TESTING AND MODIFICATION OF TWO INFRARED GAS ANALYZERS FOR CO₂ MEASUREMENT

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SOARS® Summer 2003

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ABSTRACT

The goal of the research was to test and modify two infrared carbon dioxide (CO₂) analyzers. The two analyzers are the LI-820 series and RMT DX 6100 series. They both operate on the principle of infrared light absorption. Accurate measurements of carbon dioxide play an important role in understanding global climate change resulting from the greenhouse effect. Policy makers also need more accurate measurements to manage the carbon cycle. Policy makers will be better able to manage CO₂, CH₄ and the carbon cycle with the development of the scientific basis for such societal decisions. Presently, information on carbon fluxes is only available on small or large scales with very few measurements applicable to middle scale fluxes.

The research process was divided into four steps. First, calibration requirements for the instruments were tested. The tests checked the zero value, span drift and flushing time of each analyzer. The second step tested different Nafion tube lengths to determine which will be appropriate for drying the sample air. For the third step the CO₂ analyzers and the drying system will be integrated together with other components such as a chemical drying agent (CDA), pumps and valves. Lastly, the integrated system will be tested in the laboratory and in the field to characterize its performance and to make necessary corrections. Thus far, the research has been successful.

The success of this research will provide a less expensive CO₂ instrument that will be used at different measurement sites around the globe. The success of this research, an improved instrument, will help clarify scientific uncertainties regarding CO₂ flux measurements, especially within the regional and continental areas, which constitutes the middle scale.

This work was done under the auspices of the Significant Opportunities in Atmospheric Research and Science program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric Administration, the Cooperative Institute for Research in Environmental Sciences, and the National Aeronautics and Space Administration.

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Introduction

It is currently very difficult for policy makers to develop policies regarding global climate change because of the scientific uncertainties of the budgets for the two most important greenhouse gases, methane (CH₄) and carbon dioxide (CO₂)¹. Once these scientific uncertainties are clarified, policy makers will be able to make decisions regarding the management of CO₂ within the earth system.

Presently, the flux accuracy of these gases, especially CO₂, is on large and small-scale bases². The large scale is based on average hemispherical measurements and the small-scale ranges from 0 to 1 kilometer square area.

The middle scale is one of the major areas of concern, which covers regional and continental areas. Within this scale are forest, grassland and agricultural areas that are major sources and sinks of these gases, especially CO₂, which is essentially important for photosynthesis and released during decomposition of organic matter.

There is a low level of confidence in the flux accuracy on the middle scale basis due, in part, to the fact that there is variation between the fluxes measured at different observatory stations and towers. In addition, there are a limited number of measurement sites regionally and continentally, so, the data available does not give adequate information about CO₂ concentrations in these areas.

One of the main technical problems of the middle scale atmospheric CO₂ flux measurements is the cost of developing and maintaining the instruments. Some of the maintenance aspects are gas consumption, replacement of worn out segments and manual labor. Aside from that, the degree of accuracy of average measurements can be improved.

One of the instruments used for middle scale analysis, currently in use at the Cape Grim Baseline Air Pollution Station in northwestern Tasmania, is the LOFLO analyzer system. This instrument is based on the LI-6251 model that uses non-dispersive infrared (NDIR) and incorporates several customized features such as active control of both the pressure and in the cells and flow rates through them³. One key feature is its relative flow rate through the cells at 15ml/min leading to significant economies in the consumption of calibration gases. Another instrument is the Mark II LOFLO version, which features greater portability and improved ease of use.

There are other CO₂ analyzer prototypes that are currently being developed and tested to meet the demand of greater accuracy, less cost of maintenance, portability and durability during field operation. The research described here is focused on the potential application of several recently available inexpensive CO₂ sensors.

There are various existing programs set-up to look into the scientific uncertainties of CO₂ flux measurement around the globe. Various government agencies are sponsoring this research. The major programs are the North American Carbon Program, A U.S Carbon Cycle Science Plan and the U.S Global Change Research Program. The main goals of these programs are to⁴ &⁵.

1. Quantify and understand the Northern Hemisphere terrestrial carbon sink.
2. Quantify and understand the uptake of anthropogenic CO₂ in the ocean.
3. Determine the impacts of past and current disturbance, both natural (e.g. boreal fires) and anthropogenic (e.g. land use) on the carbon budget.
4. Develop observatory infrastructures capable of accurately measuring net emissions (sources and sinks) of CO₂ from major regions of the world.
5. Develop the ability to predict and interpret changes in atmospheric CO₂ in response to climate change and inputs of CO₂, and including changes in the functional aspects of the carbon cycle.

6. Develop the scientific basis for societal decisions about management of CO₂, CH₄ and the carbon cycle.

Background and Motivation

Carbon dioxide (CO₂) is one of the major constituents of atmospheric air. It constitutes about 0.03% of air by volume. Apart from its natural existence in the atmosphere, there are several other processes, human and anthropogenic, that lead to the production of CO₂ within the earth system. Some of these processes include respiration in plants and animals including human beings, decomposition of organic matter, burning of fossil fuels (industrial and automotive) and also formation of natural minerals in the earth’s lithosphere. The lithosphere is the topmost part of the earth’s crust.

Simultaneously, other processes within the earth system lead to the consumption of CO₂. One of the major processes is photosynthesis by green vegetation. Others chemical processes take place within the atmosphere and oceans. Below is a schematic of the carbon cycle showing the processes mentioned above.

http://www.geog.ouc.bc.ca/physgeog/contents/9r.html

Figure 1  Carbon Cycle
As these processes occur simultaneously, it will be helpful to know how much CO₂ is being produced in relation to how much is consumed over a period of time and how its concentration influences certain activities.

**Why are CO₂ flux measurements important?**

CO₂ flux measurements are important because they help in better understanding the greenhouse effect and other global climate changes. One of the recent reasons for understanding the carbon cycle is to know how much CO₂ is produced and used by vegetation. It has been recently discovered that forests and grasslands are a major source and sink of CO₂. Having a better understanding of CO₂ flux measurement in the atmosphere and the carbon cycle will help policy makers clarify scientific uncertainties in order to make decisions regarding CO₂ management within the earth system.

**Project Objective**

The objective of this project is to test and modify two infrared gas analyzers (IRGA) for CO₂ measurements. The two analyzers to be worked on are the LI- 820 and RMT DX6100 series. Both instruments operate on the principle of infrared ray absorption by CO₂ molecules at a certain wavelength. The results from the tests would help in deciding the better of the two and designing a field calibration and drying system. Also, the modified analyzers are expected to be less expensive to operate and maintain over a long period of time. Another important factor to consider is the degree of accuracy of each instrument.

This is the first time the two analyzers under study are being tested for long-term field CO₂ measurements. The procedure involved in testing the CO₂ analyzers, LI- 820 and RMT DX 6100 series, is broken down into four parts.

The first step is calibrating the instruments, which involves testing the instruments for zero and span drift using two sample gases of different concentrations in the laboratory at room temperature and pressure.

The second step is testing for the most appropriate drying system. This involves passing room and saturated air at different flow rates through different length Nafion tubes, connected to a hygrometer, and flushed with air that has passed through different chemical drying agents. Results from the drying tests would be compared to determine how dry the air is with each dryer and how long the chemical drying agent for the purged gas can last. Based on the comparison the better drying system and agent will be selected.

The third step will be integrating the different components together and carrying out a test run.

The fourth and final step of the research will be testing the system in the field to determine how well it can be implemented in accurately measuring CO₂ concentrations regionally and continentally. Each analyzer comes with software that records and displays data graphically. The data obtained from the above procedures will be further analyzed using Microsoft Excel.

The success of this research will make available less expensive instruments that can be used to accurately measure CO₂ concentrations in the atmosphere. It will also provide easy accessibility to observatory sites and measurement networks, tall towers and aircraft campaigns around the globe. This will help in better understanding CO₂ distribution, sources and sinks and help clarify scientific uncertainties of the CO₂ cycle.
Method

This section of the paper will discuss the instruments tested, their theory of operations, calibration requirements, drying system tests, system integration and field testing.

Instruments

The two CO₂ analyzers tested were the LI-820 and RMT DX 6100 series. The LI-820 is a single path, dual wavelength and non-dispersive infrared (NDIR) gas analyzer. It features interchangeable optical benches; the standard 5.5" (14 cm) bench provides CO₂ measurement ranges of 0-1000 or 0-2000 parts per million (ppm), and the optional 2" (5 cm) bench provides measurement ranges of 0-5000 or 0-20000 ppm. At one end of the optical bench is the infrared light source that is a globar light reflector and on the other end is the filter and detector. The other components are the thermistors, heating elements, ribbon cable connectors, pressure transducer and a conversion system.

The RMT DX 6100 is also a non-dispersive infrared (NDIR) gas analyzer. It has a double differential frequency optical scheme that provides high accuracy in wide ranges of humidity and temperature due to the internal thermo-stabilization. The main parts of the instrument are the optical unit, controller module and optocomponent-mating module.

Instrument Operation

Both instruments operate based on the same principle, the “light absorption principle”. This principle states that, “the amount of light absorbed by CO₂ molecules is proportional to its concentration”. CO₂ molecules enter the optical path through the gas inlet at a certain flow rate. Concurrently, infrared light is emitted into the optical path at different wavelengths of 3.95nm and 4.25nm. The filter directs the different wavelengths to different detectors. A CO₂ molecule absorbs light rays over specific wavelengths, including 4.25 nm. The detector detects the amount of light absorbed by each CO₂ molecule, this is converted to concentration by a built-in calibration system and the output is displayed on the monitor. It is expected that at a wavelength of 3.95 nm, CO₂ concentration detected should approach zero. The other components also contribute to the smooth running of the instrument. The pressure transducer, which is only available in the LI-820, reduces variability due to changes in barometric pressure while the thermistors, in both instruments, tells the temperature inside the instrument at entrance and exit of the optical path. However, the instruments are sensitive to both external temperature and pressure changes, which also affect their operation. In the LI-820, the light source interior and the optical path are gold coated to increase energy transmission and also, there is a foam enclosure that surrounds the optical bench that helps to maintain a controlled thermal environment as well as protect the bench from mechanical shock and vibration.

The DX6100 is believed to be of a high stability and selectivity. It detects CO₂ molecules faster and measures concentrations over a wide range. It has low power consumption and long service life.
Figure 2 Major components of the LI-820 series

Figure 3 Interior of the RMT DX 6100 series
Calibration Requirements

One of the main tasks of the research is determining the calibration requirements of each instrument. The calibration testing process is to check for the zero value, span drift, flushing, precision and sensitivity to pressure and temperature changes of each instrument. The zero value and span drift test was used to check the zero value, which is the concentration detected by each instrument when there is no CO₂ flowing through. It should be close to zero under normal conditions. Any concentration detected at that time is due to noise effect within the instrument. The zero value is subtracted from measurements obtained to know the actual CO₂ concentration being detected. This is often carried out to check for a shift in the zero value especially, when the instrument is transported from one place to another due to handling. The span drift is how constant the difference between the measured value and zero value is over a period of time. The span drift is expected to be almost constant for a long period of time. The zero value and span drift test is also called the stability test.

The precision test is to determine how accurate and noisy each instrument is. The precision of each instrument is determined by a measure of the standard deviation of a series of measurements over a period of time. Below is a schematic of the precision and stability test set up.

Air is released into the system from a gas cylinder. The external pressure controls the airflow going into the instruments. In the above diagram, the two analyzers are connected in series. There is no major significance to this setup. The advantages are: 1) both analyzers take measurements at the same time and the data obtained can be stored together in a file. 2) An in-house written BASIC program is used to control the activities of both analyzers simultaneously. The file obtained contains time of measurement, concentrations measured by each analyzer and measurement errors of both instruments. It is also easy to compare the reading of each instrument at certain intervals from the output display. The flow meter tells how much air is flowing through each of the instruments. It can also be used to control the pressure within the instruments.

Figure 4 Precision and Stability test setup
data obtained from the tests are analyzed in different ways to identify the precision and stability of each instrument.

The flushing time is the time it takes the instrument to switch from measuring one CO₂ concentration to the other at different flow rates. In the laboratory, gas cylinders of different CO₂ concentrations are used for this test as compared to a real world situation where CO₂ fluxes change with altitude and geographical locations. Below is a schematic flushing time test. It is similar to the stability and precision test but in this case, each analyzer is connected separately.

![Flushing test setup]

The pressure and temperature tests are used to characterize the sensitivity of each instrument. This test evaluates the response of each instrument to both small and large changes in pressure and temperature as compared to field conditions where these parameters constantly change.

This is important because both external pressure and temperature changes affect the operation of each instrument, thus affecting the accuracy of CO₂ measurements. The pressure and the precision test setups are exactly the same except that the pressure test reads from a different text input file. The temperature test setup differs from the pressure setup because it reads from the same input file as the precision test while the pressures test does not. The two analyzers are placed in an oven where the temperature is varied at different time intervals. The setup is shown below.
Drying System Test

The drying system test involved determining the most appropriate Nafion tube length that would be best suitable for removing water vapor from air. A Nafion tube is made up of two concentric cylinders of equal lengths. It is a one-shell one-tube formation. Sample air flows through the inner cylinder while purged/dry air flows through the outer. The Nafion tubes tested were 24, 48, 72 and 96 inches long. Alongside the Nafion tubes, a chemical drying agent (CDA) was also tested. The CDA is made of Magnesium Perchlorate (MgClO4). The CDA was tested for durability and quality. Quality refers to how well the CDA can remove water vapor from the sample air. The water vapor content can affect CO2 concentration measured. Below is a schematic of the setup.

Air is pumped into the setup through the inner cylinder of the Nafion tube. It enters into the flow meter and then the hygrometer. The hygrometer is an instrument, which measures water vapor content in gases. There is a mirror within the instrument that detects how saturated the air molecules are. The parameters measured were dew point, ambient temperature and percentage relative humidity. On getting to the CDA, water vapor content is removed from the air molecules. The air leaving the CDA is dryer. It exits the CDA through the outer cylinder of the Nafion. As it is exiting, it dries off the incoming air sample. As this process goes on, the air entering the hygrometer gets drier over time.
Chemical Drying Agent (CDA)

Pump

Flow meter

Hygrometer

Nafion Tubes

Room/Saturated Air

Purged Air

Chemical Drying Agent (CDA)

Figure 7 Drying test setup
Results and Discussion

Presented in this section are the results to the above tests carried out to characterize the performance of each CO₂ analyzer. Each analyzer comes with a software program that collects and stores data in a tabular format. These data files are read into Microsoft Excel, which was used for most of our data analysis. The data for each of the tests are analyzed separately.

Flushing Time Test

Figure 8a and 8b show a graphical representation of the flushing time test for the RMT DX 6100 analyzer. It is a plot of concentration in part per million versus time in seconds. Shown on the graph are exponential curves that represent how long it takes each analyzer to switch between two calibration gases of different concentrations. The blue curve is a fitted curve that represents an average of both curves. Using a logarithmic equation, the flushing time for the RMT DX 6100 analyzer was calculated to be 29 seconds to 99.9%. Using the same procedure, the flushing time for the LI-820 analyzer was determined to be 24 seconds. Both times calculated were at a flow rate of 200 ml/min.

Figure 8a Result of RMT DX 6100 flushing test
The same analysis was done to data for a flow rate of 100 ml/min. The flushing time for the RMT DX 6100 and LI-820 were 36.13 and 34.54 seconds respectively. Below is a table that summarizes the results of the flushing time test.

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>LI-820 (sec)</th>
<th>DX 6100 (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>34.54</td>
<td>36.13</td>
</tr>
<tr>
<td>200</td>
<td>24.45</td>
<td>29.71</td>
</tr>
</tbody>
</table>

From the table above, it can be concluded that the LI-820 analyzer has a better flushing time than the RMT DX 6100 analyzer.

**Precision and Stability Test**

The results of the precision test are broken into two parts. The first part is the results of the short-term precision of the analyzers. Below is a graph displaying the result of the short-term precision test for each analyzer. Thirty data points were randomly selected and the standard deviations were calculated. From the graph below, it can be seen that the average standard deviation of the LI-820 from the average CO2 concentration was 1.50 and the RMT DX 6100 was 0.77.
Figure 9a Results of short-term precision test

The same analysis was done for other data set files obtained for the other tests days. The results from the analysis are summarized in the table below.

<table>
<thead>
<tr>
<th>Date / Analyzer</th>
<th>LI 820</th>
<th>RMT DX 6100</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/06/23</td>
<td>1.4200</td>
<td>0.7175</td>
</tr>
<tr>
<td>03/06/24</td>
<td>1.4911</td>
<td>0.9343</td>
</tr>
<tr>
<td>03/06/26</td>
<td>1.4769</td>
<td>0.7204</td>
</tr>
<tr>
<td>03/06/27</td>
<td>1.6124</td>
<td>0.7276</td>
</tr>
<tr>
<td>Average</td>
<td>1.5001</td>
<td>0.7749</td>
</tr>
</tbody>
</table>

Table 2 Results of the short term precision

The second part of the test was to check for the medium term precision of each analyzer. The same procedure was done for the medium precision files. These are averages of values measured by each analyzer every two minutes.
From the above graph, the average standard deviation from the LI-820 data analysis was 0.26 and the RMT DX 6100 was 0.47. The table below shows the standard deviation from the rest of the data analysis.

<table>
<thead>
<tr>
<th>Date / Analyzer</th>
<th>LI-820 Gas 1</th>
<th>RMT DX 6100 Gas 1</th>
<th>LI-820 Gas 2</th>
<th>RMT DX 6100 Gas 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/06/23</td>
<td>0.2878</td>
<td>0.5216</td>
<td>0.3132</td>
<td>0.4866</td>
</tr>
<tr>
<td>03/06/24</td>
<td>0.2595</td>
<td>0.5342</td>
<td>0.2216</td>
<td>0.3508</td>
</tr>
<tr>
<td>03/06/26</td>
<td>0.3110</td>
<td>0.4010</td>
<td>0.2423</td>
<td>0.4212</td>
</tr>
<tr>
<td>03/06/27</td>
<td>0.3571</td>
<td>0.4786</td>
<td>0.2456</td>
<td>0.5574</td>
</tr>
<tr>
<td>Average</td>
<td>0.3039</td>
<td>0.4839</td>
<td>0.2557</td>
<td>0.4540</td>
</tr>
</tbody>
</table>

From the results shown for the precision test, the RMT DX 6100 analyzer has a better short-term precision than the LI-820 analyzer but for medium term precision, the LI-820 is at an advantage.
There is also the stability test, which can also be regarded as the long-term precision. It determines how constant the zero value and span drift are for each analyzer. For the zero value, a linear fit was performed for a data set. From the linear equation, the y-intercept (b) represents the zero value and also the slope depicts the behavior of the span drift.

![Result of Stability Test (Zero Offset)](image)

**Figure 10 Result of stability test (zero value)**

From the graph above, it can be seen that the LI-820 has a more stable zero value than the RMT DX 6100. The RMT DX 6100’s zero value kept increasing throughout the test as shown on the graph. The zero value of the LI-820 was about 6 ppm and the RMT DX 6100 changed about 25 ppm for the duration of the test. It can be stated that the LI-820 has a more stable zero value than the RMT DX 6100. In addition, the LI-820 has a better span drift than the RMT DX 6100. This is illustrated on the graph shown below.
As seen from the graph, the LI-820 analyzer has a more stable span drift than the RMT DX 6100 analyzer. The span drift changes by about ±1ppm for the LI-820 while the other analyzer keeps changing throughout the test duration. Therefore, it can be confirmed that the LI-820 has a better precision and stability than the RMT DX 6100 analyzer.

In addition, the LI-820 has a better sensitivity to external pressure changes. A graphical representation of the pressure test is shown below. From the equations of the linear fits, it can be seen that for every 1 kPa change in pressure, the LI-820 concentration measured is decreased by a magnitude of 0.27 ppm while the RMT DX 6100 increases by a magnitude of 3.06 ppm. The latter analyzer has a greater magnitude change in concentration measured than the former. There will be a greater decrease in accuracy of measurement in the RMT DX 6100 if there is a continuous increase in pressure as compared to the other analyzer. In other words, the LI-820 has a better sensitivity to external pressure changes than the other analyzer.

The above is also true of temperature sensitivity. For every slight change in external temperature there is a greater change in the concentration measured by the RMT DX 6100 than the LI-820 analyzer. Below is a graphical representation of one of the temperature changes. The temperature was increased from 10°C to 20°C and as seen from the graph, there was a decrease of about 160 ppm in the concentration measured by the RMT DX 6100 while LI-820 was almost constant.
Result of Pressure Test

\[ y = -0.2749x + 402.46 \]
\[ y = 3.0574x + 103.43 \]

Figure 12 Pressure test result

Result of Temperature Test

Figure 13 Temperature test result
Drying System Test

Figure 9 shows the result of one of our drying system tests. It is a plot of dew point of air versus length of Nafion tubes. The dew point identifies how dry air molecules are. In other words, it gives an idea of how much water vapor content is present in air molecules. As expected, longer tubes do a better job of drying the air. Also, under normal conditions, it is expected that each Nafion tube length should help to dry room air better than saturated air especially at a higher flow. The higher flow for these tests was at 500ml/min. From the graph below, it can be seen that at 500ml/min, the result is as expected. But at 100ml/min, reverse is the case. There are further investigations being carried out to figure out what the causes are. One of the problems could be with the hygrometer or technical problem with the tubes. There is no full assertion at this point which of the Nafion tube lengths will be appropriate for the drying system.

![Result of Nafion Tubes Test](image)

Figure 9 Drying system test
Here is a table that summarizes the results of our findings thus far.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>RMT DX 6100</th>
<th>LI-820 Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flushing Time</td>
<td>---</td>
<td>√</td>
</tr>
<tr>
<td>Short Term Precision</td>
<td>√</td>
<td>---</td>
</tr>
<tr>
<td>Medium Term Precision</td>
<td>---</td>
<td>√</td>
</tr>
<tr>
<td>Long Term Precision / Stability</td>
<td>---</td>
<td>√</td>
</tr>
<tr>
<td>Pres. &amp; Temp. Sensitivity</td>
<td>---</td>
<td>√</td>
</tr>
<tr>
<td>Purchasing Cost</td>
<td>√</td>
<td>---</td>
</tr>
<tr>
<td>Maintenance Cost</td>
<td>---</td>
<td>√</td>
</tr>
</tbody>
</table>

Table 3 Summary of results
Future Works and Conclusion

Preliminary results have thus far shown that the LI-820 analyzer will be more suitable for measuring CO₂ fluxes in the atmosphere than the RMT DX 6100. Even though the RMT DX 6100 is cheaper to obtain in the market, the LI-820 is more suitable in terms of accuracy, precision, stability, pressure and temperature sensitivity and therefore, overall costs. The accuracy, precision and stability of an analyzer tell how often it has to be calibrated to obtain measurements. Also, the flushing time tells the amount of calibration gases needed to calibrate each instrument. All these are considered maintenance procedures. Therefore, it can be stated that the LI-820 analyzer has a better performance capability and a lesser maintenance cost and thus, lower overall costs, than the RMT DX 6100 analyzer.

Subsequently, other data sets have to be analyzed to fully characterize the performance of each of the analyzers. Afterwards, the most suitable analyzer will be connected to the drying system and other components of the final design prototype which includes pumps, pressure values, flow meters, calibration and reference gases. The final design prototype will be tested in the field to fully ascertain the suitability of the chosen analyzer and necessary modifications will be made.

The success of this research will provide an accurate, precise and less expensive CO₂ instrument that will be used at measurement sites as well as on air campaign missions around the globe. This will help clarify scientific uncertainties regarding CO₂ flux measurements, especially within the regional and continental areas, which constitutes the middle scale.
Acknowledgement

I would like to thank the SOARS program and staff for the opportunity to be a part of this summer research experience. Every minute of it has been really great, educative and exciting. Special thanks to my research mentor Britton Stephens, writing and communication mentor Catherine Shea for their time, support and love throughout the course of the research. My thanks also go to Steve Shertz, Teresa Campos and Dave McFarland for their help in different ways to accomplish the goals of this research.

Special thanks to my fellow protégés who have encouraged and stood by me when things looked blurry and were going downhill: I love you all!!! Not to forget everyone else I met this summer and have had an impact one way or the other, I’d like to say thank you.
References