Chapter 2

Literature Review: CO_2 and the oceans

2.1 SRP Project

There exists a need to know the CO_2 fluxes in the Southern Ocean. Direct measurements of pCO_2 in the Southern Ocean are limited and it is uncertain whether the Southern Ocean is a net sink or source of CO_2 [20]. Increased accuracy in the measurement of pCO_2 in the Southern Ocean may serve to increase our collective understanding of the underlying processes in the Southern Ocean, as well as the manner in which these processes vary with space and time [20].

Due to its geographical location, South Africa is one of the leading countries in the Southern Hemisphere to do carbon-climate research [58]. By focussing on the Southern Ocean, contributions can be made to improve the ability to create high resolution models on a global scale. Furthermore, this will enable researchers to gain an increased understanding of the carbon-climate system's sensitivity towards global warming [58]. The aim of the greater SRP Southern Ocean carbon-climate system project, of which this dissertation forms a part, is to strengthen South Africa's expertise in Southern Hemisphere polar climate and carbon science research [58].

Changes in the Southern Ocean have an effect on international climate negotiations [58]. One of the key global challenges for the coming decade is to determine, with increased accuracy, the sensitivity of the Southern Ocean's seasonal carbon flux cycle to variations in wind stress, rainfall, heat impacts, pack ice and various other external influences on the ocean [58]. To address the lack of Southern

Ocean CO_2 flux data, improved sampling strategies are needed. Such strategies should include *in situ* measurements as well as remote sensing data sets [58]. The Southern Ocean carbon-climate system project focusses on one of the most important sources of uncertainty in the global carbon cycle, viz. the changing dynamics of the Southern Ocean CO_2 sink/source [58].

The aim of this dissertation is the empirical estimation of pCO_2 in the Southern Ocean, and specifically to obtain this estimate with a small margin of error. Due to the sparse measurements in the Southern Ocean, as well as the seasonal bias in the quantity and quality of measurements, some empirical estimates of the pCO_2 and the CO_2 fluxes are needed in order to calculate the carbon budgets of the countries in the Southern Hemisphere. The oceanic pCO_2 depends on the state of the ocean, the ocean physics and ocean biology. Therefore, it is hypothesised that an empirical model can be developed for the estimation of pCO_2 from the variables in the *in situ* and satellite data sets. The availability of more accurate oceanic pCO_2 values will also contribute to the development of ocean models as well as to the coupling between ocean and atmospheric models.

2.2 Carbon dioxide and the oceans

2.2.1 Background

The ocean and atmosphere both contain large amounts of CO_2. Due to the increase of CO_2 in the atmosphere, the earth's climate is changing and the ecosystem is being disturbed. The ocean-atmosphere CO_2 fluxes have a significant influence on the amount of anthropogenic carbon present in the atmosphere. A more detailed explanation of these CO_2 fluxes is given in this section.

CO_2 is the main greenhouse gas that affects climate variations and is a by-product of the burning of fossil fuels [53]. Due to industrial expansion, the concentration of CO_2 in the atmosphere has increased over the past four decades. This increase in CO_2 concentration contributes to climate change and specifically to global warming [69]. According to Takahashi *et al.* [75], the increasing rate at which CO_2 is accumulated in the atmosphere is currently one of the most significant environmental concerns, since it has a big influence on the global climate system. However, this CO_2 concentration would have been considerably higher, had some of the CO_2 not been absorbed by the terrestrial and oceanic CO_2 sinks [69].

According to Deng *et al.* [31], the increase of CO_2 concentrations during the past 200 years is one of the main reasons for the warming of the planet. The warming that is predicted, together with the accompanying environmental changes, will have an influence on socio-economic stability, the global environment and the eco-system [75]. Deng *et al.* [31] states that only 40% of anthropogenic CO_2 is not absorbed by terrestrial and oceanic sinks. One of the biggest CO_2 sinks is the ocean, with an estimated uptake of 33% of the anthropogenic CO_2 per annum [53], [41]. The CO_2 taken up by the oceans reduces the rate at which CO_2 increases in the atmosphere and thus reduces the effect of anthropogenic CO_2 on climate change [32]. Gaining an understanding of the CO_2 fluxes in the atmosphere and terrestrial and oceanic sinks is essential to manage the carbon cycle and to avoid serious climate change [31]. More than 60% of the earth is covered by oceans and therefore the oceans have a great influence on climate [41].

The transfer of CO_2 between the ocean and the atmosphere plays an important role in the global carbon cycle [74]. The increasing amount of CO_2 that is taken up by the ocean is causing acidification of the oceans [74]. This is because the CO_2 is converted to other forms of carbon by chemical reactions that take place in the ocean. The CO_2 molecules react chemically with the water to produce bicarbonate (HCO_3^-) and carbonate (CO_3^-) ions. The inverse reaction of these ions with air do not take place. Only approximately 0.5% of the carbon dioxide molecules taken up by the oceanic waters is released back into the air [74]. To understand the processes that take place in the oceanic CO_2 flux and how this affects climate change, accurate observations of the changes in the CO_2 concentration are necessary [74].

An increased understanding of the variations in the CO_2 taken up and given off by the ocean is required in order to obtain a better understanding of the Southern Ocean carbon sink [55]. The Southern Ocean is sensitive to climate change as well as to the increase in anthropogenic CO_2. Thus, a need exists to understand the climate-ocean coupling in the Southern Ocean [55]. A precise spatio-temporal model of CO_2 flux between the ocean and atmosphere is essential for understanding the global carbon cycle, as well as for planning how to deal with CO_2 concentrations in the ocean and the atmosphere [75]. It is essential to develop an accurate ocean-atmosphere model to deal with some important socio-political and scientific issues, such as the restriction of carbon budgets, determining what the long term causes of changes in atmospheric CO_2 concentrations are and understanding how the ocean processes change and influence oceanic CO_2 uptake or release [32]. Doney *et al.* [32], states that it is anticipated that the warming of the planet will influence the oceanic ecosystem and have both positive and negative effects, which may play a big role in the allocation of global carbon budgets. According to Metzl *et al.* [55], seasonal carbon dioxide measurements in the Southern Ocean are extremely important to decrease the uncertainties in the allocation of carbon budgets, to authenticate ocean-atmosphere carbon estimates and to understand the variability of pCO_2 in the oceans.

2.2.2 Data availability

The quality of the research done on the Southern Oceanic environment and of the models describing this environment depends on the quantity and the quality of the data available for this region.

One of the reasons that there are very few ocean-atmosphere models that can predict the CO_2 fluxes in the Southern Ocean, is the fact that very few observations of the oceanic pCO_2 are made in this region [75]. Doney *et al.* [32] mentions that there are several oceanic regions where the coverage of CO_2 observations are still insufficient. The number of observations made are seasonally dependent, as it is more difficult to make observations during winter (since clouds obstruct the satellite views and large parts of the ocean are covered with ice [55]). More observations in the Southern Ocean will improve seasonal predictions of pCO_2 and allow for improved extrapolation [55].

Improved strategies are needed to make observations and Doney *et al.* [32] suggests that moored instruments, drifters or profiling floats can be used to make observations. Doney *et al.* [32] further suggests that it would greatly help ocean-atmosphere modelling if a global data set is compiled and the data in this database is of a high quality. It is, however, not an easy task to determine the CO_2 variability, in the ocean surface, for an area as big as the Southern Ocean. Therefore, information from boat cruises as well as historic and present biological, chemical and physical processes need to be taken into account. Some of the processes in the ocean, as well as variables affecting the CO_2 uptake or release, vary between different geographical areas. Therefore, several different regions have to be investigated [20].

The insufficient observations of CO_2 flux measurements in the ocean, and especially the Southern Ocean, creates a need for new, more dense, measurements of the pCO_2 in the Southern Ocean. This is not necessarily feasible. Thus, other strategies also need to be considered to determine the CO_2 fluxes in the Southern Ocean [58].

2.2.3 Factors affecting the CO_2 fluxes

There is no single factor that determines the amount of CO_2 taken up or released by the ocean. There are, however, several different factors that play a role in the ocean-atmosphere CO_2 fluxes. A few of these are discussed in this section.

According to Bakker [20], to calculate the long term fluxes of CO_2 in the oceanic surface layer, one needs to take into account the driving forces for the sink or source, as well as the rate at which CO_2 is transferred. These driving forces include, amongst others, wind, waves, salinity, heat, the irregularity of the seasons and the mixing of freshwater with seawater in the ocean [22]. Some of these factors will now be discussed in more depth.

Firstly, the dynamics of the ocean at the coast leads to great variability in the ocean, due to the rivers and estuaries, that serve as a source of fresh water to the ocean. This causes the water at the coasts to be substantially diverse. Thus, it is much more complex to calculate the anthropogenic CO_2 taken up or released by the oceans in these areas [53]. The mixing with fresh water thus plays a considerable role in the carbon fluxes in the ocean. Marinov *et al.* [52] mentions that in addition to the mixing of fresh water with seawater, the mixing of the ocean's surface water with the deep ocean layer alters the ocean circulation patterns, and this also has an effect on the natural carbon pumps and the CO_2 fluxes between the ocean and the atmosphere.

Secondly, the salinity of the ocean water has an effect on the pCO_2 in the water. In general, an increase in salinity results in a higher pCO_2 value in the ocean [75]. According to Williams *et al.* [79], salinity is the ocean's signature of the global water cycle. Salinity affects the circulation of the ocean and thus has a great effect on global climate change. The density of the ocean is directly related to the salinity of the ocean, and the salinity also influences the barrier layers that are formed in the ocean [79]. Studies carried out by Williams *et al.* have shown that by increasing the salinity by 35 psu (practical salinity unit - a standard measure of the salinity in seawater), the sea surface temperature increases by 0.8°C within a few years, due to a decrease in vertical mixing. This warming is then followed by a gradual global decrease in sea surface temperature by 0.4°C in a few decades [79]. Freshwater entering the ocean alters the salinity and, therefore, the density of the water. These density gradients results in thermohaline circulation (THC). THC is described as the part of ocean circulation that is driven by heat fluxes [67]. THC, which forms part of the larger circulations and mixing taking place in the ocean, in turn has an effect on the CO_2 uptake and release [79]. The thermohaline circulation is affected not only by the salinity of the ocean, but also by temperature variations in the ocean [79].

Temperature is the next parameter that plays a role in the carbon dioxide uptake or release by the ocean. When the ocean temperature increases, the ability of the ocean to store carbon is decreased. The solubility of carbon dioxide in seawater decreases with increasing temperature [32]. Cold oceanic water holds more dissolved carbon in high latitudes than warm low latitude oceanic water, because the cold carbon-rich water sinks to the deep layer of the ocean and is preserved in the deep layer [52]. Also, when the ocean surface temperature increases, it contributes to an increase in the number of layers in the ocean, which decreases the vertical mixing that takes place. Consequently, the volume of CO_2 that can be absorbed by the ocean is reduced [32]. According to Deng *et al.* [31], global warming can negatively affect not only terrestrial carbon sinks, but also oceanic carbon sinks.

The seasons also play a role in the oceanic CO_2 uptake or release. Generally in the polar frontal zone, the ocean tends to take up more carbon dioxide in the summer than in the winter. However, this is an average estimate over the entire polar frontal zone — the local uptakes and releases may differ [55]. In the winter months, the sea is partially covered with ice (which makes the uptake of carbon more difficult) and deep mixing occurs in the ocean as the cooler water sinks to the oceanic deep layer [55]. The Seasonal Ice Zone (SIZ), South of 58°S, is covered with ice in the winter months and the carbon dioxide intake from the atmosphere is limited. The SIZ in the Southern ocean tends to be a CO_2 sink in summer and a source in winter [55]. The Permanent Open Ocean Zone (POOZ) on the other hand, which is not covered with ice in the winter months, has smaller seasonal variations but the variations are still significant [55]. In addition to the seasons, different regions in the ocean also play a role in the pCO_2 values of the ocean [39].

Another factor that influences the degree to which the ocean is a sink or a source is the wind speed in the oceanic regions. According to Takahashi *et al.* [75], the result of the high wind conditions in the Southern Ocean is that the CO_2 transfer between the ocean and the atmosphere has a square dependence on wind speed. In order for bloom development to occur in the ocean, low wind speeds are required and appropriate lighting conditions are essential. From these blooms, photosynthesis takes place, and the CO_2 fixation results in an under-saturation of the CO_2 concentration in the ocean [20]. When this under-saturation exists, high wind speeds are again required in order for the transfer of CO_2, from the atmosphere to the ocean, to take place [20]. When this CO_2 enters the ocean, the ocean does not remain unchanged. As CO_2 enters the ocean, the pH of the ocean is lowered and the ocean becomes more acidic. This increase in oceanic acidity alters the plant growth and the ecosystems in the ocean.

According to Frederich [39], oceanic pCO_2 is a function of sea level air-pressure, the amount of dissolved inorganic carbon (DIC), total alkalinity of the seawater, the sea surface temperature (SST) and the sea surface salinity (SST). Rangama [68] stated that the main factors affecting pCO_2 values in the ocean are the circulation that takes place in the ocean, the temperatures of the ocean, biological factors (taken into account by considering chlorophyll-a concentrations) and the rate at which gas is exchanged between the ocean and the atmosphere.

As can be seen from the preceding discussion, the air-sea carbon fluxes are dependent on several interdependent parameters. Furthermore, it is not just the increase of CO_2 in the atmosphere that affects the ecosystem and the ocean-atmosphere CO_2 transfers. The following factors, amongst others, also play a role: overfishing, excess nutrients in the ocean from fertilizers (causing eutrophication) and geo-engineering prospects to use the ocean as a depository for carbon [32].

From this discussion it can be seen that a number of different aspects have to be taken into account when creating a model for the CO_2 fluxes between the atmosphere and the ocean. Calculating the quantity of CO_2 taken up by the ocean is more complex than merely calculating the amount of CO_2 that is released into the atmosphere. This is due to all the factors affecting the oceanic pCO_2 and the spatial and temporal variation of oceanic properties [43].

2.2.4 Ocean-atmosphere CO_2 transfers

CO_2 is one of the primary gases that contribute to global warming. CO_2 is continually being transferred between the ocean and the atmosphere. The exact rate at which the CO_2 transfer takes place is one of the key questions in ocean-atmosphere science.

The CO_2 concentrations in the atmosphere can be reduced by two primary processes. Firstly, the emissions of CO_2 into the atmosphere can be reduced. Secondly, the carbon sinks can be increased in order to increase the uptake of CO_2 from the atmosphere [69]. The terrestrial sinks are already included in the Kyoto protocol. The ocean sinks on the other hand have not yet been included due to the complexities and uncertainties in the oceanic sinks. The oceanic sinks, however, can make a significant difference in the ocean-atmosphere calculations [69].

As long as the atmospheric CO_2 concentrations are increasing, the oceanic uptake of carbon dioxide will persist, due to the concentration gradient in the CO_2 between the air and the ocean [66], [53]. The portion of anthropogenic CO_2 that is absorbed by the ocean, however, is variable due to a decreasing buffer capacity of carbon in water with an increasing uptake of CO_2 [66]. As the concentration of CO_2 increases in the atmosphere, the buffer capacity is decreased, and the efficiency of the carbon sink is reduced [69]. Thus we cannot argue that if more CO_2 is released in the atmosphere, more CO_2 would be taken up by the ocean, as there are factors other than the ocean-atmosphere equilibrium that have to be considered [69].

The oceanic CO_2 uptake should not be the only solution to decreasing the CO_2 concentrations in the atmosphere, as the oceanic carbon sink would only be effective up to a saturation level. At this point, the CO_2 concentration in the ocean would be too high and the buffer capacity would decrease. As a result, the earth's temperatures would increase, causing a decrease the effectiveness of the oceanic CO_2 sink [32].

Countries have to take responsibility for their own emissions and uptakes, in order to solve the global issue of climate change. In order to determine the quantity of CO_2 absorbed by the ocean in the coastal regions, for various countries, a specific area of the ocean is considered, viz. the exclusive economic zone (EEZ). The region of the ocean extending 200 nm (nautical miles) from the coastline of a coastal country is named the EEZ [53]. This part of the ocean plays a role in the allocation of the carbon budgets for coastal countries. The inclusion of the EEZ in carbon budget allocations can have both positive and negative effects. It may on the one hand have a positive economic effect on countries that need it, and on the other hand may result in the countries emitting more carbon dioxide because the pressure for reducing the emissions is reduced, since the oceans take up part of the anthropogenic CO_2 [53].

2.3 Conclusion

In this project the aim is to investigate the CO_2 fluxes in the Southern Ocean. The aim is to determine an empirical relationship between the pCO_2 in the ocean, and other variables that affect the ocean-atmosphere CO_2 transfer. The data that is currently available for the pCO_2 in the ocean are sparse across the Southern Ocean; however, satellite data is available for other variables such as SST, MLD, SSS and chlorophyll-a concentration. The objective of this dissertation is to determine values for the pCO_2 in the Southern Ocean from variables for which data is available.

This is a complex task, as many different factors affect the oceanic uptake or release of CO_2. In addition, there is no simple empirical relationship that exists between the variables. Furthermore, the ocean properties, and their dependence on one another, vary seasonally and regionally. This creates the need for seasonal and regional variations to be taken into account.