.6 Discussion

The comparisons presented in this chapter show that the TCCON H<sub>2</sub>O product has a dry bias relative to the MUSICA product, of approximately 1 mm PWV or about 6%. Comparisons with radiosonde measurements show a small TCCON and MUSICA wet bias. Since the MUSICA wet bias relative to the radiosondes is larger than that of the TCCON measurements, these results are consistent.

Only 55 coincidences were found between MUSICA and radiosondes at Eureka. 72 coincidences were found between TCCON and radiosondes. This relatively lower number is in part due to the absence of high latitude FTIR spectrometer measurements during polar night, which lasts for approximately 1/3 of the year in Eureka. In addition, also due to the high latitude of the site, measurements relying on sunlight are predominantly taken between the hours of 9 AM and 4 PM. This limits the overlap between solar measurements and radiosondes because radiosonde launches occur typically at 11:15 and 23:15 UTC, which is 6:15 AM and 6:15 PM local time in Eureka. Figure 6.20 illustrates this limited measurements, e.g., as shown for Izaña in Figure 6.21. A greater number of TCCON measurements than MUSICA are typically available because TCCON measurements are taken more frequently since they use a shorter OPD and do not use filters. MUSICA retrievals use only NDACC filter 3 measurements.



Figure 6.20: Eureka TCCON and MUSICA measurement histogram for hour of the day (local time, which is -5 hours UTC all year). Standard radiosonde launch times are denoted by red dashed lines. Occasional radiosonde launch times are denoted by blue dashed lines. Histograms show darker colour where they overlap.



Figure 6.21: Same as Figure 6.20 but for Izaña (local time is UTC).

Closer agreement observed between TCCON H<sub>2</sub>O and the radiosondes than between MUSICA H<sub>2</sub>O and the radiosondes may be due to the influence of the TCCON daily a priori, which is derived from NCEP reanalysis and thus relies on radiosonde data. Better agreement is observed between the TCCON retrievals and radiosonde data compared to agreement observed between the a priori and radiosondes. The results of the TCCON a priori vs. radiosonde comparisons are summarized in Figure 6.22 and Table 6.7; these suggest that the TCCON retrieval does contain information about the atmospheric water vapour column in addition to its a priori.

SEM mean  $\Delta$ SEM mean  $\Delta$ σ σ Site Ν R slope [mm PWV] [mm PWV] [mm PWV] [%] [%] [%] 1.35 Eureka 72 0.16 -3.44 8.63 73.26 0.94 -0.23 0.920 1.00 11.66 16.29 0.980 Sodankylä 398 0.07 1.36 0.82 1.01 Bremen 538 1.57 0.09 2.12 14.54 0.76 17.67 0.950 0.97 Izaña 250 0.81 2.07 104.98 0.760 0.59 0.13 52.51 6.64 Lauder 862 0.95 0.15 4.48 17.22 1.44 42.32 0.550 0.53 2120 1.06 0.07 49.97 0.869 0.89 All 3.22 18.96 0.09 All 1722 1.07 0.08 3.51 20.64 1.32 54.76 0.837 0.85 (no Sodankylä)

Table 6.7: Same as Table 6.3 but for TCCON a priori vs. radiosonde H<sub>2</sub>O total columns.



Figure 6.22: Correlation plots of radiosonde vs. TCCON retrieval (left panels) and TCCON a priori (right panels) H<sub>2</sub>O total columns at Eureka, Sodankylä, Bremen, Izaña, and Lauder.

Differences observed between the TCCON measurements at Sodankylä and the MUSICA measurements at Kiruna are different from the other site results in this study. In the TCCON vs. MUSICA H<sub>2</sub>O comparison, the magnitude of the mean difference is the opposite sign from what is seen at all other sites, i.e., there is a small TCCON wet bias. The  $\delta$ D differences are largest in the Sodankylä/Kiruna comparison as well. The scatter in the H<sub>2</sub>O and  $\delta$ D differences, i.e., the standard deviation, is largest of all site comparisons. This result is likely because of the 258 km distance between the sites. However, the measurements are highly correlated, e.g., the H<sub>2</sub>O TCCON/MUSICA comparison *R* is 0.877, and the differences are small. This result can be used to inform satellite validation comparisons conducted using TCCON water vapour products. Distance coincidence criteria should be smaller than 250 km, which is not always the case, to ensure an accurate observation of potential biases between the datasets. Distances on this scale may nonetheless be justified, depending on the accuracy of the bias determination being sought, given the reasonably good agreement and very good correlations observed; however, observed agreement should be expected to include a large scatter and interpreted to have uncertainty at least as large as the differences observed between the Sodankylä and Kiruna sites.

The TCCON-derived  $\delta D$  product shows a relatively consistent bias of approximately 40 ‰ with respect to the MUSICA measurements. The maximum depletion of the TCCON timeseries (i.e., low  $\delta D$  values) is not as large as that in the MUSICA data. This offset of 40 ‰ should be accounted for if the TCCON  $\delta D$  is used, especially for satellite validation. The TCCON HDO retrieval, unlike other products, has not had a reference available for comparison and calibration. The derivation of an offset for TCCON HDO total columns using either the MUSICA dataset or an aircraft campaign with HDO measurements could bring the TCCON and MUSICA  $\delta D$  products into agreement.

Scheepmaker et al. (2015) examined differences between SCIAMACHY  $\delta D$  and coincident TCCON and MUSICA data at ten sites (i.e., TCCON measurements at Ny Ålesund, Bremen, Park Falls, JPL, Darwin, and Lauder, and MUSICA measurements at Kiruna, Bremen, Jungfraujoch, Izaña, Wollongong, and Lauder) and found that SCIAMACHY  $\delta D$  was low biased by 35 ‰ and 69 ‰, with respect to TCCON and MUSICA respectively. Comparisons were made between SCIAMACHY and TCCON and MUSICA  $\delta D$  at two sites also examined in this study: Bremen and Lauder. At Bremen, the SCIAMACHY – FTIR mean difference was -70 % and -41 % for TCCON and MUSICA, respectively; at Lauder the difference was -86 % and

-74 ‰. This suggests overall lower  $\delta D$  values measured by the MUSICA retrieval relative to the calculated TCCON  $\delta D$ , which is consistent with the bias observed in this study. However, the latitudinal pattern seen in the differences is not observed in the results of this study.

The differences in this study showed no correlation with SZA, which can affect FTIR spectrometer retrievals. For example, the correlation coefficient for TCCON – MUSICA H<sub>2</sub>O differences and SZA was 0.11. This is illustrated by Figure 6.23, which shows the H<sub>2</sub>O and  $\delta$ D differences between all coincident TCCON and MUSICA measurements, respectively, vs. SZA at all seven sites in this study, colour-coded by year. The tight time criterion used (2 hours), nearly identical location of the instruments (except for the Sodankylä-Kiruna case), and identical instrumentation likely avoids this dependency.





Figure 6.23: (a) All TCCON – MUSICA H<sub>2</sub>O differences vs. SZA, colour-coded by year. Mean difference is denoted by dashed red line; mean difference  $\pm \sigma$  is denoted by dotted beige lines. (b) Same as (a) but for TCCON – MUSICA  $\delta D$  differences.

# 6.7 Conclusions

TCCON and MUSICA H<sub>2</sub>O and  $\delta D$  datasets were compared at seven sites and revealed close agreement. Overall, the TCCON H<sub>2</sub>O product shows a dry bias with respect to MUSICA, of approximately 6% (-1.00 ± 0.02 mm PWV). The TCCON  $\delta D$  shows a high bias, e.g., less depletion, relative to the MUSICA  $\delta D$ , of approximately 40 ‰ (39.41 ± 0.26 ‰). These biases are relatively constant across all sites, and the datasets show very good correlation, e.g., R = 0.98for H<sub>2</sub>O and R = 0.96 for  $\delta D$  using data from all sites. The exception to this observed mean agreement is the comparison performed using TCCON measurements at Sodankylä and MUSICA measurements at Kiruna, which showed larger scatter and a mean TCCON wet bias. This is likely due to the distance between the instruments. When using TCCON to validate satellite measurements, a stricter spatial criterion than the 250 km distance between Sodankylä and Kiruna is recommended to ensure that an accurate bias can be evaluated between the datasets.

TCCON spectra can be collected every 2.4 minutes. Since the TCCON H<sub>2</sub>O retrieval product has been shown to agree closely with coincident MUSICA and radiosonde measurements, TCCON H<sub>2</sub>O can be used to capture the short-term variability of water vapour total columns. This is useful for understanding variability, trends, and for validation of other instruments' datasets.

# 7 Summary, conclusions, and future work

# 7.1 Summary and conclusions

The important role of atmospheric water vapour in the chemistry, dynamics, weather, and climate of the planet has motivated the development of techniques that can measure it globally with high accuracy, and with high horizontal and vertical resolution. GCOS, for example, has set out the goal of achieving global water vapour profile measurements with 5% accuracy and total column measurements with 2% accuracy (GCOS, 2016). However, these goals have not yet been achieved. The need to develop and deploy instruments to acquire astmospheric observations is especially acute in the Arctic, where measurements are sparse and changes to the atmosphere have significant consequences for climate and atmospheric chemistry (ACIA, 2004).

The work presented in this thesis assesses improvements to atmospheric water vapour measurements at the Eureka high Arctic site using ground-based and satellite instruments. The new PEARL 125HR MUSICA dataset was shown to provide accurate water vapour measurements with a small (6%) wet bias. The ACE H<sub>2</sub>O datasets were shown to provide accurate UTLS H<sub>2</sub>O profiles near Eureka down to an altitude of around 7 km (e.g., within 13% of the 125HR). TCCON H<sub>2</sub>O and δD datasets, while having a small dry bias (6%) and high bias (40‰), respectively, relative to MUSICA, offer a global set of measurements that can be used for water vapour studies and satellite validation.

The key outcomes of this research are as follows:

- 1. Detailed comparisons between seven Eureka-based H<sub>2</sub>O datasets, which revealed that:
  - a. There was agreement between all combinations of PEARL H<sub>2</sub>O total column datasets, with mean differences  $\leq 1.0 \frac{\text{kg}}{\text{m}^2}$  and high correlation coefficients,  $R \geq 0.98$ , except between the microwave radiometer and the standard radiosonde product, which had R = 0.92.
  - b. The PEARL 125HR H<sub>2</sub>O retrievals produced using the MUSICA technique agree closely with other PEARL H<sub>2</sub>O measurements after known biases are taken into

account, revealing a high level of accuracy; however, there is a 6% wet bias that was not observed in validation studies for other MUSICA sites. This bias was not observed in an earlier version of the MUSICA retrieval (v2012) that used sitespecific a priori H<sub>2</sub>O profiles based on Eureka and other Arctic sites' radiosonde measurements, indicating that the bias may have been caused by the global a priori and microwindows used for the final retrieval version (v2015), which had abundances much larger than typical conditions at Eureka, a low-humidity highlatitude Arctic site.

- c. The AERI instruments, which measure emitted radiation from the atmosphere, were shown to produce accurate water vapour total columns, with measurements within 4% of GRUAN-processed radiosonde measurements. This result demonstrates that the AERI can be used to measure water vapour when sunlight is not available, which is a significant limitation for high-latitude sites.
- d. The lack of calibration and maintenance on the MWR at PEARL affected the H<sub>2</sub>O data significantly, causing a progressively worsening low bias in its total column measurements after mid-2010. This prompted NOAA to have the instrument removed, re-calibrated, and re-installed in 2018, and illustrates the need for regular cross-validation and comparison between measurements to monitor instrument performance.
- e. A collaboration with the GRUAN Lead Centre resulted in the generation of a Eureka radiosonde product that was processed using the GRUAN software. This provides a bias-corrected high-quality reference for temperature and H<sub>2</sub>O measurements at Eureka. Comparisons between the GRUAN-processed radiosonde data and the standard Eureka radiosonde data revealed a small dry bias in the latter, which is largest in summer. This aligns with the literature and will inform future use of the dataset, for example, in assessing new measurement techniques.

- An assessment of the accuracy and limitations of satellite-based water vapour observations in the UTLS near Eureka using the radiosondes and PEARL 125HR as a reference. This revealed that:
  - a. ACE-FTS and ACE-MAESTRO H<sub>2</sub>O profiles showed good agreement with both the radiosondes and the 125HR in the UTLS, e.g., at altitudes above 7 km. No obvious temporal trend was apparent in the differences. ACE profiles extend to lower altitudes than many other satellite-based measurements, particularly those retrieved from limb-viewing observations.
  - b. ACE-FTS showed a wet bias of approximately 6 to 13% relative to the 125HR between 7 and 14 km. ACE-FTS agreed with the radiosondes within 9% between 7 and 10 km, and showed a wet bias above 10 km up to 32%. ACE-MAESTRO profiles showed a dry bias between 6 and 11% relative to the 125HR between 6.5 and 14 km and a dry bias relative to the radiosondes of between 3% and 21% between 7 and 11 km.
  - c. Agreement between ACE H<sub>2</sub>O measurements and the Eureka 125HR and radiosondes showed closer agreement overall in the UTLS than did the other satellite datasets examined, with the exception of AIRS. Other available satellite datasets had very limited UTLS H<sub>2</sub>O measurements near Eureka. For example, MIPAS profiles are not recommended below 11 km; comparisons of MIPAS profiles below that altitude (e.g., down to 6 km) showed large differences with both the radiosondes and 125HR. MLS and SCIAMACHY profiles are limited to altitudes above 9 km and 11 km at Eureka, respectively. MLS H<sub>2</sub>O at 10 km showed a dry bias of 26% relative to radiosondes. TES H<sub>2</sub>O profiles showed large differences with the Eureka radiosondes and PEARL 125HR.
  - d. AIRS profiles showed very close agreement with both the 125HR and radiosondes at all altitudes throughout the UTLS and troposphere, i.e., the mean differences were within 5%. Given the enormous quantity of available AIRS measurements, it offers a useful dataset for quantifying the atmospheric water vapour abundances, distribution, and variability in the Arctic.

- An assessment of TCCON H<sub>2</sub>O and δD using comparisons at seven globally-distributed sites with co-located MUSICA datasets and five sites with radiosonde datasets. This revealed that:
  - a. TCCON and MUSICA H<sub>2</sub>O and  $\delta$ D datasets are in close agreement. Overall, the TCCON H<sub>2</sub>O total columns shows a dry bias with respect to the MUSICA datasets, of approximately 6%. The TCCON  $\delta$ D shows a high bias, e.g., less depletion, relative to the MUSICA  $\delta$ D, of approximately 40‰. These biases are relatively constant, and the datasets show very good correlation, e.g., *R* = 0.98 for H<sub>2</sub>O and *R* = 0.96 for  $\delta$ D.
  - b. Better agreement is observed between the TCCON H<sub>2</sub>O and radiosondes compared to agreement observed using the TCCON a priori profiles. This indicates that the TCCON retrieval contains information about the atmospheric water vapour column in addition to its a priori information.
  - c. The exception to the overall observed mean agreement between TCCON and MUSICA was the comparison performed using TCCON measurements at Sodankylä and MUSICA measurements at Kiruna. Results of this comparison showed larger scatter and a mean TCCON wet bias of 11%. This is likely due to the 258 km distance between the instruments. Nonetheless, this comparison is useful because it can inform the use of TCCON water vapour measurements in satellite validation studies, which typically need to judiciously choose a spatial criterion large enough to ensure sufficient coincident measurements to have a statistically meaningful comparison but small enough to ensure the resulting differences are due to the measurement quality and not simply the result of natural variability. A spatial distance smaller than 250 km is recommended based on the results of the Sodankylä/Kiruna comparison.

The work done in this thesis shows that progress is being made to measure atmospheric water vapour. The PEARL FTIR H<sub>2</sub>O total columns and ACE profiles are useful datasets that capture information about the high Arctic atmosphere. TCCON spectra can be collected every 2.4 minutes, and the demonstrated accuracy of its H<sub>2</sub>O retrieval means that it can be used to capture the short-term variability of water vapour at multiple global sites. This is useful for understanding variability, trends, and for validation of other instruments' datasets.

Measurements acquired using the PEARL 125HR and ACE will continue to contribute to the study of the high Arctic atmosphere. Nonetheless, despite the progress demonstrated, this thesis has also shown that work is still needed to improve water vapour measurements in the Arctic, as they do not yet meet the accuracy and data coverage needs of the climate and atmospheric science communities.

# 7.2 Future work

Suggestions are offered for improvements to the measurements acquired at PEARL and Eureka. In addition, there are a variety of research threads that have been partially pursued that offer promising avenues for future work.

### 7.2.1 PEARL 125HR operational improvements

Three opportunities to improve 125HR measurements stand out:

### Automatic liquid nitrogen (LN<sub>2</sub>) filling

The need to have an operator on-site to fill MCT and InSb detectors with liquid nitrogen every day is a barrier to maximizing the collection of MIR spectra, since operators are not always available. In addition, this is a significant limit on remote measurements. Automatic LN<sub>2</sub> filling systems have been successfully used at FTIR spectrometer sites for decades, indicating this upgrade to PEARL's 125HR system is possible.

#### Automatic weather trigger for Robodome

Currently, an on-site operator is needed to monitor local weather conditions and shut down measurements if high wind, precipitation, or other problematic weather occurs. Not only does this create measurement gaps when an on-site operator is not available, but the lack of a weather monitoring system connected to the 125HR measurement system, e.g., the 125HR, sun-tracker, and Robodome, has meant that measurements are not conducted overnight during polar day while operators are asleep. Setting up a weather monitoring system that would trigger a shut down of 125HR measurements would be a valuable step towards full automation. Since the existing 125HR macro codes automatically shut down after a loss of sufficient signal, the weather trigger could simply shut the Robodome hatch. This would protect the sun-tracker and trigger the 125HR macro to stop. Creating a system that would re-open the Robodome hatch and re-start 125HR measurements when weather (or light) is again favourable would require greater effort. Nonetheless, this level of automation has been achieved at other FTIR spectrometer sites, and should be achievable at PEARL.

#### Polar night 125HR measurements

Polar night remains a large gap in the 125HR spectra and resulting datasets. The ability of the CST to track the Moon enables the 125HR to collect lunar absorption spectra. The lower intensity of light from the Moon creates limitations; however, retrieving atmospheric total columns and profiles of various atmospheric constituents from lunar FTIR measurements has already been done by others. The previous FTIR spectrometer installed at PEARL (then called the Arctic Stratospheric Ozone Observatory, AStrO), a Bomem-built DA8, collected lunar measurements from October 2001 to March 2002. HNO<sub>3</sub> profiles were retrieved from these measurements and compared with chemistry-climate models (Farahani et al., 2007). Moreover, several species related to ozone depletion chemistry have been retrieved from lunar FTIR spectrometer measurements acquired at Ny Ålesund during polar night, e.g., during the winter of 1992/1993 (Notholt, 1994), using an MCT detector and a modified InSb detector.

The PEARL 125HR has been used to acquire lunar measurements on a few occasions using the MCT detector since March 2015; however, lunar measurements are not yet performed routinely with well-defined settings and procedures. In addition, retrievals have yet been run on the limited lunar measurements heretofore obtained. This would be a worthwhile project to pursue.

### 7.2.2 MUSICA δD analysis

The δD dataset produced by MUSICA offers an opportunity to investigate atmospheric transport and physical processes. For example, the PEARL 125HR δD could contain a signal of dehydration caused by PSC formation. ACE-FTS vertical profiles of H<sub>2</sub>O and HDO measurements might also show dehydration. Analysis of the type 2 MUSICA product's H<sub>2</sub>O and δD pairs, e.g., through H<sub>2</sub>O vs. δD plots shown in Figure 7.1, can offer insight into the transport processes that have affected the humidity reaching Eureka. This form of analysis involves the calculation of reference lines that represent different physical processes causing HDO depletion, and has been done using MUSICA retrieval data products at other sites, e.g., by González et al. (2016) at Izaña, Canary Islands. This analysis could be combined with model analysis, e.g., plot back trajectories for each data point to find seasonal shifts in sources, as has been done by Hausmann et al. (2017) using data collected at Zugspitze, Germany. Figure 7.2 shows the PEARL 125HR MUSICA δD dataset, with back-trajectories for two example dates. These results show two different transport patterns, one from across the Arctic Ocean and another from the north Atlantic Ocean, reaching Eureka with distinct δD signals.



Figure 7.1: PEARL 125HR MUSICA type 2 H<sub>2</sub>O vs. δD, using measurements acquired from 2006 to 2014. Data points are colour-coded to the day of year (DOY).



Figure 7.2: (a) PEARL 125HR δD dataset. HYSPLIT back-trajectories for two highlighted data points are shown in (b) and (c), showing different transport histories of the air parcels.

#### **Model validation**

The water vapour isotopologue measurements generated by the MUSICA project could be used to validate models. Since the isotopologues contain information about the dynamical history of the air parcel, the validation of model isotopologue values using ground-truth measurements is a check on models' ability to represent atmospheric water vapour abundances and dynamics. Initial comparisons were performed between the Community Earth System Model (CESM) daily averages of H<sub>2</sub>O and  $\delta$ D on a 2° x 2.5° degree grid and MUSICA products from nine sites. Distances between the nearest model grid point and the FTIR spectrometer site were typically small, e.g. 57 km between the PEARL RL and the nearest model grid point, 80.5°N, 272.5°E. Comparison results for the Eureka comparisons are shown in Figure 7.3; a correlation plot showing CESM vs. MUSICA H<sub>2</sub>O is shown in Figure 7.4. A detailed analysis of comparisons would be a worthwhile project that could be combined with an analysis of models' ability to reproduce the transport of water vapour into the Arctic.



Figure 7.3: Comparison of CESM and PEARL 125HR MUSICA H<sub>2</sub>O daily averages. (a) Grey squares show the full CESM timeseries of H<sub>2</sub>O from 2006 to 2014; green and red markers show coincident CESM and PEARL 125HR data, respectively. (b) Difference (CESM – 125HR). (c) Percent difference, relative to mean of both. In both (b) and (c) the red dotted line is the mean of the differences and the dashed black lines are the mean  $\pm \sigma$ .



Figure 7.4: MUSICA vs. CESM δD for nine FTIR spectrometer sites.

#### **TCCON Retrievals**

The TCCON H<sub>2</sub>O product was shown to be accurate in Chapter 6, based on comparisons to radiosondes and the MUSICA H<sub>2</sub>O product. It would be worthwhile to explore changes to the TCCON retrieval that could produce a measurement of  $\delta D$  using an approach similar to the MUSICA retrieval.

### 7.2.3 Eureka radiosonde dataset analysis

The Eureka radiosonde dataset offers opportunities for long-term trend analysis of temperatures and humidity. Surface atmospheric measurements began immediately after Eureka was established, on April 11, 1947. Upper-air measurements are available as early as 1948 (however, the number of profile levels available from the first two decades is limited). This 70-year dataset offers valuable opportunities for long-term characterization of conditions at the site and tracking long-term trends, e.g., in temperature, humidity, and the low-altitude inversion layer. Lesins et al. (2010) examined the Eureka surface and radiosonde datasets from 1961 to 2007, e.g., finding an annual average surface warming of 3.2°C since 1972 and a 10% increase in PWV since 1961. An updated analysis following from that study would be useful to pursue, especially since there has been increased attention on temperature and humidity trends globally and in the polar regions. Moreover, the time period from 2007 to 2018 corresponds to a decade of measurements and scientific output from PEARL, making an analysis of the atmospheric trends during that time additionally valuable as context for other studies.

An initial look at the Eureka radiosonde dataset suggests there are interesting features in the long-term time series worth examining:

- Overall average temperatures continue the general trend of increasing over climatological timescales.
- On a decadal timescale, near-surface temperature averages appear to peak in the final year in the Lesins et al. (2010) analysis, 2007, and decline thereafter, as shown in Figure 1.13.
- Water vapour total column trends also appear to be negative in the last decade, reducing the overall upward trend.
- The range of extreme values has been expanding: at sea level and the Ridge Lab altitude, for example, recent years have repeatedly set high temperature records during short, e.g. one to two day, periods of time.

# 7.2.4 Frostpoint hygrometer measurements at Eureka

This work assessed the accuracy and reliability of new methods for measuring water vapour. However, the best available instrument for providing reference measurements of atmospheric water vapour profiles from the surface to the middle-stratosphere, the FPH, has never been deployed at Eureka.

At the time NDACC began, it was noted that only one station recorded high quality water vapour measurements using a frostpoint hygrometer. Kurylo (1991) recommended that the FPH measurements should be expanded to a greater number of sites. 25 years later, the use of FPHs remains globally sparse.

Adding FPH measurements to the data collected at Eureka would offer a valuable dataset for precise and accurate water vapour profile measurements.<sup>29</sup> These could be used for validation of ground-based, radiosonde, and satellite water vapour measurements. Even a short-campaign using the FPH would be worthwhile, e.g., if timed during the annual ACE/OSIRIS validation campaign.

<sup>&</sup>lt;sup>29</sup> It would be ideal for ECCC to join GRUAN, which would require monthly FPH measurements as part of the radiosonde calibration requirements.

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