Fábio Lekecinskas Augusto

**An improvement on the gas transfer velocity model with application
to scatterometer data**

A thesis submitted to the Oceanographic
Institute of the University of São Paulo
in partial fulfillment of the requirements
for the degree of Doctor of Sciences in
Oceanography, with emphasis in Physical
Oceanography.

Advisor: Prof. Dr. Paulo S. Polito

São Paulo

2015

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Oceanographic Institute

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Resumo

O aumento da concentração de dióxido de carbono na atmosfera observado nas últimas décadas é responsável por alterações climáticas e ambientais em escala global. Uma das consequências desse aumento da concentração de gás carbônico é o aquecimento global. Outra consequência é a acidificação dos oceanos. Isto ocorre devido ao dióxido de carbono atravessar a interface ar-mar e se dissolver no oceano.

A quantidade de dióxido de carbono que atravessa a interface ar-mar é um dado não conhecido com precisão devido a esta quantidade depender de uma constante conhecida por velocidade de transferência do gás carbônico. Esta velocidade de transferência é normalmente uma parametrização do transporte turbulento do gás na interface oceano-atmosfera. Como o dado mais comum para essa parametrização é o vento à altura de 10 metros, muitos estudos foram desenvolvidos utilizando esta variável. No entanto, os resultados destas parametrizações possuem erros da ordem de 100%.

Este estudo desenvolveu uma metodologia para obter uma melhor estimativa da velocidade de transferência. Para isto, optou-se por relacionar esta variável à inclinação quadrática média (MSS) das ondas. Segundo a literatura científica recente, o MSS é uma variável mais relacionada à transferência gasosa do que o vento a 10 metros de altura.

Os resultados mostram que a inclinação quadrática média calculado com números de onda entre 40 e 50 radianos por metro possuem o menor erro no ajuste linear com os dados de velocidade de transferência. Este resultado indica uma mudança da dinâmica da interface nesse intervalo de número de onda. Com isso, um novo ajuste linear entre o MSS e a velocidade de transferência é sugerido como parametrização.

A aplicação desta nova parametrização a dados de satélite do tipo escaterômetro mostrou-se consistente quando comparado a um estudo recente relacionando a velocidade de transferência do gás carbônico diretamente a dados do satélite oceanográfico QuikSCAT.

Abstract

The increase of carbon dioxide in the atmosphere observed in recent decades is causing the acidification of the oceans besides the global warming. The amount of carbon dioxide that crosses the air-sea interface is not well known because this amount depends upon the partial pressure of carbon dioxide and the gas transfer velocity.

The gas transfer velocity is a variable based on Fick's Law of Diffusion and is normally parameterized as a function of wind velocity at the height of 10 meters. However, the result of this parameterization have errors greater than 100%. Newer parameterizations include the effects of temperature, friction velocity and the presence of surface waves.

Based on the simplest model of air-sea gas transfer model, the stagnant film theory, this study developed a methodology to improve the knowledge of the relation between the gas transfer velocity and the mean square slope. This variable accounts for the mean curvature of the waves in the surface. The data used was gathered within the scope of the DOGEE project in 2007. In that, a drifting buoy measured several parameters relative to the waves and the gas transfer velocity.

The results show that the mean square slope calculated with waves whose wavenumber is between 40 and 50 radians per meter has the lowest root mean square errors of the regression between the mean square slope and the gas transfer velocity. This result showed to be very consistent when applied to the QuikSCAT scatterometer data and compared to a recent published study.

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Glossary

ASIS	Air-Sea Interaction Spar Buoy
BTB	Bromothymol Blue
CCIW	Canada Centre for Inland Waters
CFT	Continuous Fourier Transform
DFT	Discrete Fourier Transform
DMS	Dimethylsulfide
DO	Dissolved Oxygen
DOGEE	Deep Ocean Gas Exchange Experiment
FFT	Fast Fourier Transform
FT	Fourier Transform
GMF	Geophysical Model Function
hPa	hectopascal
IFT	Inverse Fourier Transform
IO	Oceanographic Institute
MSLP	Mean Sea Level Pressure
MSS	Mean Square Slope
NASA	National Aeronautics and Space Administration
NOAA	National Oceanic and Atmospheric Administration
NRCS	Normalized Radar Cross-Section
NSCAT	NASA Scatterometer
NWRI	National Water Research Institute
PAR	Photosynthetically Active Radiation
PgC	Pentagram of Carbon
PSU	Practical Salinity Unity
QuikSCAT	Quick Scatterometer
SAGE	SOLAS Air-Sea Gas Exchange
SOLAS	Surface Ocean-Lower Atmosphere Study
SSH	Sea Surface Height
STD	Standard Deviation

SWH	Significant Wave Height
TKE	Turbulent Kinetic Energy
USP	University of São Paulo
WHOI	Woods Hole Oceanographic Institution

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1 Introduction

The increase in concentration of carbon dioxide (CO₂) observed in the atmosphere during the decade of 1960/1970 alerted scientists about the consequences to the environment. (KEELING, 1960) noted that the concentration of CO₂ measured at the Mauna Loa volcano at the island of Hawaii was increasing with time at an unprecedented rate. The monitoring of these values showed that in the Industrial Age the deployment of CO₂ had changed the atmosphere composition. Today, this difference in the concentration of CO₂ is about 80 PPM, raising from 320 PPM in 1965 to 400 PPM in 2013 (NOAA, 2015) and reaching an unprecedented level in Earth's history.

This new climate scenario was the background to the creation of the *Intergovernmental Panel on Climate Change* (IPCC). This organization is responsible to provide a comprehensive, objective, open and transparent understanding of the risk of human-induced climate change, its potential impacts and options for adaptation and mitigation. It's reports were developed using the most recent peer-reviewed papers from academic researchers about the state of the climate and alerted policy-makers to the impacts this event could have on a planetary scale.

The first consequence of the high concentration of CO₂ in the atmosphere is changing the planetary radiative energy budget. CO₂ is a trace gas (Table 1) and has the properties of absorbing long wave radiation in the infrared band. As the mean surface temperature of the Earth is 300 K, the maximum emission of infrared energy is precisely in the infrared band. The long-wave radiation outgoing from the Earth's surface and going to space is intercepted by the gas and re-emitted towards earth's surface again. This phenomenon is known as Greenhouse Effect. With increasing CO₂ concentration the Greenhouse effect becomes more pronounced and results in global warming and this subject is now present in academic researches as in popular television broadcasts.

The main sources of the atmospheric CO₂ are located at the surface. Volcanoes, rocks, and fossil fuel burning are located at low levels of the atmosphere and this fact contributes to the consequence about the increase of CO₂ in the troposphere that is ocean acidification (DONEY et al., 2009). Since the carbon dioxide has a molecular weight of 44 g mol⁻¹ and

Gas	Concentration (%)
N ₂	78.084
O ₂	20.946
Ar	0.9340
CO₂	0.04
Ne	0.0018
He	0.000524
CH₄	0.00018
Kr	0.000114
H ₂	0.000055

Table 1: Composition of air in percent by volume, at sea level at 15°C and 101325 Pa. Water vapor is not included because it has variable concentrations in the atmosphere. The bold letters indicate the greenhouse gases, except the water vapor (HAYNES, 2014).

dry air has a molecular weight of 28.97 g mol⁻¹, CO₂ released by man near ground level sinks in air relatively quickly rather than rising up to the upper atmosphere. This carbon dioxide stratifies from air and after sinking and stratifying, it tends to remain close to the ground and in contact with the oceans (MILLERO, 2013).

The CO₂ has low solubility in water, but once in the water, it changes the cycle of the carbonate in the ocean waters (DICKISON; SABINE; CHRISTIAN, 2007):

Equations 1a to 1d shows that CO₂ in seawater produces carbonic acid with direct consequences to biogeochemical ecosystem. One problem in changing the carbonate cycle is that it affects coral reefs and seashells that use carbonate in their exoskeleton. Another problem is that the ocean acts as a reservoir of CO₂, and may end up releasing the gas back to the atmosphere.

Although some studies discuss the global warming as a natural variability of planet Earth (JAWOROWSKI, 2007), caused by the solar variability (EDDY, 1976) or the natural

variability of water vapor in the atmosphere (MOLLER, 1963), most of the recent studies, e.g., Cook et al. (2013) pointed that anthropogenic emissions are the cause of this increase in temperature.

The general picture of the sources, sinks and effects of carbon dioxide gas has been indicated in the previous paragraphs. Some questions are open and are the subject of current investigation: How does the CO_2 crosses the boundary between the atmosphere and the ocean? What are the physical mechanisms responsible for this? How can we quantify the ocean acidification?

The answer to these questions has its roots on the global carbon cycle and in the phenomena that occur at the air-sea interface, such as surface waves, fluxes and near-surface turbulence. Section 1.1 will show the global carbon cycle in the atmosphere and the ocean, Section 1.2 briefly describes the conceptual models of the air-sea interface and Section 1.3 shows the parameterization already proposed for the CO_2 gas transfer velocity. Finally, Section 1.4 shows the recent studies of the gas transfer velocity inferred by satellites.

1.1 The Global Carbon Cycle

The importance of this study has its roots on the global carbon cycle. The CO_2 initially deployed into the atmosphere is advected by the winds and interacts with the vegetation, the soil and the oceans. The oceans play a major role in the exchange of gas, capturing 80 petagrams of carbon per year (PgC, $1 \text{ PgC} = 10^{15} \text{ gC}$) and releasing 78.4 PgC per year (Figure 1).

The total amount of carbon in the ocean increased 1.6 PgC per year. This amount of CO_2 is the result of the CO_2 crossing the air-sea interface. However, this value has a large error associated to it (SABINE et al., 2004). Additionally, Sabine and Tanhua (2010) shows that the ocean uptake of carbon has changed in the last two decades. His results show that the oceans have increased in 2.2 PgC per year and that could change, since the dynamics of the carbon in the ocean is not fully understood.

Figure 1: The global carbon cycle. The natural sources and anthropogenic effects are summed. The fluxes are in PtC year^{-1} and the stocks are in PtC . Source: Stocker et al. (2013).

1.2 The Air-Sea CO_2 Exchange

The physical processes that control the air-sea gas transfer are related to the small scale processes that occur in the first centimeter of the ocean boundary layer. According to Emerson and Hedges (2008), the near surface of the ocean can be subdivided in sub-layers with specific physical mechanisms acting in each one (Figure 2).

The layer near the air-water interface is known as *diffusive boundary layer*. This layer is 0.03 cm deep, and the transport of momentum, mass and heat are dominated by molecular diffusive processes. The transport of mass beneath the diffusive layer is mostly done by turbulent eddies. These eddies becomes small as one approaches the surface and the interface acts as a wall. There are different layer thicknesses for the transport of

Figure 2: Diffusion layers of the ocean boundary-layer. The left figure shows the horizontal velocity in the first centimeter of the ocean surface. The right figure show that the diffusive, thermal, and viscous boundary layers have different depths due to the different values of each diffusion coefficient. Adapted from Emerson and Hedges (2008).

momentum, heat, and molecular diffusion because of the different constants for momentum ($10^{-2} \text{ cm}^2 \text{ s}^{-1}$), heat ($10^{-3} \text{ cm}^2 \text{ s}^{-1}$), and mass diffusion ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$) of gases. There are three different models of the air-sea gas transfer mechanism, namely rigid wall model, stagnant film model, and surface renewal model that will be treated with more detail as follows.

1.2.1 Rigid Wall Model

The rigid wall model is the most mathematically complex model of gas exchange between the atmosphere and the ocean. It was developed by Deacon (1977) using empirically measured heat fluxes to create gas transport toward or away from a smooth surface. The study applied the formulation of the velocity profile in a turbulent flow over a smooth plane surface developed by Reichardt (1951):

$$u(z) = 2.5 \log(1 + 0.4z) + 7.8 \left[1 - \exp\left(\frac{-z}{11}\right) - \left(\frac{z}{11}\right) \exp(-0.33z) \right], \quad (2)$$

where z is the height in meters above the surface and u is the wind velocity in m s^{-1} .

The mathematical coupling of equations relating the viscous layer thickness and the flow velocity determined by Equation 2 gives:

$$\frac{k(z)}{D} = 1 + \kappa Sc \zeta_l \left[\frac{\zeta}{\zeta_l} - \tanh \left(\frac{\zeta}{\zeta_l} \right) \right], \quad (3)$$

in which k is the gas transfer velocity coefficient for the entity with the molecular diffusion coefficient is D , Sc is the Schmidt number (defined as $Sc = \mu/D$, where μ is the kinematic viscosity), κ is the von Kármán's constant, ζ is defined as $u_* z / \mu$ and ζ_l is a constant. The friction velocity (u_*) is defined as the wind velocity at the surface and the value assumed for κ is 0.41.

The Schmidt number is defined as the ratio of viscosity and mass diffusivity ($Sc = \nu/D$) and characterize fluid flows in which there are simultaneous momentum and mass diffusion processes. This number can be used as a proxy to CO_2 gas transfer and the relation between the gas transfer velocity of different substances (A and B) is given by:

$$\frac{k_A}{k_B} = \left(\frac{Sc_A(T_A)}{Sc_B(T_B)} \right)^{-n}, \quad (4)$$

where the parameter n is an empirical value. In that, $n = 1/2$ for a completely wavy water surface and $n = 2/3$ for a flat surface and T_A and T_B are the temperatures in the two media. This approach allows one to infer the k of one gas through the measurement of a different volatile gas.

The literature shows a good agreement with wind field data ($4-10 \text{ m s}^{-1}$) for Schmidt number with exponent $n = 2/3$. Although this model is theoretically consistent and advanced, the variables needed too obtain the gas transfer velocity, like u_* , is hard to obtain, making this model of difficult usage.

1.2.2 Surface Renewal Model

The intermediate complexity model is the surface renewal model (DANKWERTZ, 1970). This model considers that macroscopic parcels of water near the surface exchange gas with the atmosphere as in the stagnant film model. But these parcels are continuously

replaced by fresh, non-saturated parcels of water from the layer below (Figure 3).

Figure 3: The surface renewal model of air-sea gas transfer. The parcels of water saturated with CO_2 are replaced by non-saturated water. Adapted from Emerson and Hedges (2008).

This promotes fast exchange of gas with the atmosphere, since new parcels are unsaturated. The factor controlling the rate of gas exchange in this model is the replacement time rather than the layer thickness. As the rigid wall model, this model has some unknown variables, like the rate of the parcel replacement. This unknown parameter makes this model of difficult usage too.

1.2.3 Stagnant Film Model

The stagnant film model is the simplest model of gas transfer. It considers that the atmosphere and the ocean have both two sub-layers. The interface is a thin layer where the transport is done by molecular diffusion. The *Fick's law of diffusion* (Equation 5) describes the diffusion of CO_2 in the air or in the water as an isotropic spread of molecules of a fluid governed by Brownian movement. The parameterization of this law is given by:

$$\vec{F} = k \vec{\nabla} C, \quad (5)$$

where $\vec{F}$ is the flux of mass of CO_2 in $kg\,m^{-2}\,s^{-1}$, k is the gas transfer velocity in $m\,s^{-1}$ and $\vec{\nabla} C$ is the gradient of mass concentration of CO_2 at the interface.

The Fick's law of diffusion can be applied at both sides of the interface using the Henry's law at the interface. This law relates the amount of a gas that dissolves in a given volume of liquid as directly proportional to the partial pressure of that gas in equilibrium with the liquid, at a constant temperature:

$$C_{sg} = H C_{sl}, \quad (6)$$

where C_{sg} is the gas concentration of CO_2 at the surface of the ocean, C_{sl} is the liquid concentration of CO_2 at the interface, and H is the Henry's coefficient for CO_2 . The Henry's coefficient is dependent mostly on temperature, but the presence of electrolytes has a small influence upon the Henry's coefficient (DIAMOND; AKINFIEV, 2003).

One difficulty with the stagnant film model is the determination of the coefficient k . The gas transfer velocity (k) is a function of the state of the ocean surface. It depends on several parameters such as temperature, salt concentration, surfactants, amount of air bubbles etc. Nevertheless, the most important factor in the determination of k is the wind friction velocity (u_*), defined as the velocity of the wind in contact with the surface. However, this physical variable is difficult to measure and efforts have been made to obtain it through the use of satellites (LETTVIN; VESECKY, 2001). The u_* is related to the wind speed measured 10 meters above the ocean surface (u_{10}) and the latter is used to calculate the gas transfer coefficient k . This approach is justified because there is a much larger number of measurements of u_{10} from buoys and ships available in comparison with u_* . However, there are somewhat recent studies that discuss the relation between u_{10} and u_* that account for the vertical motion of the air-sea interface (HARA; BELCHER, 2004), and these allow for a parameterization of u_* based on u_{10} measurements.

Liss and Slater (1974) developed a two layer model based on the stagnant film model

(Figure 4). Diffusive processes occur in both layers of the atmosphere and the ocean, and at the interface the transfer of CO_2 were driven by the Henry's Law.

Figure 4: The two-layer model developed by Liss and Slater (1974)

As the molecular diffusion in water is slower than in the air, the water is the limiting factor to the diffusion. This model is not realistic because it supposes a laminar flow around the layers, however it's simple because it depends only on the measurements of CO_2 in the air and in the water diffusive layers. Their model joined the equations of Fick's Law and Henry's Law and developed a new parameterization:

$$\vec{F} = k_g (C_g - C_{sg}) \quad (7)$$

$$\vec{F} = k_l (C_{sl} - C_l) \quad (8)$$

$$C_{sg} = H C_{sl} \text{ (Henry's Law) }, \quad (9)$$

where F is the vertical flux of CO_2 , C_g is the concentration of CO_2 in the diffusive layer upon the ocean surface, C_{sg} is the concentration of CO_2 in the surface, k_g is the coefficient of diffusion in the air, k_l is the coefficient of diffusion in the water, C_{sl} is the concentration of CO_2 dissolved in the surface of the ocean, C_l is the concentration of CO_2 in the diffusive layer of the ocean and H is the Henry's coefficient for CO_2 . Joining the 3 equations yields:

$$F = \underbrace{\left[\frac{k_g k_l}{k_g H + k_l} \right]}_{k(\text{constant})} (C_g - H C_l). \quad (10)$$

Equation 10 can be rewritten as

$$F = k(C_g - H C_l). \quad (11)$$

Equation 11 simplified the determination of the flux of CO₂ between the atmosphere and the ocean. In this formulation, only three measurements are necessary: the CO₂ gas concentration over the surface, the CO₂ gas concentration beneath the surface and the variable k .

1.3 Parameterizations of the Gas Transfer Velocity

Coantic (1986) showed that the gas transfer coefficient is a function of the friction velocity, in the wind speed range where wave breaking is not important. Using data collected in-situ and from wave tanks from previous studies, the author noted a change in the gas transfer with winds between 2–3 m s⁻¹, when capillary waves appear. His conclusions show that the gas transfer depends basically on the wind velocity and the Schmidt number. The author suggests that the current models could not explain the turbulent diffusivity near the free liquid–gas interface.

Liss and Merlivat (1986) studied gas transfer velocity using both laboratory and field measurements. They found a linear relation between the wind speed at 10 meters above the surface (u_{10}) and the gas transfer velocity:

$$k_{600} = \begin{cases} 0.17 u_{10} & \text{for } u_{10} \leq 3.6 \\ 2.85 u_{10} - 9.65 & \text{for } 3.6 < u_{10} \leq 13 \\ 5.9 u_{10} - 49.3 & \text{for } u_{10} > 13 \text{ m s}^{-1}. \end{cases} \quad (12)$$

Their study measured the gas transfer velocity of sulfur hexafluoride (SF₆), a somewhat inert greenhouse gas used as a conservative tracer. The Liss and Merlivat (1986) study

adopted $S_c = 1600$ for SF_6 and $S_c = 600$ for CO_2 . Later studies adopted $S_c = 660$ as more appropriated value for Schmidt number for CO_2 , and hence the popularization of the term k_{660} . Although some comparisons with laboratory data were performed, the authors state that to improve the statistical adjustment, more in situ data would be necessary.

R. Wanninkhof developed two important studies in which he proposed the adjustment of two different polynomials to empirical data. His 1992 study (WANNINKHOF, 1992) showed that the k_{660} data obtained in laboratory experiments has a quadratic relationship with the wind speed:

$$k_{660} = 0.31 (u_{10})^2 \left(\frac{S_c}{660} \right)^{-1/2}. \quad (13)$$

Equation 13 can be used with shipboard anemometers, scatterometers and wind derived from radiometers. The author doesn't present any error estimate, arguing that "error estimates for Equation 13 are more nebulous since there are large regional variances of wind speed distributions from the Rayleigh distribution". For the averaged wind speed, the error in the gas transfer velocity is about $\pm 25\%$. The results showed in this study were obtained for a Rayleigh probability distribution function for wind speed around an average speed of 7.4 m s^{-1} . The author suggests that for lower wind speeds other mechanisms should be accounted for in the gas transfer estimate. Such as the Schmidt number used by Wanninkhof was obtained through the method developed by Jahne, Heinz and Dietrich (1987), that results in

$$S_c = A - BT + CT^2 - DT^3, \quad (14)$$

where $A = 2073.1$, $B = 125.62$, $C = 3.6276$, $D = 0.04321$ and T is the temperature in degrees Celsius.

The second study developed by Wanninkhof and McGillis (1999) used air-sea data (wind speed at 10 meters, temperature, partial pressure of CO_2 , etc) collected in the GasEx-98 (MCGILLIS et al., 2001b) cruise and the climatology of Takahashi et al. (1997). They demonstrated that the presence of surfactants at low wind speeds, changes the CO_2 flux

more than at higher wind speeds. This consideration results in a better fit with a cubic relation (equation 15):

$$k_{660} = 0.0283 (u_{10})^3 \left(\frac{Sc}{660} \right)^{-1/2}. \quad (15)$$

Nightingale et al. (2000) analyzed in situ data collected in the North Sea. They focused their efforts in the evaluation of the proxy methodology used in previous studies. A proxy is the determination of some variable based in the measurement of other physically correlated variable. They used the spores of conservative bacteria *Bacillus globigii* as a proxy for CO_2 concentration. The proposed relation (equation 16) is the one that best fits the data, and falls between those proposed by Liss and Merlivat (1986) and Wanninkhof (1992):

$$k_{660} = [0.222 (u_{10})^2 + 0.333 u_{10}] \left(\frac{Sc}{660} \right)^{-1/2}. \quad (16)$$

Ho et al. (2006) studied the air-sea exchange of $^3He/SF_6$ and CO_2 during the SOLAS Air-Sea Gas Exchange (SAGE) Experiment near the coast of New Zealand. The results showed the gas transfer velocities at relatively higher wind speeds, particularly at $u_{10} > 16 \text{ m s}^{-1}$, presents a quadratic relation (Equation 17) as in Wanninkhof (1992), instead of a cubic relation as in Wanninkhof and McGillis (1999):

$$k_{660} = 0.266 (u_{10})^2 \left(\frac{Sc}{660} \right)^{-1/2}. \quad (17)$$

The coefficient for the regression ($r^2 = 0.84$) is slightly higher than similar experiment realized in the North Sea ($r^2 = 0.78$). Their results showed that a cubic relationship developed in previous studies is inconsistent with the data of the SAGE experiment.

The parameterization of k_{660} as a function of wind speed at 10 meters from the surface has the benefit of the easy access to this measurement: it is commonly measured by anemometers in ships, buoys and satellite scatterometers. Nevertheless, errors greater than 100 % have been instigating researchers proposing new parameterizations. The ones being currently developed include the mean curvature of surface waves, microbreaking and the backscatter signal of active radars based in satellites.

One of this new approaches is the use of the Mean Square Slope (MSS) of the waves as a parameter of the gas transfer velocity. The mean square slope is a dimensionless measurement that accounts for the mean curvature of the waves in the ocean surface. Phillips (1977) defined it as:

$$MSS^2 = \int_0^{\infty} k^2 \phi(\vec{k}) d\vec{k}, \quad (18)$$

where MSS is the mean square slope, k is the wavenumber spectrum and ϕ is the wavenumber spectrum of ocean waves. As the surface height time series is the most common form of measurement, the MSS can be calculated using the dispersion relation for short gravity waves ($\omega^2 = gk$):

$$MSS^2 = \int_0^{\infty} \frac{(2\pi f)^4}{g^2} F(f) df \quad (19)$$

where F is the wave height power spectrum, f is the frequency and g is the gravity acceleration. Instead of the integration over all the frequencies, the integral of the MSS is performed in a limited range of frequencies:

$$MSS^2 = \int_{f_1}^{f_2} \frac{(2\pi f)^4}{g^2} F(f) df \quad (20)$$

As the MSS is an integral, the interval of integration changes the MSS value:

Jahne, Heinz and Dietrich (1987) reported that the mean square slope estimates based only on high wavenumber waves are more correlated with the gas transfer velocity than when integrated over all spectrum. Bock et al. (1999) studied the several factors that have influence on the air-sea gas transfer. He separated each factor and their influence in the gas transfer (Figure 6). He noted that the wind speed doesn't have a direct relation with gas transfer. He observed that the mean square slope generated by the wind on the ocean surface is more correlated to the gas transfer than the wind itself. His results are based in two circular tanks and agree with the results of Jahne, Heinz and Dietrich (1987), where the authors showed that the gas transfer velocity is better correlated with short wavelength

Figure 5: The difference in MSS depending on the integration interval.

waves than with long wavelength waves. The results showed that the correlation of short wind waves (200 rad m^{-1}) is greater than longer wind waves (50 rad m^{-1}). This implies that short wind waves are more important to the air-sea gas transfer process than longer waves.

1.4 Gas Transfer Velocity inferred by Satellite Data

The short wind waves that Jahne, Heinz and Dietrich (1987) and Bock et al. (1999) studied are similar to that obtained by orbital satellites. This fact is a new approach to infer the air-sea CO_2 exchange. The signal emitted by an active sensor onboard a satellite interacts with the ocean surface and returns to the satellite with information about the surface. The two kinds of satellite instruments used in this approach are altimeters and scatterometers. Altimeters use the specular reflection of the radar signal to infer the roughness of the surface. Scatterometers use the Bragg scattering for this same purpose. Both kinds of instruments will be described in Sections 1.4.1 and 1.4.2, however this study will use only the data provided by scatterometers.

Figure 6: Relationship between air-sea gas transfer and near surface variables. The physical processes influencing the gas exchange are represented by boxes and possible interactions among the processes are represented by arrows. The arrows indicate (1) generation of near surface turbulence through direct wind shear (shear instability), (2) generation of wind waves, (3) increase of surface drag (wind stress), (4) turbulence generation by wind waves, (5) enhanced dissipation of wind waves by near subsurface turbulence, (6) enhanced viscous dissipation of wind waves, (7) break up and accumulation of surface films by waves, (8) suppression of near surface turbulence by modified surface boundary conditions, (9) breakup and accumulation of surface films by near surface turbulence, (10) generation of bubbles by wave breaking, (11) gas exchange due to bubbles, (12) gas exchange due to wave motion, (13) gas exchange due to near surface turbulence (14) suppression of gas exchange by surface films (barrier to diffusion), and (15) enhancement of turbulence by bubbles. Adapted from Bock et al. (1999).

1.4.1 Altimeters

Altimeters are active radars with the Nadir-looking antenna emitting pulses toward the surface. To first order, the travel time determines the distance between the satellite and the Earth's surface, given that the phase speed of an electromagnetic wave through the atmosphere is known. Because the short and well defined pulse interacts with the wavy surface, the returned signal has a shape different from that of the emitted pulse. Analyzing the shape of the returned signal makes it possible to infer the capillary-gravity wave spectrum and then the gas exchange velocity. Capillary-gravity waves and air-sea gas

transfer are small scale phenomena that are connected by the viscosity and surface tension.

Glover, Frew and McCue (2007) developed an empirical relation between the gas transfer velocity and the mean square slope using data from the JASON-2 altimeter. As one of the first studies of this application of altimeter, their results shows only the comparison between the JASON-1 and the TOPEX/Poseidon altimeter. Their results showed an error of 16 cm h^{-1} on the long term global averaged k_{660} .

Frew et al. (2007) improved the algorithms used in Glover, Frew and McCue (2007) by differentiating mean square slope estimates computed from the normalized backscatter in each band of the TOPEX/Poseidon and the JASON-1 altimeters, using a simple geometric optics model. Their results showed monthly global maps of gas transfer velocity and illustrated the seasonal variations in transfer velocity over a 1-year period. The estimated overall uncertainty of their method is $\pm 30\%$ and the long-term global, area-weighted, Schmidt number corrected, mean gas transfer velocity is $14 \pm 4 \text{ cm h}^{-1}$.

Goddijn-Murphy et al. (2013) developed a parameterization of the gas transfer velocity using JASON-1 and Jason-2 altimeters. Their study shows that the sea surface roughness is more related with the gas transfer velocity than the wind speed. They suggested a new parameterization, reducing the contribution from longer waves. This is consistent with the theory that gas transfer is largely controlled by short capillary-gravity waves. Their *in-situ* data comes from a variety of cruises (GODDIJN-MURPHY; WOOLF; MARANDINO, 2012) and the RMS error of their parameterization is 3 cm h^{-1} , no error bounds were presented.

1.4.2 Scatterometers

Scatterometers are oceanographic instruments onboard satellites that emit radar pulses with different azimuths toward the ocean surface, an equipment to measure the wind speed and direction over the ocean. However, it is important to notice that the radar beam is not emitted at the nadir direction of the spacecraft, but with some predefined oblique angle relative to nadir. When the electromagnetic pulse reaches the ocean surface, it interacts with it. Part of the pulse is absorbed by the surface, part is scattered in a direction other

than the satellite direction, and part is scattered backwards towards the satellite (Figure 7). The scattered signal is a measure of the ocean surface roughness and as the main forcing of the waves is the surface wind, the satellite can infer its speed.

Figure 7: Schematic representation of microwave scattering and reflection at a smooth (a), slightly rough (b), and rough (c) ocean surface. Adapted from Stoffelen (1998).

The Bragg scattering is the scattering of part of the radar signal by the capillary-gravity waves in the surface of the ocean in a somewhat resonant fashion. The part of the energy scattered into the satellite direction is a fraction of that of the original pulse that depends on the wave geometry. This backward scattered signal is known as *Normalized Radar Cross-Section* (NRCS) or σ_0 . If there is no waves over the surface, the scattering of the signal is like the Fresnel reflection and only a minimal part of the energy of the pulse returns to the satellite. In the presence of capillary-gravity waves, a small surface of the wave will be perpendicular to the pulse and a stronger scattering will occur. The intensity of the scattering is related to the wavelength, slope and thus amplitude of the waves. Figure 8 shows the geometry of the radar beam reaching the surface.

The resonant Bragg backscattering occurs when the scatterometer radar electromagnetic wavelength and that of the surface waves are in the same order of magnitude (Figure 8). The ocean waves wavelength need to be equal an exact number of radar wavelengths such that the backscattered signal from all waves are in phase. Otherwise, a destructive interference could reduce the power received by the satellite (ROBINSON, 2004). Equation

Figure 8: Geometry of the Bragg scattering for the incident angle of 54° . λ is the surface wavelength and λ_r is the radar beam electromagnetic wavelength. Adapted from (MARTIN, 2014).

21 shows the relation between the radar wavelength and the ocean surface wavelength:

$$\lambda_w = \frac{n\lambda}{2 \sin \theta}, n = 1, 2, \dots \quad (21)$$

where λ_w is the wavelength of the ocean surface waves, λ is the wavelength of the radar beam, and θ is the angle of the incident radar beam. This effect is then modulated by longer gravity waves on the water surface and by currents which affect the sea surface roughness. The wavelength of the Seawinds scatterometer, whose frequency is 13.4 GHz, is 2.23 cm, typical of short capillary-gravity waves. This kind of waves are waves which restoring force are the gravity and the water surface tension. These waves has a dispersion relation given by:

$$\omega^2 = \left(gk + \frac{\sigma}{\rho} k^3 \right) \tanh(kh), \quad (22)$$

where g is the gravity, k is the wavenumber, H is the constant ocean depth where the wave is travelling, σ is the water surface tension (aproximately 0.074 N m^{-1}), ρ is the mean density of the water, and ω is the frequency. Figure 9 shows this relation:

Figure 9 shows that the frequency has a minimum value where the group velocity ($C_g = \partial \omega / \partial k$) is zero, meaning that waves with a critical wavelength have no dispersion. This occurs because the dispersion caused by gravity cancels out the dispersion due to the

Figure 9: The dispersion relation of capillar-gravity waves. The vertical lines divide the regions where the surface tension (capillary waves), gravity and both restoring forces are important.

capillary effect. This critical wavelength (λ_c) is 1.7 cm.

The relation between the wind speed and σ_0 is empirically determined by the *Geophysical Model Function* (GMF). The relation between both variables is made with the use of data from maritime buoys (STOFFELEN; ANDERSON, 1997). The equivalent neutral wind at 10 m is related to σ_0 and to the incident and azimuth angles of the radar beam (MARTIN, 2014) in this empirical relation. Neutral stability is important because when the ocean surface is warmer than the atmosphere above, the boundary layer is unstable and the momentum is more easily transferred from the 10-m wind to the ocean surface (BOURASSA et al., 2010). Thus, application of the GMF implicitly assumes neutral stability, regardless of the real conditions at the planetary boundary layer. Convective regions are an exception rather than a rule, thus the errors that result from this assumption are relative small in most of the global ocean. The events of rain are not considered in the present study.

The satellite used in this study is the QuikSCAT satellite (Figure 10), an oceanographic satellite launched in 1999 by NASA as a replacement for the NSCAT satellite. The spacecraft was equipped with the SeaWinds scatterometer and was active until 2009.

Figure 10: Artistic rendition of the Quikscat scatterometer. Source: <http://en.allmetsat.com/satellite-quikscat.php>

The QuikSCAT is a sun-synchronous satellite in quasi-polar orbit. The satellite altitude was 802 km and had speed of about 7 km per second. The circular antenna of the scatterometer is a 1-meter-diameter rotating dish that produces two spot beams, sweeping in a circular pattern at 18 rpm and a swath width of 1,800 km (Figure 11-a), sampling 90% of the ocean every 24

h. The SeaWinds radar operates in the Ku-band, its frequency is 13.402 GHz and its wavelength is 2.24 cm. The antenna of the satellite has two incident angles at the surface of 46° and 54° (Figure 11-a). The instrument measured winds with speeds between 3 and 20 m s^{-1} with an accuracy of 2 m s^{-1} . The nominal resolution of each wind vector was 25 km. This resolution, however has been recently enhanced through raw data reprocessing by Early and Long (2001).

Figure 11: QuikSCAT Viewing Geometry. Adapted from Spencer, Wu and Long (2000).

The σ_0 received by the Seawinds scatterometer has far more resolution than the nominal value of 25 km. The scatterometer footprint is an ellipse (or “egg”) of approximately 15 km by 25 km (Figure 11-b) at the surface. However, the satellite onboard Doppler processing unit improves this resolution. Twelve “slices” (Figure 11-c) of 4-6 km long and 20 km wide of is composed of several slices. Early and Long (2001) developed a reconstruct method aiming to preserve this finer resolution. The result of this processing has the resolution of 2.5 km per pixel. This resolution is still very poor for boundary layer studies as turbulence has a smaller scale, however, it is the best satellite resolution available at this date. This will be the dataset used in this study.

Plant (2002) showed that both the small slope approximation and the integral expansion method of the ocean wavelength distribution yield the same expression for the back scattering cross section of the sea, σ_{qp} , where q and p indicate transmitted and received polarization. His expression (Equation 23) yields the Bragg scattering result, σ_{os} , when the surface can be considered slightly rough:

$$\sigma_{os} = 16 \pi k_o^4 \cos \theta' |g'_{qp}|^2 [F_s(2k_o \sin \theta'_s, 0) + F_s(-2k_o \sin \theta'_s, 0)], \quad (23)$$

where k_o is the electromagnetic wavenumber, θ is the incidence angle, σ^2 is the mean square surface slope, g' is the antenna gain, ρ is the surface correlation function, F_s is the small-scale surface wave variance spectral density, ϵ is the dielectric constant, and primes indicate local quantities. The authors used the multiscale model that consists of applying equation 23 to three different scales of surface displacement, as in figure 7, and keeping effects of smaller scales in the mean square slope, and letting the incidence angle be the local one that includes effects of tilting by larger scales.

Bogucki et al. (2010) proposed a new parameterization for the gas transfer velocity using only the scatterometer σ_0 measurements. This new approach doesn't use the wind speed. The authors used results from Plant (2002) and proposed the parameterization for k_{660} :

$$k_{660_v} = 10^{\frac{\sigma_v + 47.4079}{21.4248}} \quad (24)$$

$$k_{660_h} = 10^{\frac{\sigma_h + 51.7545}{22.5334}} \quad (25)$$

where the indices v and h refer to the polarization.

Besides the fact that the author used only 3 points to perform the regression (Equation 24), and that model was limited only to moderate wind speeds (approximately 6 m s^{-1}), the results indicated that the model (BOGUCKI et al., 2010) agrees with others parameterizations based on surface wind speeds (U_{10}) (WANNINKHOF, 1992; NIGHTINGALE et al., 2000). The study shows that the uncertainty of his model is about 7 cm h^{-1} .

1.5 Hypothesis

The studies cited in the previous sections showed several attempts to develop a better gas transfer coefficient. The study developed by Bock et al. (1999) showed that the root mean square error in the linear regression between the gas transfer velocity and the mean square slope of capillary-gravity waves decreases with increasing wavenumbers.

The hypothesis of this study is that there is a range in the wavenumber of surface capillary-gravity waves in which the error in the regression of MSS- k_{660} decreases significantly. This wavenumber range will provide a better regression between the mean square slope and the gas transfer velocity.

This new regression will be applied to the scatterometer σ_0 data to provide a map of the gas transfer velocity along the satellite track. This will be performed in two steps. In the first step the σ_0 will be converted to wind speed using the satellite model function. The second step will be the conversion of the wind speed into MSS, using the models proposed by Cox and Munk (1954), Wu (1972), Phillips (1977), and Jackson, Walton and Baker (1985). The MSS obtained from the NRCS will then be applied to the regression described above. The results will be compared with the buoy derived k_{660} and to Bogucki et al. (2010) parameterization.

1.6 Objectives

The objectives to be performed in the calculation of the regression are as follows:

1. calculate the gas transfer velocity (k_{660}) time series of CO_2 using the theory of Section 3.1.2
2. calculate the mean square slope (MSS) for sequential ranges of wavenumbers using the sea surface height (SSH) and the theory developed in Section 1.2
3. Synchronize the k_{660} and MSS in time and perform the linear regression for the several MSS time series
4. calculate the root mean square of the linear regressions and make a plot of this error as a function of the wavenumbers range

To apply the regression to the scatterometer data, the following steps will be performed:

1. calculate the NRCS as function of the wind using the scatterometer geophysical model function
2. calculate the mean square slope as function of the wind using the parameterizations of Cox and Munk (1954), Wu (1972), Phillips (1977), and Jackson, Walton and Baker (1985)
3. relate the NRCS to the MSS calculate in the steps above
4. choose the regression with the lowest root mean square error and apply the relation NRCS-MSS
5. apply the relation NRCS- k_{660} above to the scatterometer data

The values of k_{660} found in the last item will be compared with the values of k_{660} using the *in-situ* data and with the values of the parameterization of Bogucki et al. (2010).

2 Data and Methodology

The data measured in situ was collected in the Deep Ocean Gas Exchange Experiment (Section 2.1) by the ASIS buoy (Section 2.2). Section 2.3 explain the remote sensing data collected by the *SeaWinds Scatterometer*. The main mathematical methods used in this study are the Fourier Transform discussed in Section 2.4.1 and the wavelet analysis in Section 2.4.2. The methods used to estimate the mean square slope and other variables are described in Section 2.4.2.

2.1 The Deep Ocean Gas Exchange Experiment

The *Deep Ocean Gas Exchange Experiment* (DOGEE) was part of the *Surface Ocean-Lower Atmosphere Study* (SOLAS), an international program to understand the biogeochemical-physical exchanges processes between the atmosphere and the ocean. Its main goal was to estimate the flux of CO_2 and other radiatively important gases (CH_4 , N_2O and Dimethylsulfide) and the processes of production of aerosols by sea spray (BROOKS et al., 2009). Wind-driven waves and wave withcapping are also investigated, since both phenomena have impacts on the air-sea gas exchange.

Figure 12: DOGEE cruises. Adapted from Brooks et al. (2009).

The gas transfer velocity is obtained by the measurements of the partial pressure of CO_2 in the air and the water, the flux of CO_2 between the atmosphere and the ocean and the air and water temperature. The measurements of CO_2 flux of the DOGEE campaign was performed using the direct eddy covariance method. Other measurements included water vapor, heat, and momentum, and measurements of the wave height, air-sea CO_2 partial pressure difference ($\Delta p\text{CO}_2$), and mean meteorological conditions. These data were collected in

two different cruises on board the RSS *Discovery* (Figure 12). The area of study was the North Atlantic Ocean, near Europe (40°N - 60°N , 8°W - 26°W) between 16 June and 17 July 2007.

Two air-sea interaction spar buoys were deployed during the DOGEE campaign. These buoys are thoroughly described in Section 2.2. Only the data of one of these buoys will be used in this study, due to only one wave dataset be available. No information was found in the cruise reports explaining if some problem occurred with the missing dataset.

2.2 The ASIS buoy

The *Air-Sea Interaction Spar* (ASIS) buoy is a hydrodynamically stable platform for research and industry activities. The main purpose of the buoy is to make precise measurements of directional wave spectra, meteorological parameters, and measure the concentration of several trace gases, such as Dimethylsulfide (DMS), CO_2 , SF_6 . The buoy was projected and built at Woods Hole Oceanographic Institution (WHOI).

The drifting buoy (Figure 13) consists of a 15 meters branched aluminum structure. It is made by 5 individual 8.5" tubes that provide low drag at the water surface and a spar-like open structure for the measurement of small waves using capacitance wires. The buoy is highly-damped in heave, pitch, and roll, and behaves as a wave follower for long waves. The sum of buoy motion and wave wire measurements yields directional measurement of waves with a wavelength of few centimeters.

Figure 13: Technical description of the ASIS-2 buoy. Source: Graber et al. (2000).

The design required careful attention to weight and balance to achieve the desired hydro-static characteristics, but also emphasized simple detailing for ease of manufacture and modularity. The buoy is designed to be disassembled for shipping with relative ease.

One of the most important features of the buoy is the high resolution measurement of the height of waves. The wave sensors were developed at the National Water Research Institute (NWRI) and at the Canada Centre for Inland Waters (CCIW). The physical basis of the sensor is that the capacitance changes as the wires submerge (GRABER et al., 2000). Therefore the capacitance is an indirect measurement of wave amplitude. Water in contact with the wire increase the dielectric constant of the wire and cause an increase in the capacitance of the wire. The relation between the capacitance of the wire and the height of the wave is linear and had to be calibrated in laboratory. The major advantages of this electronic design is the absence of moving parts and the high frequency of operation. This frequency is related to the physical properties of the cable and to the electronic device that measures the capacity of the wire (TUCKER; CHARNOCK, 1954). The data gathering frequency of the ASIS buoy is 10 Hz. The design of the instrument can be seen in figure 14.

Figure 14: The principle of operation of the wave detector. The electronic circuit measures the capacity of the centre wire and the Earth. Adapted from Tucker and Charnock (1954).

The wires were mounted in the moving buoy and the data has to be referenced to a fixed coordinate system. To achieve this result, the vertical position of the buoy had to be recorded to provide the correction to the wave height measurements. The buoy motion

is recorded by a six degree-of-freedom inertial package consisting of “strapped-down” orthogonal triplets of accelerometers, angular rate gyros, and a compass (DRENNAN et al., 1994). Five of them were installed in the border of the “cage” and three additional wires were installed in the center of the buoy in a isosceles configuration. The redundant array of wave staffs provided a continued measurement in the case of breaking of the wires. Fatigue, dolphins and harsh weather were the common causes of breaking wires (DRENNAN et al., 1994).

The variables measured by instruments mounted on the ASIS buoy include eddy correlation fluxes of momentum, sensible heat, latent heat and CO₂; mean values of wind speed and direction, air temperature, humidity and pCO₂ in the air; directional wave spectra and surface slopes (MSS); near surface (oceanic) profiles of sea surface temperature (4 depths, 0.5 - 5m), and salinity; TKE dissipation rates; pCO₂, light intensity (PAR), Dissolved Oxygen (DO) and chl-a fluorescence in the water (1-3 depths) and total dissolved gas (N₂). The complete list of sensors present in the ASIS buoy is in Table 2.

Table 2: List of instruments on the ASIS-2 buoy during the DOGEE campaign. The variables used in this study are those measured by the LICOR, the wave staff, SAMI, and the Huygrun Seamon thermistor.

Sensor	Measurement	Nominal Height
Solent R2A sonic anemometer	3D wind, virtual temp.	5m
LICOR LI-7500A CO ₂ /H ₂ O analyzer	CO ₂ /H ₂ O fluctuations	5m
Rotronic MP101A-T7	Humidity, air temp	4m
Huygrun Seamon thermistor	Air temperature	3m
Wave staff array (8 gauges)	Surface elevation	0 m
SonTek Dopbeam current meter	mean current, turbulence	-1.5m
SAMI pCO ₂ sensor	CO ₂ in water column	-1.5, -5m
LICOR PAR sensor	Light intensity	-1.5m
Aanderaa O ₂ sensor	DO in water column	-1.5, -5m
Huygrun Seamon	Water temperature	-3.5m
Fluorometer	Chlorophyll-a	-5m
Columbia Res Lab accelerometer	Linear acceleration	-6.5m
Systron Donner Rate Gyros	Angular motion (rates)	-6.5m
Precision Navigation compass	Compass angle (yaw)	-6.5m
URI Gas tension device	Total dissolved gas	-7m
SBE19plus	DO + CTD + Chl-a	-7m

The measurements of the wind and wind stress are estimated by direct eddy correlation using a sonic anemometer. The data is corrected for the platform motion using the

output of the motion package described before. The wind profile was measured with four anemometers at 1.5, 2.3, 3.4, and 5.1 m from the water surface.

Figure 15: The LICOR®7500A instrument.
Source: http://www.licor.com/env/products/gas_analysis/LI7500A/system_components.html

The CO₂ data in the air was measured by the LICOR®7500A instrument. This equipment measures CO₂ and H₂O densities of air in the open sample path, or the free space between the infrared source and the detector of the equipment (Figure 15). This approach does not use an air pump and it has no time delays in the data acquisition. The data sampling can be set up to the maximum of 20 Hz, and with a sonic anemometer, the eddy covariance of CO₂ can be calculated. The principle of operation of the instrument is described by the manufacturer (LI-COR, 2015):

The LI-7500A optical source emits infrared light through a chopper filter wheel and the open sample path to a temperature-controlled lead selenide detector. Some of the infrared light is absorbed by carbon dioxide and water vapor in the sample path, and the ratio of absorption to a reference is used to compute density of the gases.

The initial analysis of the CO₂ concentration data showed a significant noise and a systematic bias introduced into the high-rate CO₂ flux estimates by the mechanical deformation of the LICOR®7500A sampling head under the accelerations induced by the buoy motion (YELLAND et al., 2009). The final dataset have been correct this error.

The CO₂ in the water column was measured by the *Submersible Autonomous Moored Instrumen* (SAMI-CO₂) sensor. The manufacturer (Sunburst Sensors, 2015) states that the equipment measures the partial pressure of carbon dioxide (pCO₂) in water from 200-600 μ atm and operates up to 600 meters deep. The instrument uses colorimetric reagent method with response time of ~ 5 minutes and precision of $\pm 1 \mu$ atm.

The SAMI-CO₂ uses a calibrated reagent-based colorimetry to measure a change in the pH of the indicator, bromothymol blue (BTB). The BTB is contained in a gas-permeable membrane that is exposed to the environment. The pH change is driven by the diffusion of CO₂ across the membrane. Long-term drift-free performance is obtained by renewing the BTB reagent for each measurement, by recording the indicator absorbance at two wavelengths corresponding to the peak absorption of the acid/base forms of BTB, and by periodically measuring blank (indicator free) water in the optical cell. Changes in the light intensity (Figure 16) between blank measurements are corrected with reference detectors that monitor the light output (Sunburst Sensors, 2015; JAHNE; MONAHAN, 1995).

Figure 16: SAMI-CO₂ schematic diagram. The light used to analyse the sample is compared with the reference sample to obtain accurate color changes.

2.3 The QuikSCAT Dataset

The description of the QuikSCAT scatterometer can be seen in Section 1.4.2. The high-resolution sigma-0 data is available in the NASA PODACC website (NASA/JPL, 2015) and in the NASA Scatterometer Climate Record Pathfinder website (Brigham Young University/NASA, 2015). The data resolution varies depending on region and sampling conditions but is estimated to be 6-8 km in most areas. The temporal resolution of the data is approximately 8 hours for the buoy region.

2.4 Spectral Analysis

The usual data sampling of any variable in the environment produces a dataset with values as a function of time. The basic statistical analysis of such time-series data can reveal information about that data as the mean value, standard deviation and minimum/maximum

values, etc. The analysis of data with oscillatory shape need specific data analysis methods to extract the parameters of the oscillation, such as the frequencies and the power associated with each frequency. These variable can be important to describe the origin, forcing or other aspect of the phenomenon being studied. This technique to study oscillatory signals in the data is known as spectral analysis.

In this study, the spectral analysis is provided by the *Fast Fourier Transform* (Section 2.4.1) and the *Wavelet transform* (Section 2.4.2) described here.

2.4.1 The Fourier Transform

The Fourier Transform (FT) expresses a function as a sum of periodic components. A time series converted in a complex sum of sines and cosines has a FT whose axis are the frequency in the x-axis and a complex number resulting from the Fourier transform in the y-axis. The mathematical formulation of the Continuous Fourier Transform (CFT) is defined by Equation 26:

$$F(k) = \int_{-\infty}^{\infty} f(t) \exp(-2\pi i k t) dt, \quad (26)$$

where $f(t)$ is the time series or some function dependent of distance, k can be the frequency [s^{-1}] or wavenumber [m^{-1}] and i is the imaginary number. Equation 26 can be rewritten using the Euler formula:

$$F(k) = \int_{-\infty}^{\infty} f(t) (\cos(-2\pi k t) + i \sin(-2\pi k t)) dt \quad (27)$$

The inverse transformation, from the Fourier transform back to original time series is possible with the *inverse Fourier transform* (IFT) (Equation 28):

$$f(t) = \int_{-\infty}^{\infty} F(k) \exp(2\pi i k t) dk. \quad (28)$$

The CFT and IFT are the tools that can handle the same data in the time domain and in frequency domain. Figure 17 illustrates this domains and equations.

The FT in the form presented in equation 27 are in the complex numbers domain. To

Figure 17: Representation of the conversion between the time and frequency domains.

obtain the squared amplitude in the real *Re* domain it is necessary to work with the squared sum of the real and imaginary parts. It is called *power spectrum* and a higher value of the power spectrum in specific frequency it means that frequency is important, or the signal analyzed resembles a sin function with that frequency. A common representation of the FT is known as periodogram. The periodogram present amplitude of the FT and has units of power per unit of frequency.

In the geophysical sciences, measurements are often sampled in a regular time interval. To calculate the FT of this signal, the CFT must be dicretized because it requires the time axis be continuous. The result is to use the *Discrete Fourier Transform* (DFT), defined as

$$F(k) = \sum_{m=0}^{n-1} f(m) \exp(-2\pi i \frac{mk}{n}), \quad (29)$$

where n is the number of points of the whole time series. The inverse Fourier transform has also its discrete form:

$$f(t) = \frac{1}{N} \sum_{m=0}^{N-1} f(k) \exp(2\pi i \frac{mt}{N}). \quad (30)$$

One can observe that the power spectra is a symmetrical function considering the origin of the x-axis, and it's usual to cut the frequency axis between 0 and the *Nyquist frequency*.

To recover all Fourier components of a periodic waveform, it is necessary to use a sampling rate at least twice the highest waveform frequency. The Nyquist frequency, also called the Nyquist limit, or co-interval, is the highest frequency that can be coded at a given sampling rate to be able to fully reconstruct the original signal *via* DIFT, i.e.,

$$f_{Nyquist} = \frac{1}{2} v, \quad (31)$$

where v is the sampling rate. The *Fast Fourier Transform* (FFT) is an optimized version of

the DFT coded in the firmware of computers (COOLEY; TUKEY, 1965).

The time series is supposed to be periodic, meaning that the time series repeat itself in time. If it is not periodic, the Fourier transform will have a phenomenon known as *spectral leakage*. This spread the power of a certain frequency in the frequencies around that frequency. To avoid the spectral leakage, it's common to use *window functions*. These functions are often tapered cosines, with the extremes assuming values near zero. When the signal is multiplied by the window function, the extremes of the signal assume a zero value (or near zero) and the signal is considered periodic. The Blackman-Harris Window was used to analyze the wave data. The choice for this window offers a better suppression of noise and interference for frequencies above 0.5 (Figure 18).

Figure 18: The Blackman-Harris Window in time domain and its FFT.

The equation 32 describe the Blackman-Harris window function:

$$\begin{aligned} \omega(n) = & 0.35875 - 0.48829 \cos\left(\frac{2\pi n}{N-1}\right) + 0.14128 \cos\left(\frac{4\pi n}{N-1}\right) \\ & - 0.01168 \cos\left(\frac{6\pi n}{N-1}\right), \end{aligned} \quad (32)$$

where N is the window width. The use of more shifted trigonometric functions results in minimized side-lobe levels.

When the FFT is performed using equation 29, errors associated with the power spectrum can be estimated by the method proposed by (WELCH, 1967). His method splits the time series in several segments and performs the FFT over each segment. In the end, an average over the all FFT results in an averaged FFT with estimates based on the spread among spectra. This method will be used to calculate the MSS.

The Fourier Transform has three main limitations. The first one is that the Fourier transform cannot provide simultaneous time and frequency localization. For example, the equation

$$f(t) = \cos(2\pi \cdot 5 \cdot t) + \cos(2\pi \cdot 25 \cdot t) + \cos(2\pi \cdot 50 \cdot t) \quad (33)$$

has frequencies of 5, 25 and 50 Hz. The Fourier transform shows exactly three peaks in that frequencies (Figure).

Figure 19: Example of stationary wave and its spectrum.

Figure 19 shows that the Fourier transform has a good frequency resolution, but no time information. There is no information about the magnitude of the power relative to the three frequencies in each point of the time series.

The second problem with the Fourier transform is that it is not useful for analyzing time-variant, non-stationary signals. Taking as example the equation:

$$\omega = 25t \quad (34)$$

$$f(t) = \cos(2\pi \cdot \omega \cdot t), \quad (35)$$

where ω is the time-variant frequency. Figure 20 shows the chirp signal time series and the Fourier transform of the function.

Figure 20: Example of non-stationary waves (top) in time (below) in frequency domain.

The third problem with the Fourier transform is it not appropriate for representing discontinuities or sharp corners.

2.4.2 Wavelet Analysis

The ocean has the wind as its main source of mechanical energy, generating the wind waves and changing the height and the frequency in time. Given the limitations discussed in the preceding section, the wavelet may overcome the problems above. Wavelets are based on the process of comparison of the DFT. One way of interpreting the DFT is to associate the power with the correlation of the signal and a sinusoidal with a fixed frequency (PRESS et al., 1992). For example, suppose a Gaussian pulse:

$$P(t) = \exp(-t^2) \exp(2\pi i f t), \quad (36)$$

with a frequency of 20 Hz (Figure 21 (d)). Suppose that three sinusoidal waveforms with unitary amplitude and frequencies of 40, 20, and 10 Hz (Figure 21 (a), (b), and (c)) are correlated with the signal, the highest value of this correlation will be with the 20 Hz sinusoid (Figure 21 (e)).

Figure 21: DFT example: (a), (b), and (c) are waveforms with frequency of 40, 20, and 10 Hz, respectively. (d) is the signal of unknown frequency. (e) is the FFT of the signal, showing its highly correlated with the waveform (b).

The highest value found in the correlation can locate the frequency with precision, and can locate in what time that maximum correlation occurred. The wavelet analysis uses the same principle of the DFT, but instead of using a sinusoidal waveform, it uses a wavelet. Wavelets are short waveforms that can be stretched and shifted along the time axis, providing a correlation value for each value in the time axis. Following the example presented above, suppose again a Gaussian pulse of 20 Hz (Figure 22 (e)). Consider four wavelets (Figure 22 (a), (b), (c), and (d)) with frequencies of 40, 10, 40, and 20 Hz, respectively.

The first and second wavelets have poor correlations with the signal (e) because they have different frequencies and are not aligned with the signal in the time axis. The

Figure 22: The wavelet example: (a), (b), (c), and (d) are the Morlet wavelet with different frequencies and/or time position. (d) is a gaussian-pulse signal. The highest correlation is between the signal (e) and the wavelet (d). Both have the same frequency and are at the same position in the time axis.

third wavelet is aligned with the signal, but has a different frequency, resulting in a poor correlation. Finally, the wavelet (d) is aligned with the signal and have the same frequency, resulting in a good correlation value. The final result of the example above is presented in Figure 23.

Figure 23: Wavelet transform of the Gaussian pulse. (top) time series (below) Wavelet transform. The box right to the wavelet transform is the integral of the wavelet in time and it corresponds to the Fourier Transform of the signal.

The wavelet transform of the Gaussian pulse shows the dominant frequency during the pulse length. The box right of the wavelet transform shows the Fourier transform of the

signal, and as it is expected, the peak is in 20 Hz.

There is a curved line in the wavelet graph present over all time axis. This line is known as the *cone of influence* and represents the influence of the borders in the calculation of the transform. As the wavelet has a finite width, the values of the transform near the border are as precisely as the ones in the more central region.

The continuous wavelet transform of a discrete sequence x_n is defined as the convolution of x_n with a scaled and translated version of $\Psi_0(n)$ (TORRENCE; COMPO, 1998):

$$W_n(s) = \sum_{n'=0}^{N-1} x_{n'} \Psi^* \left[\frac{(n' - n) \delta t}{s} \right] \quad (37)$$

where the (*) indicates the complex conjugate. The term s is the *scales* of the wavelet transform. The scales are the resolvable periods of the wavelet. It is common to choose the scales as fractional powers of two (TORRENCE; COMPO, 1998):

$$s_j = s_0 2^{j \delta j}, j = 0, 1 \dots J \quad (38)$$

$$J = \delta j^{-1} \log_2 \left(\frac{N \delta t}{s_0} \right), \quad (39)$$

where s_0 is the smallest scale and J is the largest. δj is the resolution of the scale. Smaller values gives better resolution in most of the cases.

The wavelets families are functions constructed to be shorter waveforms that can be and stretched and shifted along the time axis. The wavelet must have zero mean and be localized in both time and frequency space (FARGE, 1992). Table 3 shows a set of known wavelets:

The choice of the best wavelet depends upon the signal and is somewhat subjective. Previous studies indicate that Haar wavelets are good for edge detection and reconstructing binary pulses (FUGAL, 2009). Coiflet Wavelets are good for data with self-similarities (fractals) such as financial trends (FUGAL, 2009). The wavelet used in this study is the Morlet wavelet because it resembles the shape of the ocean waves as suggested in Torrence and Compo (1998). Once the wavelet transform is defined, the wavelet power spectrum is

Table 3: Wavelet families. The Mexican Hat wavelet is not present because it's the Derivative of Gaussian (DOG) with $m = 2$. The mother function of the coiflet is the solution of the equation. See Daubechies (1992). The ϕ function in the Daubechies wavelet is the Scaling function.

Name	Mother	Waveform
Morlet	$\psi(n) = \pi^{-1/4} \exp(i\omega_0 n) \exp(-n^2/2)$
DOG	$\psi(n) = \frac{(-1)^{(m+1)}}{\sqrt{\Gamma(m+\frac{1}{2})}} \frac{\delta^m}{\delta n^m} \exp(-n^2/2)$
Haar	$\psi(n) = \begin{cases} 1, & \text{if } 0 \leq t < 1/2 \\ -1, & \text{if } 1/2 \leq t < 1 \\ 0 & \text{otherwise} \end{cases}$
Coiflet	$\int \psi(n) x^n dn = 0$
Daubechies	$\psi(n) = \sqrt{2} \sum_{k=0}^{2N-1} (-1)^k h_{2N-1-k} \phi(2n-k)$
Paul	$\psi(n) = \frac{2^m i^m m!}{\sqrt{\pi(2m)!}} (1 - in)^{-(m+1)}$

given by $|W(s)|^2$.

3 Results

The first part of this chapter describes the time series of the ASIS buoy and the synoptic events that had effects in the buoy data (Section 3.1.1). The gas transfer velocity data is analyzed in Section 3.1.2. The analysis of the wave data is presented in Section 3.1.3 and the joint analysis of the gas transfer velocity and wave data is shown in Section 3.1.5. Finally, the some results of the first part of the study are applied to the QuikSCAT satellite scattering cross section data (Section 3.2).

3.1 The ASIS Buoy Data

The ASIS buoy drifted in response to a combination of wind and current forcings, depending on the relative strength of each. During its sixteen days (Jun/26/2007-Jul/11/2007) in the ocean (Figure 24), the buoy drifted 403.7 km (174.2 km in straight line). The ASIS average drift speed was around 1.5 km h^{-1} , and it followed the path depicted in Figure 24. The relation of the data acquisition and the synoptic events are described in the Section 3.1.1.

Figure 24: ASIS-2 buoy path during the DOGEE campaign

3.1.1 The Buoy Data Time Series and Synoptic Analysis

The ASIS-2 buoy measured 64 variables when drifting in the ocean (Figure 24). The time series of the variables that are necessary to estimate both the gas transfer velocity (k_{660}) and the MSS are shown as time series in Figures 25-26.

Figure 25: ASIS-2 time series: a) Wind speed, b) Wind direction, c) Temperature, d) Atmospheric pressure, e) Dry air density, f) CO_2 density, and g) Water vapor density.

Figure 26: ASIS-2 time series: a) Turbulent transport of temperature by the vertical velocity ($\overline{w'T'}$), b) CO₂ underwater pressure by the SAMI sensor, c) Humidity mixing ratio, d) CO₂ mixing ratio, e) Turbulent transport of CO₂ by the vertical velocity ($\overline{w'\rho'_{CO_2}}$). The gaps in (l) is due to a quality flag in the data.

Figure 25-a shows the wind speed measured by the buoy during the sixteen days in the ocean. The mean wind speed is $8 \pm 2 \text{ m s}^{-1}$, with 3.2 m s^{-1} as the lowest wind speed and the maximum wind speed is 14.7 m s^{-1} measured on June 30. The highest wind speeds recorded by the buoy are due to the approximation of a cyclone. Figure 27a shows the cyclone blowing wind to the north, and can also be seen in the direction of the wind (Figure 25-b). This high wind speed contributed to enhance the air-sea gas transfer by bubbles and wave-breaking. In July 4 (Figure 27b) the buoy was under the influence of westerlies and the direction of the wind varied quickly (Figure 25-b). Finally, in July 8, the westerlies weakened over the buoy position due to the approximation of a front coming from the Arctic (Figure 27c).

Figure 27: Wind magnitude and direction near the buoy (blue dot) position. Data from the *Cross-Calibrated Multi-Platform Ocean Surface Wind Vector*.

Source: <ftp://podaac-ftp.jpl.nasa.gov/allData/ccmp/L3.0/flk>

The buoy experienced normal temperatures (Figure 25-c) for the northern hemisphere in the summer (Figure 28). The average temperature recorded is $17.6 \pm 0.7^\circ\text{C}$, with the minimum temperature equal to 15.3°C . The increasing in temperature in June 30 is provoked by the advection of warmer air from the tropics by the cyclone. The temperature is an important factor in the gas transfer velocity because the Schmidt number depends on it.

(a) June

(b) July

Figure 28: Temperature climatology for the ASIS buoy region. Data from the World Ocean Atlas (LOCARNINI et al., 2013) for the 1955–2012 period.

The Mean Sea Level Pressure (MSLP, Figure 25-d) has the averaged value of 1021 ± 6 hPa. The lowest pressure is 1009 hPa in June 30, not surprisingly coinciding with the approximation of the cyclone. In the following days, the pressure increased, getting

its highest value (1030 hPa) in July 9. The pressure will be used in calculation of the atmospheric density of CO₂.

The dry-air density time series (Figure 25-e) is similar to pressure time series. The mean value is $41.3 \pm 0.3 \text{ mol m}^{-3}$. The dry-air density had the lowest value (40.7 mol m^{-3}) with the approximation of the cyclone. This occurs due to the advection of moist and warmer air and decrease the dry-air density. The highest value is 41.9 mol m^{-3} .

The water vapor density (Figure 25-g) shows a continuous increase with the advection of moist air from the tropics made by the cyclone. The humidity mixing ratio (Figure 26-c) shows variations similar to the water vapor density. The mean value is $10 \pm 2 \text{ mmol m}^{-3}$, with the lowest value equal to 5 g kg^{-1} and the maximum equal to 12 g kg^{-1} . These values are important to apply the Webb correction to the fluxes and remove the influence of the water vapor density in the fluxes of CO₂.

Turbulent transports (Figures 26-a, 26-e) cannot be analyzed with synoptic scale dynamics because they are micro-scale phenomena. The gaps observed in Figure 26-l are due to the presence of bad *quality flags* in the data. The quality flags are associated with the tilting of the buoy in the ocean. When the vertical axis of the buoy is not perpendicular to the ocean surface, the measurements of the vertical (w') fluxes are subject to a correction. Values recorded above the upper limit for the inclination of the buoy are defined as bad values. The bad values were removed from the time series, with its position appearing as white spaces.

3.1.2 The Gas Transfer Velocity

To calculate the gas transfer velocity for CO₂ using the development made in section 1, the difference of pressure of carbon dioxide between the atmosphere and the ocean ($\Delta p\text{CO}_2$) was computed using

$$\Delta p\text{CO}_2 = p\text{CO}_{2\text{ o}} - p\text{CO}_{2\text{ a}}, \quad (40)$$

where $p\text{CO}_{2\text{ o}}$, $p\text{CO}_{2\text{ a}}$ are the partial pressures of CO₂ in the ocean and in the atmosphere, respectively. Each pressure was calculated using Equation 41 (WALLACE; HOBBS, 2006)

and Equation 42 (SENSORS, 2013):

$$pCO_{2a} = CO_{2mixRatio} \cdot p \cdot 0.0001 \quad (41)$$

$$pCO_{2o} = pCO_{2SAMI5m} \cdot 0.101325. \quad (42)$$

The CO_2 atmospheric mixing ratio ($CO_{2mixRatio}$), atmospheric pressure (p), and the CO_2 partial pressure under water ($pCO_{2SAMI5m}$) were measured by the instruments on the buoy (Figure 26). The mixing ratio is in PPM, the underwater pressure of CO_2 is in μatm and pCO_{2atmos} and pCO_{2ocean} are in Pa. The difference of partial pressure of CO_2 between the atmosphere and the ocean can be observed in Figure 29.

Figure 29: Time series of the difference of partial pressure of CO_2 between the ocean and the atmosphere

The averaged value of ΔpCO_2 taken in the whole time series (16 days) is $-38.8 \pm 0.9 \mu atm$. These values are lower than those obtained by McGillis et al. (2001a). Their study was performed during the GasEx-98 experiment near $46^\circ 6' N$, $20^\circ 55' W$. The stations were performed across the Atlantic Ocean finishing near Lisbon, Portugal, near the site of the DOGEE campaign. The experiment was realized during the the month of June of 1998 in a warm region. The values encountered by McGillis et al. (2001a) is $-85.8 \pm 16 \mu atm$. McGillis et al. (2001a) states that their values of ΔpCO_2 are greater than expected because of a possible algal bloom near the measurement site. Krasakopoulou et al. (2009) analyzed

the $\Delta p\text{CO}_2$ in the Aegean Sea (Greece) and found values between -34 and -61 μatm . The result shown in Figure 29 is in the range of values presented in the studies cited above. The values of $\Delta p\text{CO}_2$ are negative because the values of $p\text{CO}_{2\text{a}}$ are greater than $p\text{CO}_{2\text{o}}$. This occurs due to the main sources of CO_2 are concentrated in the atmosphere and the low solubility of the CO_2 in the ocean. Additionally, the CO_2 diffusion constant/turbulent transport is greater in the air than in the water, generating a greater spatial variability.

The second variable to calculate the CO_2 gas transfer velocity is the flux of CO_2 between the atmosphere and the ocean. The method used in this study to obtain this flux is the *Eddy covariance method*, as described in Section 1. It assumes that the flux of CO_2 crossing the air–sea interface is due to the turbulent transport of CO_2 by the vertical velocity:

$$F_{\text{CO}_2} = \overline{w' \rho'_{\text{CO}_2}}, \quad (43)$$

where F_{CO_2} is the flux of CO_2 ($\text{kg m}^{-2} \text{s}^{-1}$), w' is the deviation of the instantaneous vertical velocity from its temporal mean, and ρ'_{CO_2} is the deviation of density of CO_2 from its mean. The vertical velocity was obtained using an sonic anemometer, due to its higher data sampling. The overbar in Equation 43 indicates the averaged value of both deviations. The dataset used in this project had the CO_2 flux previously calculated by the DOGEE staff.

The flux calculated with Equation 43 needs a correction to eliminate the influences of the vertical turbulent fluxes of temperature and water vapor. For this reason, the flux calculated with Equation 43 is known as raw flux of CO_2 . One simple way to visualize the effects of the fluxes of temperature and water vapor on the flux of CO_2 is to imagine a bowl with CO_2 inside. When the bottom of the bowl is heated, a convective process starts. The flux of temperature creates a convection process that move some mass of CO_2 upwards. This flux of CO_2 mass is due only to the flux of temperature, and not to w' . The consequence is that $\overline{w' T'}$ is affecting the value of $\overline{w' \rho'_{\text{CO}_2}}$. The variation of water vapor has a similar effect. Imagine that the bowl has water in its bottom. This water releases molecules of water vapor inside the bowl. The gas inside the bowl is not a pure gas, its a mixture of CO_2 and water vapor. When molecules of water vapor are transported

by fluctuations of vertical velocity together with molecules of CO_2 , the flux of CO_2 is lower because molecules of water vapor replaced part of the molecules of CO_2 . The consequence is the $\overline{w'\rho'_v}$ causes variations in $\overline{w'\rho'_{\text{CO}_2}}$. A correction is needed to remove both fluctuations of temperature and water vapor density from the raw flux. With this correction, measurements of flux of CO_2 with different values of $\overline{w'T'}$ and $\overline{w'\rho'_v}$ can be corrected and comparable to the values of CO_2 fluxes from the literature. Webb, Pearman and Leuning (1980) developed a method aptly named *The Webb correction*:

$$F = \overline{w'\rho'_{\text{CO}_2}} + \mu \frac{\overline{\rho_{\text{CO}_2}}}{\overline{\rho_a}} \overline{w'\rho'_v} + (1 + \mu\sigma) \frac{\overline{\rho_{\text{CO}_2}}}{\overline{T}} \overline{w'T'}, \quad (44)$$

where $\overline{w'\rho'_{\text{CO}_2}}$ is the vertical turbulent transport of carbon dioxide density, $\mu = M_a/M_v$ is the ratio of molecular mass weight between the dry air and water vapor, $\sigma = \overline{\rho_v}/\overline{\rho_a}$ is the ratio between the vapor and dry air densities, $\overline{\rho_{\text{CO}_2}}$ is the mean density of CO_2 , $\overline{T}$ is the mean temperature, and $\overline{w'T'}$ is the turbulent transport of temperature. The raw (Equation 43) and the corrected fluxes (Equation 44) are shown in Figure 30.

Figure 30: Raw and Webb-corrected flux of CO_2 measured by the ASIS buoy.

The Webb correction shows its importance in the ocean removing the flux of water vapor from the raw flux of CO_2 . Figure 30 shows that the Webb correction changes the direction of the CO_2 flux. This result is in consonance with other studies in the literature. Kondo and Tsukamoto (2007) studied the air-sea gas transfer in the Indian Ocean near Indonesia. In one point of their data, the raw flux of CO_2 obtained is $-0.052 \text{ mg m}^{-2} \text{ s}^{-1}$

and the Webb correction gives $+0.062 \text{ mg m}^{-2} \text{ s}^{-1}$. Other point with a raw flux of $-0.063 \text{ mg m}^{-2} \text{ s}^{-1}$ has a Webb corrected flux of $+0.064 \text{ mg m}^{-2} \text{ s}^{-1}$. The Liebethal and Foken (2003) study shows similar results for a grassland field in Germany.

The last correction needed to calculate the gas transfer velocity is the solubility factor. The solubility of a gas in the sea water is a parameterized function of temperature and salinity. Following Wanninkhof (1992), the solubility is given by:

$$\text{Sol} = B(T, S) \cdot \left(\frac{T}{273.15} \right) \quad (45)$$

where $B(T, S)$ is the *Bunsen coefficient*, defined as:

$$B(T, S) = -60.2409 + 93.4517 \cdot \left(\frac{100}{T} \right) + 23.3585 \cdot \log \left(\frac{T}{100} \right) + S \cdot \left(0.023517 - 0.023656 \cdot \left(\frac{T}{100} \right) + 0.0047036 \cdot \left(\frac{T}{100} \right)^2 \right), \quad (46)$$

and T is the temperature in degrees Kelvin and S is the salinity in PSU. The salinity measured by the ASIS buoy is presented in Figure 31. The values are in the expected range for the summer in that area when compared to the climatology (Figure 32).

Figure 31: Salinity measured by the ASIS buoy. The averaged time series salinity is 35.87 ± 0.03 PSU.

Figure 32: Salinity climatology for the ASIS buoy region. Data from the World Ocean Atlas (ZWENG et al., 2013) for the 1955-2012 period.

The solubility time series can be seen in Figure 33. The averaged solubility is $0.00147 \pm 0.00003 \text{ kg kg}^{-1}$. This value is in the expected range according to the chemical oceanography literature. Weiss (1974) shows a table with a solubility of 2.968 g Kg^{-1} for 24°C and 36 PSU. Diamond and Akinfiev (2003) shows a solubility of 1.5 g kg^{-1} at 1 atm and 24°C . Salinity is not considered in this last study.

Figure 33: Solubility of CO_2 in water calculated with Equation 45.

With the values of F_{CO_2} , solubility, and $\Delta p\text{CO}_2$, the gas transfer velocity can be calculated as (Section 3.1.2):

$$k = \frac{F_{CO_2}}{Sol(S, T) \Delta p_{CO_2}}. \quad (47)$$

Equation 47 is the expression for the gas transfer velocity. To compare the gas transfer velocities to the results of others studies carried out in different temperatures, the k value is normalized to a *Schmidt number* (Sc) of 660. This value is due to the Schmidt number of CO_2 in seawater at $20^\circ C$ is equal to 660 (WANNINKHOF, 1992). The Schmidt number is parameterized and dependent only on temperature (WANNINKHOF, 1992):

$$Sc = 2073.1 - 125.62T + 3.6276T^2 - 0.043219T^3 \quad (48)$$

Therefore, the gas transfer velocity (k_{660}) shown in is obtained from:

$$k_{660} = k \left(\frac{Sc}{660} \right)^{-1/2}. \quad (49)$$

The averaged value of the k_{660} time series (Figure 34) found in this study is 48.4 ± 0.5 $cm\ h^{-1}$. This result shows values in the known range from the literature (WANNINKHOF, 1992).

Figure 34: Time series of the CO_2 gas transfer velocity from Equation 49.

The spike in July 01 is due to the cyclone near the buoy (Figure 27b). The high wind speed enhanced the gas transfer velocity by wave-breaking and bubbles (Section 1.2). The

gas transfer velocity as a function of wind speed (u_{10}) can be seen in Figure 35. For this figure u_{10} was measured by the buoy anemometer and k_{660} was obtained from formula 49 using buoy measurements of T , $\Delta p\text{CO}_2$, w' and ρ' .

Figure 35: Relation between the CO_2 gas transfer velocity and the wind speed at 10m.

The distribution of k_{660} with respect to the wind speed shows an agreement with the literature as can be seen in Edson et al. (2008) and Wanninkhof (1992). In Figure 35, 26% of the k_{660} values are below 10 m s^{-1} and in the y-axis, the interval of $20\text{--}40 \text{ cm h}^{-1}$ is occupied by 58% of the points. For higher wind speeds, the spread of k_{660} becomes relatively larger. A non-linear dependence between u_{10} and k_{660} is expected at wind speeds above 10 m s^{-1} because that is where the theory developed by Liss and Merlivat (1986) and Wanninkhof (1992) show significant differences.

Figure 36: Histogram of the distribution of the values of k_{660} and the assumed gaussian distribution.

The histogram of distribution of the k_{660} values (Figure 36) shows good agreement with the expected values from the literature (BENDER et al., 2011).

3.1.3 The Wave Measurements

The wave data collected by the ASIS buoy had a data acquisition frequency of 10 Hz. This frequency produced more than 10^7 data points in the 22 days of the cruise. The entire time series was split in 49 files with a variable number of arrays with 30 minutes of continuous data each. The measurements have irregular gaps of a few minutes between each 30 minutes segment. For example, the time stamp of one segment of data is 09:25 AM and the next one is 10:00 AM, not 09:55 AM. Figure 37 shows the time gaps in minutes between all the data files.

Figure 37: Time gaps between consecutive arrays of data. These intervals contained no wave measurement.

In this analysis, the gaps between the segments were ignored and the segments were joined. This is justified by the argument that we are only interested in frequencies much higher than the longest harmonic of each individual data segment (i.e. periods much shorter than 10 minutes). The signal we are most interested is due to capillary-gravity waves that are intermittent, in bursts that are observed to last on the order of 4-10 seconds. The entire time series of surface wave height and the power spectrum are presented in Figure 38. The

higher variance around June 30 (top plane) was due to the wind waves generated by the cyclone. These waves are among the highest values measured by the ASIS buoy. The entire time series has a mean value of 0.0 ± 0.5 m. The lowest SSH value in the time series is -5.5 m and the maximum value is 9.5 m.

Figure 38: Wave height measured by the ASIS buoy. (Top) Time series (Bottom) Power spectrum of the time series.

The initial computation of the frequency analysis (lower plate) of the SSH data raise some concerns about the presence of white noise in the FFT. To evaluate this possibility, the frequency analysis was performed using the Welch method (Section 2.4.1). Figure 39 shows 3 segments of 10 minutes of data and their respective power spectrum. The FFT of each segment was calculated splitting it in 10 and 15 subdivisions. The purpose of this computation is to evaluate the presence of a flat part in the power spectrum, a white noise in a determined band of the spectrum. The results are statistically identical and the number of averaged segments in the Welch method found to be the best was 15. Using 10 yields a flat part of the spectrum around 5×10^{-2} Hz.

The shape of the power spectrum is in good agreement with the Pierson-Moskowitz formulation (PIERSON; MOSKOWITZ, 1964). Their formulation shows that for a fully

Figure 39: Time series of wave height and the power spectrum of three segments of data. Ns is the number of averaged segments in the Welch method.

developed sea, the peak in the power spectrum is 0.1 Hz. The peak in our case is 0.104 Hz, and is taken as an indication that we observed a fully-developed sea. With a power spectrum for every 10 minutes of data, the power spectrum of the entire time series can be obtained by averaging the 10 minutes segments. Additionally, this approach can be used to calculate the standard deviation of the time series. Figure 40 reinforces the spectrum of Pierson-Moskowitz and the fully developed sea. The linear fit (red line) shows an angular coefficient of $-4.033 \pm 0.008 \text{ m}^2 \text{ Hz}^2$, that agrees with the study of Elfouhaily, Chapron and Katsaros (1997), where the power spectrum $\sim k^{-4}$ is related to the fully developed ocean with short wind waves. The result obtained here shows that waves with frequencies above 0.104 Hz have an intense power decay, making the waves around the peak the most powerful of the wind generated waves.

Figure 40: Averaged power spectrum of 10 min of data. The linear fit is in log-log space.

The mean square slope (MSS) of sea surface is defined as the variance of surface slope. This variable is dimensionless and quantifies the mean curvature of the waves in the ocean surface. It can be interpreted as a measure of roughness of the ocean, since higher values of MSS indicated a wavy sea. Phillips (1977) defined MSS as:

$$MSS^2 = \int_0^\infty k^2 \phi(\vec{k}) d\vec{k} \quad (50)$$

where k is the wavenumber vector and $\phi(\vec{k})$ is the wavenumber spectrum of ocean waves. Combining the above definition of MSS with the surface gravity-wave dispersion relation

$$\omega^2 = gk, \quad (51)$$

where ω is the angular frequency ($\omega = 2\pi f$), f is the frequency and g is gravity, assumed equal to 9.80665 m s^{-2} , yields (LI et al., 2013):

$$MSS^2 = \int_0^\infty \frac{(2\pi f)^4}{g^2} F(f) df, \quad (52)$$

where $F(f)$ is the Fourier transform of the wave data. The original continuous fast fourier transform (CFFT) was replaced by the discrete fourier transform (DFT) to process the discrete sampled data. The FFT was calculated in every 10 minutes window over all the time series.

To assure that the mean square results are trustworthy, a comparison with another variable that accounts for the variability of the ocean surface can be done. The *Significant Wave Height* (SWH) is a measure of the wave state of the sea. Originally, it was defined as the mean wave height (trough to crest) of the highest third of the waves (SVERDRUP; MUNK, 1947). Nowadays, the SWH is defined as (WMO, 1998):

$$SWH = 4STD(SSH), \quad (53)$$

where STD is the standard deviation of the sea surface height. Both time series of mean square slope and sea surface height show the expected range of values (ELFOUHAILY; CHAPRON; KATSAROS, 1997; BOGUCKI et al., 2010). It is noticeable the peak in MSS as SWH showing the presence of high winds of the cyclone (Figure 27b).

Figure 41: Mean Square Slope (black) and Significant Wave Height (blue) of the ASIS wave data.

3.1.4 The Wavelet Analysis

The wavelet analysis indicates how the power spectrum of some variable changes in time and the cross-wavelet shows how the power spectrum of two variables changes in time. This should be the analysis performed between the MSS and the k_{660} .

Due to the different data sampling of the $\Delta p\text{CO}_2$ (1 measurement every 30 minutes or a Nyquist interval of 1 hour) and the SSH (10 Hz or a Nyquist interval of 0.2 seconds), its not possible analyze the cross-wavelet spectrum for periods less than one hour. To cope with this limitation, the wavelet analysis will be performed using the continuous wavelet of the SSH and compared with the time series of k_{660} .

Figure 42: (a) Gas transfer velocity (k_{660}) with the mean removed and normalized by the standard deviation. (b) Continuous wavelet transform of the SSH time series. The original data at a resolution of 0.1 s has been averaged to 1 s. (c) The integral of the wavelet tranform along the time axis. It corresponds to the FFT. (d) Averaged variance of the SSH obtained from the wavelet transform.

Figure 42 shows that when high values of k_{660} starts to appear (2000 s), an increase in power is observed in the SSH wavelet transform. This energy is concentrated in waves with periods of 8 to 1024 seconds, with a peak in 256 seconds. Using the surface gravity-waves

dispersion (Equation 51), the wavelength of these period are 99 meters and 102 kilometers.

The approach of observing the regions with higher energy in the wavelet power spectrum cannot provide information about the microscale physics of the interaction of the waves with the gas transfer velocity. The next section a new approach to study the MSS- k_{660} will be developed to isolate the short wave wavelengths.

3.1.5 The Wave- K_{660} Analysis

The analysis of the relationship between the mean square slope and the gas transfer velocity is initially based in the studies of Bock et al. (1999) and Jahne, Heinz and Dietrich (1987). The last study showed that the MSS has a linear relation with the gas transfer velocity:

$$k_{660} = \alpha \cdot MSS + \beta, \quad (54)$$

where α is the angular coefficient of the line and β is the linear coefficient. Figure 43 shows that the MSS and K_{660} from the DOGEE data has a linear relationship as the tank experiments in Bock et al. (1999) study. The data showed included all the available points.

Figure 43: Linear relationship between the MSS and k_{660} . The red line is the linear fit between both variables.

The results showed here incited some doubts about how the presence of outliers points could impact the dispersion in MSS and the k_{660} . Table 4 shows the number of points that is between one, two and three standard deviations of the MSS and k_{660} .

Table 4: Number of points inside the mean plus one, two, and three standard deviations of k_{660} and MSS.

	k_{660}	MSS
All data	310	310
1 STD	232	261
2 STD	291	305
3 STD	303	308

Figure 44 shows the k_{660} data, the mean and one standard deviation of the data. The same was done to the MSS.

Figure 44: (top) k_{660} time series, mean (red line) and standard deviation (blue lines). (below) MSS time series, mean (red line) and standard deviation (blue lines).

The result showed that only a few points are outside the standard deviation range. The periods of the cyclone and the passage of the front are related to the outside points.

The analysis of the data with the MSS calculated with data integrated in bands of $10 \text{ radians m}^{-1}$ was performed for the raw data and to data in the range of one standard deviation (Figures 45-46).

Figure 45: Linear fit between MSS and k_{660} . The left column is the raw data and the right column is the data in the range of 1 standard deviation. The rows are the MSS integrated in the range 0-10 and, 10-20, 20-30, 30-40, 40-50, 50-60 rad m^{-1} .

Figure 46: Linear fit between MSS and k_{660} . The left column is the raw data and the right column is the data in the range of 1 standard deviation. The rows are the MSS integrated in the range 60-70, 70-80, and 80-90, 90-100 radians m^{-1} .

Figures 45-46 shows the linear fit between the MSS and the gas transfer velocity for several intervals of integration of the MSS. One can see that the points are more spread in the range $0 < k < 10 \text{ rad } m^{-1}$ than in the range $80 < k < 90 \text{ rad } m^{-1}$. This indicates that the higher the wavenumbers, the better is the linear fit. The Root Mean Square (RMS) error of each fit from Figures 45-46 can be seen in Figure 47.

Putting aside the fact that there is a small number of points in figure 47, there is an apparent regime shift near $40 \text{ rad } m^{-1}$. In that, the points associated to $k > 50 \text{ rad } m^{-1}$ follow a smooth progression and for $k \leq 50 \text{ rad } m^{-1}$ the arrangement is less organized. The largest difference in the error between waves with wavenumber between 30-40, and

40-50 suggest that a distinct physical mechanism is actuating in this wavenumber range.

Figure 47: Root Mean Square (RMS) error of each linear fit from Figures 45-46

The difference between the original MSS and the MSS calculated only with wavenumbers in the range 40-50 can be seen in Figure 48. The values of MSS obtained in the limited 40-50 rad m⁻¹ range are (in average) 26% lower than the MSS calculated over all wavenumbers and both time series preserve the overall shape (top plane).

Table 5 shows the linear regression coefficients from Figure 45-46. The correlation coefficient (r) shows that the best fit is for the segment with wavenumbers between 40 and 50 radians m⁻¹. The p-value shows how statistically significant is the result, and p-values greater than 0.05 (WILKS, 2011) are interpreted as not significant. Only the MSS with wavenumbers between 10 and 20 rad m⁻¹ are greater than 0.05.

Table 5: Linear regression between mean square slope and the gas transfer velocity (k_{660}).

	Slope	Intercept	correlation	p-value
0 < k < 10	$2.1 \times 10^{-4} \pm 4 \cdot 10^{-5}$	$-1.29 \cdot 10^{-5}$	0.09	0.00
10 < k < 20	$1.1 \times 10^{-4} \pm 6 \cdot 10^{-5}$	$9.39 \cdot 10^{-6}$	0.17	0.11
20 < k < 30	$1.7 \times 10^{-4} \pm 6 \cdot 10^{-5}$	$4.70 \cdot 10^{-6}$	0.16	0.00
30 < k < 40	$1.4 \times 10^{-4} \pm 6 \cdot 10^{-5}$	$8.70 \cdot 10^{-6}$	0.23	0.03
40 < k < 50	$2.09 \times 10^{-3} \pm 7 \cdot 10^{-5}$	$5.23 \cdot 10^{-6}$	0.52	0.00
50 < k < 60	$2.01 \times 10^{-3} \pm 7 \cdot 10^{-5}$	$4.94 \cdot 10^{-6}$	0.38	0.00
60 < k < 70	$2.15 \times 10^{-3} \pm 7 \cdot 10^{-5}$	$5.42 \cdot 10^{-6}$	0.29	0.00
70 < k < 80	$2.36 \times 10^{-3} \pm 8 \cdot 10^{-5}$	$6.84 \cdot 10^{-6}$	0.37	0.00
80 < k < 90	$2.22 \times 10^{-3} \pm 8 \cdot 10^{-5}$	$4.51 \cdot 10^{-6}$	0.40	0.00

Figure 48: The original MSS time series and the MSS computed with wavenumber between 40 and 50 radians m^{-1} .

Finally, for the best correlation coefficient, the equation relating MSS and k_{660} is:

$$k_{660}(mss) = 2.09 \cdot 10^{-3} mss + 5.23 \cdot 10^{-6}, \quad (55)$$

where k_{660} is in m s^{-1} . This relation has a correlation of 0.52 and provides a linear relation between MSS and k_{660} . Equation 55 allows us to infer the gas transfer velocity based on the mean sea surface slope of capillary-gravity waves with k between 40 and 50 rad m^{-1} . It is necessary to keep in mind that its applicability is limited to areas where the wind speed is in the $2\text{-}14 \text{ m s}^{-1}$ range, and that no bubbles or foam develops at the interface.

The next step of this study is to establish a mathematical relation between the normalized radar cross-section (NRCS) and the mean square slope. Finally, using Equation 55 will yield the relation between k_{660} and NRCS that will allow us to relate the scatterometer measurements to k_{660} .

3.2 Application: monitoring gas transfer velocity with satellite data

The development of a relation between the gas transfer velocity (k_{660}) and the mean square slope (MSS) has been achieved in Section 3.1.5. To develop an estimate of the air-sea gas transfer using satellites, a relation between MSS and the Normalized Radar Cross-Section (NRCS) is necessary. The literature provides some relationships between the MSS and the wind speed. The link between the wind speed and the NRCS is the essence of the satellite model function, an empirical relationship between the wind speed and the σ_0 signal received by the satellite.

Cox and Munk (1954) deduced slopes of the sea surface from the brightness distribution of photographs of sun glitter on the sea surface. One of their main results is this linear relationship between the MSS and the equivalent neutral wind speed at 10 meters above the sea surface:

$$MSS(U_{10}) = 0.003 (3.0 + 5.12 U_{10}), \quad (56)$$

where U_{10} is the wind at 10 meters from the sea surface.

An alternative relationship was developed by Wu (1972). He found that the relation between the MSS and U_{10} vary logarithmically, not linearly. In his study, the capillary part of the wave spectrum was considered together with the boundary-layer regimes of the wind. He proposed that MSS and wind speed at 10 meters are related as follows:

$$MSS(U_{10}) = \begin{cases} 0.01 \left(3.2 + 1.2 \log \left(\frac{U_{10}}{7.0} \right) \right) & , 1 \text{ m s}^{-1} \leq U_{10} < 7 \text{ m s}^{-1} \\ 0.01 \left(3.2 + 6.0 \log \left(\frac{U_{10}}{7.0} \right) \right) & , U_{10} \geq 7 \text{ m s}^{-1} \end{cases} \quad (57)$$

$$(58)$$

His results showed that the growth of small surface waves is due to the direct effect of the wind.

Phillips (1977) developed an expression for the fully developed sea using the logarithmic approach of Wu (1972). He applied a “cut-off” wavenumber $2\pi/0.3$ due his simplifying assumption that wave components shorter than 30 cm are not significant for

the MSS. In this situation the lowest wavenumber in the equilibrium range is close to the wavenumber of the spectral peak. His final expression is:

$$MSS(U_{10}) = 0.0046 \log \left(\frac{2\pi}{0.3} \frac{U_{10}^2}{g} \right), \quad (59)$$

where g is gravity.

Finally, Jackson, Walton and Baker (1985) developed a linear relation (Equation 60) between MSS and U_{10} using aircraft and satellite measurements of the ocean surface. The technique they applied in their study is measuring the vector wave number spectrum of the ocean surface using short-pulse, noncoherent radars in a conical scan mode near vertical incidence, a strategy for both aircraft and satellite applications. This new approach differ from the others considered above by considering remote sensing techniques to infer the MSS.

$$MSS(U_{10}) = 0.0028 U_{10} + 0.009, \quad 5.0 \text{ m s}^{-1} \leq U_{10} \leq 18.0 \text{ m s}^{-1}. \quad (60)$$

The conversion of wind speed into Normalized Radar Cross-Section is done with the *QuikSCAT Geophysical Model Function*, a computer program whose source code written in the FORTRAN language (Attachment A) and it is public available at <http://podaac.jpl.nasa.gov/>. The relationship between MSS and NRCS are obtained through the insertion of the winds in equations 56 to 60 into the model function algorithm.

Figure 49 shows the newer relations (Jackson et al., Phillips) are more restrictive than the first studies (Cox and Munk, Wu). In the range 0-0.05 of the MSS the results are very similar. The relation proposed by Cox and Munk and Wu are valid for a wider range of MSS.

In the next section the different MSS relations given by equations 56 to 60 will be used to calculate the gas transfer velocity adopting equation 55. The satellite data is the Ultra High Resolution QuikSCAT data developed by Professor D. Long (EARLY; LONG, 2001).

Figure 49: Relationship between Mean Square Slope and Normalized Radar Cross-Section

3.2.1 Comparison between the satellite and buoy data

This section shows the comparison between the k_{660} obtained by the regression (Equation 55) using the QuikSCAT σ_0 with the gas transfer velocity from the ASIS buoy. The comparison is performed by calculating the difference between the k_{660} from the buoy data with the k_{660} derived from the satellite data (Figure 50) and the regression (Equation 55) at the specific position of the buoy. Around four MSS-sigma-0 relations (Equations 56 to 60) presented in Figure 49, only the relation proposed by Wu (1972) is shown in this section. The choice of this parametrization is due to the higher difference in NRCS to small variations of MSS. This enhance the values k_{660} from regions of low and high values of sigma-0 in satellite images. The figures from the others parameterizations are in Appendix B.

Figure 50: The k_{660} obtained from the MSS parameterization proposed by Wu (1972) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy. The values of k_{660} from the buoy and equation 55 are in lines 2, 6, and 10 of Table 6.

The gas transfer map (Figure 50) of 2007/06/30 shows the buoy near a region of high values of k_{660} . The presence of the cyclone (Figure 27a) contributed to the high agitation of the sea surface and higher values of the gas transfer velocity. Both polarizations (vertical and horizontal) have similar patterns, but the horizontal polarization has not so strong values in the upper-left corner of the figure. The parameterizations of Cox and Munk, and the parameterization of Jackson (Appendix B) have similar patterns, but with higher k_{660} values. The parameterization of Phillips produces more homogeneous fields and with smaller values of k_{660} . The Jackson's parameterization shows large areas of missing information due to the parameterization be defined only in a range of wind speed.

The second day (Figure 50) analyzed is 2007/07/04 at 10:40 AM. The synoptic pattern (Figure 27b) shows the North Atlantic wind regime caused by the subtropical high pressure system near the buoy and higher wind speed with a zonal orientation. A region of higher values of k_{660} is near the coast of Portugal, as the general aspect of the synoptic events. The last day analyzed is 2007/07/08 at 10:30 AM and resembles the day 2007/07/04. The synoptic pattern (Figure 27c) shows a zonal wind and the subtropical high at the south. The Phillips parameterization has an almost linear relation between NRCS and MSS (Figure 49) and this generates figures with small differences between lower and higher values of MSS. This relation have the greatest slope for values of NRCS between -40 and -10 dB. The relation generates values smaller than 0.05 in the MSS axis, making values of MSS not very spread.

The comparison between the values of k_{660} obtained by the ASIS buoy and the k_{660} obtained by the equation 55 using the MSS from equations 56 to 60 applied to the vertical and horizontal polarization is presented in Table 6. The mean difference between the k_{660} obtained by the vertical and horizontal polarization for the three days is 0.7 ± 0.5 cm h^{-1} and the lowest values is obtained with the parameterization of Phillips (1977). The parameterizations of Cox and Munk (1954) and Wu (1972) presented the highest differences.

Table 6: Values of the k_{660} from the ASIS buoy, the k_{660} obtained from the vertical polarization, the k_{660} obtained from the horizontal polarization, the difference of k_{660} from both polarizations, and the difference of the buoy k_{660} and each polarization. The C, W, P, and J refers to the relations proposed by Cox and Munk (1954), Wu (1972), Phillips (1977), and Jackson, Walton and Baker (1985), respectively. The time in the first column is the buoy measurement time. The NaN values are due to the MSS relation cannot be valid in that region.

Time/MSS	k_{660} (buoy)	k_{660} (v)	k_{660} (h)	$ v - h $	$ \text{buoy} - v $	$ \text{buoy} - h $
2007/06/30-10:29 (C)	39.70	32.22	31.92	0.30	07.47	07.77
2007/06/30-10:29 (W)	39.70	27.79	27.31	0.48	11.90	12.38
2007/06/30-10:29 (P)	39.70	18.26	18.18	0.08	21.43	21.51
2007/06/30-10:29 (J)	39.70	24.01	23.85	0.16	15.68	15.84
2007/07/04-10:46 (C)	04.77	12.50	13.74	1.24	07.73	08.97
2007/07/04-10:46 (W)	04.77	15.39	16.64	1.25	10.62	11.87
2007/07/04-10:46 (P)	04.77	09.87	10.83	0.95	05.10	06.05
2007/07/04-10:46 (J)	04.77	NaN	NaN	NaN	NaN	NaN
2007/07/08-10:03 (C)	11.03	32.17	31.30	0.87	21.14	20.27
2007/07/08-10:03 (W)	11.03	27.71	26.28	1.43	16.68	15.25
2007/07/08-10:03 (P)	11.03	18.24	18.03	0.22	07.21	05.99
2007/07/08-10:03 (J)	11.03	23.98	23.50	0.47	12.95	12.47

The comparison with the buoy data showed that the parameterization of Phillips (1977) produced the lowest differences (around 5 cm h^{-1}), except in Jun 30. This day presented higher wind values and the parameterization is not realistic in this situation. The others parameterizations didn't worked too, with the relation of Jackson, Walton and Baker (1985) having a difference of more than 15 cm h^{-1} . The last day show the parameterization of Jackson, Walton and Baker (1985) with a difference of $\sim 13 \text{ cm h}^{-1}$ while the relation of Phillips (1977) is around $6\text{-}7 \text{ cm h}^{-1}$.

3.2.2 The satellite gas transfer velocity comparison with Bogucki's approach

This section shows the comparison between the k_{660} obtained from Equation 55 combined with the parameterizations proposed by Cox and Munk (1954), Wu (1972), and Phillips (1977), with the parameterization proposed by Bogucki et al. (2010). This parameterization is the first to correlate the NRCS direct to the k_{660} . Among the four MSS-sigma-0 relations (Equations 56 to 60) presented in Figure 49, only the relation proposed by Wu (1972) is shown in this section. The figures from the others parameterizations are in Appendix B.

Figure 51: The k_{660} difference between the MSS parameterization proposed by Wu (1972) and the parameterization proposed by Bogucki et al. (2010). Values are in cm h^{-1} . The black dot is the position of the ASIS buoy.

Figure 52: The k_{660} difference between the MSS parameterization proposed by Wu (1972) and the parameterization proposed by Bogucki et al. (2010). Values are in cm h^{-1} . The black dot is the position of the ASIS buoy.

Each of the parameterizations (Equations 56-60) have different results when compared to the relation proposed by Bogucki et al. (2010), which is dependent only upon σ_0 , and doesn't need any NRCS to wind conversion. The difference map (Figures 52-51) between the k_{660} proposed by Wu (1972) and that proposed by Bogucki et al. (2010) shows values that exceed 10 cm h^{-1} (white shade) to regions of 5 cm h^{-1} . The relation proposed by Cox and Munk (1954) (Appendix B) shows lower difference ($7\text{-}10 \text{ cm h}^{-1}$) than Wu (1972). The Phillips (1977) relation shows differences of $1\text{-}5 \text{ cm h}^{-1}$ in regions of low wind speeds and values that exceed 10 cm h^{-1} in regions of high wind speeds. Finally, the relation of Jackson, Walton and Baker (1985) presented the lowest differences ($0\text{-}4 \text{ cm h}^{-1}$) of the four parameterizations, although the parameterization of the MSS be very restrictive (defined only in small range of MSS), generating wide regions of unavailable information.

In the absence of others studies of the relation of the MSS with the gas transfer velocity, the Bogucki's study can be used as a validation to the regression presented here. The

parameterizations of Phillips (1977) and Jackson, Walton and Baker (1985) have the lower difference when compared to Bogucki's parameterization.

4 Summary and Conclusions

This study analyzed the gas transfer velocity (k_{660}) of the carbon dioxide (CO_2) between the atmosphere and the ocean and its relation with the short wavelength gravity waves. The gas transfer velocity is one of the parameters relating the partial pressure difference of CO_2 between the atmospheric layer above the surface of the ocean and the layer immediately under the sea surface. This information is important to improve the knowledge of how much CO_2 will enter into the ocean in a global warming future scenario.

The data used in this study was collected during the DOGEE campaign of the UK-Solas project (BROOKS et al., 2009). The wave data and the partial pressure of the CO_2 of the atmosphere and the ocean were gathered by an automatic drifting buoy, released by the RRS *Discovery* in the northern Atlantic Ocean, during the months of June and July of 2007.

The partial pressure difference was measured by the buoy in intervals of 30 minutes. The CO_2 flux was calculated using the eddy covariance method. The Webb correction (WEBB; PEARMAN; LEUNING, 1980) was applied to remove turbulent fluctuations of temperature and water vapor from the CO_2 flux. Finally, the solubility was calculated and the gas transfer velocity (k) could be calculated. The result obtained was normalized by the Schmidt number of 660 to produce estimates of k_{660} that are comparable to results in the literature.

The wave data was measured by the buoy in intervals of 0.1 seconds. The power spectrum of the wave data showed a spectrum compatible with that proposed by Pierson and Moskowitz (1964). The presence of a cyclone (Figure 27a), large scale winds (Figure 27b) and a front (Figure 27c) during the experiment created a fully developed ocean, with waves with maximum height of 9.5 meters from the sea surface.

The mean square slope (MSS) was calculated with the sea surface height time series. The mean square slope is related to the curvature of the ocean waves and is directly correlated with the gas transfer velocity of CO_2 . The wavelet analysis (Figure 42) of the mean square slope showed high values during the passage of the cyclone over the buoy.

The analysis of the relation between the mean square slope and the gas transfer velocity

was based on the previous studies of Jahne, Heinz and Dietrich (1987) and Bock et al. (1999). These studies proposed a linear parameterization between the MSS and the k_{660} . Both studies showed that waves with higher wavenumber is better correlated with k_{660} than waves with lower wavenumber values.

This study tried to improve on this methodology by calculating the MSS for narrow ranges of wavenumber and calculating the regression (Equation 55) between the gas transfer velocity and each one of the MSS models proposed by Cox and Munk (1954), Wu (1972), Phillips (1977), and Jackson, Walton and Baker (1985).

The results showed that waves with wavenumbers less than 40 radians m^{-1} present higher RMS values in the regression of k_{660} with the MSS. Waves with wavenumbers between 40 and 50 radians m^{-1} have an abrupt decrease in the RMS value, keeping a relative low and constant value for wavenumbers greater than 50 radians m^{-1} . This result suggests that waves in the range 40-50 radians m^{-1} trigger some physical mechanism that increase the relation between the MSS and the k_{660} . This is probably related to the phenomenon of microbreaking.

Microbreaking is the breaking of waves of short wavelength without the penetration of air bubbles in the ocean (ZAPPA et al., 2004). When the microbreaking occurs, a parcel of fluid near the surface goes into layers above the surface (Figure 2). This parcel of fluid is replaced with a non-saturated parcel coming from the deeper layers of the boundary layer of the ocean. This process is related to the viscosity of water. The link between waves with 40-50 radians m^{-1} (wavelength of 12-15 cm) with microbreaking seems to be the viscous parameter of the momentum equations. Stokes (STOKES, 1845) showed that the viscous parameter is responsible for the decay of the wave amplitude. Kinsman (1984) states that viscosity acts to reduce the mean square slope of the sea surface. This transfers energy to small wavelengths waves and to microbreaking.

The QuikSCAT scatterometer Normalized Radar Cross-Section (NRCS) data was used to compare and validate the regression (Equation 55) developed with the ASIS buoy data. The conversion of NRCS to MSS was performed in two steps using the Geophysical Model Function of the satellite that converts NRCS to U_{10} and the parameterizations developed

by Cox and Munk (1954), Wu (1972), Phillips (1977) and Jackson, Walton and Baker (1985) that converts U_{10} to MSS, which, in turn will ultimately be converted into k_{660} . The best results were obtained with the parameterizations of Phillips (1977) (difference of $\sim 6 \text{ cm h}^{-1}$). The horizontal polarization produced a slightly greater ($< 0.5 \text{ cm h}^{-1}$) difference than the vertical polarization in the first and second day. In the third day, the horizontal polarization have the lower differences ($< 1 \text{ cm h}^{-1}$). This can be related to the wave direction in the sea. The wind in Jun 30 (Figure 27a) and Jul 04 (Figure 27b) are approximately zonal near the buoy. In Jul 08 the wind is bowing from the north (Figure 27c).

The k_{660} obtained using satellite data as described above can be compared with the k_{660} parameterized by Bogucki et al. (2010) to visualize similarities and differences. The results of this comparison shows that the parameterizations of Phillips (1977) ($1\text{-}5 \text{ cm h}^{-1}$) and Jackson, Walton and Baker (1985) ($0\text{-}4 \text{ cm h}^{-1}$) have the lowest difference when compared to Bogucki et al. (2010) model.

The flux of CO_2 between the atmosphere and the ocean can be obtained using the regression (Equation 55) proposed in this study. The flux of CO_2 is calculated using equation 5, where k is the gas transfer velocity and $\vec{\nabla}C$ is the CO_2 partial pressure difference between the atmosphere and the ocean. This last variable can be obtained in-situ by buoys or research vessels, or by numerical modeling. This can help to create future scenarios of ocean acidification in a global warming world.

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Attachment A

The QuikSCAT Model Function (MF) used in Section 3.2.1. This source code is public available at <http://podaac.jpl.nasa.gov/>. The file QSCAT2.asc is a *Look-up table*, a table with several NRCS values, incidence angles and wind speeds determined from observation. Its available together with the MF source code.

```

! -----
! MODULE lqsca
! -----
MODULE lqscat

IMPLICIT NONE

CONTAINS

FUNCTION nracs(azi, tht, u, phi)
! -----
! Version for use with SeaWinds model functions
! Author:  R. Scott Dunbar           12 January 2001
! -----
! Purpose:
!
! Look up and interpolate the value of the sigma-0 model function
!   for the given values of wind direction and wind speed.
!
! Uses multilinear interpolation among the nearest 8 model function
!   values in the model function table.
!
! INPUTS:
!     azi = cell azimuth w.r.t. north (deg)
!     tht = incidence angle (deg)
!     u   = wind speed (m/s)
!     phi = wind direction (deg)
! OUTPUT:
!     nracs = model sigma-0 from table
! -----

! Data declarations
IMPLICIT NONE
INTEGER, INTENT(IN) :: azi, phi, tht
INTEGER, PARAMETER :: REAL_SIZE = 4
REAL(KIND = REAL_SIZE), INTENT(IN) :: u ! wind velocity
INTEGER :: kt1, kt2, ku, kchi, ichi, ju, j, i, k, htth
REAL(KIND = REAL_SIZE) :: q, q1, p, p1, at1, at2, chi
INTEGER :: openStatus, & ! opening file status flag

```

```

        readStatus      ! reading file status flag
LOGICAL :: lexist ! logical file presence
! returned value of model function
REAL(KIND = REAL_SIZE) :: nrCs
! intermediate table of interpolated values
REAL(KIND = REAL_SIZE) :: mfun(2,2)
! table loaded from file
REAL(KIND = REAL_SIZE) :: table(40:60,0:50,0:90)
INTEGER, PARAMETER :: kt1min = 40, kt1max = 59

! Open ascii model function table file
INQUIRE(FILE = 'QSCAT2.asc', EXIST = lexist)
IF(.NOT. lexist) CALL fatalError("cannot find file QSCAT2.asc")

OPEN(17, FILE = 'QSCAT2.asc', STATUS = 'OLD', FORM = 'FORMATTED',
      IOSTAT = openStatus)
IF(openStatus > 0) CALL fatalError("cannot open file QSCAT2.asc")

! Reading table
DO k = 0, 90
  DO j = 0, 50
    DO i = 40, 60
      READ(17, *, IOSTAT = readStatus) table(i,j,k)
      IF(readStatus /= 0) CALL fatalError("error in file QSCAT2.asc")
    ENDDO
  ENDDO
ENDDO

CLOSE(17)

! -----
! Adjust the relative azimuth into the range (0.,180.) degrees
! and get interpolation coefficient q:

chi      = azi - phi
chi      = AMOD(chi, 360.0)
IF (chi < 0.0) chi = chi + 360.0
IF (chi > 180.0) chi = 360.0 - chi
ichi     = INT(chi/2.0)
q        = chi/2.0 - ichi
q1       = 1.0 - q

! -----
! Get interpolation coefficients w.r.t. incidence angle:

htht     = tht
kt1       = INT(htht)      ! first index
IF(kt1 <= kt1min) kt1 = kt1min

```

```

IF(kt1 >= kt1max) kt1 = kt1max
kt2          = kt1 + 1          ! second index
at2          = ht1t - kt1      ! second coefficient
at1          = 1.0 - at2       ! first coefficient

! -----
! Get interpolation coefficient w.r.t. u:
ju          = INT(u)           ! primary speed index
p           = u - ju
p1          = 1.0 - p

! -----
! Interpolate with respect to incidence angle:
DO i = 1, 2
  kchi = i + ichi - 1
  IF (kchi > 90) kchi = 180 - kchi
  DO j = 1, 2
    ku = j + ju - 1
    IF (ku == 0) THEN
      mfun(j,i) = 0.0
    ELSE
      mfun(j,i) = at1 * table(kt1, ku, kchi) + at2 * table(kt2, ku, kchi)
    ENDIF
  ENDDO
ENDDO

! -----
! Do bilinear interpolation of the working table to find nracs(i):

nracs = p1 * q1 * mfun(1,1) + p * q1 * mfun(2,1) + q * p1 * mfun(1,2) +
        p * q * mfun(2,2)

END FUNCTION nracs

SUBROUTINE fatalError(message)
! -----
! SUBROUTINE fatalError
! -----
IMPLICIT NONE
CHARACTER*(*) :: message

WRITE(*,*)"Fatal error: "//message
WRITE(*,*)"Now exiting to the system"
STOP

END SUBROUTINE fatalError

END MODULE lqscat

```

Appendix A

This appendix contains the figures of gas transfer velocity (k_{660}) calculated with the relations proposed by Cox and Munk (1954), Phillips (1977), and Jackson, Walton and Baker (1985). More information about these figures are in Section 3.2.1.

Figure 53: The k_{660} obtained from the MSS parameterization proposed by Cox and Munk (1954) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 54: The k_{660} obtained from the MSS parameterization proposed by Cox and Munk (1954) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 55: The k_{660} obtained from the MSS parameterization proposed by Phillips (1977) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 56: The k_{660} obtained from the MSS parameterization proposed by Phillips (1977) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 57: The k_{660} obtained from the MSS parameterization proposed by Jackson, Walton and Baker (1985) and Equation 55. Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Appendix B

This appendix contains the figures of the difference between the gas transfer velocity (k_{660}) calculated with the relations proposed by Cox and Munk (1954), Phillips (1977), Jackson, Walton and Baker (1985), and the parameterization proposed by Bogucki et al. (2010). More information about these figures are in Section 3.2.2.

Figure 58: The k_{660} obtained from the MSS parameterization proposed by Cox and Munk (1954) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 59: The k_{660} obtained from the MSS parameterization proposed by Cox and Munk (1954) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 60: The k_{660} obtained from the MSS parameterization proposed by Phillips (1977) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 61: The k_{660} obtained from the MSS parameterization proposed by Phillips (1977) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 62: The k_{660} obtained from the MSS parameterization proposed by Jackson, Walton and Baker (1985) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.

Figure 63: The k_{660} obtained from the MSS parameterization proposed by Jackson, Walton and Baker (1985) the parameterization proposed by Bogucki et al. (2010). Values are in cm s^{-1} . The black dot is the position of the ASIS buoy.