Development, Aircraft Integration, and Field Deployment of a CO2 Herriott Cell to Measure Arctic Carbon Fluxes

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:37944962

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Abstract

The warming of the Arctic, as mediated by climate change, will precipitate a feedback effect. Should the carbon in soil be processed and emitted as the greenhouse gases CO$_2$ and CH$_4$, the feedback effect will be positive; if, however, increased plant growth draws down sufficient atmospheric CO$_2$ to overwhelm emission mechanisms, the feedback will be negative. High resolution measurements of CO$_2$ and CH$_4$ emissions are critical to understanding how the changing Arctic biome will respond to, and, in turn, influence climate change. Yet the sparsity of infrastructure and population in the Arctic precludes widespread monitoring of carbon emissions and uptake in the Arctic, hindering understanding of the mechanisms which control the feedback effects of a warming Arctic.

In response to these issues, we present a new CO$_2$ Herriott Cell that operates in conjunction with a NOAA Best Air Turbulence probe on a lightweight DA-42 aircraft. The CO$_2$ Herriott cell employs a tunable mid-IR Quantum Cascade Laser to measure CO$_2$ and its isotopologues via direct absorption in a Herriott Cell. The CO$_2$ Herriott cell demonstrates in-laboratory precision of 1 ppmv (1 sec). We describe the development of the instrument, as well as our calibration and precision assessment protocols in the laboratory, in detail. In chapter 2, we
report on the field deployment of the instrument suite in the North Slope of Alaska in August of 2013. Owing to differences between field deployment conditions and laboratory conditions, our instrument did not perform to specification in the field. Thus, in chapter 3, we examine the sources of instrument performance deterioration in the field. We provide as well corrections to field data carried out in the laboratory after the mission, and the subsequent recovered $^{12}$CO$_2$ data from five flights of the field campaign, demonstrating proof-of-concept of the CO$_2$ Herriott instrument. Finally, we offer suggested instrument augmentations to ensure the capacity to measure fluxes in-situ during future field deployments.
Abstract ......................................................................................................................... iii

1: Introduction and Motivation .................................................................................. 1

1.1 Climate Change Background .................................................................................. 1

1.1.1 Energy Production and Use ............................................................................ 2

1.1.2 Consequences of Climate Change .................................................................... 8

1.1.3 Climate Feedback Effects ................................................................................ 10

1.1.4 Arctic Carbon Feedback Effect ......................................................................... 12

1.2: Arctic Biogeochemistry and Geomorphology .................................................. 14

1.2.1 Natural Processes that Control Carbon: Photosynthesis, Respiration, Methanogenesis, and Methanotrophs ................................................................. 14

1.2.2 Geomorphology of the Arctic and Natural Processes of Emissions and Uptake ........ 18

1.2.3 Anthropogenic CH₄ and CO₂ in the Arctic .................................................... 24

1.3 Isotope Ratios ........................................................................................................ 25

1.4 Recent Measurements and Models ........................................................................ 31

1.4 Aircraft Flux Measurement and Comparison with Tower ..................................... 33


Chapter 2: CO₂ Instrument Development ................................................................... 38

2.1 Instrument Design and Requirements .................................................................... 38

2.1.1 Light Source and Optics ................................................................................ 41

2.1.2 Herriot Cell ....................................................................................................... 47

2.1.3 Electronics ........................................................................................................ 48

2.1.4 Fitting Software ............................................................................................... 49

2.1.5 Pneumatics System .......................................................................................... 52
2.2 Laser Spectral Region Shift and Ramifications ................................................................. - 54 -

2.3 Final Integration into FOCAL ................................................................................................ - 60 -

3: Results .................................................................................................................................. - 64 -

3.1 Lab Performance and Water Calibration .............................................................................. - 64 -

3.2 Inconsistencies Between Lab and Field ................................................................................ - 71 -

3.2.1 Calibration Mismatching ................................................................................................. - 72 -

3.2.2 Ruling Out Simple Temperature Corrections ................................................................. - 73 -

3.2.3 Etalon and Laser Feedback ............................................................................................... - 74 -

3.2.4 Detector Shortcomings and Laser Feedback Shortcomings and Laser Feedback .......... - 77 -

3.2.5 Making a New Algorithm to Recover Field Data ............................................................. - 78 -

3.2.6 Recovered $^{12}\text{CO}_2$ data ............................................................................................ - 82 -

3.2.7 Cavity Etalon Fitting Issues ............................................................................................ - 84 -

3.2.8 Temperature Measurement and Control ......................................................................... - 87 -

3.3 Field results of the $^{12}\text{CO}_2$ Data ....................................................................................... - 91 -

3.3.1 North Slope, AK, Field Test and Mission ....................................................................... - 92 -

3.3.2 Field Mission and $^{13}\text{CO}_2$ results .............................................................................. - 94 -

3.3.3 Field Mission and Measured $^{13}\text{CO}_2$ ......................................................................... - 100 -

3.3.4 Back-Trajectory Analysis, Regional Trends, and Tower Comparison ......................... - 100 -

3.3.5 Brief Analysis of NOAA Flux Tower near Deadhorse, AK .......................................... - 113 -

3.4 Next Generation $\text{CO}_2$ Instrument ..................................................................................... - 116 -

3.4.1 Off Gassing Anodization ................................................................................................. - 117 -

3.4.2 Laser Wavelength ........................................................................................................... - 118 -

3.4.3 In-Flight Calibrations ...................................................................................................... - 119 -

3.4.4 Lab Testing Optical Changes ......................................................................................... - 119 -
3.4.5 Temperature Control and Measurement ................................................................. - 120 -
3.4.6 Anticipated Results of Fixes .................................................................................. - 121 -

4 Conclusion ................................................................................................................. - 122 -

Appendix ......................................................................................................................... - 124 -

Beer’s Law Code and Description for Matlab ............................................................... - 124 -

Fitline File ....................................................................................................................... - 127 -

Steady State Heat Transfer Model for Lower Glass Temperatures ....................... - 128 -

List of Figures

Figure 1: Worldwide GHG emissions by gas from 1970-2010........................................ - 4 -

Figure 2: GHG emission by sector in 2010................................................................. - 5 -

Figure 3: Relative CO₂ equivalent emissions of the major types of powerplants .... - 7 -

Figure 4: Abundant lakes in Arctic Alaska ............................................................... - 19 -

Figure 5: Thermokarsting causing mass wasting ....................................................... - 22 -

Figure 6: A schematic of a permafrost lake in the arctic ........................................... - 23 -

Figure 7: Carbon emissions in the North Slope ...................................................... - 30 -

Figure 8: BAT probe displayed in a wind tunnel calibration .................................... - 36 -
Figure 9: CO2 Instrument Design.................................................................- 39 -

Figure 10: CO2 instrument installed in the airplane, with support electronics.........- 40 -

Figure 11: Concept art of the instrument suite ..............................................- 41 -

Figure 12: Laser housing schematic.............................................................- 43 -

Figure 13: A diagnostic etalon scan. ..............................................................- 46 -

Figure 14: Spectral region of CO2 instrument and field spectra. .......................- 52 -

Figure 15: Intended spectral region vs. what he had.......................................- 56 -

Figure 16: Carbon cell etalon. ....................................................................- 57 -

Figure 17: Fitting results with a cavity etalon.................................................- 58 -

Figure 18: Discrete Fourier Transform of fitted data........................................- 59 -

Figure 19: Fitting results after accounting for the cavity etalon. .......................- 60 -

Figure 20: The BAT probe and boom installed and mounted on the aircraft. .......- 61 -

Figure 21: Large ICOS cell and Pump System................................................- 62 -

Figure 22: Allan Variance plots of CO2 axis in lab tests.....................................- 65 -

Figure 23: Bubbler system schematic for water corrections. ...........................- 67 -

Figure 24: Water broadening correction........................................................- 69 -

Figure 25: 12CO2 instrument linearity.............................................................- 70 -

Figure 26: Field mixing ratios before algorithm augmentation...........................- 72 -

Figure 27: Calibration cycle before correction...............................................- 72 -
Figure 28: First derivative of fit of the etalon function. - 75 -

Figure 29: Schematic diagram of LPV thermal expansion and laser feedback. - 77 -

Figure 30: Tuning rate of the laser during calibration. - 80 -

Figure 31: Flow diagram of correcting the fit of the CO2 instrument. - 81 -

Figure 32: Scan using our former algorithm (top) and corrected algorithm (bottom). - 83 -

Figure 33: Calibration cycles during flight. - 84 -

Figure 34: A zoomed in cavity etalon from the field data. - 85 -

Figure 35: Etalon fit causes fitting errors. - 86 -

Figure 36: Glass Sample Cell Temperature of a flight on August 26th, 2013. - 88 -

Figure 37: Table of temperature effects on measurements. - 89 -

Figure 38: Temperature profile of the CO2 cell. - 91 -

Figure 39: CO2 vs. Temperature for all five runs, 10s data. - 95 -

Figure 40: Compilation of [CO2] for five runs, and land types. - 96 -

Figure 41: CO2 concentration and land type and colored by temperature. - 98 -

Figure 42: CO2 measurements vs. Air Temperature on Aug. 26th. - 99 -

Figure 43: Geospatial view of CO2 on August 26. - 99 -

Figure 44: The CO2 concentrations along the flight path of flight 26.1. - 103 -

Figure 45: backward trajectory analysis of the flight data for 26.1. - 103 -

Figure 46: The CO2 concentrations along the flight path of flight 26.4. - 105 -
List of Tables

Table 1: Table of carbon pathways and how they affect carbon isotope ratios. ....... - 26 -

Table 2: Harvard Anderson CO₂ instrument measured laboratory performance vs. commercially available instruments............................................................... - 71 -
Acknowledgements

This dissertation would not be here if it were not for those who supported me along the way. Most important, I would like to thank my four siblings for their support after we lost our parents at a young age. I never would have made it to start my PhD if it were not for their support.

As for surviving my PhD, the thanks must be liberally spread. Mark Witinski, a former Anderson Group post doc, was one of my earliest academic mentors. His early one-on-one lab technique sessions gave me what I needed to complete this work, and his push to learn machining and the hardware aspect of all provided me with a niche in the group that no one else filled. David Sayres’ analytical and programming techniques rounded out the skills I needed to develop my own analytical and data processing applications. I’ll be using the skills these two taught me for the rest of my life. The engineering team in the Anderson group, beyond providing invaluable design and guidance, was a source of moral support in and out of the office. Through Chris’s indirect guidance, I more than doubled my squat and deadlift over my seven years in the Anderson group. A special thanks goes out to David Sayres and Jessica Smith in the Anderson group, and the administration of SEAS, and Suzanne Smith at the writing center for helping me over the finish line of the PhD. Finally, Josh Klobas and Reem Hannun have been a source of constant support and inspiration that were vital to me sticking it out.

Throughout my PhD, three other groups kept me sane. First is my group of friends outside of academics, especially Meghan, Dandan, and Scott, who made sure that when things did not work in lab that I would have a place to decompress. Usually the Tam. Second, I would
like to thank the community at Mather House, where I am a resident tutor, for both supporting and inspiring me, especially Ravi Parikh. Finally, I need to thank the Harvard Business School Rugby Football Club. The highlight of my time as a PhD was when we won the MBA Rugby World Championship. I never would have survived my PhD if I did not have an opportunity to get my exuberance and energy out on the rugby pitch.
1: Introduction and Motivation

Climate change stands to alter the world dramatically, with potentially devastating effects for a large swath of the world population. The burning of fossil fuels continues to be the primary contributor to climate change, and will remain so for the coming decades. Increases in global temperature are predicted to lead to rising sea level, extreme weather events, threats to crop productivity, and direct health impacts. A better understanding of the complex dynamic systems, both natural and produced by man, that influence climate change will aide us in making policy choices.

1.1 Climate Change Background

The climate system is unequivocally warming, as demonstrated by an increase in the average surface temperature of the earth by 0.85°C since 1880 (IPCC 2014). Scientific consensus is that this phenomenon is driven primarily by increasing concentrations of greenhouse gases (GHGs) in our atmosphere, consisting primarily of CO₂, CH₄, N₂O, and H₂O. These gases accumulate in the Earth’s atmosphere and prevent the emission of radiant energy, which the Earth, like all matter, emits as electromagnetic radiation. The amount of energy and wavelength of radiation serve as a function of surface temperature. The Sun supplies $5.4 \times 10^{24}$ J/yr or energy to the Earth, 30% of which is reflected back to space, with the remaining $3.8 \times 10^{24}$ J/yr being absorbed by Earth’s surface. In steady-state, the Earth must emit the energy is absorbs. Basic physics indicates the average surface temperature of the Earth would be 255 °K. The presence of GHGs shifts this equilibrium temperature upwards by absorbing outgoing infrared radiation and
reemitting it, with half passing further into the upper atmosphere and half directed towards the surface, increasing surface temperature. As a result of this increase in energy flux to the surface, the average temperature of the Earth is 288 °K, owing primarily to GHGs (IPCC 2014). Given the primacy of GHGs in conditioning atmospheric temperature, a characterization of GHGs in further detail is necessary.

GHG emissions are characterized by both volume and potency. The volume of emissions minus GHG sinks, reservoirs that absorb or sequester emissions, determines atmospheric concentrations. Potency is characterized by the relative Global Warming Potential (GWP). The GWP is the relative greenhouse forcing per molecule. While CO$_2$ can remain in the atmosphere for millennia, other molecules have a shorter average atmospheric lifetime due to chemical and biological consumption. As a result, when comparing GWP, a relative timescale needs to be taken into account. CH$_4$, for example, is approximately 25x stronger than CO$_2$ on a 100-year timescale (IPCC 2007). The reason for this relative strength is that CO$_2$ is somewhat saturated in the atmosphere in terms of infrared absorbance, and further increases in concentration have relatively smaller marginal heat-trapping effects. CH$_4$, on the other hand, is less saturated, and will absorb and trap a greater amount of outgoing infrared radiation per molecule.

1.1.1 Energy Production and Use

The concentrations of GHGs in the atmosphere have increased concurrently with the rise of industrialization. Atmospheric CO$_2$ has increased from a pre-industrial level of 280 parts per million by volume (ppmv) to over 400 ppmv today, while CH$_4$ has risen from 715 ppbv in 1750 to 1,787 ppbv in 2008 (Dlugokencky et al. 2009, Conrad 2009). Anthropogenic emissions and land use changes have largely shaped CO$_2$ emissions over the last two centuries.
Driving the anthropogenic rise in GHGs are emissions from energy production, industry, transportation, agriculture, and land use practices (Figure 1 & Figure 2). Industry emits GHGs directly and indirectly. As an example, one to two tons of CO$_2$ are emitted during steel and concrete per ton of production and aluminum production produces trace sulfur hexafluoride, with a 22,800 greater warming potential per molecule than CO$_2$. These emissions are directly related to the chemical changes of the materials. In addition, all industrial processes use energy that often is produced at fossil-fuel burning power plants. As for other sources, nearly all transportation burns fossil fuel to directly contribute to the GHG burden in the atmosphere. Slash-and-burn agriculture, forestry, and animal husbandry also contribute greatly to GHG emissions and reduction of the Earth’s ability to draw down CO$_2$ from photosynthetic storage of CO$_2$ in plants. All told, these processes currently release more than 49 gigatons of CO$_2$ equivalent emissions per year, and they are estimated to increase with population growth and development (IPCC 2014). For a deeper breakdown of 2010 emissions by sector, see Figure 2.
Figure 1: Worldwide GHG emissions by gas from 1970-2010. Emissions are weighted by GWP relative to CO₂. CO₂ emissions in orange are mostly from industrial and energy processes, including transport. CO₂ in red is forestry and other land use changes. Annual average growth rates are periodically defined in brackets, with percent of total emissions broken out each decade. F-gases are CFCs, PFCs, and SF₆. The various emissions have different 90% confidence intervals, with ~20% for CH₄ and F-gases, ~60% for N₂O (largely from agriculture) and CO₂ land use changes, and 8% for CO₂ fossil fuel and industrial emissions (IPCC 2014).
Figure 2: GHG emission by sector in 2010. Emissions are converted into CO₂ equivalent emissions on a 100 year timescale to determine relative GWP. The chart makes it clear that incremental reductions in emissions can come at a cost. Industry, which drives GDP growth in most countries, accounts for 32% of emissions, and transport to move goods and to get to work accounts for a further 14% of emissions. Cutting emissions from these proves difficult when a country is choosing between emissions cut and GDP growth. Image from IPCC (2014).

These anthropogenic emissions sources, and their increase, are integral to nations developing out of poverty by increasing living standards with increased use, and also saving and preserving lives by raising health standards. Moreover, each scales directly with population increase. As a society, how are we to weigh the cost of climate change versus the needs of developing countries and preserving lives? We seek to enrich this discussion by contributing to a deeper understanding of factors that contribute to climate change. We consider as well limitations in our options to sustainable expand energy production while mitigating emissions, and the consequences of climate change. Unfortunately, the answer to the dilemma posed by climate change is not as simple as building cleaner energy sources.
Low-emission energy production are mechanisms of energy production, including wind, solar, hydropower, nuclear, and others, that result in significantly lower GHG emissions than fossil fuel power plants. No matter the pathway to energy production, however, it produces CO$_2$ (Figure 3). Fossil fuel power plants produce CO$_2$ both in the steel and concrete used to produce them, and in burning the fuels that create heat and steam to spin generator turbines. Nuclear power plants, wind turbines, hydroelectric dams, and solar power plants do not emit CO$_2$ once complete, but they all have a CO$_2$ cost in the steel, concrete, and other materials used to produce them. Thus, while it is inescapable that providing the electricity that drives our society will produce GHGs, the power sources that do not emit GHGs during energy production will have a far lower environmental impact (Figure 3). Why, then, are low-emission energy sources not the clear solution to climate change?

First, according to the IEA (IEA 2015), the cost of solar PV is more than 50% higher than natural gas or coal, putting these energy sources out of the price range of many developing economies. Second, it is impossible currently to supply all the world’s energy from non-nuclear clean energy sources. In the past five years, world energy production has grown at 200 GW per year. To supply just this growth with enough materials for solar power would require 1 kiloton of tellurium, a vital component of solar PV, compared to current total world production of 0.5 kilotons (Moss et al. 2013). Given that solar power uses only 8% of current world Te production, solar PV would require triple production of this material to meet the needs of current Te use and of solar PV. This calculation excludes replacement of the current 3600 GW of installed fossil fuel generation capacity that would need to be replaced to reduce GHG emissions from power production.
Figure 3: Relative CO₂ equivalent emissions of the major types of powerplants. Data taken from IPCC (2014). Over an entire lifetime, in optimal conditions, solar PV will emit roughly 10% the CO₂ equivalent emissions as the current natural gas power plants. While this graphic serves to compare the CO₂ costs of various sources of energy, it fails to account for limited suitable locations for the low-emitting sources of power. Solar PV is this efficient only in areas of high sunlight, and requires significant amounts of rare earth elements, and the current world production rate is relatively small and largely limited to China. Similarly, onshore wind will emit 2.5% of what natural gas plants will, but there are relatively few sites with sufficient wind to bring costs low enough to make this a viable tradeoff.

Third, location limitations for all region-specific clean sources preclude cost-effective emplacement. Hydro power is largely tapped out in most developed countries, and can be environmentally disastrous. Wind power is cost-effective and available in limited locations. Solar power is only effective in regions with limited cloud cover and strong direct insolation, often far from population centers.

Fourth, the likelihood of societal changes that would allow for an immediate shift to cleaner technologies is small. Shifting transportation from fossil fuels is impossible on short timescales. Few cities in the world have infrastructure or space to build infrastructure that would allow for sufficient public transportation to supplant personal vehicles. Thus, changing the
suburban commuter lifestyle of the US, would entail a generational shift rather than a short-term one. The replacement of all personal vehicles with electric vehicles would not only result in rare earth production issues similar to solar PV technology, it would also require undertaking extensive electrical capacity development, further stressing natural resources.

Fifth and finally, while nuclear power could solve most of these problems, most of the world finds nuclear power unacceptable as an energy source for perceived safety reasons. From these limitations, it becomes clear that until we develop newer technology, fossil fuel power plants will still need to be built. Any power plants built now will last an estimated 40-60 years, prolonging emissions into the latter half of the century. As a result, we can anticipate high levels of global CO$_2$ emissions from energy generation for decades to come, and the concomitant climate forcing resulting from these emissions. Our options are to endure climate change, or to curtail lifestyles in developed countries while reducing the development of third world countries.

### 1.1.2 Consequences of Climate Change

While estimates of the cost of consequences of climate change vary widely, from -$3 (a net benefit) to $100 per ton CO$_2$ emitted, with an average of $12 in the literature (IPCC 2014), it is certain that areas that are unprepared, highly exposed, and with limited ability to adapt will bear the brunt of the cost (IPCC 2014). In other words, poorer regions will suffer more than wealthier regions. Some harmful events will be transient, occurring infrequently but often with devastating effects, while others will be prolonged or permanent.

Transient events include heat waves, erratic storm patterns, short term droughts, and floods, while examples of prolonged impacts include sustained regional or national droughts and...
sea level rise. These events have increased related to climate change across mid latitudes over the past two decades, and will likely become more frequent as climate change progresses (Pachauri and Meyer 2014). Transient events cannot easily be prepared for, with death as a potential result. A heat wave in Europe in 2003, for example, killed over 30,000 people.

Although it is possible to prepare for the prolonged impacts of climate change, they will unavoidably entail the devastation of regions and local and regional economies, due to drought or complete loss of fresh water supply. Increased evaporation rates under warmer climate scenarios which will desiccate some areas, leading to drought. Drought can lead to crop failure, reducing agricultural output of regions that rely on agriculture for their economy, and endangering food supplies. Owing to extreme events destroying crops through drought and flood, the world food supply is at risk in the face of climate change. Models suggest “severe and widespread droughts” in the next 30-90 years (Dai 2013). In addition, as sea level rises, saline waters will inundate the fresh groundwater of several regions, poisoning the water needed to grow crops.

Sea level has risen nearly 10cm since 1850, from both melting land ice and from thermal expansion of the ocean. As sea level rises, storm surges will produce a surge height on top of the additional sea level, and the risk of catastrophic flooding of the likes after hurricanes Katrina and Irene increases. In the US, projected sea level rise by 2050 will result in some areas experiencing historic 100-year storm surges annually, and up to 30% of coastal regions in the US experiencing historic 100-year surges at least once a decade (Tebaldi, Strauss and Zervas 2012). Indeed, it is possible that climate change will increase the frequency of the most devastating hurricanes,
causing massive coastal property damage (Knutson et al. 2010). Preparing cities for events like this is immensely costly; as such, many developing countries cannot afford to do so.

A final devastating effect of sea level rise is the inundation of fresh water supplies by rising ocean water, which will disproportionately impact poor areas and already water-stressed areas (Dasgupta et al. 2009), poisoning wells and irrigation water and rendering regions uninhabitable. One meter of sea level rise in Bangladesh, for example, will deprive 17 million impoverished people of fresh water, and force them to move deeper inland in an already-overpopulated region (Sarwar 2005)

Understanding how climate change unfolds will help us craft policy to mitigate its effects, and where emissions cannot be avoided, how to best adapt. Unfortunately, anthropogenic emissions alone do not capture the complexity of climate change. Many feedbacks, both positive and negative, have the potential to exacerbate and limit climate change. Monitoring and understanding these interactions is necessary to increase confidence in predictions of climate change and its associated impacts.

1.1.3 Climate Feedback Effects

Climate feedback effects are effects of climate change that, in turn, affect further climate change. Several feedback effects are prominent in relation to climate change. The scale and timing of these feedback effects vary greatly; some occur over years, while others occur over epochs. The most important of the climate feedback effects is the several-hundred-thousand year negative feedback effect of silicate weathering. This is the thermostat of the Earth that takes advantage of the fact that the Earth’s surface temperature is near the triple-point of water that
ensures habitable temperatures. Silicate weathering is the chemical transformation of rocks into weathered minerals. The composition change that draws CO\(_2\) into the chemical structure of sediments, typically carbonate sediments, governed by the equation \(\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2\). This process is mediated by rain. During warmer periods on Earth, there is more rain that contributes directly to more rapid weathering, causing more CO\(_2\) to be sequestered in sediments, and ultimately cooling the Earth. Conversely, during cooler periods on Earth, rainfall is reduced, less CO\(_2\) is drawn into the sediments, atmospheric CO\(_2\) increases (albeit at a rate much slower than we are currently experiencing), and the buildup of CO\(_2\) pushes the Earth to warm sufficiently to restore liquid water. This is the feedback effect that has allowed life on Earth to flourish over the past 500 million years. It will eventually force the atmosphere back into equilibrium by burying excess atmospheric CO\(_2\), but the several hundred thousand year timescale to re-equilibrate will not help us over the next century of development.

Several major climate feedback effects are vital to understanding Earth’s climate evolution over the next hundred years. Sea ice reflects 80-90% of incoming radiation, but open ocean left from melted sea ice absorbs 90% of incoming radiation, further heating the Earth and melting more ice. Warmer air can lead to drying forest biomes, resulting in less plant growth, and less above-ground CO\(_2\) storage in plant matter(Enquist and Enquist 2011). Countering this is the negative feedback loop, CO\(_2\) fertilization, whereby plants will grow faster with more CO\(_2\) in the atmosphere. Increasing cloud cover based on greater moisture in warmer climates can cause both negative and positive climate feedbacks. Increasing low-altitude clouds can reflect incoming shortwave radiation, preventing the Earth from absorbing that energy, while increasing high-altitude clouds absorb outgoing longwave radiation from Earth, trapping heat (Soden and Held 2006).
This project focuses on the climate feedback of warming in the Arctic. As a consequence of climate change, the poles will warm more than the rest of the world, and the permafrost in the Arctic can melt (IPCC 2014). The Arctic contains labile carbon from millennia of growth-freeze cycles. As the permafrost melts, this labile carbon can be exposed to the atmosphere, and released into the atmosphere as the greenhouse gases $CO_2$ and $CH_4$ in a positive feedback effect.

### 1.1.4 Arctic Carbon Feedback Effect

The Arctic carbon feedback effect is the potential emission of $CO_2$ or $CH_4$ from the Arctic on a scale that rivals emissions of the largest emitting countries. The concomitant rise of tropospheric temperature with increases in greenhouse gas mixing ratios could trigger a feedback effect in the Arctic. The melting permafrost exposes organic carbon to decomposition, and the subsequent release of this carbon to either $CO_2$ or $CH_4$. The timing, mechanisms, and scale of this release are not well understood (Crawford et al. 1996, Sitch et al. 2007, Zhu and McGuire 2016), but the *potential* effect is massive, with the arctic permafrost holding twice as much carbon as the entire atmosphere (Tarnocai et al. 2009, Hugelius et al. 2014). Conversely, it is possible that warmer growing conditions and thawing permafrost will allow for more and larger plant matter to take root and grow in the Arctic, effectively drawing down carbon from the atmosphere. It is imperative to conduct field research to reach a better understanding of the timescale and magnitude of potential carbon release or uptake from this region. As the Arctic climate warms and arctic permafrost begins to melt, the net carbon exchange will be determined by the balance of net primary production and heterotrophic respiration (Hicks Pries, Schuur and Crummer 2012, Friborg et al. 2003, Koven et al. 2011, Natali et al. 2011, Merbold et al. 2009),
both of which increase with increasing average annual temperatures in the Arctic (Euskirchen et al. 2009).

Measurements of carbon emissions are crucial as models of the Arctic landscape have varied in their assessment of whether the region will be a net sink or source of carbon, with the results dependent upon the inputs and parameterizations used (Koven et al. 2011). Sitch et al. (2007) cite many early models that indicated the Arctic would take up more CO₂ than it released, whereas some literature suggests that the Arctic will become a net carbon source (Schuur et al. 2008, Schuur et al. 2009, Natali et al. 2011, Koven et al. 2011, Dutta et al. 2006, Hayes et al. 2011, Oechel et al. 2000). The most recent and comprehensive research indicates that the Arctic could be a strong sink for carbon (Zhu and McGuirre 2016), with even dry areas measured to have slight carbon uptake in the summer, and wet areas having 300x carbon uptake as the dry areas (Emmerton et al. 2015). The effect on climate, however, depends not only upon net carbon emissions, but also upon the composition of the emissions. Because of the 25x enhanced GWP of potential of CH₄, wetland and lacustrine CH₄ emissions could result in net warming (Zhu and McGuire 2016), even in the presence of net carbon uptake. The complicated systems presented here require a detailed analysis of process-based understanding of the geomorphology and biogeochemistry of the melting Arctic.
1.2: Arctic Biogeochemistry and Geomorphology

The widely varying landscapes of the Arctic reveal a complicated interplay of biology, chemistry, and natural environment. Knowing how the biogeochemistry unfolds throughout Arctic warming will help us better understand the trade-offs of preventing versus preparing for climate change. This rich biodiversity over vast landscapes, however, hinders our understanding of the contributions to climate change from the melting Arctic. Presented here is a detailed discussion of the major biogeochemical processes, the physical environments they occur in, the field data to-date that analyzes and models this potential feedback effect.

1.2.1 Natural Processes that Control Carbon: Photosynthesis, Respiration, Methanogenesis, and Methanotrophs

Photosynthesis and Respiration (NPP – Net Primary Production)

As the Arctic warms, the balance of increased photosynthesis and respiration of plant matter into CO₂ will determine whether the Arctic is a sink or source of CO₂. Photosynthesis (\(6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2\)), the primary biochemical method to store atmospheric CO₂, is likely to increase in the Arctic for two reasons. First, the warming of cold regions such as the Arctic, in combination with rising atmospheric CO₂, will very likely lead to more above-ground storage of atmospheric CO₂ in plant matter, with up to 20-30% faster plant growth in a more CO₂ rich atmosphere (IPCC 2014). Second, regions that previously could not support complex root structures owing to permafrost will shift from tundra regions to graminoid and shrub regions, or even to growing trees, sequestering carbon from the atmosphere above ground. In other words,
plants such a trees and shrubs that do not give all their biomass to respiration at the end of the season will be growing in larger tracts of land.

Counteracting photosynthesis is respiration, which is the heterotrophic conversion of easily processed carbon from plant matter, defined as labile carbon, to $\text{CO}_2$ ($\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 -> 6\text{CO}_2 + 6\text{H}_2\text{O}$). In much of the world, plant matter can be sequestered by burial in alluvial fans, burial in other plant matter, burial underwater, or burial under sediment. In the Arctic, plant matter has historically been sequestered by permafrost. As the permafrost melts, that sequestered biomass is subject to heterotrophic respiration. This is the likely source of increased emissions from the Arctic as it warms. In addition, a longer growing season will reduce permafrost sequestration of plant matter and promote more heterotrophic respiration of plant matter back to $\text{CO}_2$ at the end of each year.

The balance of photosynthesis and respiration is called Net Primary Production (NPP). While the primary driver of photosynthesis is Photosynthetically Active Radiation (PAR, at 400nm to 700nm wavelength) NPP is temperature dependent. Specifically, the rate of photosynthesis depends on canopy temperature, or the temperature at the top of the plant matter where most growth is, in conjunction with PAR. Respiration depends primarily on surface and topsoil temperature, where most of the respiration occurs, and oxygen availability. In much of the Arctic where low tundra and graminoid landscape dominates, surface temperature and canopy temperature are nearly the same.

Depending on plant type, photosynthetic efficiency peaks between 15 and 30 °C, whereas respiration rates tends to steadily increase even beyond these temperatures. Above a threshold temperature specific to a given environment, typically beyond 20-30 °C, respiration rate will
always meet or exceed photosynthesis. The Arctic summer temperatures, however, are in a regime whereby an average temperature increase of up to 10 °C will result in strongly increased photosynthesis, and marginally increased respiration. The balance of NPP in a warming Arctic is almost certain to be in favor of photosynthesis. As a result, Alaska and the Arctic are likely to become massive sinks of carbon as the Earth warms (Zhu and McGuire 2016).

**Biomass burning**

Counteracting increased plant growth from warmer temperatures will be greater biomass burning from warmer, dryer landscapes (Chapin et al. 2010), with climate change indicated as a primary driver for increasing natural fires in the Arctic (Gillett et al. 2004). Biomass burning releases both CO$_2$ and CH$_4$. Biomass burning can effect more than the carbon stored in the above-ground plant matter in that it can disturb all soil above the permafrost to burn off carbon stored in the soil (Genet et al. 2013, Burn, Mackay and Kokelj 2009).

**Methanogens**

In aerobic sediments where the water table is sufficiently low to leave soil unsaturated, respiration of organic matter via oxidation to CO$_2$ is dominant (Merbold et al. 2009, O'Connor et al. 2010). We define the heterotrophic processing of labile carbon in the absence of oxygen as methanogenic decomposition, owing to the CH$_4$ byproduct in place of CO$_2$. Anoxic environments are typical in environments with the water table at or proximal to the surface. Without oxygen as a mediator, methanogens produce CH$_4$ either via acetate fermentation (CH$_3$COOH $\rightarrow$ CH$_4$ + CO$_2$) or via CO$_2$ reduction (2CH$_2$O+2H$_2$O $\rightarrow$ 2CO$_2$ + 4H$_2$ and then CO$_2$ + 4H$_2$ $\rightarrow$ CH$_4$ + H$_2$O) (O'Connor et al. 2010, Nakagawa et al. 2002).
Methanotrophs

Methanotrophs are microflora that metabolize CH₄ to fuel themselves. They exist in the soil and water, both in anoxic and oxic environments. Methanotrophs in oxic environments rapidly convert CH₄ in the soil into CO₂, so the CH₄ produced beneath oxic soils never reaches the atmosphere (Raghoebarsing et al. 2005). In many areas, particularly in the Arctic, methanotrophs in the soil draw down CH₄ from the atmosphere: in non-waterlogged soils, equilibrium with the atmosphere is fast relative to microbial oxidation (Whalen and Reeburgh 1990), meaning that lowering Arctic water tables could result in negative CH₄ fluxes. In lakes, CH₄ produced in anoxic bottom waters can be rapidly consumed by methanotrophs in both anoxic and oxic water columns.

River Transport

As the Arctic permafrost melts, drainage can lead to stream and river formation (Walvoord, Voss and Wellman 2012), and subsequent physical transport of carbon and labile plant matter. Rivers themselves are sources of emissions, as respiration happens throughout transport, resulting in roughly 50% of the total carbon export being via emission, and the other 50% being via transport. Given that rivers are not stagnant, they are rarely anoxic. The lack of anoxia promotes respiration rather than methanogenesis, resulting in less than 0.4% of the total carbon loss in rivers going to CH₄ emissions.

Natural Seeps

Any region that has natural gas or oil underground will also have seeps. Seeps are natural pathways that slowly leak trapped hydrocarbons. Both CO₂ and CH₄ leak from these sources.
Siberia and The North Slope of Alaska both are regions of prodigious hydrocarbon production, indicating there are local sources of hydrocarbons. It is extremely likely that there are local CH\(_4\) and CO\(_2\) seeps that confound measurements, and are entirely unrelated to the temperature regime in the Arctic.

### 1.2.2 Geomorphology of the Arctic and Natural Processes of Emissions and Uptake

Geomorphology is the physical features of a region relating to its natural structures. The geomorphology of a region determines which natural process dominates in a given region. The Arctic permafrost region is a complex system physically and biochemically. Moreover, ice content in the permafrost ranges from low to 90% (Lee et al. 2012, Zimov, Schuur and Chapin 2006). As the ice melts, critical structure holding the soil together crumbles, creating new architecture and revealing buried soils for processing via methanogenesis or respiration. As a result of moisture being trapped in soil as ice, and subsequent melting through secular warming of the Arctic, much of the Arctic, and particularly the North Slope of Alaska, is dominated by lakes (Koven et al. 2011, Smith, Sheng and MacDonald 2007) (Figure 4). The confluence of soil carbon content, soil ice content, land elevation, and regional water level define the geomorphology, and thus the dominant biogeochemical processes relevant to climate change and GHG emissions. As our project focuses on flat lake regions, we describe in detail the geomorphology specific to flat Arctic tundra.
Organic Rich Soils and the Active Layer

Carbon is stored in the arctic permafrost in two primary sediment types that are distinguished by carbon content: organic rich soils and yedoma deposits. The organic soils have built depth over the past 5-6 thousand years (KY) in North America, and for the past 10-12 KY in Eurasia (Koven et al. 2011, Zimov et al. 2006, Jones, Peteet and Sambrotto 2010), and are known to contain up to 50 kg of C per m$^3$ in the top 1 m of soil (Schuur et al. 2008). The active layer, or the part of the soil that thaws in the summer, is estimated to range from 76 to 84 cm, with organic soils underlying 8 to 30% of Alaska (Zhu and McGuire 2016). The total estimated carbon stored in this active layer is estimated to be between 48 and 77 Pg. The organic-rich deposits experience little heterotrophic respiration, as the summer growing season is short, and
much of the carbon is locked up in permafrost prior to respiration, though this stands to change under climate change, with a potential increase in soil respiration from thawing soils.

Several mechanisms control the thawing of permafrost (Schuur et al. 2008), and therefore pathways to heterotrophic respiration and decomposition of the stored organic carbon. The primary mechanism is the increase of active layer thickness. The active layer is the maximum annual depth of permafrost melting. Carbon in this layer is unlocked from ice and exposed to decomposition. In general, as the Arctic warms, greater heat flux into the soil for longer periods each year increases the active layer depth, potentially exposing more carbon. If the active layer gets deep enough, a talik can form. In a talik, the surface re-freezes in the winter with an unfrozen portion remaining at depth, squeezed by freezing from both above and below. Here, year-round heterotrophic respiration can continue (Friborg et al. 2003). If this occurs rapidly enough, the heat produced by heterotrophic respiration can be sufficient to counteract the freezing from above and below, creating a self-sustaining region of heterotrophic respiration for the entire year (Heimann and Reichstein 2008). This could result in chronic, sustained emissions of CO₂ and CH₄ (Tarnocai et al. 2009).

**Yedoma Deposits**

The other primary form of carbon storage is a yedoma, comprised primarily of ice and minerals. Yedomas, formed during the Pleistocene (Jorgenson et al. 2010) are generally 1-3 m wide wedges, averaging 25m deep, comprised of 50-90% ice (Figure 6), and carry wind-blown sediments with 2-5% composition of largely unprocessed carbon (Lee et al. 2012, Zimov et al. 2006). Accounting for deeper deposits and yedomas, the Arctic region contains an estimated
1300 Pg of C. For comparison, the entire atmosphere of the Earth contains approximately 800 Pg C (Zimov et al. 2006, Hugelius et al. 2014).

Melting yedomas involve more complex geomorphology (Walter et al. 2008, Walter, Smith and Chapin 2007, Brosius et al. 2012). As ice wedges melt, they can either form small lakes or the water can drain away. Small lakes can often have anoxic soils with high labile carbon content that can produce CH$_4$ (Figure 6). In either case, the removal of the structural support provided by the ice wedge causes subsidence and surface collapse, increasing thaw rates and progressively exposing more buried carbon to decomposition. The size of these blocks can easily reach 1-2 meters on a side, depending on the terrain, exposing meters-deep carbon to the atmosphere for decomposition (Figure 5). This process leads to a structure type called thermokarsting.
Figure 5: Thermokarsting causing mass wasting. In drained areas, thermokarsting exposes labile carbon to the atmosphere to be readily respirated to CO\textsubscript{2}. This process can easily expose 3 meters depth of high-carbon-content soil to the atmosphere. Thermokarsting can calve off up to 2m chunks of sediment.

**Thermokarst Lakes**

Melting permafrost in yedoma regions has a high probability of soil subsidence, whereby the soil elevation recedes locally. Melting permafrost in regions of subsidence can fill these holes with water, creating lakes. Moderated by the more efficient heat transport of water from the atmosphere to the soil, warming lake banks can contribute to rapid thermokarsting that continuously delivers labile carbon to lake beds. In oxic waters, labile carbon is rapidly consumed via heterotrophic respiration to CO\textsubscript{2}, much as it is in soils causing CO\textsubscript{2} release. Anoxic regions of thermokarst lakes and undergo methanogenesis, causing CH\textsubscript{4} release (Figure 6). The first estimates placed total Arctic lake CH\textsubscript{4} emissions at approximately 24±10 Tg CH\textsubscript{4} per year (Walter et al. 2007), or 0.6 Gt CO\textsubscript{2} equivalent. More recent models suggest this could
be grossly overstated, and that the balance of long-term emissions and uptake is anything but clear (Schuur et al. 2015). Measurements of Arctic lakes over the past several years have shown that total lacustrine emissions could be as much as 16.5 Tg of CH$_4$/year, accounting for nearly 2/3 the CH$_4$ emissions as shown by inversion models (Wik et al. 2016, Zhu and McGuire 2016). However, only 1/3 of these emissions, or 2/9 of total emissions from the inversion models, come from thermokarst lakes, with the remainder of lacustrine emissions having provenance in post-glacial lakes.

![Figure 6](image_url)

**Figure 6:** A schematic of a permafrost lake in the arctic. Taken from Walter et al. (2008). When the ice wedge on the side of the lake thaws, it will deprive the surrounding organic soils of structural support, causing collapse of the soils and subsequently feeding peat into the anaerobic lake bottoms. Methanogenic decomposition of the carbon produces CH$_4$. The CH$_4$ comes out in hotspots of rapid ebullition of CH$_4$ and point sources of lesser amounts of CH$_4$ production.

**Wetlands**

Melting permafrost regions that remain wet produce wetlands, which prodigiously produce CH$_4$ in the Arctic (Zhu and McGuire 2016). Wetlands and lakes can and often do exist alongside each other. According to the best and most recent models, wetland CH$_4$ emissions account for roughly 28 Tg of CO$_2$ equivalent emissions per year, but current models indicate
they could account for as much as 37 to 90 Tg of CO₂ equivalent per year by 2090, with the median model prediction around mid-40s Tg per year (Zhu and McGuire 2016).

**Drained Basins**

Talik formation, whether in wetlands or lake regions, can eventually leading to drying (Yoshikawa and Hinzman 2003). Models indicate that the high-emission scenarios all result in a drastic drying of lakes in the Arctic (Avis, Weaver and Meissner 2011). Methanogenesis relies on wet, anoxic environments. As regions dry and become oxic, they tend to emit CO₂ via heterotrophic respiration, and natural biogeochemical processes that produce CH₄ are reduced (Striegl et al. 2012).

**Long Term Large Plant Matter**

As permafrost melts, more complex plant matter can take root, whether the soil remains dry or wet. Roots cannot penetrate into permafrost, currently precluding the growth of trees. As the permafrost melts and the active layer depth increases, trees and other large plants can take root. This results in draw-down of atmospheric CO₂ into plant matter, contributing to long term CO₂ sequestration in the plant matter.

As the climate structure in the Arctic evolves through climate change, these processes are likely to change. The best available field work right now suggests that the local evolution of these regions as permafrost degrades is to increase groundwater discharge to rivers, drying out areas, but it remains unclear how widespread temperature change will effect this paradigm, and it needs to be closely monitored to better understand this evolution (Walvoord et al. 2012).

**1.2.3 Anthropogenic CH₄ and CO₂ in the Arctic**
Anthropogenic emissions are, by definition, caused by man. Vast fossil fuel reserves in many Arctic environments, including the North Slope and Siberia, influence and compound with natural emission processes. During production of hydrocarbons, CH$_4$ can escape, or, more likely, is flared during oil production, but flaring is typically only 97% effective, leaving remnant CH$_4$. In addition, flaring produces massive amounts of CO$_2$. Either of these scenarios can artificially inflate the CH$_4$ level and CO$_2$ levels in the region, confounding attempts to measure these species in the field.

**1.3 Isotope Ratios**

Approaching a better understanding of the evolving emissions in the warming Arctic necessitates a framework to parse and subsequently model these processes. The isotopic ratios of the carbon in both CO$_2$ and CH$_4$ can help provide insight into the emission and uptake processes in the Arctic. As chemical reactions like photosynthesis, methanogenesis, and combustion take place, heavier or lighter isotopes are preferentially selected for the reaction, leaving one side of the chemical equation isotopically enhanced with a greater abundance of the heavy molecules, and the other more isotopically depleted with fewer of the heavy molecules. The isotope fractionation is expressed as $\delta^{13}C$ of the sample, where

$$\delta^{13}C = \left[ \frac{^{13}C_{sample}}{^{12}C_{sample}} \right] - 1 \right] \times 1000$$

And is expressed as a parts-per-mil deviation (‰), with respect to the Pee Dee Belemnite (PDB), with negative deviations meaning there is relatively less of the heavier isotope. The most
common is mass-dependent fractionation, where a reaction “selects,” or preferentially chooses, the more or less stable molecule based on mass. In short, we expect methanogenesis, for example, to fractionate CH₄ further from the source material roughly by -25 or -55‰, depending on the CH₄ pathway (Whiticar 1999). The precursor sediments in the Arctic range from a δ¹³C of -22‰ to -34‰ (Jones et al. 2010). By comparing the isotopic fractionation changes of CO₂ and CH₄ to their bulk changes, we can reliably isolate sources of carbon emissions from the Arctic (Table 1).

<table>
<thead>
<tr>
<th>Pathway</th>
<th>CO₂</th>
<th>δ¹³C CO₂ in atmosphere (global mean is -8)</th>
<th>CH₄ (CH₄)</th>
<th>δ¹³C CH₄ (global mean is -47.1)</th>
<th>1ppm change effect on δ¹³CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3 photosynthesis</td>
<td>decreases</td>
<td>Enriches ¹³C (selects up to -36)</td>
<td>-</td>
<td>-</td>
<td>+0.1</td>
</tr>
<tr>
<td>C4 photosynthesis</td>
<td>decreases</td>
<td>Enriches ¹³C, but relatively less</td>
<td>-</td>
<td>-</td>
<td>+0.1</td>
</tr>
<tr>
<td>Respiration</td>
<td>increases</td>
<td>-6 δ¹³C (relative to background)</td>
<td>-</td>
<td>-</td>
<td>-0.06</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>Increases</td>
<td>Depletes (source material is depleted -20-30)</td>
<td>increases</td>
<td>Varies</td>
<td>-.05</td>
</tr>
<tr>
<td>CO₂ reduction methanogenesis</td>
<td>1:1 increase of CO₂ w/ CH₄</td>
<td>enriches</td>
<td>increases</td>
<td>depletes (up to -84 in Arctic)</td>
<td>+0.1</td>
</tr>
<tr>
<td>Acetate fermentation methanogenesis</td>
<td>1:1 increase of CO₂ w/ CH₄</td>
<td>enriches</td>
<td>increases</td>
<td>depletes (not as much as CO₂ red., but from -58 to greater dep.)</td>
<td>+0.05</td>
</tr>
<tr>
<td>Methanogenesis then respiration</td>
<td>1:1 increase of CO₂ with decrease of CH₄</td>
<td>depletes</td>
<td>-</td>
<td>-</td>
<td>0 to -0.1</td>
</tr>
<tr>
<td>Natural CH₄ seeps</td>
<td>no change to increase</td>
<td>varies</td>
<td>increases</td>
<td>enriches (-40)</td>
<td></td>
</tr>
<tr>
<td>CH₄ flaring*</td>
<td>increase</td>
<td>depletes (thermogenic CH₄ is -40 C13)</td>
<td>increases</td>
<td>enriches (-40)</td>
<td>-4</td>
</tr>
</tbody>
</table>

Table 1: Table of carbon pathways and how they affect carbon isotope ratios. The table shows the standard pathways of carbon fluxes in the Arctic, and their effects on the δ¹³CO₂ assuming a ~20 δ¹³C for precursor materials. This effect is shown with the idea that every bit of the reactant or product can be measured, which is
meant to show what an end-member state would look like. In reality, it would never be as clear as this. C3 photosynthesis is the only photosynthesis to occur in tundra, whereas C4 photosynthesis occurs in larger flora, such as trees. Methanogenesis processes carbon into CH$_4$ and leaves CO$_2$ behind, where the CO$_2$ can be used in other biogeochemical processes, though here the effect on atmospheric $\delta^{13}$CO$_2$ is shown as though we would be able to measure the entire effect from an airplane. In an end-member state, methanogenesis followed by respiration will first enrich CO$_2$ during methanogenesis, and then deplete it back to equilibrium once it is respirated by methanotrophs. CH$_4$ flaring, which is typically only 97-99% effective, will produce a massive amount of CO$_2$ and thus greatly influence $\delta^{13}$CO$_2$. Data taken from Lee et al. (2012), (Nakagawa et al. 2002, Walter et al. 2006, Jones et al. 2010). All changes in CH$_4$ on $\delta^{13}$CO$_2$ are below standard 1σ-1s detection limits of CO$_2$ instruments.

**CO$_2$ Processes and Isotope Ratios**

CO$_2$ has three primary production mechanisms and one consumption mechanism in the Arctic. C3 plants, the dominant type in the Arctic, prefers the lighter isotopologue of CO$_2$ for photosynthesis, and selects as low as -36 $\delta^{13}$C for photosynthesis to leave behind slightly less CO$_2$ and a relatively enriched $\delta^{13}$C in the local atmosphere. Respiration, on the other hand, increases CO$_2$ and depletes the $\delta^{13}$C of the atmosphere to a lower level. This depletion is caused in part because the respirated plant matter is already depleted, and because respiration has a mass-dependent fractionation preference for the lighter isotope. For biomass burning, the background material is the local plant matter at $\delta^{13}$C of -22‰ to -34‰ (Jones et al. 2010). We expect the CO$_2$ ratios from biomass burning to be relatively similar to the background material. CH$_4$ flaring in the Arctic is expected to produce $\delta^{13}$C near -40‰, owing to the thermogenic properties of the source CH$_4$ producing this ratio.

**CH$_4$ Processes**

CH$_4$ has five primary production methods and three consumption methods in the Arctic. Natural Methanogenic pathways cause fractionation by preferentially using the lighter isotope to produce CH$_4$, so the CH$_4$ produced is isotopically depleted in $^{13}$C relative to its precursor carbon, and the remnant carbon pool is relatively enriched in $^{13}$C than the precursor carbon (Nakagawa et al. 2002).
The first CH\(_4\) production pathway is CO\(_2\) reduction, common in large wetland areas that have less labile carbon per unit area, which preferentially selects light CO\(_2\) to produce CH\(_4\), leaving relatively heavier CO\(_2\) behind in the wetland (Nakagawa et al. 2002). The second method, acetate fermentation, dominates in small wetland areas, where the labile carbon per unit area of lake tends to be greater. Typical $\delta^{13}$C-CH\(_4\) in the Arctic tundra range from about -58‰ for acetate fermentation and -84‰ for CO\(_2\) reduction (Walter et al. 2006).

The third production pathway of CH\(_4\) in the Arctic is natural seeps of CH\(_4\) from underground hydrocarbon traps that slowly produce and leak methane. Thermogenic CH\(_4\) has an isotope ratio of near -40‰. The fourth production pathway, CH\(_4\) flaring and leaking from hydrocarbon production, also produces an isotope ratio near -40‰. The fifth and final CH\(_4\) production pathway is biomass burning, producing isotope ratios in a range similar to the isotope ratios of the source material.

The first CH\(_4\) consumption process is methanotrophic decomposition of CH\(_4\) to CO\(_2\) in the soil. CH\(_4\) produced in the subsurface can be oxidized very efficiently if it travels through an oxic layer in the soil (Raghoebarsing et al. 2005). If there is a sufficient aerobic soil depth, all of the CH\(_4\) produced will be oxidized (Parmentier et al. 2011a), leaving no trace of methanogenic processes. The second process occurs in anoxic environments if sphagnum moss is present, whereby a symbiotic relationship between the moss and methanotrophic bacteria in its roots allows CH\(_4\) oxidation (Kip et al. 2010). In these instances, the bacteria in sphagnum roots oxidize up to 50% of the potential CH\(_4\) flux to CO\(_2\) (Parmentier et al. 2011a), but data on isotope ratio changes from this process in unavailable. The third process is CH\(_4\) drawn down from the
atmosphere into the soil, where methanotrophs consume the CH₄, creating a CH₄ sink (Whalen and Reeburgh 1990), and converting it to CO₂.

Both CH₄ production and consumption processes can influence the isotopic signature on CO₂. In incubation studies from soils in the Alaskan tundra, Lee et al. (2012) showed that CO₂ fractionation under anaerobic conditions from soils in the Alaskan tundra produced δ¹³C-CO₂ of -23.45 to -11.01 ‰, while aerobic conditions produced from -27.56 to -23.09 ‰. Nakagawa et al. (2002) found average δ¹³C-CO₂ ranges in emissions from Siberian lakes of -16.7 to -6. In short, less depleted δ¹³C-CO₂ in the presence of increased CH₄ flux is very strong evidence of methanogenesis as the provenance of increased CH₄ fluxes. See Figure 7 for more details. While a fielded CO₂ instrument may be able to detect a signature of CH₄ processes on CO₂ ratios, it would likely require a more precise instrument remaining in a single place with longer averaging times, precluding our airplane-mounted instrument from reporting these CO₂ signatures.
Figure 7: Carbon emissions in the North Slope. The major processes for carbon emission on the North Slope (and in most places) are biomass burning, fossil fuel consumption, methanogenesis, respiration, and photosynthesis. Shown here are the major pathways, and their effect on the CO$_2$ and CH$_4$ levels and their major isotopologues. Chemicals in green have mixing ratios increased and isotopically heavy isotopes enriched. Those in red have mixing ratios decreased or isotopically depleted.

Taken together, CH$_4$ flux and CO$_2$ exchange with the environment determine whether a region is a source or sink of radiative forcing. As the permafrost thaws, it can either retain water in thermokarst lakes and produce more CH$_4$ (Walter et al. 2006), or it can drain water to lower elevations and dry out the area, potentially reducing CH$_4$ emissions but temporarily increasing CO$_2$ emissions through more efficient heterotrophic respiration in the soil (Merbold et al. 2009). In regions of retained moisture, the increased plant uptake of CO$_2$ associated with longer
growing seasons can be offset by a local source of CH$_4$, making a region that is an overall carbon sink into a region of net positive radiative forcing (Friborg et al. 2003). The variability of soil types, vegetative types, and water levels render measurements from only a few isolated sites incapable of accurately describing the tundra as a whole (Parmentier et al. 2011b). Measurements from an aircraft provide a means of capturing the full spatial diversity of this region. These measurements can expand the temporal advantage of tower measurements to a wider area, and can establish a more representative analyses of differences in emissions from differing vegetation types (Zulueta et al. 2011). Measuring fluxes for both CO$_2$ and CH$_4$ is vital to determining the net radiative forcing associated with carbon exchange as the Arctic warms.

Put more succinctly: Simultaneous measurements of $\delta^{13}$C of both CO$_2$ and CH$_4$ may provide insight into current Arctic carbon processes. The balance of photosynthetic uptake and respiration from plants, respiration from the soil, and methanogenesis from the soil provides a first-order estimate of carbon emissions and uptake from the melting Arctic permafrost. Given the large areal extent of the Arctic, and the requirements for high-resolution information to inform scientific models, in-situ field measurements via aircraft are vital to assess the current carbon flux, and to predict future carbon fluxes from the Arctic.

1.4 Recent Measurements and Models

Over the past two decades, Arctic research has revealed a potential feedback effect of carbon in the Arctic. In 2006 Walter et al. (2006) showed that Arctic lakes produce CH$_4$, and proposed that Arctic CH$_4$ production could be a potentially massive climate feedback mechanism. Recent research has dampened these fears. Recent regional fly-overs have shown
little melting permafrost CH$_4$ signature on the North Slope lakes, but have shown significant wetland sources (Chang et al. 2014).

Models, however, lack the process-level understanding to forecast whether the Arctic will be a sink or source of GWP in the coming century (Fisher et al. 2014, Zhu and McGuire 2016). The best current models suggest that Alaska and the Arctic in general is projected to be a source of carbon for the next 30 years as labile carbon is exposed to the atmosphere, and a sink of carbon thereafter as primary production dominates. The caveats, however, are that the best available data are too sparse so that no clear evolution of the biogeochemistry can be modeled (Zhu and McGuire 2016), and the ranges too wide to know the ultimate fate of Arctic carbon, according to the summary of the most recent report (Zhu and McGuire (2016), emphasis mine):

Our simulations indicated that terrestrial uplands and wetlands would act as sinks for greenhouse gases from 2010 through 2099 with GWP ranging from –24.5 to –91.6 TgCO2-eq/yr. … Although we project that biogenic CH$_4$ emissions from wetlands will increase between 17 and 187 percent depending on the climate simulation, the increases do not offset the net increase in CO2 uptake by upland and wetland ecosystems of Alaska for five of the six climate simulations in this assessment. This contrasts with our analysis for the historical period, which indicated that uplands and wetlands of Alaska were sources of greenhouse gas forcing. Because we did not assess the future dynamics of CH$_4$ emissions from lakes, we do not know if Alaska would be a net sink or source for greenhouse gases in the future (Zhu and McGuire 2016).

Moreover, the report elucidated its limitations: there is very little field data, CH$_4$ simulations were based on one wetland distribution map, and observation systems, process-based research, and modeling all need to be vastly improved in the Arctic

This synthesis report makes clear that though Alaska is projected to be a net sink of GWP, the data has a wide range, and the modeling has massive data gaps that need to be addressed by robust measurement systems. In order to have a process-level understanding of how the Arctic currently is, and how it is likely to evolve, the scientific community needs to develop a
high-resolution map of CO₂ and CH₄ concentrations and fluxes over a vast geographical area. In response, the Anderson group at Harvard embarked on a multi-prong approach to develop a platform for measuring CO₂ and CH₄ fluxes, and their isotopologues, via an aircraft. First, we developed and tested a new Best Air Turbulence probe in conjunction with NOAA and report the requirements and outcome below. Second, we developed a CO₂ Herriott instrument and report that progress in Chapter 2. Third, we developed two CH₄ detection axes to work in conjunction with the CO₂ Herriott cell. Fourth, we integrated the instrument suites into a Diamond Aircraft DA-42, owned and operated by Aurora Flight Sciences. Finally, we field tested the instrument and showed proof-of-concept.

1.4 Aircraft Flux Measurement and Comparison with Tower

The eddy covariance technique has been used for decades to measure fluxes. It is best when used to measure turbulent vertical fluxes of constituents assuming no sinks and sources between the ground and the instrument (Baldocchi, Hicks and Meyers 1988). In other words, we are assuming a sink/source on the ground, and that there are no other sinks/sources between the ground and the aircraft.

Fluxes are the result of vertical advective turbulence represented by the covariance of the vertical component of the wind and the concentration of the constituent. If \( w \) is the vertical wind component, and \( c \) is concentration, flux \( F \) is

\[
(1) \quad F = \bar{wc}
\]

where the bar represents the time average. Representing the terms via Reynold’s decomposition (2), taking the average value of each component and their deviations and multiplying these sums
against each other, the time average of the deviations goes to zero (3) and the system simplifies to (4) (Baldocchi et al. 1988):

\[
\begin{align*}
(2) \quad F &= (\bar{w} + w')(\bar{c} + c') \\
(3) \quad F &= (\bar{wc}) + (\bar{w}c') + \bar{w'}c + w'c' \\
(4) \quad F &= \bar{w'c'}. 
\end{align*}
\]

Measuring the vertical wind speed component is often done with a sonic anemometer. Sonic anemometers take high-frequency measurements of wind speeds in three dimensions. When combined with an instrument capable of measuring chemical component concentrations, flux measurements can be obtained. For measurements made from a tower, the sampled footprint is dependent on the height of the tower, wind speed, and wind direction (Baldocchi et al. 1988).

Flux towers have the advantage of gathering excellent temporal data, but to increase the area represented by flux tower, you must increase its height. In this process, spatial resolution is lost. In places such as the arctic tundra it is logistically impossible to have sufficiently widespread towers to allow for representative measurement of carbon fluxes (Crawford et al. 1996). Aircraft measurements can augment the spatial resolution of towers, spatially expanding the higher temporal resolution of the measurements by flux towers, and increasing regional flux measurement accuracy. In the North Slope of Alaska, the region of focus for this project, Zulueta et al. (2011) showed that one of their towers underestimated local CO₂ flux by 22% through an inability to incorporate some local nearby features that were captured with the aircraft. Moreover, Parmentier et al. (2011b) showed that different vegetation types are sampled when wind direction changes, which can change tower-measured CH₄ fluxes by as much as an order of
magnitude in the Arctic. Thus, aircraft CO$_2$ and CH$_4$ measurements provide a means of enhancing accuracy and assuring a representative measurement of the region.

Measuring eddy covariance fluxes from an aircraft is currently done with a Best Air Turbulence (BAT) probe (Crawford and Dobosy 1992) combined with an instrument to measure chemical concentrations. The Anderson group has worked with the NOAA Air Turbulence and Diffusion Division to update, calibrate, and test our own BAT probe for deployment with a DA-42 aircraft. A BAT probe measures both direct and differential air pressures. Working with NOAA, we post-processed the BAT probe data to provide vertical wind speeds for covariance with our concentration measurements. We used the pressure measurements in conjunction with a GPS-INS system (Novatel) to compute derive the vertical wind speeds. Latent and sensible heat fluxes for flux measurement corrections are measured via a sensor mounted on the bottom of the BAT probe, near three inlets that sample air for the instruments. The probe samples at a rate of 50Hz. In order to accurately describe the covariance of concentration with vertical wind speed, the concentrations must be sampled at a rate of at least 10Hz (Crawford and Dobosy 1992, Crawford et al. 1996).

Garman et al. (2006) showed that BAT probes differ from theory and have systematic errors that can be corrected. Our team tested the BAT probe in the Wright Brothers wind tunnel at MIT (Figure 8) twice in 2010 to calibrate and find potential systematic errors. We estimate being able to meet or exceed prior BAT probe vertical wind measurements with a precision of 3cm/s (Garman et al. 2006).
Figure 8: BAT probe displayed in a wind tunnel calibration at MIT Wright Brothers wind tunnel prior to testing. The testing calibrated the BAT probe for speeds of winds up to 100mph. The testing required that we tilt the BAT probe 15 degrees across several axes to measure how the BAT probe responded. Using the data acquired from the tests, the BAT probe was calibrated for field operation.

The CO$_2$ Herriott instrument, described in detail below, was designed to fly in the North Slope of Alaska alongside the NOAA ATDD probe, using Aurora Aerospace’s DA-42 aircraft. The flight paths followed procedures developed to minimize systematic and random errors in flux measurement, such as following straight flight paths over level land (Mahrt 1998). We aimed to fly at about 10-30 m above the surface to maintain high spatial resolution, dividing the flight tracks into 4-5 km lengths to minimize systematic inaccuracies the arise as a result of insufficient averaging (Martins et al. 2009). Furthermore we repeated flight tracks multiple times to reduce random errors in the measurements (Lenschow, Mann and Kristensen 1994).

1.5 Thesis Outline: Instrument Design, Testing, and Suggested Corrections

With the goal of measuring carbon fluxes in the Arctic, we deployed an instrument suite on a low-flying aircraft in August of 2013 out of Deadhorse, AK.
Chapter 2 describes in detail the specifications and testing of the instrument, focusing on constraints associated with a small, low-flying aircraft, and how these constraints informed the design of the instrument. Following is a description of the performance of the instrument in the laboratory, and special considerations for field deployment.

Chapter 3 reports our August 2013 field deployment and results of the instrument in Deadhorse, AK. Post-processing showed instrument errors that arose in the field, but were not seen in the laboratory. Our methods to diagnose a predictable error are described, and our eventual discovery of a poorly constrained laser feedback error are discussed in detail. A method to partially correct this field anomaly is introduced and reviewed, as are the limitations of this method. Several other field-specific errors are identified, alongside instrument issues that persist throughout the laboratory analyses, and corrections are suggested. Finally, we report on CO₂ concentration data from five flights. While the remainder of the data proved irrecoverable, methods to correct the instrument for future missions are laid out in conclusion.
Chapter 2: CO$_2$ Instrument Development

2.1 Instrument Design and Requirements

In this prior chapter we laid out the need for a better understanding of Arctic emissions processes in the changing climate. In order to meet the needs of this goal, here we describe in detail the development of the instrument. In order to measure concentrations of CO$_2$ via an aircraft and covary these concentrations with vertical wind speed measurements to determine CO$_2$ fluxes, the instrument was obligated to have a 90% recovery time of at least 10 Hz. This is measured by the time required to reach 90% of the true value after a step function of concentration. 10 Hz the desirable rate for covariance with 50 Hz vertical wind speed measurements (Crawford and Dobosy 1992, Crawford et al. 1996). Second, the instrument needed to demonstrate a sensitivity of at least 1ppm (1σ-1s) to have sufficient resolution for expected changes in the field. Finally, the instrument also had to be small and light enough to fit in one side of the nose compartment of a DA-42 aircraft. The largest modification compared to commercially available equipment is the 10Hz 90% recovery time, which is 100x faster than many comparable commercially available instruments.

The instrument was part of a suite comprising a CO$_2$ Herriott Cell (Herriott, Kogelnik and Kompfner 1964) (Figure 9) and two CH$_4$ ICOS cells (Witinski, Sayres and Anderson 2011) that were designed to work together to develop a total flux carbon measurement. The CO$_2$ instrument operates alongside the fast response CH$_4$ instrument, where water measurements are
also acquired and subsequently used to correct and report the dry \( \text{CO}_2 \) mixing ratio, or what the \( \text{CO}_2 \) mixing ratio would be in the absence of water vapor in the sample.

![CO2 Instrument Design](image)

**Figure 9:** CO2 Instrument Design. The optical instrument schematic showing the laser, the laser pressure vessel and optics (including a second CaF\(_2\) wedge to dump laser power into the absorbing LPV), the sample cell, and the TE cooled Vigo MCT detector. Light from the laser passes into the LPV and is split, with part going to a diagnostic etalon, and the rest going towards the cell. A coaxial alignment visible laser can be attached to LPV for alignment purposes. The light leaves the LPV and enters the Herriott Cell, passing between the mirrors multiple times before exiting and reaching the detector.

The CO2 Herriott instrument comprises a Quantum Cascade Laser (QCL) light source and optical system contained in a Laser Pressure Vessel (LPV), a Herriott absorption cell (Herriott et al. 1964), and a detector. The cell is much smaller than commercially available CO2 measurement instruments of similar performance, and associated electronics are designed in our research group to be lightweight and to fit into a very small compartment in the nose of an aircraft (Figure 10).
Temperature instabilities could have the potential to cause alignment drift, which would require corrections and could reduce precision and accuracy, with a 1ppm inaccuracy in reported CO₂ mixing ratios per 1 °C of sample temperature control and assessment inaccuracy. To ensure temperature stability of the cell, optical train, and sample gas, the laser, LPV, detection axis, and detector were insulated using Nomex wrapped in Kapton tape.

Flux measurement by our instrument suite is enabled by a three-part integration of the instruments with a DA-42 aircraft (Aurora Flight Sciences) and NOAA’s BAT probe (Figure 11). The aircraft has a modular nose section to allow for installation of instrumentation, and space behind the pilot to house large or heavy equipment: the large CH₄ ICOS cell, scroll pumps, and the data acquisition and management system. In March of 2011, our team integrated the CH₄ and CO₂ instruments and associated electronics into the airplane for equipment fit-up.
Figure 11: Concept art of the instrument suite (1 and 2) and BAT probe (3) integrated into the DA-42 aircraft. The pumps, data storage and processing, large CH$_4$ ICOS cell, and calibration gases were housed in the back of the aircraft. Hoses connected them to the CO$_2$ and mini CH$_4$ cells in the front of the aircraft. The inlets were co-located with the pressure sensors on the BAT probe to ensure we were sampling the same air that the BAT probe was assessing the vertical wind velocities of.

Detailed below, in order and by section, are specifications of the optical designs, the laser housing design and testing, the CO$_2$ Herriott cell design, the detector system, electronics, the fitting software, and the pneumatics system and pneumatics cooling system. Following this is a discussion of the laser deviation from the initial specification, and the instrument design and software fitting augmentations implemented to account for this deviation. Next we describe the integration into the aircraft, and test flights. Finally we describe the laboratory calibration procedure and assess the instrument performance which includes the calibrations, water broadening and dilution corrections, and linearity testing.

2.1.1 Light Source and Optics
Each instrument we installed in the aircraft contains a tunable mid-IR Quantum Cascade Laser (QCL) (Faist et al. 1994). Until the advent of QCLs, the mid-IR spectral region was largely inaccessible. QCLs can produce in the mid-IR, a region with little absorption overlap with other primary atmospheric constituents. A QCL can scan over several wavenumbers in the region of interest by applying a ramped current, controlled by a custom low-noise voltage-to-current converter (Witinski et al. 2011), to fractionally modulate the temperature of the QCL. The precise temperature ramping necessitated the design of a custom laser housing to effectively audit and govern laser temperature. Moreover, instrument precision demanded our custom laser housing minimize optical noise, e.g. optical effects such as interference, often caused by reflections that can mask or even degrade the signal. We iteratively designed and assessed a novel QCL laser housing to meet the optical and temperature control needs of the laser.

**Laser Housing Mechanical Design and Evaluation**

QCL control requires highly accurate and precise temperature control of the housing in order to achieve the desired laser wavelength and stability, dictating use of an insulating material for the housing. Ultem, a machinable composite, was chosen for the housing material due to its strong insulating capacity, extreme light weight, and coefficient of thermal expansion, which closely mirrors that of the aluminum blocks used to control the temperature of the laser. The laser mounting package (Figure 12) comprised the ultem housing, a mount for the laser, a collimating optic for the laser, a window to transmit the mid-IR light, and a thermo-electric cooler and heat sink to control the mounting block temperature.
The lasers are mounted on an aluminum block, the temperature of which is governed by a heating element and a Thermo Electric Controller (TEC) (Laird Technology). A thermistor mounted in the block relays the block temperature to a PID controller located in the adjacent electronics. This, in turn, proportionally drives an appropriate current to the TEC connected to the aluminum block, which relies on the Peltier effect to control cooling via an electrical current that cools one side of the TEC and heats the other. The aluminum block is cooled until the laser operating temperature is reached, whereupon the TEC stabilizes the aluminum block temperature at the appropriate laser temperature. An aluminum heat sink and fan, secured to the TEC with thermal grease, dissipates heat accumulation from the TEC. Once the aluminum block reaches laser operating temperature, micro-adjustments to laser temperature are controlled by a current ramp applied directly to the QCL.

The housing is hermetically sealed and back-filled with N₂ to inhibit sample contamination in the laser path by ambient air. A delrin ring compresses the ZnSe wedged
window against an O-ring seal in the housing. The remainder of the seals at the top of the housing, the aluminum block and base, and entry ports for adjustments are sealed with vacuum-greased O-rings, with the grease providing an enhanced seal without off-gassing hydrocarbons that could interfere with accurate sample measurements.

**Laser Housing Optical Design and Evaluation**

A QCL emits a beam of light in a 40x60 degree arc, while direct absorption spectroscopy dictates the light sight be coherent and collimated for the path length of absorption, or 8.4 m in the CO₂ Herriott instrument. After laying out the mechanical design for the structure and heat control of the laser housing, we focused on the optical mechanism to control the QCL beam. Beams can be collimated either with a series of optics to serially reduce the beam to the desired diameter or with a single optic with high-finesse controls placed within several millimeters of the QCL. We chose a single optic within the QCL to reduce the quantity of optics, which therefore reduces degrees of freedom of beam steering and allows for a more robust instrument in preparation for field deployment.

Instrument design constraints dictate the maximum beam diameter for a collimated light source. The entry and exit holes in the mirrors of the Herriott cell are 2.5mm. Overfilling these entry holes causes optical effects that impinge on the viability of the instrument measurement; if a portion of light overfills the Herriott mirror exit hole, it will reflect back into the cell and create interference in the beam. This results in increased optical noise and reduced signal to noise ratio of the instrument, which in turn impairs the precision of the instrument. Moreover, the detector for the CO₂ instrument had a 1mm immersion lens. Overfilling this lens could result in large increases in optical noise. As a result, we employed an initial 5mm aspherical collimating lens
(Hamamatsu A11331-02) to constrain the beam diameter to less than 1mm, forgoing an additional focusing lens preceding the detector to maintain the most minimal optical design.

The focal length of the 5mm Hamamatsu lens is much shorter than the prior 25mm lens, and required a re-design of pushing the optic closer to the laser. Proportionally, the control of distance and angle of the optic relative to the laser required far more precision than our prior designs permitted. We therefore created a four-axis micrometer response optical mounting system for our 5mm collimating optic that employed 0-80 set screws for fine control that could be manipulated while operating, granting both more rapid and precise laser collimation. The new optical collimating lens and mechanical system in conjunctions with Ultem laser housing and electronic heat controls resulted in a stable laser system while reducing the need of further collimating optics further downstream.

**Laser and Optical Train of the CO$_2$ Herriott Cell**

The CO$_2$ cell employs a 4.3 μm QCL (Hamamatsu LC0324) operating from 2311 cm$^{-1}$ to 2309 cm$^{-1}$. After collimation, the beam passes through a wedged ZnSe (ISP Optics, CF-WW3-25-3) window with anti-reflective (AR) coating with a band-pass filter around 4.3 μm and into the LPV where the remainder of the optical train is housed. Attached to the walls of the LPV is a thorlabs ½” cage system, a rigid yet modular structure to emplace optics and aid in optical alignment. The first optic after the laser housing is a CaF$_2$ beam splitter. The beam splitter is not AR coated on either side, so each side causes 7% of the beam being diverted. In our CO$_2$ Herriott cell, 7% of the beam is split into the black wall of the laser pressure vessel where it is absorbed. Another 7% travels through a 0.5" diameter Ge-etalon (LightMachinery) to a detector (Vigo Systems, PVI-8). Diagnostic etalons are solid cylinders of a material that can pass light of a
specific wavelength, with Germanium (Ge) typically used in the mid-IR. The two parallel faces of the cylinder are highly polished, which allows for the internal reflection of light that passes into the diagnostic etalon. When light passes out, the detector shows the regions of constructive and destructive interference (Figure 13). This diagnostic etalon is used to evaluate the laser tuning rate and thus to convert scan numbers into wavenumber space.

![Figure 13: A diagnostic etalon scan.](image)

The second optic moving towards the cell is an additional CaF$_2$ beam splitter, employed primarily as a beam dump to shed excess power, owing to the fact that our laser produces 60mw of power, or nearly 60x the amount of light that our detector can process linearly at its 1mw rating. A majority of the excess power is dumped into the black walls of the LPV where it will be absorbed, and only 6% of the laser light passes into the cell (86% reached the second optic, and 7% of this passes into the cell). The third and final optic prior to the cell is a final $\frac{1}{2}$” silver steering mirror used to direct the laser towards an AR-coated ZnSe window, coated with a band-pass around 4.3 μm, into the cell. The laser passes through the first Herriott mirror into the
detection axis, reflects off the Herriott mirrors, and exits the other side to pass through a final ZnSe window into the detector. Both ends of the cell are hermetically sealed from the rest of the instrument with a face-seal to each window. Before operation, the laser housing and the optical pressure vessel are purged with nitrogen to remove CO$_2$.

2.1.2 Herriot Cell

Mechanically, the CO$_2$ Herriot instrument consists of six distinct zones (Figure 9), with all except the sample cell being made of aluminum. All zones are sealed together using greased O-rings to prevent leaks into the sample volume. The first zone is an aluminum connector between the LPV and the Herriott cell. A 30 kΩ thermistor on the body of this zone measures temperature, and a 25W Minco thermofoil heater controls the temperature of the zone. As the sample passes into the zone, it is heated through contact with the aluminum component.

The second zone is the portion of the instrument that holds the entrance Herriott mirror. Surrounding the Herriott mirror is a set of sample entrance holes designed to reduce eddies in the cell, which can result in trapped volumes of sample air, effectively mixing samples and reducing accuracy of the instrument. The reduction of eddy formation is accomplished by pulling the air through a radial set of 2.5mm holes around the mirror, which causes the flows to merge together, and thus reduces trapped volumes of samples that could confound measurement. A 100 kΩ thermistor in this zone measures and records the sample temperature at 10 Hz.

The Herriott mirrors in this zone are 2.5cm diameter gold-plated mirrors with 15cm radius of curvature, with a 1% per reflection estimated loss of reflection off of each surface. Both mirrors have 2.5mm holes at a radial distance of 2cm, allowing for the laser to enter one side of
the cell and leave the other side with an odd number of passes. The cell is 23.8 cm long.

Depending on entry angle, the laser has two stable pathways: a 5 pass pattern for a 1.2 m path length and a 35 pass pattern for an 8.4 m path length.

The third zone of the instrument is the sample area of the cell. The sample cell itself is made of glass for alignment purposes. To align the QCL beam in the Herriott cell, we co-aligned the beam with a visible laser, and the glass cell allowed us to see through the cell and visualize the spot pattern on the Herriott mirrors.

The fourth zone of the instrument is a mirror image of the second zone with the exception of a pressure port. This zone holds the exit Herriott mirror, a 100 kΩ thermistor to measure sample temperature at 10 Hz, a high-precision pressure measurement apparatus (MKS Baratron) to measure and control pressure at 10 Hz, and sample exit ports in the same configuration as zone two. The temperature measurements from this zone and from zone 2, both directly in the sample flow stream, are combined with the pressure measurement as part of the data fitting used to derive the CO₂ mixing ratio (see section 2.1.4).

The fifth zone of the instrument is the outlet to the pump. The sample flows through this zone and out of the instrument. The laser passes through this zone and into the sixth and final zone, which serves to connect the cell to the detector.

2.1.3 Electronics

Electronics for the instrument are either contained within the LPV or co-located near the instrument, bolted in narrow locations in the nose of the aircraft. Data acquired from the MCT detector is conditioned by 350 kHz low-pass filter to reduce high-frequency noise. The signal is
then passed through an anti-aliasing filter and transmitted as differential signal, whereby the signal is duplicated and flipped 180 degrees so that both signals travel to the analog-to-digital converter. Here, the signal is flipped again and recombined with its duplicate so that any EM interference induced in transit is effectively cancelled.

The spectra are oversampled using our Scalable Signal Processing board at 100 MHz. We sample by sweeping over the entire region of interest at 800 Hz, which allows us to average every 56 points. The averaged spectra are then co-added to achieve a 10 Hz sample rate. Telemetry data, including but not limited to the cell temperature and other temperatures, cell pressure, inlet temperatures, LPV and laser pressures and temperatures, and diagnostic etalon signals are combined with the absorption spectra, given a timestamp, and stored on a field-hardened solid-state drive. 50Hz BAT probe data also receive a time stamp and are stored for later co-variance.

### 2.1.4 Fitting Software

In general, converting the acquired spectra into measured mixing ratios is achieved by performing a least-squares analysis comparing them to modeled spectra derived using parameters from the HITRAN database (Rothman et al. 2009). The HITRAN database contains frequency, temperature, and pressure dependent spectra characteristics for atmospherically relevant molecular absorption features.

The spectra fit a Voigt line shape (Liu et al. 2001), whereby Doppler and Lorentzian broadening profiles of the spectral absorption features convolve to create the line shape. The Doppler and Lorentzian profiles of an absorption feature are associated with the pressure and
temperature of the samples. The absorption coefficient, $k(\nu)$, is governed by the spectral line intensity $S_{nn'}$, the Voigt lineshape function $V$, and the Lorentzian and Doppler half-widths, $\gamma_L$ and $\gamma_D$ (Rothman et al. 2009):

$$k(\nu) = \frac{S_{nn'}}{\gamma_D} \sqrt{\frac{\ln(2)}{\pi}} V(\nu, v_{nn'}, \frac{\gamma_L}{\gamma_D})$$

whereby $\gamma_L$ and $\gamma_D$ are

$$\gamma_L(p, T) = \left(\frac{T_{ref}}{T}\right)^n \gamma_{air} p$$

$$\gamma_D = v_{nn'} \sqrt{\frac{2kT\ln(2)}{mc^2}}$$

and temperature-dependent $S_{nn'}$ is

$$S_{nn'}(T) = S_{nn'}(T_{ref}) Q(T_{ref}) \frac{e^{-c_2E_n/T}}{e^{-c_2E_{n'}}/T_{ref}} \frac{e^{-c_2E_n/T_{ref}}}{e^{-c_2E_{n'}/T_{ref}}}$$

The pressure and temperature are derived from the baraton and thermistors described in section 2.1.2. The parameters $S_{nn'}(T_{ref})$, $E_n$, $v_{nn'}$, $\gamma_{air}$ and $n$ are obtained from the HITRAN database, $c_2$ is the second radiation constant, $Q(T)$ is the total internal partition sum, $k$ is Boltzmann’s constant, and $c$ is the speed of light. These equations and parameters are utilized in an in-house fitting algorithm to derive mixing ratios.

The fitting algorithm begins with fitting the data from the diagnostic etalon (Figure 13) within the sample region to convert sample numbers to wavenumber space. The data from the
etalon fit is output into a file with the temperature and pressure of the cell during that scan. Next, an empirical fit of the baseline is derived, representing laser transmission in the absence of absorbers. The baseline is generated with a 4th order polynomial fit to regions of the spectrum lacking absorption features and interpolated to absorption features using the generated polynomial. The baseline is then used to determine the max absorption depth of the absorption features.

The output of the etalon fit and the empirically determined baseline are combined with a third data file containing the temperature and pressure dependent spectral coefficients for the selected absorption features from the HITRAN database. The spectral data (Figure 14) is transformed using the temperature and pressure relationships described above and fit to model absorption features using a non-linear least-squares fit, deriving mixing ratios.

After fitting the data, minor linear adjustments are carried out using calibrated gas standards, typically around 400ppm CO2, which are sampled every 20 minutes in flight and in the laboratory. Final corrections are made based on the ambient water mixing ratio, which is measured simultaneously by the fast response CH4 instrument.
Figure 14: Spectral region of CO$_2$ instrument and field spectra. A model of the spectrum in the wavelength region of the CO$_2$ instrument (left), using spectral parameters from HITRAN. A 770cm path length and a pressure of 65 torr shows several CO$_2$ absorption features. Our spectra from the instrument (right) shows the matching absorption features in conjunction with the diagnostic etalon. The data we fit on are the short peaks surrounding the major feature at 2310.5.

2.1.5 Pneumatics System

The CO$_2$ cell was operated at 65 torr in the field. This cell pressure was chosen to provide a sufficient absorption depth to meet our precision requirements. We use a Varian Tri-Scroll 300 scroll pump to achieve flow through the instrument. An inlet co-located with the NOAA BAT-probe on the boom, which was mounted on the nose of the aircraft, sampled the ambient air. A 2m long, 1cm diameter Synflex tube transports the sample to a proportional solenoid valve, which controls the pressure of the cell and additionally is heated to 25 °C to initially condition the sample temperature. The sample continues through a 1m tube to the CO$_2$ axis. The sample flows through the cell and exits, leading to a 2.5 cm reinforced rubber tube that connects to the scroll pump, located 3 meters aft in the passenger compartment of the airplane. The flow rate is measured at 17.5 SLM at 65 torr. The volume of the cell is 0.115 L, resulting in a cell flush rate of 35 Hz. Given that a 10 Hz response rate is necessary to capture all scales of eddies that are important for covariance (Auble and Meyers 1992), this high flush rate is ideal as it accounts for signal flattening, or the turbulent mixing of samples, that can happen from the inlet to the
detection axis. If, for example, a sample mixes with both the sample ahead and behind it, then a flush rate that is 3x faster than the sample rate will effectively obscure the signal flattening. Consequently, our cell 90% response rate is faster than our 10 Hz measurement.

The CO\textsubscript{2} instrument was sealed to prevent sample contamination from air in the ambient environment, as air pulled from the front compartment of the airplane into the instrument during operation would combine with the sample and distort the signal. Sealing was tested by capping the inlet of the instrument, pumping out the CO\textsubscript{2} axis, and closing the Edwards valve that leads to the pump. The instrument was pumped below 1 torr and left for 8 hours, over which time the pressure crept up to 17 torr, indicating a leak of less than 2 torr/hour. Given that the instrument operates in the field at 65 torr and that the flush rate of the instrument is 35 Hz, the contribution of leaks to the measurement in flight is negligible.

**Pneumatic Cooling System**

A cooling system is required to prevent the scroll pumps from over-heating and shutting down. During this project, we developed and tested our own cooling system for our pneumatic systems. Using a liquid pump and pump controller (Fluido-Tech), we circulated a 1:4 mix of propylene glycol coolant and water through a heat exchanger and fan system near the pumps to provide cooling air. The pump pulled from a reservoir of cooling fluid, pushed the fluid through a radiator with a fan that cooled the air surrounding the pump, and recycled the fluid back into the reservoir.

The viability of this cooling system was measured by housing the cooling system in 4’x4’x4’ styrofoam housing, a volume roughly similar to the airplane space available, and
measuring the heat buildup. Heat was measured by thermistors connected to a digital multi-meter, with a thermistor for each pump head. Within 20 minutes of their first tests, the pumps reached within 10 °C of the melting point of their Teflon tip seals. The temperature within the Styrofoam enclosure was much cooler than the pump heads, which indicated that the enclosed space and heat exchanger with fans were not sufficient to move heat from the pump heads quickly enough.

This problem was remedied by augmented the cooling system by replacing the standard air-cooling fairings on the pumps with fairings that allowed for liquid cooling as well as replacing the radiator with an external heat-exchanger. Unfortunately, this would require a source of external cooling while in flight. To meet this requirement, we designed and installed a passive heat exchanging radiator on the bottom of the aircraft. This heat exchanger proved sufficient for cooling in environments as warm as 35 °C. For colder environments, like our site of deployment in Arctic Alaska, we drew air flow from the ambient environment to cool our reservoir to maintain sufficiently cool pump operation temperatures.

2.2 Laser Spectral Region Shift and Ramifications

The instrument originally meant to target CO$_2$ absorption features at 2298 cm$^{-1}$. This wavelength region would have achieved the desired absorption depth, and thus the requisite precision, with a five-pass pattern in our Herriott cell. Instead, our laser operated at 2310 cm$^{-1}$, capturing CO$_2$ absorption features with less than 1/10$^{th}$ the absorption depth. As a result, we needed a 35 pass pattern and higher pressure to achieve the desired absorption depth. The 2310 cm$^{-1}$ region is also more crowded with absorption features (Figure 15) that could make fitting a baseline more difficult. The 35 pass pattern, however, resulted in an overlap of our laser path on
our Herriott mirrors. This overlap created an etalon interference pattern (hereafter referred to as a cavity etalon, to distinguish it from the diagnostic etalon), a constructive and destructive interference pattern based on partial overlap of reflection points on the cell mirrors. These cavity etalons affect both the baseline and the absorption features of our laser scans (Figure 16).
Figure 15: Intended spectral region vs. what he had. Intended absorption region (top) vs. absorption region of our instrument (bottom). The intended absorption region would have exhibited a five-pass pattern with no cell etalon to achieve 15% absorption at 400ppm CO2 and 30 torr. Instead we had to go with a 35 pass pattern with overlap, resulting in a cavity etalon, and operate at 60 torr. This led to baseline overlap resulting in fitting difficulties to achieve half the desired absorption depth.
Figure 16: Carbon cell etalon. Our 35 pass pattern resulted in overlapping points on the mirrors. Optical interference resulted in a cavity etalon. This etalon looks like a sine function (actually an Airy function) traveling through the scan line. This cavity etalon affects both the baseline and the absorption features, making the fitting of the data more difficult, since data fitting relies on flat baselines and characteristic absorption curves.

Running the data with a cavity etalon through our fitting program results in a poor fit, with 0.75% residual fit mismatch around the $^{13}$CO$_2$ feature, and up to 0.6% residual fit mismatch around the $^{12}$CO$_2$ feature (Figure 17). This would be inconsequential if the cavity etalon were stationary on the absorption features, as it would create an accuracy error that we could correct. The cavity etalon, however, changes location in the scan owing to the thermal expansion of the optics and cells. This results in a sinusoidal signal being overlaid into the mixing ratios. A 0.6% precision limit on CO$_2$ would make the precision of the instrument no better than 2.4ppm, which is far below standards for measuring CO$_2$ as suggested by the literature for measuring isotopic signatures in the field (Tohjima et al. 2009).
Figure 17: Fitting results with a cavity etalon. Bottom: The fit of the baseline baseline (red) and the fit of the data (smooth green curve) is compared with the actual scan data (blue sinusoidal line). The baseline is modeled as flat, the data fit is modeled as a standard absorption curve, and the cavity etalon is apparent in the actual scan data. The fit residual (top) shows a 0.75% residual error of fit around the $^{13}$CO$_2$ absorption feature, and a 0.6% residual fit error over $^{12}$CO$_2$. Mismatch of fitting would consistently result in poor data quality well below reporting standards.

We attempted to account for the cavity etalon by adjusting the fitting routine described above. We performed a Discrete Fourier Transform (DFT) on the results to determine its dominant frequency (Figure 18). The cavity etalon can then be closely approximated with trigonometric functions. Applying this etalon shape to the empirical baseline results in a more accurate measurement of the concentration. The results diminish the residuals of the data fit (Figure 19), creating mixing ratios with better precision and accuracy. Through this, we can achieve nearly the same precision through a 35-pass pattern as we could in the planned 5 pass pattern of the original specifications.
Figure 18: Discrete Fourier Transform of fitted data. The resulting fit data of the fitting algorithm are fed into the DFT. Because the cavity etalon effects the mixing ratios of the fitting algorithm output, a DFT reveals the frequencies at which the etalon is present. Using this, we can create a baseline that accounts for the etalon, reducing sinusoidal noise in the fit and increasing both the accuracy and precision of the measurement.
2.3 Final Integration into FOCAL

The instruments were integrated into the DA-42 in Manassas, VA, along with the BAT probe (Figure 20) and radiator. Initial integration allowed for final placement of the large ICOS cell, designed to measure the isotopologues of CH$_4$, and the pneumatics system in the rear of the aircraft (Figure 21), as well as the final placement of the small, fast-response CH$_4$ (“mini-CH$_4$”) and CO$_2$ cells in the front of the aircraft.
Figure 20: The BAT probe and boom installed and mounted on the aircraft. The inlets to the instruments are the metal tubes protruding from the rear of the BAT probe. The boom is made of carbon fiber, and the BAT probe is made of aluminum.

Best practices for eddy covariance flux measurements require that the inlet for the instrument measuring concentration be co-located as close as possible to the BAT probe, which measures vertical wind speeds. Variations in the vertical wind speed, $w'$, are used for the eddy covariance flux calculations. The closer the CO$_2$ and CH$_4$ instrument is to the inlet, the better for covarying, as this reduces the mixing of samples that can result in signal dampening. The sample inlet is co-located adjacent to the BAT probe (Figure 20), and a 2m tube carries the sample to the CO$_2$ Herriott cell and mini CH$_4$ instruments mounted in the nose of the DA-42 aircraft. The larger CH$_4$ isotopologue ICOS instrument was in series pneumatically with the mini-CH$_4$ instrument with an additional further 2m tube of 1.5” diameter running into the back of the aircraft, where the larger CH$_4$ instrument and scroll pumps operated.
Instrument electronics were co-located with each instrument. Each instrument has a Serial Signal Processor (SSP) that manages all channels of data associated with it. The data are passed to a central connector board adjacent to the instrument, combined, and processed by our Parallel Digital and Analog Converter (PDACs). Data are stored on a solid-state drive. The PDACs is located adjacent to the scroll pumps in the rear of the aircraft (Figure 21).

Figure 21: Large ICOS cell and Pump System. Shown here is the instrument payload laid out in the configuration used in the aircraft. The pumps are located beneath the large CH₄ ICOS cell and the PDACs, the data acquisition and control system. These instruments are deeply recessed once in the aircraft, preventing pictures of the installed payload.

Each DA-42 is hand-built, and specifications for size and shape on these airplanes are rarely precise. As a result, our first major field effort was focused on fitting all of the instruments
into the airplane with proper alignment. To carry this out, we worked out of Aurora Flight Sciences, our partner and owner of the DA-42 we used, in Manassas, VA.

To certify the airplane for flight, all equipment was uninstalled and transported to an FAA reviewer in Greensboro, NC, where the DA-42 was then flown. All the instruments were re-installed using a bolt-by-bolt instruction set under the guidance of FAA reviewers. The airplane received experimental aircraft certification and test flights were initiated.

**Wallops Field**

Test flights were conducted from Manassas to Wallops Field. These aimed to better integrate the BAT probe data and our instrument data, as well as test the temperature stability of the instrument. The instrument performed to specification.

Prior to fielding the full instrument payload to Alaska, additional test flights were carried out from Hanscom Air Force Base outside of Boston. The instrument again performed according to specification. In early August 2013, the system took off from Hanscom Air Force Base, and flew to Deadhorse, AK, for our field mission.
3: Results

As we emphasized in Chapter 1, the uncertainties associated with emissions of CO₂ and CH₄ from the warming Arctic demand a robust platform to measure and report high-fidelity CO₂ and CH₄ concentrations and fluxes over a massive areal extent in the Arctic. However, the workhorse method of flux towers is impossible in the Arctic. To remedy this, we report here the performance of the CO₂ Herriott instrument in laboratory and field testing. The performance of the CO₂ instrument in the laboratory was nearly as good as commercially available instruments, but with a 100x faster response time. Furthermore, our instrument successfully demonstrated proof-of-concept in the initial field integration with the NOAA BAT probe on the DA-42 aircraft. While the performance deteriorated during flights over the North Slope of Alaska, we have identified all the major instrumental problems, proposed solutions for each one, and in the laboratory tested solutions for the largest of the problems.

The first section of this chapter briefly described the instrument calibration procedure, demonstrates the linearity of the instrument, and reviews post-processing water vapor corrections. The second section discusses the several instrument issues that were discovered while reducing and interpreting data from the field campaign. The third section discusses the recommended augmentations to the instrument, and includes results from laboratory tests of a new detector type that will likely address the largest of the problems encountered in the field. Finally, the remainder of the data acquired over the North Slope of Alaska, five runs of CO₂ concentration data, are presented in the context of ambient temperature, moisture, and land type.

3.1 Lab Performance and Water Calibration
The instrument was calibrated and its precision assessed during a series of two-hour long operations using a gas standard. The performance is assessed with Allan Variance analysis. Allan Variance is an estimate of stability due to noise, and not that of systematic errors such as frequency drift or temperature effects. Allan variance plots show the statistical variance of instrument precision compared to what would be expected from white noise. This indicates the averaging time over which instrumental noise is nearly equivalent to white noise, and the precision achieved at that averaging time. Allan variance plots for this run show that the CO$_2$ instrument has a lab precision of 550 ppb (1σ-1s) for $^{12}$CO$_2$ and 2.2‰ δ$^{13}$ for $^{13}$CO$_2$ (Figure 22).

![Allan Variance plots](image)

Figure 22: Allan Variance plots of CO$_2$ axis in lab tests. The instrument currently shows a 0.5ppm precision (1σ-1s) at 10 Hz, and 2.2‰ δ$^{13}$ for $^{13}$CO$_2$. In future deployments we can increase this by a factor of three by moving from 2310 cm$^{-1}$ to 2298 cm$^{-1}$ for the next instrument (this wavelength was not available at the time of instrument development).

**Water Dilution Correction**

Additional laboratory tests were carried out to determine the appropriate corrections for ambient water vapor in the sample, which can range from a few hundred parts per million to a few percent by volume in the troposphere. During the mission, we witnessed water vapor ranging
from 0.4% to 1.5%. The preliminary CO₂ data need to be corrected for two independent effects to do with water vapor. The first is dilution. As the amount of water vapor increases in the sample, the effective mixing ratio of the molecule of interest proportionally decreases. Reporting the dry CO₂ mixing ratio standardizes the results for comparison. As the dry mixing ratio of CO₂ is ultimately what is desired, the effect of water vapor must be accounted for via the following equation:

\[
CO_{2\,\text{dry}} = CO_{2\,\text{wet}} \frac{1}{1 - [H_2O]}
\]

where \(CO_{2\,\text{dry}}\) is the reported mixing ratio, \(CO_{2\,\text{wet}}\) is measured CO₂ mixing ratio, and \([H_2O]\) is water vapor mixing ratio.

**Water Broadening Correction**

In addition, water can directly affect the spectral characteristics of individual features in the CO₂ spectrum. Collisions with water molecules lead to additional line broadening that needs to be accounted for. Calibrating an instrument over a range of water vapor concentrations encountered in the field campaign provides the relationship to convert measured CO₂ to standardized convention of reporting dry mixing ratios. Water concentrations are measured in the field by the adjoining fast-response CH₄-H₂O detection axis and calibrations to empirically determine the total water corrections were carried out in the laboratory.

Water correction coefficients were determined by introducing sample air with known water vapor mixing ratios. The water vapor content of the air was varied over a range representative of values encountered in flight. The concentration of the sample is controlled by
mixing air that has been fully saturated through a dual-stage bubbler with a primary dry air flow. The temperature of the water in the bubbler was measured with a 30kΩ thermistor, and the water vapor mixing ratio of the moistened air was determined using the Clausius-Claperyon relationship. The proportion of saturated to dry air is controlled by a pair of flow controllers (Figure 23), with the total flow and the pressure in the CO₂ Herriott cell remaining constant. The source for both the wet and dry flows is a calibrated tank of dry air with 389 ppmv of CO₂.

**Bubbler System Design**

![Bubbler System Schematic](image)

Figure 23: Bubbler system schematic for water corrections. Dry calibration air is split into two channels, and the proportion of saturated to dry air is controlled by two separate flow controllers. One flow controller (bottom path) regulates the flow through a bubbler where the sample becomes saturated with water vapor. The temperature of the bubbler system is monitored to determine the amount of water vapor that absorbs into the sample. The saturated flow recombines with the dry calibration flow (top path), and flows into the instrument. An overflow valve vents excess combined sample gas into the room to ensure the instrument can control the pressure within the sample cell. By adjusting the relative flow rates of each flow controller, we can adjust the water ratio to run water calibrations.

Measurements of the dry CO₂ mix ratio are plotted against the water mixing ratio of the sample in Figure 24. Water broadening effects are accounted for after accounting for the water dilution effect, thus, the remaining difference between CO₂ measured and CO₂ dry is due to the line-broadening effect. A linear fit to the data is used to generate the empirically determined correction factor. The dry mixing ratio can be represented by:
\[ CO_{2\ dry} = \frac{CO_{2\ wet}}{[H_2O] \ast m} \]

where \( m \) is the slope of the relationship between water and dry mixing ratio. The resulting equations are:

\[ CO_{2\ dry} = \frac{CO_{2\ wet}}{[H_2O] \ast 366} \]

\[ ^{13}CO_{2\ dry} = \frac{^{13}CO_{2\ wet}}{[H_2O] \ast 4.93} \]

for up to 1.5% water vapor. Relationships between water vapor mixing ratios and corrections can become non-linear with higher water vapor mixing ratios. The range of water vapor mixing ratios seen in the field did not exceed .008, remaining within the range of water vapor correction linearity demonstrated in the laboratory.
Figure 24: Water broadening correction. Water broadening corrections of $^{12}\text{CO}_2$, using 10 Hz data. Using a calibrated tank of 389ppm CO$_2$, we see the measured dry mixing ratio of CO$_2$ decrease as the water vapor mixing ratio increases. Note that the dry mixing ratio of CO$_2$ is constant during this run. A linear fit to data yields a slope of -366 for $^{12}\text{CO}_2$ and -4.93 for $^{13}\text{CO}_2$. At 1.5% water vapor the correction is 5.5ppm and 0.074ppm for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, respectively.

**Instrument Linearity**

We assessed the linearity of the instrument response over the range of CO$_2$ mixing ratios we expected to see in the field: 360 and 400ppm. Using a tank of 400ppm CO$_2$, a tank of zero air, and two flow controllers, we adjusted the ratio of CO$_2$ to zero air from 100% to 95% to 90%. Each flow was held for 30 minutes. A plot of the CO$_2$ expected vs. the CO$_2$ observed shows a linear 1:1 relationship (Figure 25).

Because the CO$_2$ instrument performs linearly over all expected values in the field, we determined we could use a single calibration tank rather than a span calibration system. It would
have been ideal to use a span of calibration tanks as well as a tank of N$_2$ to achieve a baseline, but space and weight constraints prevented this on our first field campaign.

![CO2 Linearity Diagram](image)

Figure 25: $^{12}\text{CO}_2$ instrument linearity. The CO$_2$ instrument performs linearly for $^{12}\text{CO}_2$. The residuals of the fits are clustered symmetric, clustered around zero, and contain few outliers, indicating a good fit.

The CO$_2$ axis proved capable of high-precision measurements of CO$_2$ concentrations for flux analyses when used in conjunction with a NOAA BAT probe onboard a small, low-flying aircraft (see table 1). Compared to commercially available instruments, our instrument has a far better response time, a lower volume profile, and a weight profile that minimizes mass in the front of the airplane, with only a modest trade-off in precision.
3.2 Inconsistencies Between Lab and Field

We fielded our instrument suite in the North Slope of Alaska in August 2013. Upon returning, we began data analysis and reduction from the field campaign data. Our in-house fitting algorithms failed to produce data quality consistent with the performance seen in laboratory. This section reports in detail the insufficiencies of instrument field performance. In particular, the fitting algorithm resulted in periodic anomalies (Figure 26) that masked the signal. In addition, while the instrument was supposed to be stable over several hours, the in-flight calibrations showed up to 6ppm deviations despite occurring only 20 minutes apart. An exhaustive search for correlations with a wide range of variables, including instrument and cell temperatures, cell pressure, and electronic noise was carried out, but no clear, correctable trend was established. We discovered a laser feedback effect when reflections from the diagnostic etalon that produced deviations from the standard performance, and developed and tested a correction mechanism to correct the data. Additionally, through instrument modification and testing, we discovered a sample temperature measurement and reporting problem that we could not address retroactively. Ultimately, several problems with temperature control, laser feedback, and detection resulted in only $^{12}\text{CO}_2$ data being recoverable from the field mission, with a lower precision than expected from laboratory characterization of the instrument.
Figure 26: Field mixing ratios before algorithm augmentation. Overlaying the field data is a period oscillation that overwhelmed our signal, reducing precision and obscuring relationships to ambient parameters such as temperature, moisture, and land cover type.

3.2.1 Calibration Mismatching

Performance in flight did not match performance in the laboratory or either of the two preliminary field tests, showing a 6ppm accuracy drift not observed in the laboratory. During post-processing, we diagnosed an issue on several runs whereby our calibrations, taken every 20 minutes, did not align (Figure 27), despite the fact that our instrument was stable in lab over two hours.

Figure 27: Calibration cycle before correction. Calibrations during flights show a 6ppm difference in concentrations between three calibration cycles. Calibration cycles were separated by 20 minutes of flight time, and ran for two minutes
3.2.2 Ruling Out Simple Temperature Corrections

We suspected the cause of these errors was related to the far colder temperatures encountered in the Arctic than what we experienced in the laboratory, where temperatures were stable, or in either of our initial field trials, where the temperature was warm and controlled. Colder temperatures could overwhelm the instrument ability to self-heat, and could result in unstable instrument temperatures. This would result in changing optical train length, and thus a change in the beam path. If this were the case, we would see a predictable relationship between instrument temperature and concentration change during both the field operation and during laboratory tests. Diagnosing and recreating the effect in the laboratory would establish a correction method to recover the field data. Recorded instrument temperatures in the field did not show correlations between temperature and the instrument oscillations, however.

We returned to the laboratory and stripped the CO₂ cell of its thermal insulation. While running a long calibration test, we slowly changed the temperature of the instrument while measuring temperatures all over the instrument with thermistors. We used a calibration gas of known and constant concentration during these temperature tests. We saw clear deviations in measured concentration of the known standard as the temperatures changed, but there was no periodic relationship in temperature that matched the period shifting we witnessed in mixing ratios. Regressions with respect to electronics performance, pump temperature, pressure control, and potential electronic feedback from other instruments also showed no clear cause of the degradation.

The problem was not caused by electronic feedback or signal processing, and it was not in the optical train, leaving the laser and the detector. Both of these also showed within-
parameter performance. Thus, every potential first-order problem had been accounted for. This led to a time-consuming search of second-order problems, evaluating every upstream and downstream data input, fitting parameters, calculation of fits, and storage method.

3.2.3 Etalon and Laser Feedback

Delving into the entire fitting algorithm and analyzing all of the inputs and outputs revealed the culprit: we were having what appeared to be laser feedback. Here, we define a scan as a single pass of the laser over the spectral region of study, and each scan has ~1800 data points within the scan. An analyses of our diagnostic etalon revealed that the tuning rate of the laser (cm$^{-1}$/s) was changing frequently between scans. However, this should have been accounted for by the fitting algorithm using the diagnostic etalon.

Tunable lasers are expected to have a constant tune rate within a single scan. They operate by applying a linear current ramp (I/s yielding cm$^{-1}$/s, with a constant cm$^{-1}$/sample point). By analyzing the fitted tuning rate at a single point of each scan, and comparing through all scans, we discovered that the tuning rate at that in the scan was oscillating (i.e. getting faster and slower over time) with a period that changed over time. We should only expect changes in tuning rates between scans. Looking at the rate of change around a single point in each scan, we would expect to see smooth transitions over time indicating a slow drift of scan speed. Instead, we saw frequent jagged transitions (Figure 28). This aberrant behavior indicated that our laser was suffering from laser feedback.

This is uncharacteristic behavior of a laser, and makes fitting the etalon, and thus the scan rate and expected shape of a spectral feature, unpredictable. A faster scan rate would result in
narrower absorption features, which, in turn, would result in a smaller measured absorption feature area, and lower reported mixing ratios. This indicated the source of our problem.

![First Der. Laser Tuning Rate at a Single Point](image)

Figure 28: First derivative of fit of the etalon function. This is the scan rate of the laser at a single point along the scan, moving across every scan of a calibration test. This would be expected to be a smoothly transitioning function over time. The jagged format indicates that our laser was experiencing feedback, and that feedback occurred at different places in the scan over periods of time.

QCLs produce light by manipulating coupled quantum wells to create population inversions, the process whereby electrons are at a high energy state and, in relaxing, emit photons (Faist et al. 1994). The layer thickness of varying layers of a QCL controls the general wavelength region of photon production. The laser can be tuned across several wavenumbers in this general wavelength region by applying a current to the QCL to vary the temperature of the QCL. A consistent current ramp will produce a consistent laser scan rate. Laser feedback with a QCL can result in scan rate changes in a scan by “locking” the quantum well that produces the photons in place. Within fractions of a second the increasing laser temperature overcomes the
locking, and the scan must accelerate to resume the programmed overall scan rate. The result is measured absorption features with widths that are changing within and between scans, leading directly to inaccurate reported mixing ratios.

From this, we found a potential temperature dependence. Part of the laser beam is likely reflecting off the surface of the diagnostic etalon and back into the laser. Thermal expansion and contraction of the system causes micro-scale changes in the distance between the laser and the face of the germanium etalon, leading to changing laser feedback. As the distance between the laser and the etalon minutely changed, the interference that caused feedback slightly shifted in the scan location of the laser (Figure 29). An additional related mechanism could be the temperature of the diagnostic etalon itself. Light that enters the etalon is trapped for a time, but then photons leave through both sides of the etalon. As thermal expansion changed etalon length, the light coming out of the diagnostic etalon can return to the laser. Shifts in the length of the diagnostic etalon will result in shifts of etalon peaks and troughs in wavenumber space, varying the location of the laser feedback over the tuning range.
Figure 29: Schematic diagram of LPV thermal expansion and laser feedback. Here we use “feedback 1” and “node 1” to designate that this is the same interference happening in different locations based on the distance from the laser to the etalon. Minute changes in the distance between the laser and the reflective surface of the diagnostic etalon result in shifts of the feedback pattern.

### 3.2.4 Detector Shortcomings and Laser Feedback

A lack of isolating optics to prevent laser feedback helped give rise to this problem. Our detector precluded implementation of standard methods to block laser feedback. In addition, our detector had several flaws that reduced instrument precision in the laboratory, and contributed to deteriorated instrument performance during the field campaign.

First, the lens material chosen for the Vigo detector is incapable of passing circularly polarized light. The typical method to prevent laser feedback is a polarizer followed by a quarter wave plate. The polarizer passes the laser through, and the quarter wave plate circularly polarizes the light and shifts the phase by 45 degrees. The circularly polarized light then travels towards the optical train. Any back-reflections would pass back through the quarter wave plate, become linearly polarized, and be at 90 degrees to the initial laser beam. The polarizer would then block
the light from passing back into the laser. Because the lens material for the Vigo detector could not pass circularly polarized light, we were precluded from using this optical isolation technique.

Second, the detector uses an immersion lens that is 1\,mm$^2$ in area, focusing light to a 0.1\,mm$^2$ MCT detector. Immersion lenses suffer from several nearly crippling optical issues: overfilling them results in inaccuracies, changing the entrance angle results in the detector recording a different signal for the same incident power, and holding a stable alignment can be difficult, particularly with thermal expansion of the optics train and detection axis. This may have been remedied with a focusing optic prior to the detector, but laboratory tests showed that we could not achieve proper alignment of a focusing optic with this instrument design. The result was that thermal expansion of the instrument could alter reported mixing ratios given the same sample and light source.

Third, in our wavelength of interest in the mid-IR, the material surrounding the MCT detector is reflective. Any light that is not incident on the 0.1\,mm$^2$ semiconductor of the detector will reflect back into the immersion lens, with a portion returning to the semiconductor detector, creating optical interference by reflection. Put succinctly, our detector has an inherent design flaw that causes self-optical interference, reducing instrument precision.

### 3.2.5 Making a New Algorithm to Recover Field Data

The primary culprit of compromised instrument field performance was laser feedback. Eliminating feedback would allow the use of our standard fitting algorithms. Two laser feedback behavior types would allow averaging of the feedback to reduce inaccuracies. The first resolvable feedback is if there exists a characteristic timescale whereby feedback were
completely random, akin to white noise. Averaging the data over time would average the results of the feedback effect, creating an averaged data set that could be fit with our fitting algorithms. The second resolvable feedback would be if the feedback were periodic, allowing binning of the data to groups of equal size. Averaging within these bins would reduce the effects of feedback.

Unfortunately, our feedback showed neither of these characteristics. Our CO₂ Herriott instrument has a diagnostic etalon and a cavity etalon. Each should have consistent ratio of wavenumbers per fringe within a scan, and similar ratios between scans. Comparing the difference between the fits of these two etalons, and subtracting the cavity etalon spacing, shows the signal error due to feedback that prevented proper fitting of the etalons (Figure 30). The results approximately relates the tuning rate discrepancies within and between scans. This is not the actual tuning rate, an estimate of the error, so we cannot use these results to repair our data by assigning a new tuning rate to each data point of our field data. Moreover, we cannot replicate this experiment for field conditions to attempt to model a correction for each data point. In short, the feedback experienced in the field could not be corrected via further experiments in the laboratory.
Figure 30: Tuning rate of the laser during calibration. The x-axis represents individual scan numbers, while the Y-axis represents the position of each individual scan. The plot is colored by the difference in wavenumbers per fringe between the diagnostic and the cavity etalon, and approximates the error signal in the laser tuning rate. The black lines running horizontally across the graph show the location of our absorption features. The tuning rate change, caused by feedback error, is not consistent between the two absorption lines, changes with time, and becomes very unpredictable, precluding averaging to correct feedback.

Because our in-house fitting algorithm relies on area of the absorption feature to derive mixing ratios, and the feedback created unreliable areas of absorption features, we designed an algorithm that relies only on absorption feature depth and not area to fit the data (see appendix for the commented code for this algorithm). Our method, generally, establishes a baseline, removes the cavity etalon, adjusts parameters for each molecule based on HITRAN parameters and then carries out Beer’s law rather than fitting an area under the absorption feature (Figure 31).
Figure 31: Flow diagram of correcting the fit of the CO2 instrument. Fixing the problem with our system by augmenting our original algorithms and creating new fitting algorithms, we were able to circumvent several of the problems posed by our detector and laser feedback to recover some of the field data. First we establish a baseline, then remove the cavity etalon. We augment the scan with temperature and pressure correction coefficients, and then apply Beer’s law to arrive at a concentration.

Beer-Lambert’s law relates concentrations of an absorber to the attenuation of light passing through the medium wherein the absorber resides. In our data, it relates the mixing ratio of our absorber, CO₂, to the attenuation of specific regions of our tuned laser. The relationship is governed by the equation:

\[- \ln \left( \frac{I}{I_0} \right) = c \times k(v) \times l\]

Where \(I\) and \(I_0\) represent transmitted and initial light intensity, respectively, \(c\) is the concentration of the absorber, \(k\) is the absorption coefficient accounting for pressure and temperature broadening, and \(l\) is the instrument path length. By using peak absorption depth of the feature, we eliminate the changing area of an absorption feature caused by changing laser tuning rate. In a sample without laser feedback, this method would reduce precision of fit by going from an area fit to a linear depth fit, causing up to a \(\sqrt{2}\) decrease in precision. In a system with laser feedback, this precision reduction is superior to the precision and accuracy errors in the fitting algorithm produced by laser feedback.
This Beer’s law fitting algorithm follows the initial steps and transformations used in-house algorithm described in section 2.1.5 and the cavity etalon fitting algorithm described in section 2.2. The spectral data is then augmented by subtracting the cell etalon from the spectral data. The algorithm then locates each absorption feature in the scan. Each absorption feature has over 18 points, but this is insufficient resolution to pinpoint the absorption peak simply by taking the minimum value. We fit the points near the peak with a 2nd order polynomial, and interpolate from 18 points to 300 points on both the absorption feature and the baseline. Taking a minimum on the polynomial fit resulted in an absorption depth, \( I \), and taking the value of the baseline directly above the minima provides incident light \( I_0 \). Using absorption coefficients from the HITRAN database, we correct for pressure and temperature for specific molecule by carrying out the calculations in Rothman et al. (1998) (also described in section 2.1.5) to derive \( k(\nu) \). We solve for \( c \) in the above equation to derive mixing ratio, and linearly adjust the results based on the calibration cycles during flight.

### 3.2.6 Recovered \( {^{12}\text{CO}_2} \) data

The new algorithm resulted in more stable \( {^{12}\text{CO}_2} \) measurements over changing temperatures in lab measurements (Figure 32). Applying this algorithm to field data showed improvement in the viability of the data. Prior to this application, in-flight calibration cycles did not show the same concentrations, despite using the same calibration gas. The corrections using our Beer’s Law refined algorithm eliminated this discrepancy, allowing us to recover some of the \( {^{12}\text{CO}_2} \) data from the mission, despite laser feedback issues. Using the new algorithm on field calibration cycles showed that we had rectified the mode hop seen while using our old algorithm (Figure 33).
Figure 32: Scan using our former algorithm (top) and corrected algorithm (bottom) with 10 Hz data. The new fitting algorithm during calibration tests in the laboratory shows consistent measurements over a long period, eliminating the mode hop that we saw in changing temperature regimes in both the laboratory and the field environments. These plots do not make the final correction in mixing ratio based on the calibration standard, further illustrating the difference in results of the fitting algorithms. In each case, there would be a final step to adjust to the calibration standard mixing ratio.
3.2.7 Cavity Etalon Fitting Issues

Figure 33: Calibration cycles during flight, using the former algorithm (top) and the new algorithm (bottom). Calibration cycles on a field mission flight on August 28th. The in-house algorithm results in a 6ppm shift between calibration cycles (top), making the measurement between the two calibration cycles unreliable. Using the modified Beer’s Law algorithm, the three calibration cycles now exhibit the same resulting measurement, indicating our field measurements were reliable.
The cavity etalon fitting algorithm proved less effective when applied to data acquired during the field campaign field. A cavity etalon should be consistent within a single scan if a laser tuning rate is consistent throughout the scan. Because our tuning rate changed within a scan, a fitted etalon would match well in some regions of the scan, and match poorly in other regions. In addition, the thermal expansion of the cell resulted in the etalon changing frequency between scans. In short, the etalon was shifting both within and between laser scans, making it more difficult to fit (Figure 34). The resulting mismatch between the modeled etalon for the fit and the etalon in the actual data confounded our $^{12}\text{CO}_2$ mixing ratios over very short time scales on the order of a second by as much as 0.4%. This is shown in Figure 35.

![Figure 34: A zoomed in cavity etalon from the field data. The DFT performed over a 20 minute section of field data shows that the primary etalon occurs over three frequencies. As a result, fitting the etalon accurately over a 20 minute section of the field data is imprecise, reducing viability of data.](image)
Figure 35: Etalon fit causes fitting errors. These plots show relative strength of the absorption features with an arbitrary scaling and the residuals to the fits in the same units. The absorption features from left to right are $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ (this one is too deep and is saturated), and $^{13}\text{CO}_2$. One scan on $^{13}\text{CO}_2$ shows a residual fit of -50 (top) while the next scan, 1.3s later, shows a residual of +100, for a total residual difference of 2.5% of the entire feature strength in just one second.

While this fitting errors is minor in relation to our overall $^{12}\text{CO}_2$ instrument precision, it occurs at a rate on the order of the covariance rate with the NOAA BAT probe. This confounds
the covariance of concentration with vertical wind data, precluding use of these data for flux measurements for this mission. Eliminating the cavity etalon would entirely eliminate this problem for future deployments.

The cavity etalon lack-of-fit proved more fatal to the $^{13}\text{CO}_2$ data. We report here a 2.5% fit residual on the $^{13}\text{CO}_2$ absorption feature. Our augmented fitting algorithm is completely reliant on absorption depth, and a 2.5% fitting error could directly translate to a $^{13}\text{CO}_2$ fractionation ratio error in excess of 25‰. Our measured $^{13}\text{CO}_2$ fractionation ratio variances are in excess of this. Given that a 4‰ change is the maximum expected in an entire growing seasons, our $^{13}\text{CO}_2$ field precision did not warrant reporting this data.

### 3.2.8 Temperature Measurement and Control

The field campaign in the North Slope of Alaska was significantly colder than our instrument was exposed to in the laboratory, in the test flights at Wallops Air Field in Virginia in June, and again in Boston in July, creating the largest instrument flaw. Our CO$_2$ Herriott Cell used a glass tube in the sample area for alignment purposes. The glass tube where nearly all of the absorption took place had no heating. Were it aluminum, we could have heated part of it and the high thermal conductivity of the aluminum would have allowed the entire tube to heat. The low thermal conductivity of glass prevented us from heating the glass tube in this manner. This resulted in the glass staying at a lower temperature relative to the intended flow, and to cooling of the glass from the ambient conditions in the nose of the aircraft. While we did pre-condition and measure the sample temperature prior to the cell, we later concluded that cooler glass could cause a cooling of the sample, and we didn’t measure this temperature change within the flow.
We could only measure the temperature at the inlet and outlet of the cell, before and after absorption had taken place.

The glass tube did not present this problem in the laboratory and during the field flights in the continental US, where the glass tube was consistently near the sample temperature. For these measurements, we simply averaged the temperatures at the end of the cell and assumed the sample at the center of the cell would hold the same temperature. After the field campaign, we suspected that the colder temperature of the arctic resulted in temperature control issues. Post-campaign analysis showed that the glass tube on the instrument was significantly colder than the sample temperature (Figure 36), and so it quite likely caused a sample temperature deviation from what we measured at the entrance and exit of the cell.

Figure 36: Glass Sample Cell Temperature of a flight on August 26th, 2013. The inlet temperature is the temperature of the gas measured at the inlet of the instrument. The glass cell temperature is the temperature of the
glass, as measured by a thermistor placed on the outside of the glass, underneath the Nomex insulation. The heating of the glass very likely came from the sample itself, indicating that the sample temperature was changing when contacting the glass.

In the field, the temperature of the gases was measured in the aluminum components before and after the sample cell. The temperature of the aluminum component at the end of the sample cell was similar to the temperature at the start of the cell, since they were heated off the same control circuit. The sample air was in contact with the aluminum component at the end of the cell before reaching the thermistor at the exit. If the glass had cooled the sample, thus making all the spectroscopy happen at a lower temperature than we measured, and then the aluminum in the end of the cell re-heated the sample, we would have been doing spectroscopy at a temperature that was several degrees different from our measured temperatures. Using HITRAN parameters, we calculated the potential effect this would have on the samples (Figure 37).

<table>
<thead>
<tr>
<th>Sample</th>
<th>290k transmission</th>
<th>295k transmission</th>
<th>Delta</th>
<th>Change/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$CO$_2$</td>
<td>84.75</td>
<td>83.5</td>
<td>1.25%</td>
<td>1ppm</td>
</tr>
<tr>
<td>$^{13}$CO$_2$</td>
<td>80.45</td>
<td>80.15</td>
<td>.3%</td>
<td>3‰</td>
</tr>
</tbody>
</table>

Figure 37: Table of temperature effects on measurements. Temperature affects can create precision and accuracy errors in measurements if they are not accounted for. To calculate the change per degree C, we took the difference in transmission, divided by 5 °K, and multiplied by the constituent mixing ratio for $^{12}$C and by permil ratio for $^{13}$C.

To assess whether this could have been a problem in the field, we replaced the glass tube with a Delrin tube in lab, and mounted thermistors in the tube to measure the sample temperature directly. We ran the instrument without any heating and allowed the heat to equilibrate across the thermistors, and then turned on the heating elements for the samples. The goal was to mimic the temperature changes that the instrument might undergo from frequent temperature changes to the glass tube in the field. The data showed that the temperatures preceding the final thermistor were cooled by the Delrin tube (Figure 38), and the temperature we used to fit is not only likely several degrees off from the actual sample temperatures, but that the deviation between the
actual sample temperature and the measured sample temperature changes over time, precluding a simple temperature correction after the fact. Because we did not measure the sample flow temperature in the glass tube during the flight, and because we cannot easily replicate temperature profiles from flight, we have to assume that our temperature measurements were 0-3 °C too high, resulting in up to 0-3 ppm differences in CO₂ measured. While this error is well within the 15ppm differences we saw within individual flights in the field, it is near the 4ppm standard deviation of all combined data. This indicates the data is still viable for drawing some relationships, but interpretations are not strongly supported. See the appendix for a steady-state model of the total heat that could pass to the sample from the glass tube given the temperature of the glass tube measured in the field.
Figure 38: Temperature profile of the CO\textsubscript{2} cell. The final cell temperature is the thermistor in the aluminum component at the end of the cell. The first thermistor was unavailable for this test, and would be unavailable for months, as it was under use for the CH\textsubscript{4} project. The temperature measured by the first thermistor, however, closely tracks the last thermistor. The 2\textsuperscript{nd}, 3\textsuperscript{rd}, and 4\textsuperscript{th} thermistors were linearly placed prior to the final thermistor in the instrument flow. The data show that the temperatures we measured in flight were likely unrepresentative of the actual sample temperature, since we only had the thermistors in the aluminum blocks to measure temperature. Note that the section from 2500 to 4000 overlapping indicates that these thermistors all registered the same equilibrium temperature, indicating that these deviations are highly unlikely to be from improper thermistor calibration.

3.3 Field results of the $^{12}$CO\textsubscript{2} Data

We recorded CO\textsubscript{2} data from 11 flights, and, after accounting for issues in the field, successfully analyzed $^{12}$CO\textsubscript{2} data from five flights. Because water and temperature data were taken at above-ground altitudes, and not at the canopy or ground-level where the relevant temperatures for photosynthesis and respiration occur, we do not attempt to carry out any statistical measurements on CO\textsubscript{2} concentrations in relation to moisture and temperature to derive process-level relationships relating to NPP. Comparison to several fly-overs of ground-level
measurements of temperature and water mixing ratios support that the discrepancies between water mixing ratios between the ground and our airplane varied between 10-20\%, and temperature measurement discrepancies varied between 3° and 6° C. As a result, the relationships are reported and discussed, but no process-level conclusions can be drawn.

3.3.1 North Slope, AK, Field Test and Mission

Flights were operated out of Deadhorse, Alaska, on days of low fog. A total of 14 flights were carried out. Several flights were test flights, and others resulted in adverse conditions shutting down instrumentation. Finally, several flights produced data that could not be accurately fit, and the data were discarded. Due to constraints that the CO$_2$ cell cannot measure water, and does not desiccate samples, we were unable to fit CO$_2$ data on runs where the CH$_4$ instrument did not function well. What remained was five flights worth of data: 26.1, 26.4, 27.1, 28.1, and 28.3 (28.3 can be interpreted as the 28$^{th}$ of August, UTC time, and the third run of the day, with the other flights all following the same naming convention. Some flights occurred locally in the evening of the prior day).

Corrections to field data were carried out based on analyzing the data using the methods described in sections 2.1.5 and 2.2. The $^{13}$CO$_2$ measurements were unreliable, showing 50\% differences in places where there should have been a maximum of 2-4\% differences. While the data are unreliable, they seem directionally correct, showing directional changes associated with respiration and photosynthesis that are in-line with the $^{12}$CO$_2$ measurements.

The data were quality controlled as previously described and forwarded to colleagues at NOAA, experts in BAT probe data and aircraft eddy covariance methods. While the
concentration measurements of $^{12}\text{CO}_2$ are robust, they indicated that noise constraints in the $^{12}\text{CO}_2$ data were shown to prevent flux measurements in these flights. As discussed in section 3.2.8, this was likely caused by the fitting errors arising from the instrument’s cavity etalon. Thus, only concentration measurements are presented geographically, and flux measurements could not be calculated.

Lacking both fluxes and robust $^{13}\text{CO}_2$ data, as well as soil moisture and canopy temperature data, limits the science and relationships that can be drawn from our results. Robust isotopologue data would allow for confirmation of relationships between temperature and total CO$_2$ mixing ratios, indicating whether our observed CO$_2$ came from respiration or photosynthesis. Similarly, successful flux measurements would also provide proof that our measured concentrations were reliable indicators of respiration or photosynthesis.
3.3.2 Field Mission and $^{12}$CO$_2$ results

CO$_2$ measured in the field ranged from 375 ppm to 390 ppm. Data were conditioned by removing values acquired above 100m, when the pilot was flying to a site, away from a site, or maneuvering. Data was also excised when the CH$_4$ instruments failed or were doing in-flight calibrations, because the water corrections could not take place without the water data from the CH$_4$ cells.

All five flights were compiled together to compare CO$_2$ concentrations, land type (dark blue is water, light blue is wet sedge, orange/red is drier tussock), and temperature (Figure 39 & Figure 40). Land types were acquired from the North Slope Science Initiative (Payne 2013). Land type was determined by taking the mode of each land type for a 75 m$^2$ area around the measurement. Overall, the relationship between CO$_2$ and temperature was not strong (Figure 39), with a correlation of only 0.15.
Figure 39: CO₂ vs. Temperature for all five runs, 10s data. The relationship between CO₂ and temperature is not well correlated. The entire range of CO₂ measurements are witnessed over the entire range of temperature measurements.
Figure 40: Compilation of [CO$_2$] for five runs, and land types. Data were taken from all five successful CO$_2$ flights and compiled in a single map. The concentration of CO$_2$ (top) shows regionally heterogenous CO$_2$ concentrations ranging from 375 to 390ppm. There is little clear relationship between [CO$_2$] and land type (middle). There is also no clear relationship between CO$_2$ and H$_2$O (bottom).
Photosynthesis and respiration should vary by land type, so we expected to report variants in $^{12}\text{CO}_2$ by land type. There are three major land types in the NSSI database: open water (lakes), wet sedge (wet areas), and dry tussock (dry areas). If CO$_2$ concentrations were related to land types, we would expect higher CO$_2$ levels for drier land types, owing to lower NPP. There is no clear relationship between CO$_2$ and land type (Figure 41). Indeed, the average of all concentrations measured for each of the three land types is 380ppm, 380ppm, and 381ppm for water, wet sedge, and dry tussock, respectively, and standard deviations of 3.4ppm, 3ppm, and 4ppm, respectively. The 1ppm difference in averages is well below the estimated 3-4ppm precision allocated to imprecise sample temperature measurement, and the standard deviations are on par with the estimated precision, precluding the establishment of well constrained relationships between land cover type and ambient CO$_2$ mixing ratios.
Figure 41: CO₂ concentration and land type and colored by temperature. The left most bin is measurements taken over water, the next two are measurements taken over wet sedge, and the final is measurements taken over dry tussock. While the temperatures measured over dry tussock tended to be slightly higher, there is no trend between CO₂ concentrations and land type.

Only the flight on the morning of August 26th showed the expected inverse relationship between CO₂ and temperature (Figure 42 & Figure 43), with a correlation of -.55. In other words, lower levels of CO₂ were measured in areas with warmer air temperature (Figure 42).
Figure 42: CO2 measurements vs. Air Temperature on Aug. 26th. Total CO2 tended to decrease with increasing temperatures, a sign that photosynthesis is occurring. Water has a less clear relationship with total CO2, indicating that temperature is more dominant than water in terms of CO2 concentrations.

Figure 43: Geospatial view of CO2 on August 26. In general, warmer temperatures corresponded with lower measured CO2. This falls in-line with the idea that higher temperatures lead to more photosynthesis.

In short, while individual days show meaningful correlations between [CO2] and temperature, the dataset as a whole does not support any notable relationships between [CO2]
and any of temperature, air moisture content, land type, and altitude above ground level (below 100m).

3.3.3 Field Mission and Measured $^{13}$CO$_2$

Expected ranges of $\delta^{13}$CO$_2$ in an area of heavy photosynthesis and no photosynthesis, respectively, are from -9 to -3‰ (Lai et al. 2005). In a given day, they are not expected to move more than 1‰ in a specific location. Unfortunately, even with long-term averaging, our measured differences in $\delta^{13}$C had ranges of over 40‰. All attempts to reduce the range reliably failed. Methods to rectify this in future missions are covered in the discussion section.

3.3.4 Back-Trajectory Analysis, Regional Trends, and Tower Comparison

None of the flights showed strong relationships between measured CO$_2$ and temperature, altitude, water mixing ratio, or land type. Before attributing the differences in mixing ratio to local biogeochemistry, however, we must consider the movement of air masses into the measurement region. Differences in measured CO$_2$ concentrations could be caused by air masses moving into the region from outside the region, rather than local biochemistry or anthropogenic activity. We carried out backward trajectory analysis using the HYSPLIT trajectory modeling tool provided by NOAA to show the provenance of air masses moving into the measurements locations. These data are limited to 0.5° resolution, limiting the scope of conclusions that can be drawn, but providing insight into possible mechanisms for differences in measured CO$_2$ concentrations.

In two of the five flights, back trajectory modeling indicated that differences in measured CO$_2$ concentrations are likely from air masses coming from several outside regions, indicating
the effect of air movement influencing CO$_2$ concentrations rather in addition to local biochemical signatures on CO$_2$ concentrations. This highlights the value of obtaining in-situ flux measurements in addition to concentration measurements: flux measurements help characterize the local biochemistry of a region, while concentration measurements may be affected by biochemistry from other regions. Back trajectory analysis shows that two of the additional flights show some evidence that regional air movement could have affected the measurements, the back trajectory analysis of flight 26.1 reveals no pathway for the air movement to cause differential signals in measured CO$_2$. What follows is a brief analysis of each flight with consideration to regional airflow patterns. In addition, two flights overlapped with a NOAA CO$_2$/CH$_4$ flux measurement tower, and we present and discuss a comparison of the measurements in these flights.

During **Flight 26.1**, measured CO$_2$ concentrations ranged from 374 to 389 ppm, with the majority of the measurements falling between 376 and 384 ppm (Figure 44). Backward trajectory analysis (Figure 45) reveals that the entire measurement region for this flight has consistent sources of air masses moving into the region. The differences in measured CO$_2$ concentrations thus cannot be attributed to differences in outside our masses flowing into the region of study, and it’s likely that the differences measured were caused by local biochemistry.
Figure 44: The CO$_2$ concentrations along the flight path of flight 26.1. The measured CO$_2$ mixing ratios vary along the transect, indicating likely biochemical differences. The tower is located on the upper right-hand part of the transect.

![NOAA HYSPLIT MODEL](image)

Backward trajectories ending at 0200 UTC 26 Aug 13
GFSG Meteorological Data

Figure 45: Backward trajectory analysis of the flight data for 26.1. The analysis shows a homogenous source location of air masses entering this region, with stratified movement causing air masses to remain within 100m of ground for the preceding 24 hours. The prevailing source of air for this region comes in from the Arctic coast and from altitude, and likely entrained coastal and riverine components. Like most regions, the balance of photosynthesis and respiration depends on local conditions of the source region, and both photosynthesis and respiration can thrive in most coastal regions.

This flight overlapped with a NOAA CO$_2$/CH$_4$ flux tower in the northeastern portion of the transect. The tower and aircraft showed similar values, with the aircraft measuring between 380 and 382ppm at this time and location, the tower measuring between 382 and 384. While this discrepancy could be a result of the aircraft sampling air 30m above ground while the tower samples within several meters of the ground, this discrepancy is also within the precision limits imposed by the temperature measurement and control constraints on the instrument.
Nevertheless, the close agreement between the tower and the instrument provides strong evidence for adequate field performance of the instrument during this engineering flight series.

**Flight 26.4** (Figure 46) was a regional survey flying in the direction of Barrow, Alaska. Measurements of CO₂ concentrations ranged from 373 to 382, with data taken over 3 hours beginning at 1pm local time. Back trajectory analysis shows a regional flow of air from the coast to the measurement location (Figure 47). The earlier measurements of the flight show markedly lower measured CO₂ mixing ratios. We suggest two possible scenarios to explain this. First, as the solar radiance reduced in the afternoon, respiration may have become dominant over photosynthesis, increasing measured CO₂ mixing ratios. An alternative pathway is suggested by the back-trajectory analysis. The lower measured CO₂ mixing ratios in the lower right leg of the transect shows a backwards trajectory with an air mass that passes over significantly more land than the upper leg of the transect. This air mass remained low to the ground, likely entraining air that had passed over more regions with photosynthesis, lowering the CO₂ mixing ratio.
Figure 46: The CO$_2$ concentrations along the flight path of flight 26.4. The measurements occurred over a 3-4 hour time period, and passed over a region dense with lakes. Measured CO$_2$ concentrations approximately increased throughout the duration of the flight.
Figure 47: Backward trajectory analysis of the flight data for 26.4. The analysis shows a homogenous source location of air masses entering this region, with stratified movement remaining within 100m of ground for the preceding 24 hours. The lower latitude measurements, however, sample air masses that have passed over significantly more land where greater amounts of photosynthesis could have drawn down entrained CO$_2$ levels.

**Flight 27.1** (Figure 48) is a regional transect, with measured CO$_2$ mixing ratios ranging from 378 to 387 ppm. As with flight 26.4, back trajectory analysis (Figure 49) suggests a possible factor for the apparent bimodal and regional differences is that the lower right transect may have been in a region with entrained air masses that had flowed over more land with greater amounts of photosynthesis. Given that the air masses all moved from the same direction, however, it’s also possible that the measured differences in CO$_2$ concentrations are due to different local biochemistry.
Figure 48: The CO2 concentrations along the flight path of flight 27.1. The measurements show two distinct regions of concentrations, with lower concentrations in the lower right and higher concentrations in the upper left.
Figure 49: backward trajectory analysis of the flight data for 27.1. The analysis shows a homogenous source location of air masses entering this region, with stratified movement remaining within 100m of ground for the preceding 24 hours.

**Flight 28.1** (Figure 50) was a transect overlapping with the NOAA CO$_2$/CH$_4$ flux tower in the uppermost part of the transect. The majority of measured mixing ratios were between 377 and 382 ppm. The flights began at 5pm local time and ended at 8pm local time, with the earliest parts of the flight on the left side of the transect. Back trajectory analysis (Figure 51) shows two converging air masses flowing into this region. The bimodal distribution of measured CO$_2$ between the left and right legs could be a result of measuring two separate air masses in the region. This interpretation is supported by the massive discrepancy between our measurements and the measured CO$_2$ mixing ratio at the NOAA tower. The NOAA tower recorded CO$_2$ mixing
ratios on the order of 410ppm. If our flyover was sampling only local air, it would have more closely matched the tower data. Instead, it is likely that our sample was heavily influenced by outside air sources.

Figure 50: The CO2 concentrations along the flight path of flight 28.1. The measurements show two distinct regions of concentrations, with lower concentrations in the left and higher concentrations in the right. The NOAA flux tower is located at the apex of the intersection of the left and right legs.
The ground temperature explains the anomalously high CO$_2$ concentrations measured at the tower. The air temperature measured by the aircraft during this transect was 10° C, but the ground and soil temperature was 4° C, limiting photosynthesis. The much higher mixing ratios recorded at the ground are thus likely a product of ground temperature that was sufficiently cold to prevent photosynthesis, but not sufficiently cold to prevent respiration. Further explanation is required to explain the discrepancy between the tower CO$_2$ concentration measurements and those of our flight. Of our flights during the campaign, this flight occurred latest in the afternoon and evening. Given that the boundary layer in the Arctic can approach the ground at night, it is possible that the aircraft was not sampling within the bottom of the boundary layer, and instead was sampling a mix of background atmospheric CO$_2$ mixing ratios and emissions from the
ground. This would result in measured CO₂ mixing ratios from our aircraft being more similar to background than to the ground measurements for this flight.

**Flight 28.3** (Figure 52) is a regional transect with CO₂ measurements ranging from 375 to 383. The flight occurred during the late morning. The back-trajectory analysis (Figure 53) shows the likely provenance of the measured CO₂ mixing ratios. The measurements in the lower right part of the transect are from relatively stagnant local air masses. Photosynthesis likely drew down the CO₂ locally. The measurements from the left and north are from air masses that have been flowing over much colder uplands, where photosynthesis is inhibited by the cold conditions, contributing to higher background CO₂ levels. Finally, the region in the middle appears to have contributions from both stagnant local areas and coastal winds, leading to both higher and lower mixing ratios.
Figure 52: The CO2 concentrations along the flight path of flight 28.3. This regional transect shows complex differences in measured CO2 concentrations, with rapid changes from low to high concentrations.

Figure 53: Backward trajectory analysis of the flight data for 28.3. The analysis shows a heterogeneous source locations of air masses entering this region, with air masses traveling over the North Slope to reach the
location on the left, and air masses traveling from the ocean on the upper right, and stagnant air masses not traveling far in the middle portions of the transect. This complexity of this source attribution exceeds the resolution of the backward trajectory analysis, but provides a rough detail of the complex mixing of air masses measured during the transect.

We have shown five flights with varying degrees of influence from outside air sources. The influence of these outside air masses on concentration measurements serves to underscore the necessity of obtaining in-situ flux measurements alongside regional concentration measurements, particularly on the flight 28.3. At the same time, flight 26.1 shows close agreement with the NOAA tower measurements, and flight 28.1 shows marked disagreement with the tower, indicating that some wind conditions result in measurements at 30m that correspond with net ecosystem exchange, while other conditions result in measured CO₂ that seems unrelated to net ecosystem exchange. In summary, this series of engineering flights showed capability to measure local and regional CO₂ concentrations with our instrument platform, and provided the necessary data to upgrade our instrument for flux capability.

3.3.5 Brief Analysis of NOAA Flux Tower near Deadhorse, AK

The NOAA Air Turbulence and Diffusion Division emplaced a tower at 70.085°N, 148.57°W. The tower measured CO₂ and CH₄ concentration and fluxes, air and ground temperature, wind direction and speed, photosynthetically active radiation (PAR), and water mixing ratios. Here we examine several relationships within the tower data to demonstrate the potency of concentration and flux measurements together, and to consider the drivers of CO₂ fluxes.

The CO₂ mixing ratios measured every half hour by the NOAA tower in August of 2013 (Figure 54) range from 370 to 420ppm, with the majority of measurements falling between 380 and 395ppm. The tower uses the eddy covariance technique to derive flux measurements from
the concentration measurements. CO\textsubscript{2} fluxes are generally negative during this time, indicative of photosynthetic CO\textsubscript{2} uptake being dominant over respiratory CO\textsubscript{2} release.

Figure 54: CO\textsubscript{2} concentration and flux measurements from NOAA Tower near Deadhorse, AK. The day of the year is the day number, with 213 corresponding to August 1 and 243 corresponding to August 31. A data gap exists for five days in late August. Measured CO\textsubscript{2} concentrations oscillate around 382ppm. Measured CO\textsubscript{2} fluxes are predominantly negative, indicating uptake by a photosynthetic dominant biochemical regime. Positive fluxes occur at night.

The relationship between measured CO\textsubscript{2} concentration and measured CO\textsubscript{2} fluxes at the tower site is bimodal (Figure 54). When fluxes are negative, and CO\textsubscript{2} is being drawn into the ground, measured CO\textsubscript{2} drops. When fluxes are low and positive, typically during night when PAR is low or during the day when temperatures are low, CO\textsubscript{2} rates rise. An attempted first order polynomial fit shows the relationship for measured CO\textsubscript{2} concentration and fluxes is represented by the equation:

\[
\text{Flux} \frac{mg}{m^2s} = 0.0188 \times [CO_2] - 7.3104
\]

with an R\textsuperscript{2} of .223. This low fit value indicates that the relationship between CO\textsubscript{2} fluxes and concentrations is not direct, indicating that in the absence of in-situ flux measurements, transport
models applied to precise CO₂ concentration measurements would be necessary to derive flux measurements.

![Figure 55: NOAA tower CO₂ flux compared to CO₂ concentration measurements.](image)

The two regimes are photosynthetic and non photosynthetic. When conditions allow for photosynthesis, measured CO₂ concentrations decrease. Stronger uptake is generally associated with lower measured CO₂ concentrations, but the relationship is not strong enough to generally apply. When photosynthesis shuts down, the ground emits CO₂ and measured CO₂ concentrations begin to increase.

The three major drivers for CO₂ flux are PAR, moisture, and temperature. Tower data shows no relationship between moisture and fluxes, and a mild but weak relationship between PAR and fluxes (Figure 56). The relationship between air temperature or 2cm depth soil temperature and fluxes (Figure 57) is stronger, indicating that temperature is a potent driver for both respiration and photosynthesis in the Arctic in August. Nevertheless, any given temperature has a wide range of fluxes associated with it, further clarifying that the complex biochemistry and wind patterns of a region preclude drawing simple relationships between fluxes and locally measured attributes. This dictates that in-situ measurements of fluxes are necessary to provide
the process-level details required for a better fundamental understanding of how the Arctic responds to climate change, and whether the Arctic will contribute to or help curb climate change.

Figure 56: PAR compared to CO₂ fluxes. The data show a slight trend for increased CO₂ uptake with increased PAR, but the relationship is not strong.

Figure 57: Measured temperatures compared to measured fluxes. While both air temperature and soil temperature have a negative relationship with CO₂ fluxes, temperature at 2cm soil depth shows a very similar relationship to temperature at 1m above ground.

3.4 Next Generation CO₂ Instrument
Our initial field campaign showed proof-of-concept of the CO$_2$ Herriott instrument, and revealed opportunities for instrument improvement. The next generation CO$_2$ instrument will greatly benefit from technical advances since its inception. First, we can reduce endogenous infiltration of CO$_2$ into the sample path. Second, improvements in laser sources will solve several optical noise issues. Third, expanded in-flight calibrations will enhance fitting and precision assessment. Fourth, newly available InAsSb detectors can increase detector precision and allow resolution of our laser feedback issue. Fifth and finally, replacing the glass tube with an aluminum tube and thermistors will allow precise sample temperature control and measurement.

### 3.4.1 Off Gassing Anodization

Standard practice for instrument measurements is to purge the optical path prior to the absorption cell of absorbents. Given that the LPV has twelve times the pressure of the cell during operation, and the cell has 35 passes, the LPV could potentially contribute 25% to the CO$_2$ measured if it was not purged. Moreover, because the cell LPV is at a higher pressure, we expect more pressure broadening, which can interfere with the establishment of the baseline used for fitting the laser scan.

Our practice was to purge the LPV and laser and backfill them with nitrogen. We noticed that our LPV would build up CO$_2$, so we would frequently need to backfill the LPV. In the field, this became more difficult. It was time-consuming, requiring disassembly and removal of the instrument from the aircraft. Given the rapid turn-around time between flights, this was not always possible. As a result, we would over-pressure the LPV to prevent its leaking.
Upon returning from the field and analyzing the data, it became clear that our LPV did not leak. It maintained over-pressure throughout the entire set of runs, and CO₂ still seemed to build up in the LPV. If we did not have a leak, the only possible source was off gassing inside the LPV. This means throughout every flight, we had an unknown and constantly changing amount of CO₂ in the LPV. Because we over pressured the LPV to 1000 torr, we also increased the pressure broadening of this CO₂, which is quite likely the reason we had trouble fitting a baseline in our fitting algorithms.

We discovered the source of this infiltrating CO₂ was our choice of color for the instrument. All aluminum layers of the instrument are anodized to prevent oxidation of the aluminum. Black anodization was chosen for our instrument. Our field data analysis led us to realize that organic dyes are used in black anodization, and these dyes can off-gas CO₂. Future instruments would use the standard anodization without dye for instrument anodization, and prevent this error.

3.4.2 Laser Wavelength

We intended to conduct spectroscopy in the 2298 cm⁻¹ region, but our laser could only reach to 2308 cm⁻¹, where absorption depths were 10% as deep. We altered our instrument’s path length to account for this, and in the process we introduced cavity etalons that prevented high-precision fitting. In addition, we increased the cell pressure to account for the decreased absorption, despite that the features were more crowded in our new region. There was possible overlap in the bases of absorption features, preventing an accurate baseline fit and reducing accuracy and precision.
A year after our flight, ICL, or Intraband Cascade Lasers, became commercially available. These lasers are better capable of achieving targeted wavelengths while still being tunable in the mid-IR like a QCL. Utilizing an ICL will eliminate the cavity etalon, increasing precision, and allow operation at lower pressures to reduce absorption feature overlap, further improving instrument accuracy and precision.

3.4.3 In-Flight Calibrations

In flight calibrations are typically carried out over a span of concentrations similar to what would be measured in the field. The calibration gases have known amounts of the molecule being measured, and known amounts of ratios of the isotopes being measured. The span of calibrations shows that the instrument performs consistently over the course of a flight, and allows for minute adjustments to the data to increase accuracy. In addition to span calibrations, in-flight calibrations often have a zero-gas calibration. This is a gas, like N₂, that does not absorb in the region of instrument operation. Running a zero gas provides a signature of a scan with no absorbance. This can be used to establish a baseline of laser power for far more accurate baseline fit. Due to space and weight limitations, we flew with a single calibration gas during flight, and no zero gas. Future missions would account for this error by including a span calibration gas and a zero calibration gas in-flight.

3.4.4 Lab Testing Optical Changes

As discussed in section 3.2.4, our fielded detector has shortcomings in back-reflections, preclusion of optical isolators to prevent feedback, and problems inherent to immersion lenses. We burrowed a new Hamamatsu InAsSb detector for the mid IR wavelength for laboratory tests
to demonstrate potential improvements. The Hamamatsu detector remains linear well past 3 mW of power, whereas the Vigo detector saw deteriorated performance above an estimated 1 mW. In addition, the Hamamatsu detector is a true 1 mm$^2$ detector rather than the Vigo 1 mm$^2$ immersion lens with 0.1mm$^2$ detector. This reduces precision losses from slight changes in alignment due to thermal expansion. Finally, the Hamamatsu detector is capable of passing circularly polarized light, allowing the use of an optical isolator system to prevent laser feedback.

In order to test this device, we designed and 3D printed a specialized connector to test the Hamamatsu detector. The greater linear operation threshold for the Hamamatsu detector also allowed us to test the originally designed 5-pass pattern. Instrument performance with the InAsSb detector at five passes matched instrument performance with the Vigo MCT detector at 35 passes. Additionally, the cavity etalon was reduced. With this detector, we could eliminate laser feedback by using an optical isolator and solve the remaining detector issues.

3.4.5 Temperature Control and Measurement

In section 3.2.8 we discussed sample temperature control and measurement inadequacies present throughout the field deployment. Direct absorption instruments demand excellent temperature control and measurement to function accurately, particularly in the section of the instrument between the Herriott mirrors where absorption takes place. The CO$_2$ cell had only one zone of temperature control, and we do not measure the temperature of the sample along the entire absorption cell. Moreover, the CO$_2$ cell used a glass tube for the cell. Not only did this glass tube prevent us from controlling heat or measuring temperature with temperature ports, it likely cooled the samples in ways we did not measure. The next iteration will use the glass tube during initial alignment, and then replace the glass tube with an aluminum tube that can be heat
controlled and have thermal measurement ports along several points of the axis for better temperature determination and data fitting.

3.4.6 Anticipated Results of Fixes

Changing the laser and detector, and including optical isolators, will directly increase incident power on the detector by 5x. It will also completely eliminate the laser feedback and the cavity etalon, likely more than further doubling efficiency, allowing us to reach 10x. Fixing the remainder of the issues will likely net a similar increase, all told, conservatively resulting in an instrument that is 20-40x more precise than our current instrument.
4 Conclusion

As of yet, no low-cost method to measure the processes controlling the potential feedback effect from the rapidly warming Arctic exists. Here, we have presented the development and initial deployment of an instrument suite to measure high-resolution CO$_2$ concentration and isoflux data to be used in conjunction with high-resolution CH$_4$ concentration and flux data to help resolve this gap. As part of this project, the Anderson group has developed novel high-finesse laser housings, field-tested brand new laser and optic types, built three cutting-edge instruments, and mounted the instruments on a DA-42 aircraft to create a highly flexible research platform. Several additional equipment pieces to the DA-42 were created and tested, including a mounting system in the passenger compartment of the aircraft, and a radiator cooling system below the aircraft.

The CO$_2$ Herriott Instrument was deployed as part of this revolutionary instrument suite, capable of measure flux in-situ over vast areal expanses for a relatively low cost of operation of $600/hr. The primary need of the instrument was to have an extremely fast-response, with a 90% recovery time faster than 10Hz. Laboratory performance of the instrument was nearly as good as commercially available instruments that have 100x longer recovery times. The instrument was deployed in Deadhorse, AK during August of 2013. Field deployment showed proof-of-concept of the entire instrument suite, providing a powerful platform to monitor GHG emissions in-situ.
Although field performance of the CO\textsubscript{2} instrument did not match laboratory performance, we produced and analyzed CO\textsubscript{2} concentration data over a geographically large area. Our results showed initial proof-of-concept of measuring CO\textsubscript{2} concentrations locally. Furthermore, we have identified and tested several improvements that will drastically benefit the next generation CO\textsubscript{2} Herriott instrument for the aircraft platform, and allow for in-situ CO\textsubscript{2} isoflux measurements.
Beer’s Law Code and Description for Matlab

This code was used to circumvent the feedback-derived inconsistent laser tuning rate within a scan that prevented the in-house algorithm from working. It uses the same underlying algorithms, but rather than matching the area of an absorption feature to HITRAN parameters, it uses Beer’s law.

function concentration=newbeer(icosout,scannums)

%This script is to fit with absorption depth using beer's law rather than FWHM. It is useful when laser feedback skews the line.

%It first calculates a sigma, or absorption cross-section for concentration, based on absorption cross-section modified for temperature and pressure. It feeds this into beers law, comparing the absorption depth to the

%concentration=newbeer(icosout,scannums); Concentration is the beer's law concentration resulting from taking the depth of the line. It uses the
%line centers from icosout to find the lines. icosout is the actual icosout %file, like ICOSout.r2.p3. Scannnums is the scan numbers. You can choose to %designate this if you want to fit a subset of the data. If you leave it %empty, it will choose the entire data set to fit.

%This program can be run on a dataset that has a cavity etalon in the %writeetlbase program

%Note that this program retains inherent errors in fitting from the cavity %etalon. Any residuals that exist after doing a dft and accounting for a %cavity etalon will transfer to this program.

S = ICOS_setup(icosout);
%ICOS_setup is an Anderson group tool to unpack data from an ICOS output
if isempty(scannums)
    %This tells the program to use the entire ICOS output if the user %doesn't designate otherwise
    scannums=S.scannum;
end

load('therm1t.mat');
%this requires a prior step of getting and converting the HCI_eng. It
%interpolates 1Hz parameters to 10Hz parameters to match the concentration
%data

%How to create therm1t: go to the engineering files and run this script:
% load('HCIeng_10.mat')
% load('HCIeng_1.mat')
% SSP_C_10=interp1(THCIeng_1,SSP_C_Num,THCIeng_10);
% SSP_C_Num=SSP_C_10;
% CT1=CCel1T;
% CT2=CCel2T;
% save('therm1t','CT1','CT2','SSP_C_Num','THCIeng_10')

%The loop below finds the location of the absorption features in sample space
%using the ICOSout output. It then builds the absorption depth vs. baseline
%to get transmission percent, both from raw data and from fitted data

warning('off','MATLAB:polyfit:RepeatedPointsOrRescale');
%this gets rid of annoying warning.

%As of 10-16-14 I have made this 10hz data.

for j=1:length(scannums)
    % this make a loop for the length of the info to get temp, a fit, and absorption
    [m,I]=min(abs(SSP_C_Num-S.scannum(j)));
    %This is to make sure it finds the nearest SSP number
    temp(j,1)=CT1(I)+273.15;
    %this pulls in the temperature for each scan in kelvin
    Tmetrics(j,1)=(SSP_C_Num(I));
    %records SSP number for future matching to CH₄ and BAT data
    Tmetrics(j,2)=(THCIeng_10(I));
    %records time for for future matching to CH₄ and BAT data
    fit=load(mlf_path(icosout,S.scannum(j)));
    % this loads the fit of this particular scan number
    pos=round(interp1(fit(:,2)+S.nu_F0(j)+S.nu0,1:size(fit,1),S.nu));
    %this finds the positions of the lines, which is needed to find absorption
    % no polyfit trans(j,1:(length(pos)))=fit(pos,3)./fit(pos,5);
    %this is the transmittance based on the raw data
    %The following loop greatly reduces noise by fitting a line locally to
    %the absorption feature. It used a polynomial fit with very high
    %resolution to reach the minima of the feature. This gets around the
    %resolution limits of the data
    for k=1:length(pos)
        %This accounts for the fact that there are an equal number of
        %positions to fitted lines
        polycos=polyfit(rot90(fit(:,2)+S.nu_F0(j)+S.nu0,1,size(fit,1),S.nu));
        %The choice of + and - 3 is dictated by line width. It gives 7
%points to fit the line shape. Wider lines will need more than 7. 
fitted(k,1)=min(polyval(polycos,pos(k)-3:.02:pos(k)+3));
  \%This builds up the fit based on the minimum.
end

%Noise fitting loop done

testfit(j,1:(length(pos)))=fitted./fit(pos,5);
trans(j,1:(length(pos)))=fit(pos,3)./fit(pos,5);
  \%this is the transmittance based on the raw data
trans2fit(j,1:(length(pos)))=fit(pos,4)./fit(pos,5);
  \%transmittance based on fitted data
base(j,1:(length(pos)))=fit(pos,3);
  \%baseline
fit(j,1:(length(pos)))=fit(pos,4);
  \%the fitted line
scanline(j,1:(length(pos)))=fit(pos,5);
  \% This is the actual raw line
end

assignin('base','Tmetrics',Tmetrics)

warning('on','MATLAB:polyfit:RepeatedPointsOrRescale');

\%% Okay now do temperature and pressure correction\%%

\%%Simple formula
\%second radiation constant c2 = hc/k (cm*K)
c2 = 1.438789;
Tref=296; \%this is the reference temperature for temp corrections
F=load('fitline.dat');
  \%Fitline contains HITRAN parameters. This step gets the HITRAN numbers for
  \%later use. If you change the fitline.dat file, you need to change anything
  \%that references it to make sure you are working with the correct lines.
SnnC13 = F(13,4);
  \%strength of C13 absorption, need to change for other components. column 4
SnnC12 = F(18,4);
  \%is Snn, column 13 is C13 **NEED TO CHANGE if fitline.dat changes!
SnnC12 = F(18,4);
  \%strength of C12 absorption. **CHANGE if fitline.dat changes!
S13cTemp = SnnC13*(Tref./temp).^(3/2).*exp(c2*F(13,6)*(temp-Tref)./(Tref*temp)).*(1-exp(-c2*F(13,3)./temp))./(1-exp(-c2*F(13,3)./Tref));
  \%F(13,3) is the line in cm-1
S12cTemp = SnnC12*(Tref./temp).^(3/2).*exp(c2*F(18,6)*(temp-Tref)./(Tref*temp)).*(1-exp(-c2*F(18,3)./temp))./(1-exp(-c2*F(18,3)./Tref));
  \%F(18,3) is the line in cm-1
G = F(13,5)*65/760;
  \%lorentz correction for pressure, need to make dynamic if instrument P
  \%changes. This is for 12C
G12 = F(18,5)*65/760;
% lorentz correction for pressure, need to make dynamic if instrument P changes. This is for 13C
Fv = 1/(pi * G);
% for getting sigma
Fv12 = 1/(pi * G12);
sigma = S13cTemp.*Fv;
% this is our sigma adjusted for temperature to be used in Beer's
sigma12 = S12cTemp*Fv12;
% same story.

% From here on out is all Beer's Law
% These three lines are absorption depth
A=2-log10(100*trans(:,2)); % For using raw line as opposed to fit
Apoly=2-log10(100*testfit(:,1)); % This uses the fitted line for 12C
Apoly12=2-log10(100*testfit(:,3)); % fitted line for 13C
b= 21.9*35;
% length of cell in cm
% Need S for molar absorbivity in L/(mol*cm)
c = A./(b.*sigma);
% This is gives concentration in mols/L

Cppmpoly = Apoly./(b.*sigma)*(10e-21*400/.164/22.4).*temp/273.15;
Cppmpoly12 = Apoly12./(b.*sigma12)*(10e-21*400/.164/22.4).*temp/273.15;
% These give concentration in PPM instead.

Cppmpoly = Cppmpoly*1.1031;
% These are scale factors that I derived to get the output to match calibrations
Cppmpoly12 = Cppmpoly12*1.1031;
assignin('base','C13Con',Cppmpoly)
assignin('base','C12Con',Cppmpoly12)

**Fitline File**

This file is called by the above program. It can be created via HITRAN parameters.

Changing which lines are referenced here will require alteration of the above code.
Our inability to control or measure the heat of the sample cell in the field resulted in subsequent lab tests to ascertain whether we used an incorrect temperature for fitting. The lab tests showed up to of 4 °C difference in temperature between the measured heat in the thermistors we used in the field, and the cell itself. At 17SLM, our sample flows 1050 liters of air per hour. STP air has a specific heat of ~1 kJ/kg°C, and 1050 liters of air is 1.3 kg of air. It would require 3.25 kJ of heat transfer to support this cooling of the sample air.

To ascertain whether the temperature difference between the glass cell and the sample could transfer sufficient heat to warm the sample, we compare the measured values to a steady-state heat transfer model. The temperature of the inside (sample location) and outside of the cell

<table>
<thead>
<tr>
<th>HITRAN molecule</th>
<th>HITRAN isotope</th>
<th>Wavenumber</th>
<th>absorption cross-section</th>
<th>Lorentz Correction</th>
<th>Energy Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>2309.541</td>
<td>4.40E-22</td>
<td>0.0774</td>
<td>113.958</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2309.5961</td>
<td>6.32E-20</td>
<td>0.0688</td>
<td>1054.7607</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2309.64</td>
<td>1.72E-22</td>
<td>0.0853</td>
<td>1954.3514</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2309.6905</td>
<td>2.44E-22</td>
<td>0.0788</td>
<td>729.5555</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2309.7078</td>
<td>2.44E-22</td>
<td>0.0788</td>
<td>729.455</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2309.8061</td>
<td>3.55E-21</td>
<td>0.0726</td>
<td>1552.0433</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2309.8078</td>
<td>6.23E-23</td>
<td>0.0871</td>
<td>2088.5681</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2309.9824</td>
<td>4.23E-22</td>
<td>0.0683</td>
<td>476.8538</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2310.0024</td>
<td>4.86E-21</td>
<td>0.0748</td>
<td>1454.9686</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2310.1859</td>
<td>7.24E-23</td>
<td>0.0748</td>
<td>2467.5957</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2310.2055</td>
<td>4.60E-21</td>
<td>0.0695</td>
<td>278.2797</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2310.3332</td>
<td>4.40E-22</td>
<td>0.0782</td>
<td>100.5525</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2310.3472</td>
<td>6.70E-21</td>
<td>0.0678</td>
<td>639.6307</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2310.4449</td>
<td>1.50E-22</td>
<td>0.0863</td>
<td>1948.9209</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2310.4973</td>
<td>2.35E-22</td>
<td>0.0798</td>
<td>719.9585</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2310.506</td>
<td>6.87E-20</td>
<td>0.0689</td>
<td>1031.1292</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2310.5118</td>
<td>2.36E-22</td>
<td>0.0798</td>
<td>719.8724</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2310.6861</td>
<td>5.89E-21</td>
<td>0.0726</td>
<td>1449.3831</td>
</tr>
</tbody>
</table>

**Steady State Heat Transfer Model for Lower Glass Temperatures**

Our inability to control or measure the heat of the sample cell in the field resulted in subsequent lab tests to ascertain whether we used an incorrect temperature for fitting. The lab tests showed up to of 4 °C difference in temperature between the measured heat in the thermistors we used in the field, and the cell itself. At 17SLM, our sample flows 1050 liters of air per hour. STP air has a specific heat of ~1 kJ/kg°C, and 1050 liters of air is 1.3 kg of air. It would require 3.25 kJ of heat transfer to support this cooling of the sample air.

To ascertain whether the temperature difference between the glass cell and the sample could transfer sufficient heat to warm the sample, we compare the measured values to a steady-state heat transfer model. The temperature of the inside (sample location) and outside of the cell.
are at steady-state, at 32 °C and 19 °C, respectively, and use the equation for steady state heat transfer through a solid:

\[
\frac{Q}{t} = \frac{kA(T_{hot} - T_{cold})}{d}
\]

where \( Q/t \) is heat transfer over time, \( k \) is thermal conductivity, and \( d \) is wall thickness. Thermal conductivity of glass is 0.8 W/m°C, and wall thickness of the cell is .3 cm. The total area of the glass cell is .015 m\(^2\). This results in a heat transfer of 52W/hr. 52 Wh is 187KJ. This model shows there is more than enough heat loss available in the cell to change the temperature of the sample for a long period.
References


