Chapter 1

Introduction and Objectives

The current increase of carbon dioxide (CO_2) in the atmosphere, and its possible consequences for climate change, have led to more scientific interest in the global carbon cycle. This thesis deals with the role of the oceans in the global carbon cycle, with emphasis on two key regions: the North Sea as a case study of coastal seas, and the Southern Ocean.

1. The natural and enhanced greenhouse effect

The greenhouse effect is related to the Earth's radiation balance. About 45% of the solar radiative energy incoming at the top of the atmosphere is absorbed by the surface of the Earth. The solar energy absorbed by the Earth's surface is re-emitted as infrared radiation (long-wave radiation, 8-13 μm) and about 55% of this radiative energy is absorbed in the lower atmosphere (first 10-15 km, *i.e.* troposphere) by various gases and water vapour. It is then either released as heat or re-emitted as infrared radiation towards the surface of the earth. This natural greenhouse effect by trace gases and water vapour, warms the surface of the earth and the troposphere by about 33 ^{o}C and thus maintains favourable conditions for life on the planet (without the greenhouse effect the planetary surface temperature would be -18 ^{o}C). Natural atmospheric gases such as water vapour (H_2O), carbon dioxide (CO_2), tropospheric ozone (O_3), methane (CH_4) and nitrous oxide (N_2O) as well as anthropogenic atmospheric gases such as chlorofluorocarbons (CCl_3F and CCl_2F_2), that absorb outgoing infrared radiation, are called greenhouse gases.
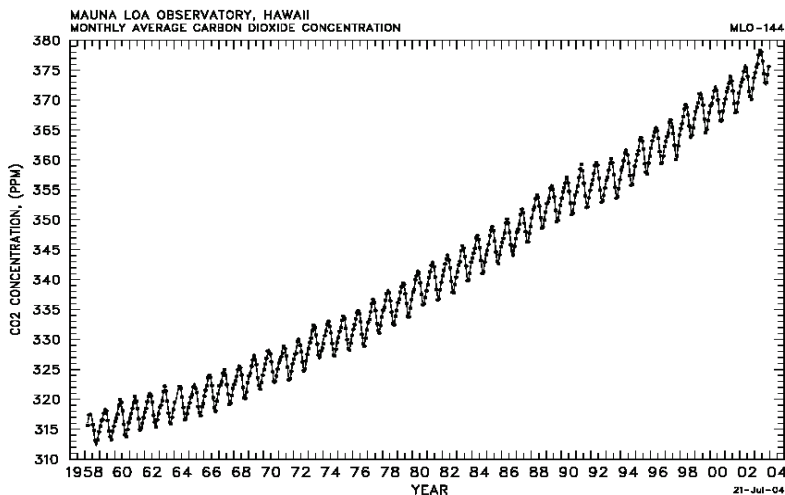

Figure 1: *Evolution of atmospheric carbon dioxide since 1958 to present at Mauna Loa site (Hawaii) from Keeling and Whorf (2004).*
Available on internet at http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm.

In 1957 Dave C.D. Keeling from Scripps Institute of Oceanography started the well-known time series of atmospheric CO_2 measurements at Mauna Loa, Hawaii, far away from local industrial sources (Keeling, 1960). The first values of about 315 μatm were rapidly rising at a rate of ~2 μatm yr^{-1} (Keeling and Whorf, 1999). Soon, this rise was attributed to the burning of fossil fuels by mankind. Nowadays in 2005 the values are approaching 380 μatm and continue to rise (Keeling and Whorf, 2004) (Figure 1).

In order to know what the natural CO_2 was in the atmosphere before the onset of the Industrial Revolution, many efforts and approaches to reconstruct the past CO_2 have been conducted (for overview see Gammon et al., 1985). Eventually, the drilling of ice-cores at Greenland and Antarctica provided well-preserved records of CO_2 in air bubbles enclosed within the ice (Petit et al., 1997). Ice cores collected in regions with high precipitation (snow which in the upper ~0.5 m rapidly converts to ice with gas bubble enclosures) have proven that over the preceding ~1000 years, and ~10,000 years, of the Holocene, the CO_2 in air was quite constant at ~280+3 μatm (Petit et al., 1999). Then, from 1780 A.D. onwards, it increased rapidly, and from 1957 onwards, the ice core record perfectly overlaps with the Anthropocene atmospheric record of Keeling (Keeling et al., 1989). Moreover, by deep ice drilling at central Antarctica where is very little precipitation, ice cores with lower resolution but very long records were obtained, first over the past ~160,000 yr (Barnola et al., 1987), next over the past ~420,000 yr (Petit et al., 1999) and recently over the past 740,000 yr (EPICA, 2004). The first cores showed regular oscillation of atmospheric CO_2 over the well-known 100,000 yr glacial/interglacial cycle, with minima and maxima of ~190 and 290 μatm. For the recent 740,000 yr ice core, 8 complete glacial/interglacial cycles were shown (EPICA, 2004). Its air bubbles record has not yet been completely analyzed, but preliminary CO_2 results thus far confirm the oscillations and minima/maxima of the previous cores. The regular CO_2 oscillations are correlating with the temperature record as derived from stable isotope signals in the ice. This shows a minimum local temperature at the Vostok drilling site which is ~6-7 $^{\circ}$C below the interglacial or "warm" periods like the modern Holocene interglacial era.

Summarizing the above, the atmospheric CO_2 value of today (~375 μatm) is ~100 μatm higher than the past 10,000 yr Holocene. This rise is the same magnitude (~100 μatm), but beyond, the regular oscillation between 190 and 290 μatm over the past >420,000 yr (Petit et al., 1999). Latter oscillation co-varying with a ~6-7 $^{\circ}$C warming and cooling, there is concern that the current 100 μatm excess CO_2 will give rise to an excessive global warming of similar magnitude because of the anthropogenic enhancement of the greenhouse effect.

Currently we know that several other greenhouse gases also are increasing due to activity of mankind (CH_4, N_2O, CCl_3F and CCl_2F_2). Because of the much more important global warming effect of CO_2 compared to other increasing greenhouse gases, many investigations have been focused on the CO_2 in context of the global carbon cycle.

2. Ocean Carbon Cycle

2.1 Main reservoirs of the Global Carbon Cycle

Towards unravelling the fate of the anthropogenic CO_2 and related global warming, it is important to identify the major reservoirs involved in the natural global carbon cycle. The data presented in Table 1, mainly focus on the oceanic reservoirs and are based on the review articles by Gruber et al. (2004) and Sabine et al. (2004b).

Table 1: *Relevant reservoirs for the global carbon cycle in Peta grams of Carbon (Pg C) (1 Pg C = 1 Gt C = 10^{15} g C) for the 1980s and 1990s based on Gruber et al. (2004) and Sabine et al. (2004b). Inventories (Pg C) of DIC = Dissolved Inorganic Carbon; DOC = Dissolved Organic Carbon and POC = Particulate Organic Carbon.*

Reservoir		Pg C
Atmosphere		751
Ocean	Surface waters	915 DIC + 3 POC + 25 DOC
	Deep and intermediate waters	37195 DIC + 700 DOC
Terrestrial biosphere	Soils	3150
	Plants	650
Lithosphere	Limestone	60×10^6
	Organic carbon	15×10^6
	Recoverable fossil fuels	4×10^3

The sediment reservoirs of both limestone and organic carbon are by far the largest carbon reservoirs but on a time-scale of 100 years these carbon reservoirs are not expected to react to an additional input of atmospheric CO_2. The actual atmospheric content of 751 PgC comprises a natural background component as well as an increasing anthropogenic component. Latter is due to the airborne fraction (about 60%) of the emissions by mankind in past 200 years through net deforestation, the burning of fossil fuels and cement making (see below section 3). Among the "reactive" carbon reservoirs, the deep ocean is the largest and holds about 50 times more carbon than the atmosphere. Some 98% of this carbon in seawater is in the pool of dissolved inorganic carbon (DIC), this pool is also increasing, because part (~40%) of anthropogenic CO_2 emissions into the air is absorbed by the ocean.

2.2 Chemistry of the Dissolved Inorganic Carbon in seawater

In order to understand the role of the oceans in the carbon cycle, it is necessary to define the DIC pool in seawater. Here, based on the extensive descriptions by Skirrow, (1975); Millero (1995); DOE (1997); Zeebe and Wolf-Gladrow (2001), we define and summarize the relevant parameters of the inorganic carbon chemistry in seawater used in the different chapters of this thesis. For a recent and most detailed overview of the CO_2 system in seawater the reader should refer to Zeebe and Wolf-Gladrow (2001).
Exchange of the CO_2 gas occurs at the air-sea interface. The gaseous CO_2 reacts with the water to form the unstable carbonic acid (H_2CO_3), which further dissociates. Dissolved inorganic carbon, also called in literature total CO_2 (C_T, TCO_2) is the sum of the dissolved inorganic species in seawater:

$$DIC = [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (1\text{-}1)$$

where brackets represent total stoichiometric concentrations. Direct measurement of DIC is in molar units (μmol L^{-1}), then converted to molality (μmol kg^{-1} seawater) as to avoid density change of seawater with increasing depth (pressure) in seawater. The bicarbonate (HCO_3^-) ion constitutes about 90% of the overall DIC pool. The carbonate (CO_3^{2-}) ion is in the order of 9%, free carbon dioxide ($CO_2(aq)$) of 1% and carbonic acid of 0.001%. Since the concentration of H_2CO_3 is much smaller than that of $CO_2(aq)$, the sum of the two electrically neutral forms, carbonic acid, H_2CO_3, and aqueous carbon dioxide, $CO_2(aq)$, which are chemically not separable, is usually denoted by CO_2:

$$[CO_2] = [CO_2(aq)] + [H_2CO_3] \qquad (1\text{-}2)$$

Note that this notation will be used in the following equations. This gives the following relative proportions:

$$[CO_2] : [HCO_3^-] : [CO_3^{2-}] \approx 1 : \approx 90 : \approx 9 \qquad (1\text{-}3)$$

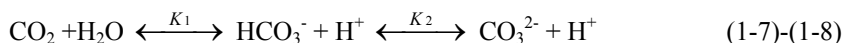In thermodynamic equilibrium with gaseous carbon dioxide ($CO_2(g)$)

$$CO_2(g) \longleftrightarrow [CO_2] \qquad (1\text{-}4)$$

the concentration of CO_2 in seawater is given by the Henry's law formula:

$$[CO_2] = K'_0 (S,T) \times fCO_2 \qquad (1\text{-}5)$$

where the solubility coefficient of CO_2 in seawater (K'_0) depends on temperature (T) and salinity (S) (Weiss, 1974) and fCO_2 (μatm) is the fugacity of CO_2. The partial pressure of CO_2 (pCO_2) can be used after correction for non-ideal behaviour of the gas mixture in the air with the fugacity coefficient γ using the following equation:

$$f\text{CO}_2 = \gamma \times p\text{CO}_2 \tag{1-6}.$$

The three inorganic carbon species in the seawater are in thermodynamic equilibrium according to the following equations:

$$\text{CO}_2 + \text{H}_2\text{O} \xleftrightarrow{\;K_1\;} \text{HCO}_3^- + \text{H}^+ \xleftrightarrow{\;K_2\;} \text{CO}_3^{2-} + \text{H}^+ \tag{1-7)-(1-8}$$

where K_1 and K_2 are the first and second dissociation constants of carbonic acid, respectively. These equilibria are the natural buffer for the pH of seawater, which therefore is very constant ≈ 8.1 in surface waters. For the description of the carbonate system in seawater, stoichiometric equilibrium constants, which are related to concentrations, are used:

$$K_1^* = [\text{HCO}_3^-][\text{H}^+]/[\text{CO}_2] \tag{1-9}$$

$$K_2^* = [\text{CO}_3^{2-}][\text{H}^+]/[[\text{HCO}_3^-] \tag{1-10}$$

Stoichiometric equilibrium constants depend on T, S and pressure (p) and are conventionally denoted by a star. These two constants only apply for the pH scale, the concentration scale and the composition of the ionic medium, for which they have been determined (see for details Millero (1995)).

The above description started with the CO_2 in air and therefore would in itself be adequate if equilibration and exchange with the air would have been the major source for DIC in seawater. In reality the major source is and always has been the continuous input of DIC into the oceans by rivers from the weathering of continental limestone:

$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \tag{1-11}$$

thus bringing both dissolved $[\text{Ca}^{2+}]$ and DIC into the oceans. This is one of several reasons for introduction of the Alkalinity concept, as required for a complete understanding and description of the DIC system in seawater.

2.3 Total Alkalinity

Total Alkalinity (TA) is an essential variable for the understanding of the inorganic carbon system in seawater. When adding together the electrical charges of the cations of the strong bases (cations of fully dissociated bases such as Na^+, K^+, Ca^{2+}, Mg^{2+}) in seawater with given salinity (here taken as salinity S = 35), we come to a charge equivalent of 605.0 mmol kg^{-1}. Subtracting the charge equivalent of the anions of strong acids (Cl^-, SO_4^{2-}, NO_3^-; = 602.8 mmol kg^{-1}), we come to a difference of 2.2 mmol kg^{-1}, which is then compensated by the charges of the anions of the weak acids such as CO_3^{2-},

HCO_3^- and as $B(OH)_4^-$ and a suite of other but very minor species in common seawater. Thus, TA is defined as the equivalents of all bases that can accept a proton to the carbonic acid endpoint (close to a pH of 4.5, see Dickson, (1981)). The proton acceptors are the bases formed from weak acids with dissociation constants $K \leq 10^{-4.5}$ ($pK \geq 4.5$) at 25ºC, and proton donors are acids with dissociation constant $K > 10^{-4.5}$ ($pK < 4.5$):

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] +$$

$$[NH_3] + [HS^-] + 2[S^{2-}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \qquad (1\text{-}12)$$

One might say that in seawater, DIC (equation 1-1) keeps track of the carbon and Total alkalinity (equation 1-12) keeps track of the charges. Bicarbonate and carbonate constitutes approximately 98% of the total alkalinity, the carbonate alkalinity (CA) is defined as:

$$CA = [HCO_3^-] + 2[CO_3^{2-}] \qquad (1\text{-}13)$$

In other words, when taking into account and correcting for both the borate and all the minor species in above (1-12) it is possible to derive, from the measured Total Alkalinity, the Carbonate Alkalinity (Millero, 1995). This is feasible because borate, sulphate and fluorine are proportional to salinity in ocean seawater, and the nutrients phosphate, silicate (and ammonia where present) can be measured independently.

2.4 Governance by set of four equations

The variables and equations introduced above are used for the quantitative description of the carbonate system in seawater. The mass balance for total inorganic carbon (equation 1-1), the two equilibrium conditions (equations 1-9 and 1-10) and the charge balance (1-13) together constitute four equations with six unknown variables $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$, DIC and CA. As a result, when 2 variables are known, the system is determined and all other components can be calculated. Theoretically, this goal could be achieved by measuring any two of the six quantities. In practice, only $[CO_2]$ (or in fact via fCO_2), DIC, $[H^+]$ (or in fact via pH) and TA can be measured directly. Obviously it is preferable to measure the concentration of a parameter directly, rather than to calculate it from two other observed variables. For this thesis, we measured the DIC and pCO_2 directly during our cruises, using the most robust techniques with the most satisfactory accuracy and precision for the determination of these two parameters (for more details see the method parts of the different chapters of the thesis). If a parameter can not be measured directly, the choice of the two variables used in the calculation, and the inherent accuracy of the constants K_1^* and K_2^*, together determine the precision of the obtained value (Millero, 1995).
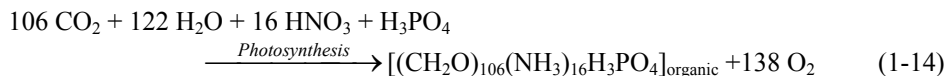
2.5 Inorganic Carbon Dynamics

Inorganic carbon dynamics depend on the combination of various processes such as biological activity, air-sea exchange, water mass mixing and temperature variations. These are superimposed on the very large background content of DIC and TA in seawater as part of the overall dissolved salt content or salinity in seawater. Here we briefly present the main processes driving the inorganic carbon system, which are discussed in this thesis.

2.5.1 Salinity

As mentioned, most of the DIC in seawater originates from the long time river input due to weathering of limestone on land. Therefore at any given place and time in the oceans, the absolute values of both DIC and TA are largely corresponding with the salinity of that seawater. Within the open oceans, the salinity is constituted from dissolved cations and anions in constant proportions, and varies only within a narrow (33-37) range. Therefore, in the central North Sea and the southern Ocean, we can focus on other change of DIC and TA, notably photosynthesis and respiration, which are of major interest for this thesis and described below. However some caution is required when in coastal seas approaching rivers (coastal areas of the North Sea) and enclosed seas, notably the Baltic Sea, or various fjords. Here one may encounter salinity well below 33. Moreover the major ion composition of any given river may deviate strongly from that of the open oceans, such that general relations of salinity with DIC and TA are not necessarily valid anymore in the region where river water is mixing with seawater. Such deviations may also be the case to lesser extent in the Baltic Sea or any given fjord.

2.5.2 Photosynthesis/Respiration

The most fundamental biological processes involved in the dynamics of dissolved inorganic carbon are photosynthesis and aerobic respiration:

$$106 \; CO_2 + 122 \; H_2O + 16 \; HNO_3 + H_3PO_4$$
$$\xrightarrow{\textit{Photosynthesis}} [(CH_2O)_{106}(NH_3)_{16}H_3PO_4]_{organic} + 138 \; O_2 \qquad (1\text{-}14)$$

Equation (1-14) corresponds to photosynthesis by algae, which on average, produces organic matter with Redfield ratios, i.e. C:N:P of 106:16:1 with concomitant production of 138 O_2. During photosynthesis, 106 moles of CO_2 are consumed, corresponding to a decrease of 106 moles of DIC. Moreover, the TA increases slightly by 16 moles or equivalent due to the consumption of strong anion nitrate (NO_3^-). The overall decrease of DIC and slight increase of TA lead to adjustments within the set of 4 equations (1-1, 1-9, 1-10, 1-13) and, as a result, the $[HCO_3^-]$ and $[CO_2]$ hence fCO_2 have decreased while the $[CO_3^{2-}]$ has increased. The ensuing change in ratio of $[HCO_3^-]$ and $[CO_3^{2-}]$ furthermore controls a concomitant decrease of $[H^+]$ hence increase of the pH (pH = - ^{10}log(H+)).

Eventually, the algal organic matter will, virtually completely, be degraded by aerobic respiration. This is the exact opposite of equation (1-14).

2.5.3 Formation/dissolution of CaCO₃

Formation and dissolution of calcium carbonate ($CaCO_3$) are also important processes controlling dissolved inorganic carbon dynamics. Calcification is the formation of carbonates that is biologically mediated from either planktonic (coccolithopores, foraminifera, pteropods…) or benthic (bivalves, corals, marine calcareous algae…) organisms. However, carbonates are present in various forms, calcite and aragonite. Calcite and aragonite are both calcium carbonate forms that differ in their crystallographic structure. The precipitation of $CaCO_3$ is given by the following equation:

$$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3 \tag{1-15}$$

From equation (1-15) and rearranging equations (1-7) and (1-8), we obtain the following equation:

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O \tag{1-16}$$
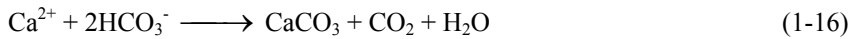
which is the inverse of the above dissolution reaction (1-11). According to the above equation (1-16), for each mole of $CaCO_3$ precipitated, one mole of CO_2 is produced. However, this CO_2 interacts through thermodynamic equilibria (equations 1-7 and 1-8) with the bases present in seawater (buffer effect), and this adjustment can be calculated exactly from the set of 4 equations, leading to the $[CO_2]$ increase being less than 1. The $[CO_2]$ increase is 0.6 mole for each mole of $CaCO_3$ precipitated, for "standard" seawater conditions. The ratio of CO_2 production to $CaCO_3$ precipitation is defined by the letter Ψ. Carbonate dissolution is controlled by the solubility product according to:

$$CaCO_3 \xleftrightarrow{K_s} Ca^{2+} + CO_3^{2-} \tag{1-17}$$

where K_s is the solubility product:

$$K_s = [Ca^{2+}]_{eq} \times [CO_3^{2-}]_{eq} \tag{1-18}$$

Equation (1-17) and (1-18) correspond to equilibrium conditions between the solid and dissolved inorganic carbon phases. The K_s is larger for calcite than for aragonite, and both dependent strongly on temperature and pressure. A convenient parameter is the degree of saturation (Ω) that is defined as the ratio of the product of the *in situ* concentrations of Ca^{2+} and CO_3^{2-} to the solubility product:

$$\Omega = ([Ca^{2+}]_{in\ situ} \times [CO_3^{2-}]_{in\ situ})/K_s \tag{1-19}$$

Oversaturation, saturation and undersaturation with respect to calcium carbonate are defined by $\Omega > 1$, $\Omega = 1$ and $\Omega < 1$. These two parameters (K_s and Ω) are defined here in order to discuss the impact of increasing atmospheric CO_2 on the inorganic carbon chemistry in the ocean (see below section 4.2).

2.6 Air-Sea gas exchange

In the preceding section we considered the main parameters of the carbonate system in seawater and several processes involved in the dynamics of this system. Another key issue of dissolved inorganic carbon dynamics is the exchange of CO_2 between the atmosphere and surface waters resulting from the gradient of CO_2 across the air-sea interface.

The rate of exchange of any given gas across the surface of the sea will be driven by both the concentration difference of the gas between air and seawater, and the existing turbulence at the air-sea interface. This turbulence is directly related with the sea-state where wind velocity (both present and in preceding hours and days), swell, surface slicks, bubbles by breaking waves all play a role. The unraveling of all these various forcing on sea state hence overall turbulence is an actively pursued, yet difficult, research topic (Zemmelink, 2003). In general it is agreed that wind velocity is the major forcing of sea state and turbulence, and this is adequate for this thesis.

Gas transport across the air-sea interface is dominated by turbulence but can be parameterized following Fick's first law of molecular diffusion:

$$F = -D \times \frac{\partial C}{\partial z} \qquad\qquad (1\text{-}20)$$

where the gas flux, F (mol m^{-2} s^{-1}), is given as the product of the molecular diffusion coefficient D (m^2 s^{-1}) and the concentration gradient ($\partial C / \partial z$, mol m^{-4}) across a boundary layer.

This equation has been adapted to the air-sea exchange of CO_2 according to:

$$F = k \times ([CO_2]_{sea} - [CO_2]_{air}) = \alpha \times k \times (pCO_{2sea} - pCO_{2air}) \qquad (1\text{-}21)$$

where F is the air-sea flux of CO_2 (mol m^{-2} s^{-1}), k (m s^{-1}) is the exchange coefficient or gas transfer velocity of CO_2, α is the solubility coefficient of CO_2 (mol atm^{-1} m^{-3}), $[CO_2]_{sea}$ is the concentration of CO_2 in the bulk of mixed layer and $[CO_2]_{air}$ is the concentration of CO_2 in the atmosphere above the air-sea interface (mol m^{-3}), and pCO_{2sea} and pCO_{2air} are the respective partial pressure (atm).

For CO_2, the resistance for the exchange across the air-sea interface is mainly in the aqueous phase through a micro-layer of water where the exchange depends on molecular diffusion (Liss, 1983). Besides molecular diffusivity (D), the exchange coefficient k depends, among other processes, on turbulence at the interface. To take this into account, the Schmidt number was introduced. The Schmidt number is the ratio of

transfer coefficients for momentum and mass, which are respectively the kinematic viscosity of water ν (m^2 s^{-1}) and the molecular diffusion coefficient D of the gas in seawater:

$$Sc = \frac{\nu}{D} \qquad\qquad (1\text{-}22)$$

The Schmidt number depends on the given gas, the salinity and temperature. The Schmidt number for CO_2 at 20ºC is 600 in freshwater and 660 in seawater (Liss and Merlivat, 1986). Three main conceptual models for air-sea exchange of CO_2 have been developed that differ in the way they take the Schmidt number into account.

In the *Film Model* (Whitman, 1923), air-sea exchange is only limited at the air-sea interface by molecular diffusion through a perceived stagnant micro-layer of water with a constant thickness for a given set of conditions. In this model, air-sea exchange is limited by molecular diffusion and the thickness of the micro-layer, so that the exchange coefficient is proportional to molecular diffusion:

$$k \sim D \leftrightarrow k \sim Sc^{-1} \qquad\qquad (1\text{-}23)$$

The *Surface Renewal Model* (Higbie, 1935; Danckwerts, 1951) is based on the film model, but the micro-layer is periodically replaced by fluid from the underlying bulk. Air-sea exchange is then limited by the rate of renewal of the micro-layer and K is given by:

$$k \sim D^{0.5} \leftrightarrow k \sim Sc^{-0.5} \qquad\qquad (1\text{-}24)$$

In the *Boundary Layer Model* (Deacon, 1977) for smooth or rigid water surfaces, the gas transfer velocity K is proportional to $Sc^{-2/3}$:

$$k \sim D^{2/3} \leftrightarrow k \sim Sc^{-2/3} \qquad\qquad (1\text{-}25)$$

Based on the above conceptual considerations, various field and laboratory experiments have been carried out to attempt to parameterize k as a function of wind speed. The interest of the development of theoretical and empirical relationships between k and wind speed is that air-sea fluxes can then be easily computed since wind speed is a relatively easy parameter to measure. The effect of other factors on air-sea exchange such as waves, air bubbles, surface films, heat exchange at the interface have also been investigated, although wind speed is recognised as the main forcing factor on k. Furthermore, the occurrence of some of these factors (*e.g.* waves, air bubbles) are more or less directly related to wind conditions. For an extensive review of the various field and laboratory experiments used for the parameterization of k as a function of wind speed (wind tunnel experiments, carbon balance method, the bomb ^{14}C produced method, the [222]Rn

deficiency method, the sulphur hexafluoride (SF_6) and [3]He deliberate tracer) see Broecker and Peng (1974); Liss (1983); Wanninkhof et al. (1985); Liss and Merlivat (1986); Frankignoulle (1988); Watson et al. (1991); Donelan and Wanninkhof (2002). Here we give the main k versus wind speed relationships obtained from the above experiments with a particular emphasis on those used in this thesis:

The Liss and Merlivat (1986) k-wind speed relationship has been deduced from deliberate tracer experiment with SF_6 at a lake (Wanninkhof et al., 1985) for wind speeds up to 13 m s^{-1} and from wind tunnel data (Broecker and Siems, 1984) at higher wind speeds. Three wind speed regimes are distinguished: a smooth surface regime (1-26), a rough surface regime (1-27) and a breaking wave regime (1-28) with the gas transfer velocity k (cm h^{-1}) and wind speed u (m s^{-1}) at a height of 10 m (Liss and Merlivat, 1986):

$$k = 0.17u \times (Sc/600)^{-2/3} \qquad u \leq 3.6 \qquad\qquad (1\text{-}26)$$

$$k = 2.85u - 9.65 \times (Sc/600)^{-0.5} \qquad 3.6 \leq u \leq 13 \qquad\qquad (1\text{-}27)$$

$$k = 5.9u - 49.3 \times (Sc/600)^{-0.5} \qquad u > 13 \qquad\qquad (1\text{-}28)$$

For the *Wanninkhof (1992) k-wind speed relationship,* Wanninkhof proposed that gas exchange shows a non linear dependence of wind speed. As a result k determined from a particular average wind speed will depend on the wind speed variability during the measurement interval. Because of the disproportionate influence of higher wind speeds on gas exchange, estimates of k over long periods with variable winds, will be somewhat higher than corresponding estimates over short time scales with steady winds. Using the ^{14}C data from Broecker et al. (1985) and Cember (1989), Wanninkhof derived the following relationship for long term averages of wind speed

$$k = 0.39u_{av}^2 \times (Sc/660)^{-0.5} \qquad\qquad (1\text{-}29)$$

where u_{av} is the long term average wind velocity at ten meter elevation. For short term, steady winds, (derived from spot measurements by ship borne anemometers and wind speeds inferred from scatterometers and radiometers) Wanninkhof suggested

$$k = 0.31u^2 \times (Sc/660)^{-0.5} \qquad\qquad (1\text{-}30)$$

The *Wanninkhof and McGillis (1999) k-wind speed relationship* is based on the results from SF_6 and [3]He tracer experiment in the north Atlantic (for winds up to 14.5 m s^{-1}) that were cross-checked with the global ^{14}C inventory in the ocean (Broecker et al., 1985). Wanninkhof and McGillis (1999) propose two formulations for short-term (1-31) and long term (1-32) wind speeds:

$$k = 0.0283u^3 \times (Sc/660)^{-0.5} \qquad\qquad (1\text{-}31)$$

$$k_{av} = [1.09u_{av} - 0.333u_{av}^2 + 0.078u_{av}^3] (Sc/660)^{-0.5} \qquad (1\text{-}32)$$

where k and k_{av} are the exchange coefficients (cm h^{-1}) for respectively the short-term and long average of wind speed measured at 10 meters height.

Finally, another *k-wind speed relationship by Nightingale et al. (2000)* found a quadratic dependence between air-sea gas exchange rates obtained from deliberate tracer experiments in the southern North Sea:

$$k = (0.222u^2 + 0.333u) \times (Sc/660)^{-0.5} \qquad (1\text{-}33)$$

The k-wind relationships are so far the only available parameterizations for the CO_2 exchange coefficient. No consensus has yet been achieved and the various relationships give fairly different k values, in particular at high wind speeds. Thus, in this thesis, we applied the various most widely used k-wind speed relationships mentioned above to provide a range of computed air-sea fluxes of CO_2.

3. Global anthropogenic CO_2 budgets and uptake by the Oceans

Having described the inorganic carbon chemistry and the air-sea exchange at the air-sea interface, we can now consider the role and the response of the ocean in the context of the increasing atmospheric CO_2. The increase of atmospheric CO_2 accurately measured by Keeling and others, is much less than the annual emissions from fossil fuel burning. These emissions also are known fairly accurately from the annual production statistics of the petroleum and natural gas companies, and coal mining. Similarly, the emissions due to cement production can be assessed rather precisely. However, the emissions due to land use change (notably deforestation as well as restoration of forests) are very difficult to quantify directly.

Only about half of the anthropogenically emitted CO_2 remains in the atmosphere. The atmosphere is in contact with two major carbon reservoirs: terrestrial systems and the oceans. These two reservoirs are the two most likely candidates for present-day storage of the remainder of the emitted CO_2. The rate of the net oceanic uptake of CO_2 is primarily determined by the physico-chemical equilibria of the inorganic carbon system in seawater and the renewal times of surface water, rather than by the air-sea exchange of CO_2. Large spatial and temporal variability of the air-sea exchange of CO_2 has complicated estimates of net oceanic uptake of CO_2 from direct observations. Based on such observations, Takahashi et al. (2002) estimated an ocean uptake of 2.2 Pg C yr^{-1}, applying the Wanninkhof (1992) relationship mentioned above, for a reference year of 1995.

Several independent estimates of the net oceanic uptake of CO_2 exist. During the 1970's, an extensive dataset for DIC was collected during GEOSECS (Geochemical Ocean Sections Study) and allowed the first estimates of the CO_2 anthropogenic in the ocean based on tracer separation technique (Brewer, 1978; Chen and Millero, 1979). However, it took until the 1990's before the oceanic measurement of DIC and pCO_2 were accurate enough to refine the approach for such estimates (Gruber, 1996). The large international projects such as the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS) as well as many national programs have been devoted to understand and asses the ocean's role in the global carbon cycle. Thus, the large amount of now very accurate data for DIC and pCO_2 collected in the ocean during the different expeditions of the these programs allowed the scientific community to constrain, with improved accuracy, the oceanic uptake of CO_2. Based on a separation tracer concept applied to the accurate JGOFS/WOCE Ocean CO_2 survey, Sabine et al. (2004a) calculated the latest estimate of the anthropogenic CO_2 inventory of the world oceans (Table 2). Since the onset of the industrial revolution (~1800) until ~1994 the oceans have accumulated an estimated 48% of CO_2 emissions from fossil fuel burning and cement production. Over the final 20 years of the century this ocean uptake was a third of the previous 200 years, but relatively less at 31% of the emissions. By absorbing 31-48% of fossil fuel emissions, the oceans have slowed down the atmospheric CO_2 increase accordingly.

Table 2: *Anthropogenic CO_2 budget for the Anthropocene (1800 to 1994) and its most recent decades 1980-1999 from Sabine et al. (2004a).*

	CO_2 Sources and Sinks	1800-1994	1980-1999
	[Pg C] = [Petagram C] = [10^{15} gram Carbon]	[Pg C]	[Pg C]
	Constrained sources and sinks:		
(1)	Emissions from fossil fuel and cement production	244 ± 20	117 ± 5
(2)	Storage in the atmosphere	-165 ± 4	-65 ± 1
(3)	Uptake and storage in the oceans	-118 ± 19	-37 ± 8
	Inferred net terrestrial balance:		
(4)	Net terrestrial balance = [-(1) - (2) - (3)]	39 ± 28	-15 ± 9

4. Global change and change in the ocean

In this section, we relate the increase of pCO_2 and DIC observed in the atmosphere and the ocean, respectively, to the observed and predicted changes in these two reservoirs. A review of predictive models of climate change and of the biological and chemical changes in the ocean is clearly out of the scope of the present work, however, it is interesting to outline a few elements to emphasize the relevance of studying and improving our understanding of the global carbon cycle. Moreover, mankind and the planet have risen well outside the CO_2 versus temperature 'calibration' of past >420,000 yr, which means the CO_2-temperature correlation of the past is, on its own, not necessarily valid for the future and global climate change take place in unpredictable proportions.

4.1 Climate Change

Recently, the Intergovernmental Panel on climate Change (IPCC) reported an observed global warming over the past century (IPCC, 2001). While recognizing the complexity of the climate system, the most straightforward, hence most acceptable explanation of this observed warming is due to the rise of CO_2 in the atmosphere. This is consistent with the most recent climate models, which, when taking into account all other variations (solar cycle, volcanism, etc.), cannot reproduce the observed warming trend, unless also taking into account the anthropogenic enhancement of the natural CO_2-greenhouse mechanism by the rising CO_2 in the atmosphere (see http://www.acia.uaf.edu/). Climate models predict the most rapid global warming at high latitudes, notably in the Arctic (Hassol, 2004). The recent Arctic Climate Impact Assessment (ACIA) predicts a temperature rise of ~5-7 ^{o}C in 2100 in the Arctic, when the CO_2 would have risen well over 800 µatm (see http://www.acia.uaf.edu/). Arrhenius also foresaw this, one century ago: "A simple calculation shows that the temperature in the Arctic regions would rise about 8°C to 9°C, if the carbonic acid increased to 2.5 or 3 times its present value." Using the atmospheric CO_2 value of 296 µatm in 1896, one arrives at 740-880 µatm to achieve the 8-9°C (Arrhenius, 1896).

The predictions by Arrhenius (1896) and ACIA in 2004, are major reasons for caution for the possibility of irreversible climate changes due to the global warming. Climate change over the past ~30 years has produced numerous shifts in the distribution and abundance of species and has been directly related to increasing extinction risk of several species (Thomas et al., 2004).

4.2 Change in the ocean

While contributing to about 55% of the anthropogenic enhancement of the greenhouse effect (Mackenzie, 1998), the increasing atmospheric CO_2 content has also been related to major changes in chemical and biological processes in the ocean. Although time series measurement of DIC for the ocean do not cover periods as long as for the atmosphere, increasing DIC content of seawater was reported, notably at the BATS station in the western North Atlantic (Bates et al., 2002) and at station ALOHA in the subtropical North Pacific Ocean (Keeling et al., 2004). These recently measured increases are consistent with long known physical-chemical predictions by Revelle and Suess (1957) and others. General circulation models as cited and summarized by the IPCC, indicate that surface water DIC could probably increase by 12% by the end of the century when the atmospheric CO_2 level will be over 800 ppm. The carbonate ion concentration would then decrease by almost 60% (Brewer, 1997) because of the shift in above chemical equilibria (1-4, 1-7, 1-8) of the DIC pool, which can be summarized as follows:

$$[CO_2] + [CO_3^{2-}] + H_2O \rightarrow 2[HCO_3^-] \quad\quad\quad (1\text{-}34)$$

The corresponding pH drop would be about 0.4 pH units in surface waters (Caldeira and Wickett, 2003). Moreover, the actual invasion of CO_2 in the ocean has a direct impact on the horizon depth of the degree of saturation of seawater with respect to aragonite and calcite (Ω) (Feely et al., 2004).

Because the upper ocean is supersaturated with respect to all phases of $CaCO_3$, the carbonate chemistry was not previously considered as a limiting factor in biogenic calcification. However, more recently it was shown that the lesser degree of supersaturation slows down the rate of calcification in corals and coralline macroalgae (Gattuso et al., 1998a; Langdon et al., 2000; Langdon et al., 2003). In other words, at lower ambient $[CO_3^{2-}]$, the rate of bio-calcification appears to decrease accordingly.

The majority of marine calcification occurs in planktonic organisms: bio-calcification is virtually the only route, spontaneous abiotic precipitation of $CaCO_3$ is deemed to be exceptional, if occurring at all. The formation of these calcareous skeletons by marine planktonic organisms and their subsequent sinking to depth generates a continuous rain of calcium-carbonate to the deep ocean and underlying sediments. This is important in regulating marine carbon cycling and ocean-atmosphere CO_2 exchange. Here, the concept of rain rate ratio of sinking organic carbon versus inorganic (but biogenic) $CaCO_3$ is known to be very crucial in ocean carbon cycle simulation models of past, present and future oceans (Heinze et al., 1991; Zeebe and Wolf-Gladrow, 2001). It was also shown that the present invasion of CO_2 in the ocean reduced the calcite production of dominant marine calcifying phytoplankton species, thus slowing down the production of calcium carbonate in the surface ocean. This corresponds to a shift of equation (1-16) to the left and therefore constitutes a negative feedback of the increasing atmospheric CO_2 content (Riebesell et al., 2000; Zondervan et al., 2001) that would result in a diminution of the release of CO_2 from the ocean to the atmosphere between 6 an 32 PgC for the period between 1950 and 2100 (Riebesell et al., 2000). However, Armstrong et al. (2002) have derived that a downward settling flux of organic carbon is strongly coupled with the settling flux of $CaCO_3$. This "ballast effect" of $CaCO_3$ enhancing a downward flux of organic carbon may decrease, due to the diminishing production of calcite shells, such that the efficiency of the biological pump mentioned in the next section, will overall decrease as well. Thus, by less "ballast", there is a reducing of the CO_2 uptake capacity of the ocean, this by definition constituting a positive feedback of the rise of atmospheric CO_2. In other words, bio-calcification has opposing effects, chemical release of CO_2 versus carbon settling by the physical ballast, and the overall net impact on the CO_2 budget varies with subtle changes in each of these processes (Buitenhuis et al., 2001). Moreover, Tortell et al. (2002) suggested that increasing CO_2 concentrations could potentially influence competition among marine phytoplankton taxa and affect oceanic nutrient cycling.

These few examples, among others, underline the potential and poorly understood feedbacks of anthropogenic CO_2 on our climate and the chemistry and biology of the ocean. These feedbacks particularly affect the biological pump which is defined in the next section. Thus, it is of particular importance to understand the process that control this biological pump for the uptake of CO_2, in particular in regions where the uptake of CO_2 has not yet been entirely constrained (i.e the coastal seas), or where this biological pump could

be stimulated (Southern Ocean). This thesis aims at improving our knowledge and understanding of this biological pump in these two key regions.

5. Mechanism of the oceanic CO_2 pump

The net uptake of anthropogenic CO_2 takes place via two well known mechanisms: the so-called "physical pump" and the "biological pump". More recently, the "continental shelf pump", which constitutes a specific case of the biological pump has been defined. Here we briefly describe these three mechanisms for the oceanic pump of CO_2, with particular emphasis on the latter two, which are particularly investigated in the different chapters of this thesis.

5.1 The physical pump

In the North Atlantic, north of Iceland, the surface water cools down during the northern hemisphere winter. As a result it contracts, its density increases, and once the density is higher than that of the deeper water layers, the surface water sinks to greater depths. When sinking it takes along all its dissolved substances, thus dissolved CO_2. The same processes occur in the Weddell Sea during austral winter. The process of deep water formation has taken place for a very long time and the deep water has entered into the deep Indian and Pacific Oceans, where it arrives ~ 1000 years or more after it has left the surface in Arctic or Antarctic winter. Due to the higher atmospheric CO_2, the polar winter waters are nowadays taking up some more CO_2 than before industrial times, by this extra CO_2 driving the physical pump for net uptake of anthropogenic CO_2.

In temperate and tropical regions, the transfer of anthropogenic CO_2 into the deep ocean is hindered by the thermocline, acting as a barrier for mixing between the surface ocean and the deep ocean. Nevertheless, some anthropogenic CO_2 has entered and continues to enter the surface waters, and is slowly mixed down into the deep oceans. At global scale this is much less than the CO_2 uptake by above deep water formation, nevertheless it also contributes to the worldwide physical pump.

Since CO_2 has a large natural background and biogeochemical cycling, the physical CO_2 pump is not as immediately discernible as the invasion of truly anthropogenic tracers, such as the Chlorofluorocarbons (CFC's), or the excessive radioactive tritium (^{3}H) introduced by atomic bomb testing. The invasion of CFC's and ^{3}H into the oceans is a striking analogue of the physical CO_2 pump, and indeed used to quantify the latter.

5.2 The Biological pump

The natural biological pump was described, in essence, with the forward and backward reactions of equation (1-14). Before the industrial revolution, this presumably was in balance, i.e when averaging out the biological pump over one year and all oceans regions, the net exchange of CO_2 with the atmosphere due to the natural biological pump is assumed to be zero. With rising CO_2 levels, or by iron fertilization, this biological pump could be stimulated, i.e the overall biological pump gets stronger, and the net increase would be the "extra" biological pump bringing down "extra" CO_2. The iron fertilizations of High Nutrients Low Chlorophyll (HNLC) regions as a stimulus for the biological pump of CO_2, is based on the hypothesis that low concentrations of iron in these three vast oceanic regions (the Southern Ocean, the North Pacific and the Equatorial Pacific), limit the phytoplankton growth and therefore the biological pump of CO_2 (Martin and Fitzwater, 1988. Martin (1990), and more recently Markels and Barber (2001), suggested that large-scale iron fertilization of the HNLC regions would remove CO_2 from the atmosphere and would sequester it into the deep ocean. However, other parameters such as depth of the Wind Mixed Layer (WML) that induces light limitation, are deemed to be mostly responsible for the limited phytoplankton growth in HNLC regions, and might be an obstacle for the efficiency of such fertilization in HNLC regions (De Baar et al., 2005). Moreover the magnitude and duration of carbon storage remain uncertain and difficult to quantify (Gnanadesikan et al., 2003). In chapters 6 and 7 of this thesis, we will examine the potential of the stimulation of the phytoplankton growth in the Southern Ocean on the uptake of CO_2 during an iron fertilization experiment carried out during austral spring.

5.3 The Continental shelf pump

The "continental shelf pump" (Tsunogai et al., 1999) consists of a biological uptake of CO_2 in the coastal regions, which is then transported and stored for a longer period in the deeper layer of the open ocean. This continental shelf pump is of particular importance since the various assessments of the oceanic CO_2 sink (Sarmiento et al., 2000; Gruber and Keeling, 2001; IPCC, 2001; Orr et al., 2001; Thomas et al., 2001; Sarmiento and Gruber, 2002; Takahashi et al., 2002; Sabine et al., 2004a) do not take into account these fluxes in the coastal zone. Coastal and marginal seas play a key role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric reservoirs (Walsh, 1991; Wollast, 1998; Andersson and Mackenzie, 2004). They occupy only 7% of the global ocean surface area but house 10-30% of the global marine production (Gattuso et al., 1998b). Moreover, the net biological community production in coastal margins, which is related to the magnitude of the CO_2 air-sea fluxes, varies from net autotrophic to net heterotrophic (Smith and Hollibaugh, 1993; Gattuso et al., 1998b; Andersson and Mackenzie, 2004; Mackenzie et al., 2004). It is therefore essential to acquire complete field datasets for DIC and pCO_2 in various coastal regions of the world, in order to quantify the overall CO_2 air-sea fluxes of these regions and the processes driving the continental shelf pump of CO_2.

In chapters 2, 3, 4 and 5 of this thesis we will test the hypothesis of a continental shelf pump of CO_2 in the North Sea and assess the mechanisms involved in this pump.

6. This thesis

6.1 Objectives

This PhD thesis was carried out in the context of increasing atmospheric CO_2 observed since the beginning of the industrial revolution, which is closely related to the concomitant CO_2 uptake by the ocean, with two major objectives: 1) To quantify this uptake by coastal seas with a case study in the North Sea 2) To assess the response of the biological pump of CO_2 to an *in-situ* iron fertilization in the Southern Ocean during austral spring.

The continental shelf pump of CO_2 in the North Sea

The work was carried out in the framework of the CANOBA program with the following objectives:
The acquisition of a complete new field dataset for the CO_2 system and related parameters for the North Sea based on four consecutive cruises, of one month each, covering every season of the year, between 2001 and 2002. The determination of the air-sea fluxes of CO_2 in the North Sea as part of the overall assessment of the CO_2 air-sea fluxes in the coastal zone. The assessment of the biological, chemical and physical processes controlling the inorganic carbon system in the North Sea. The elaboration of a comprehensive budget for carbon in the North Sea based on the dataset acquired during this thesis combined with results from precedent investigations.

Fe fertilization in the Southern Ocean

The work was carried out as part of the CARUSO program with the following objectives:
To follow the evolution of an *in-situ* iron enriched patch during a two month cruise under contrasting meteorological conditions. To determine the factors influencing the inorganic carbon uptake throughout the experiment. To relate the observed changes for inorganic carbon to the observed changes in other inorganic nutrient. To assess the potential net carbon uptake of such iron fertilization.

6.2 Outline

The chapters of this thesis have either been published in (2, 3, 5, 6, 7) or are in revision for (4) peer-reviewed journals. We kept the content of each chapters in the particular format of the journal where the article was published. Therefore, for each chapter, here a more detailed introduction completes this general introduction and describes the particular context and objectives of each article. The analytical method used is detailed in each "method" section of each chapter and the results are presented and discussed. Chapters 2, 3, 4 and 5 are focused on the continental shelf pump of CO_2 in the North Sea, whereas chapters 6 and 7 discuss the results from the EisenEx iron enrichment experiment in the Southern Ocean.

Chapter 2 focuses on the late summer distribution of the inorganic carbon in the North sea, highlighting the strong difference between the southern ($\approx$ south of 54ºN) and the northern North Sea (54ºN-61ºN). The different processes driving the DIC and pCO_2 variations at that time of the year are assessed. The fluxes of CO_2 in both regions as well as in the whole North Sea are computed and a mechanism driving theses fluxes for that period of the year is proposed.

In **chapter 3**, based on the very large amount of continuous pCO_2 data collected during the four cruises of our CANOBA program and the wind speeds acquired during the period of observations, we compute the annual CO_2 air-sea exchange for different areas of the North Sea and the whole North Sea. We compare the results obtained with the different k-wind speed formulations given in section 2.5 and underline the importance of the late summer situation discussed in **chapter 2** for the annual CO_2 air-sea fluxes. The computed CO_2 air-sea fluxes are compared to the fluxes calculated in other coastal regions and to the latest estimates of the net oceanic uptake of CO_2, in order to highlight the significance of the coastal regions in the overall oceanic uptake of CO_2.

In **chapter 4**, we use the seasonally resolved dataset of DIC, pCO_2 and inorganic nutrients to assess the abiotic and biological processes in the whole water column of the North Sea throughout the year. The North Sea's regional variability is accounted for by using the 15-boxes scheme as proposed by the International Council for the Extrapolation of the Seas (ICES) (ICES, 1983). We use the changes in DIC due to biological processes calculated for different regions of the North Sea to assess the Net Community Production (NCP) based on inorganic carbon. This is compared to the NCP based on inorganic nutrients and previous calculation. The NCP based on inorganic carbon for every region of the North Sea is used to compute the overall NCP for the whole North Sea, thus taking into account the internal spatial variability for this parameter. The NCP estimate allows the determination of the trophic state of the North Sea, which can then be related to the annual CO_2 air-sea fluxes calculated in **chapter 3**.

In **chapter 5**, a complete carbon budget is established for the whole North Sea, based on the data collected during our cruises and previous investigations. A gross and a net budget are established in order to identify the key players of the budget. Moreover, inorganic and organic carbon budgets have been established to quantify the internal sources of dissolved inorganic carbon. Finally, this one-box carbon budget approach is use to assess the trophic sate of a larger area than in **chapter 4**.

Chapter 6 presents the evolution of DIC, in relation with the inorganic nutrients changes observed, during the course of the EisenEx iron enrichment experiment in the southern Ocean. The variations of the wind mixed layer under contrasting meteorological conditions during such experiment is related to the evolution of the uptake of CO_2. Finally, a preliminary budget of the net uptake of CO_2, based on DIC measurements is elaborated.

In **chapter 7**, a more comprehensive budget of the net uptake of CO_2, based on the fCO_2 data is established using the finalized data set of the Fe-enriched patch tracers. The same method as for the precedent iron enrichment experiment carried out in the southern Ocean (SOIREE) is applied in order to compare the net CO_2 uptake estimates in both experiments.

Finally, in **chapter 8**, results from the preceding chapters are synthesized and the implications of the research presented in this thesis are discussed in a wider context.

References

Andersson, A.J. and Mackenzie, F.T., 2004. Shallow-water oceans: a source or sink of atmospheric CO_2. Frontiers in Ecology and the Environment, 2(7): 348-353.

Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S. and Wakeham, S.G., 2002. A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Research II, 49: 219-236.

Arrhenius, S., 1896. On the influence of carbonic acid in the air upon the temperature on the ground. Philosophical Magazine, 41: 237-276.

Barnola, J.-M., Raynaud, D., Korotkevich, Y.S. and Lorius, C., 1987. Vostock ice cores provides 160,000-year record of atmospheric CO_2. Nature, 329: 402-408.

Bates, N.R., Pequignet, A.C., Johnson, R.J. and Gruber, N., 2002. A short-term sink for atmospheric CO_2 in subtropical mode water of the North Atlantic Ocean. Nature, 420: 489-493.

Brewer, P.G., 1978. Direct measurement of the oceanic CO_2 increase. Geophysical Research Letters, 5: 997-1000.

Brewer, P.G., 1997. Ocean chemistry of the fossil fuel CO_2 signal: The haline signal of "business as usual". Geophysical Research Letters, 24(11): 1367-1369.

Broecker, W.S. and Peng, T.-H., 1974. Gas exchange rates between air and sea. Tellus, 26: 21-35.

Broecker, W.S., Peng, T.-H., Ostlund, G. and Stuiver, M., 1985. The distribution of bomb radiocarbon in the ocean. Journal of Geophysical Research, 90: 6953-6970.

Broecker, W.S. and Siems, W., 1984. The role of bubbles for gas transfer from water to air at higher windspeeds: experiments in wind-wave facility in Hambourg. In: W. Brustaert and G.H. Jirka (Editors), Gas transfer at water surfaces. Reidel Publishing compagny, Dordrecht, pp. 229-238.

Buitenhuis, E.T., van der Wal, P. and De Baar, H.J.W., 2001. Blooms of *Emiliana huxleyi* are Sinks of atmospheric Carbon Dioxide: a field and Mesocosm Study derived Simulation. Global Biogeochemical Cycles, 15(3): 577-587.

Caldeira, K. and Wickett, M.E., 2003. Anthropogenic carbon and ocean pH. Nature, 425: 365.

Cember, R., 1989. Bomb radiocarbon in the Red Sea: a medium scale gas exchange experiment. Journal of Geophysical Research, 94: 2111-2123.

Chen, C.-T.A. and Millero, F.J., 1979. Gradual increase of oceanic CO_2. Nature, 373: 412-415.

Danckwerts, P.V., 1951. Significance of liquid-film coefficients in gas absorption. Industrial Engineering Chemistry, 43: 1460-1467.

De Baar, H.J.W., Boyd, P.W., Coale, K.H., Landry, M.R., Tsuda, A., Assmy, P., Bakker, D.C.E., Bozec, Y., Barber, R.T., Brzezinski, M.A., Buesseler, K.O., Boyé, M., Croot, P.L., Gervais, F., Gorbunov, M.Y., Harrison, P.J., Hiscock, W.T., Laan, P., Lancelot, C., Levasseur, M., Marchetti, A., Millero, F.J., Nishioka, J., Nojiri, Y., van Oijen, T., Riebesell, U., Rijkenberg, M.J.A., Saito, H., Takeda, S., Timmermans, K.R. and Veldhuis, M.J.W., 2005. Synthesis of 8 Iron Fertilization Experiments:

from the Iron age in the Age of Enlightenment. Journal of Geophysical Research (Oceans), in press.

Deacon, E.L., 1977. Gas transfer to and across an air-water interface. Tellus, 29: 363-374.

Dickson, A.G., 1981. An eaxact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep-Sea Research I, 28: 609-623.

DOE, 1997. Handbook of methods for the analysis of the various parameters of the carbon system in seawater, version 2.11. In: A.G. Dickson and C. Goyet (Editors). ORNL/CDIAC 74.

Donelan, M.A. and Wanninkhof, R., 2002. Gas Transfer at Water surfaces-Concepts and Issues. In: M. Donelan, W.M. Drennan, E.S. Saltzman and R. Wanninkhof (Editors), Gas transfer at water surfaces. American Geophysical Union, Washington, pp. 1-10.

EPICA, 2004. Eight glacial cycles from an Antarctic ice core. Nature, 429: 623-628.

Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., kleypas, J., Fabry, V.J. and Millero, F.J., 2004. Impact of Antropogenic CO_2 on the $CaCO_3$ System in the Oceans. Science, 305: 362-366.

Frankignoulle, M., 1988. Field measurements of air-sea CO_2 exchange. Limnology and Oceanography, 33: 313-322.

Gammon, R.H., Sundquist, E.T. and Fraser, P.J., 1985. Hystory of carbon dioxide in the atmosphere. In: J.R. Trabalka (Editor), Atmospheric Carbon Dioxide and the Global Carbon Cycle. United States Department of Energy, Oak Ridge National Laboratory, Washington, DOE/ER-0239, pp. 25-62.

Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S. and Buddemeier, R.W., 1998a. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. Global and Planetary Change, 18: 37-46.

Gattuso, J.-P., Frankignoulle, M. and Wollast, R., 1998b. Carbon and carbonate metabolism in coastal aquatic ecosystems. Annual Reviews of Ecological Systems, 29: 405-434.

Gnanadesikan, A., Sarmiento, J.L. and Slater, R.D., 2003. Effects of patchy ocean fertilization on atmospheric carbon dioxide and biological production. Global Biogeochemical Cycles, 17(2): 1050, doi: 1029/2002GB001940.

Gruber, N., 1996. An improved methode for detecting anthropogenic CO_2 in the oceans. Global Biogeochemical Cycles, 10: 809-837.

Gruber, N., Freidlingstein, P., Field, C.B., Valentini, R., Heimann, M., Richey, J.E., Lankao, P.R., Schulze, E.-D. and Chen, C.-T.A., 2004. The Vulnerability of the Carbon Cycle in the 21st Century: An Assessment of Carbon-Climate-Human Interactions. In: C.B. Field and M.R. Raupach (Editors), The global carbon cycle: integrating human, climate and the natural world. SCOPE, ISSN, Washington, D.C., pp. 45-77.

Gruber, N. and Keeling, C.D., 2001. An improved estimate of the isotopic air-sea disequilibrium of CO_2: Implications for the oceanic uptake of anthropogenic CO_2. Geophysical Research Letters, 28(3): 555-558.

Hassol, S.J., 2004. Impacts of warming Arctic: Arctic Climate Impact Assessment. Cambridge University Press. http://www.acia.uaf.edu/

Heinze, C., Maier-Reimer, E. and Winn, K., 1991. Glacial pCO_2 reduction by the world ocean: Experiments with the Hambourg Carbon Cycle Model. Paleoceanography, 6: 395-430.

Higbie, R., 1935. The role of absorption of a pure gas into a still liquid during short periods of exposure. Transactions of the American Institute of Chemical Engineering, 35: 365-373.

ICES, 1983. Flushing times of the North Sea. ICES Cooperative Research Report. 123.

IPCC, 2001. The scientific basis. In: J.T. Houghton et al. (Editors), Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, New York, USA, pp. 881.

Keeling, C.D., 1960. The concentration and isotopic abundances of carbon doxide in the atmosphere. Tellus, 12: 200-203.

Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, W.G. and Roeloffzen, H., 1989. A three dimensional model of atmospheric CO_2 transport based on observed winds: Analysis of data. In: D.H. Peterson (Editor), Aspect of climate variability in the Pacific and the Western Americas. Geophysical monograph 55, pp. 165-236.

Keeling, C.D., Brix, H. and Gruber, N., 2004. Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii. Global Biogeochemical Cycles, 18(GB4006, doi:10.1029/2004GB002227).

Keeling, C.D. and Whorf, T.P., 1999. Atmospheric records from sites in the SIO air sampling network. In: T.A. Boden, D.P. Kaiser, R.J. Sepanski and F.W. Stoss (Editors), Trends: A compendium of data on global change, ORNL/CDIAC., Oak Redge, Tenessee, pp. 983.

Keeling, C.D. and Whorf, T.P., 2004. Atmospheric CO_2 records from sites in the SIO air sampling network., In Trends: A compendium of data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S Department of Energy, Oak Ridge, Tennessee, USA. http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm

Langdon, C., Broecker, W.S., Hammond, D.E., Glenn, E., Fitzsimmons, K., Nelson, S.G., Peng, T.-H., Hadjas, I. and Bonani, G., 2003. Effect of elevated CO_2 on the community of an experimental coral reef. Global Biogeochemical Cycles, 17(1): 1011, doi:10.1029/2002GB001941.

Langdon, C., Takahashi, T., Sweeney, C., Chipman, D.W., Goddard, J., Marubini, F., Aceves, H., Barnett, H. and Atkinson, M.J., 2000. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. Global Biogeochemical Cycles, 14(2): 639-654.

Liss, P.S., 1983. Gas transfer: experiments and geochemical implications. In: P.S. Liss and W.G.N. Slinn (Editors), Air-sea exchange of gases and particle. D. Reidel Publishing Compagny, pp. 241-298.

Liss, P.S. and Merlivat, L., 1986. Air-sea gas exchange rates: Introduction and synthesis. In: P. Buat-Ménard (Editor), The Role of Air-Sea Exchange in Geochemical Cycling. D. Reidel Publishing Company, pp. 113-127.

Mackenzie, F.T., 1998. Our Changing Planet. Prentice-Hall, Englewood Cliffs, New York, 486 pp.

Mackenzie, F.T., Lerman, A. and Andersson, A.J., 2004. Past and present of sediment and carbon biogeochemical cycling models. Biogeosciences, 1: 11-32.

Markels, M. and Barber, R.T., 2001. Sequestration of CO_2 by ocean fertilization. In: N.E.T. Laboratory (Editor), First National Conference on Carbon Sequestration.

Martin, J.-M., 1990. Glacial to interglacial CO_2 change: the iron hypothesis. Paleoceanography, 5: 1-13.

Martin, J.-M. and Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the northeast Pacific subarctic. Nature, 331: 341-343.

Millero, F.J., 1995. Thermodynamic of the carbon dioxide system in the oceans. Geochimica et Cosmochimica Acta, 59(4): 661-677.

Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J. and Upstill-Goddard, R.C., 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochemical Cycles, 14(1): 373-387.

Orr, J.C., Maier-Reimer, E., Mikolajewicz, U., Monfray, P., Sarmiento, J.L., Toggweiler, J.R., Taylor, N.K., Palmer, J., Gruber, N., Sabine, C.L., Le Quéré, C., Key, R.M. and Boutin, J., 2001. Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models. Global Biogeochemical Cycles, 15(1): 43-60.

Petit, J.R., Basile, I., Leruyet, A., Raynaud, D., Lorius, C., Jouzel, J., Stievenard, M., Lipenkov, V.Y., Barkov, N.I., Kudryashov, B.B., Davis, M., Saltzman, E. and Kotlyakov, V., 1997. Four climates cycle in Vostock ice core. Nature, 387: 359-360.

Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappelaz, J., Davis, M., Delaygue, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pépin, L., Ritz, C., Saltzman, E. and Stievenard, M., 1999. Climate and atmospheric history of the past 420,000 years from the Vostock ice core, Antarctica. Nature, 399: 429-436.

Revelle, R. and Suess, H.E., 1957. Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO_2 during the Past Decades. Tellus, 9: 18-27.

Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R.E. and Morel, F.M.M., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature, 407: 364-367.

Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, T. and Rios, A.F., 2004a. The Oceanic Sink for Anthropogenic CO_2. Science, 305: 367-371.

Sabine, C.L., Heimann, M., Artaxo, P., Bakker, D.C.E., Chen, C.-T.A., Field, C.B., Gruber, N., Le Quéré, C., Prinn, R.G., Richey, J.E., Lankao, P.R., Sathaye, J.A. and Valentini, R., 2004b. Current Status and Past Trends of the Global Carbon Cycles. In: C.B. Field and M.R. Raupach (Editors), The global carbon cycle: integrating human, climate and the natural world. SCOPE, ISSN, Washington, D.C, pp. 17-44.

Sarmiento, J.L. and Gruber, N., 2002. Sinks for anthropogenic carbon. Physics Today, 55(8): 30-36.

Sarmiento, J.L., Monfray, P., Maier-Reimer, E., Aumont, O., Murnane, R.J. and Orr, J.C., 2000. Sea-air CO_2 fluxes and carbon transport: A comparison of three ocean general circulation models. Global Biogeochemical Cycles, 14(4): 1267-1281.

Skirrow, G., 1975. The dissolved gases-carbon dioxide. In: J.P. Riley and G. Skirrow (Editors), Chemical Oceanography, 2, 2nd edition, Academic Press, pp. 1-92.

Smith, S.V. and Hollibaugh, J.T., 1993. Coastal metabolism and the ocean organic carbon balance. Reviews of Geophysics, 31(1): 75-89.

Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N.R., Wanninkhof, R., Feely, R.A., Sabine, C.L., Olafsson, J. and Nojiri, Y., 2002. Global sea –air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. Deep-Sea Research II, 49: 1601-1622.

Thomas, C.D., Cameron, A., Green, R.E., Bakkenes, M., Beaumont, L.J., Collingham, Y.C., Erasmus, B.F.N., de Siqueira, M.F., Grainger, A., Hannah, L., Hughes, L., Huntley, B., A.S., V.J., Midgley, G.F., Miles, L., Ortega-Huerta, M.A., Townsend-Peterson, A., Phillips, O.L. and Williams, S.E., 2004. Extinction Risk from climate change. Nature, 427: 145-148.

Thomas, H., England, M.H. and Ittekkot, V., 2001. An off-line 3D model of anthropogenic CO_2 uptake by the oceans. Geophysical Research Letters, 28(3): 547-550.

Tortell, P.D., DiTullio, G.R., Sigman, D.M. and Morel, F.M.M., 2002. CO_2 effects on taxonomic composition and nutrient utilization in an Equatorial Pacific phytoplankton assemblage. Marine Ecology Progress Series, 236: 37-43.

Tsunogai, S., Watanabe, S. and Sato, T., 1999. Is there a "continental shelf pump" for the absorption of atmospheric CO_2? Tellus, 51B: 701-712.

Walsh, J.J., 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. Nature, 350: 53-55.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research, 97(C5): 7373-7382.

Wanninkhof, R., Ledwell, J.J. and Broecker, W.S., 1985. Gas exchange wind speed relation measured with sulphur hexafluoride on a lake. Science, 227: 1224-1226.

Wanninkhof, R. and McGillis, W.R., 1999. A cubic relationship between air-sea CO_2 exchange and wind speed. Geophysical Research Letters, 26(13): 1889-1892.

Watson, A.J., Upstill-Goddard, R.C. and Liss, P.S., 1991. Air-sea gas exchange in rough and stormy seas measured by a dual tracer technique. Nature, 349: 145-147.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry, 2: 203-215.

Whitman, W.G., 1923. The two-film theory of gas absorption. Chemical Metallurgy Engineering, 29: 146-148.

Wollast, R., 1998. Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean. In: K.H. Brink and A.R. Robinson (Editors), The Sea. John Wiley & Sons, Inc., New York, pp. 213-252.

Zeebe, R.E. and Wolf-Gladrow, D.A., 2001. CO_2 in seawater: equilibrium, kinetics, isotopes, 65, Elsevier Oceanography Series, 346 pp.

Zemmelink, H.J., 2003. Dimethly Sulphide: Measuring emissions from the ocean to the atmosphere. Ph.D Thesis, Rijksuniversiteit Groningen, Groningen, 166 pp.

Zondervan, I., Zeebe, R.E., Rost, B. and Riebesell, U., 2001. Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO_2. Global Biogeochemical. Cycles, 15(2): 507-516.

Chapter 1