Non-Dimensional Gradient Functions for Water Vapor and Carbon Dioxide in the Marine Boundary Layer

Dimensionslösa gradientfunktioner för vattenånga och koldioxid i det marina gränsskiktet

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Abstract

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A better understanding of the exchange processes taking place over the oceans is of great importance since the oceans cover about 70% of the Earth’s surface. With better knowledge the turbulent fluxes can be more accurate parameterized, which is essential in order to improve the weather- and climate models.

In this study, the non-dimensional gradient functions for water vapor ($\phi_q$) and carbon dioxide ($\phi_c$) in the marine boundary layer have principally been studied. The quality of the instrumentation used in the study has also been evaluated. The study is mainly based on tower measurements of turbulent fluxes and vertical profiles of water vapor and carbon dioxide, taken from the Östergarnsholm Island located in the Baltic Sea. The measurements have been shown to represent open-sea conditions for most situations when the winds are coming from the east-south sector, even though the measurements are obtained over land.

It was found that the best fitting non-dimensional gradient functions for water vapor during unstable conditions were $\phi_q = 2(1–18z/L)^{-1/2}$ and $\phi_q = 1.2(1–14z/L)^{-1/2}$ at the 10 and 26 m level on the tower, respectively. No unique relationship could be established for $\phi_q$ during stable conditions.

$\phi_q$ showed a dependence with wind direction and could for winds coming from the sector $80^\circ$–$160^\circ$ be described with the relationship $\phi_q = 1.2 + 10.7z/L$ during stable conditions. For the wind sector $50^\circ$–$80^\circ$ the relationship for $\phi_q$ was found to be $\phi_q = 1.8 + 7.1z/L$ during stable conditions.

A high degree of scatter was apparent in the calculated values of $\phi_c$ during both stable and unstable conditions and did not seem to show any Monin-Obukhov similarity behaviour. The results indicate that there might be measurement problems with the instruments measuring the turbulent fluxes of carbon dioxide, but further studies are needed in order to draw a firm conclusion about the quality of the instruments. The profile measurements of water vapor seem to work fine, but more studies of carbon dioxide are needed before a statement can be made regarding the quality of the profile measurements of carbon dioxide.

Keywords: Monin-Obukhov similarity theory, non-dimensional gradient functions, water vapor, carbon dioxide, marine boundary layer, turbulent fluxes.

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Caroline Vahlberg

Skiktet närmast marken kallas det atmosfäriska gränsskiktet och karaktäriseras av turbulens, dvs. oregelbundna virvelförråd och uppstånd av vindens friktion mot jordytan (land eller hav) eller av luftens utbytning av värme och koldioxid. Genom turbulens kan utbyte av värme, vattenånga, momentum, koldioxid och andra gaser ske mellan jordytan och atmosfären.

Turbulenta utbytesprocesser i det atmosfäriska gränsskiktet är viktiga att studera för att kunna beräkna ett turbulent flöde från en yta i väder- och klimatmodeller. Genom en ökad förståelse av flödena kan dessa bli mer noggrant parametriserade (dvs. en fysikalisk process som sker på en mindre skala eller är för komplex för att kunna beskrivas i en modell förenklas genom att beskriva processen med hjälp av ett antal kända parametrar som kan upplösa i modellen), vilket är grundläggande för att kunna förbättra modellerna. Flödena beräknas med hjälp av de s.k. dimensionslösa gradientfunktioner, vilka relaterar flödet av en viss turbulent kvantitet, t.ex. värme, momentum, vattenånga, koldioxid etc., till dess vertikala gradient. Enligt Monin-Obukhovs similaritetsteori ska funktionerna vara universella och endast bero på den atmosfäriska stabiliteten.

I denna studie har de dimensionslösa gradientfunktionerna för vattenånga ($\phi_q$) och koldioxid ($\phi_c$) i det marina gränsskiktet huvudsakligen analyserats. Kvaliteten på de instrument som har använts i studien har också utvärderats. I studien har främst data av turbulent flöden och vertikala profiler av vattenånga och koldioxid använts som erhållits från ett torn på ön Östergarnsholm i Östersjön. Även om måtttagningen sker över land har det visat sig att de för de flesta situationer när vinden blåser från sektorn ost-syd representerar likvärdiga förhållanden som gäller över öppet hav.

Resultaten visade att uttrycket $\phi_q = 2(1-18z/L)^{-1/2}$ respektive $\phi_q = 1.2(1-14z/L)^{-1/2}$ bäst beskriver de dimensionslösa gradientfunktionerna för vattenånga under instabila förhållanden på mäthöjderna 10 respektive 26 m. Något unikt uttryck för $\phi_q$ under stabila förhållanden kunde inte fastställas.

$\phi_q$ visade ett beroende av vindriktning och kunde under stabila förhållanden beskrivas med uttrycket $\phi_q = 1.2 + 10.7z/L$ för vindsektorn $80^\circ - 160^\circ$. För vindar i sektorn $50^\circ - 80^\circ$ kunde $\phi_q$ beskrivas enligt $\phi_q = 1.8 + 7.1z/L$ under stabila förhållanden.

En stor spridning syntes i de beräknade värdena av $\phi_c$ under både stabila och instabila förhållanden och verkade inte följa Monin-Obukhov’s similaritetsteori. Resultatet tyder på att det kan vara måtproblem med de instrument som mäter de turbulenta flödena av koldioxid, men fler studier behövs för att kunna dra en definitiv slutsats om instrumentens kvalitet. Profilmätningarna av vattenånga verkar fungera bra, men fler studier om koldioxid måste utföras innan ett uttalande angående kvaliteten på profilmätningarna av koldioxid kan göras.

Nyckelord: Monin-Obukhov similaritetsteori, dimensionslösa gradientfunktioner, vattenånga, koldioxid, marina gränsskiktet, turbulenta flöden

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1 Introduction

1.1 Background

Although oceans cover the largest area of the Earth’s surface, about 70 %, the exchange of momentum, heat, water vapor, carbon dioxide (CO$_2$) and other trace gases between the ocean and the atmosphere is not that well understood compared to the exchange processes taking place over land. It is thus of great importance to get a better understanding of the air-sea interactions in the marine boundary layer, not least in order to improve the numerical weather- and climate models. However, it is often difficult to measure fluxes of turbulent quantities over the ocean due to that moving platforms, e.g. ships or buoys, are influenced by water waves which disturb the measurements. Salt particles can also stick to the instrumentation which can result in a reduced quality of the measurements (e.g. Sahlée 2007). Furthermore, the fluxes and gradients are often small over the ocean and thereby giving uncertainties (e.g. Baklanov et al. 2011). Due to these difficulties it is often assumed that exchange processes in the marine boundary layer behaves in the same manner as the ones in the boundary layer over land, which is not always the case. Studies (e.g. Smedman et al. 1999; Rutgersson, Smedman & Högström 2001) have shown that the turbulence characteristics and therefore also the exchange processes in the marine boundary layer are affected by the wave field, i.e. differences exist between boundary layers over land and ocean and cannot always be treated in the same way.

In 1946, Monin and Obukhov (1954) postulated the Monin-Obukhov similarity theory (see section 2) – a theory based on that turbulent fluxes in the atmospheric surface layer only depends on the atmospheric stability and can be described with universal functions. These universal functions are often referred to as flux-profile or flux-gradient relationships since the functions relate the flux of a turbulent quantity to its vertical gradient (Arya 2001). In this thesis the universal functions will however be referred to as non-dimensional gradient functions. These functions are important in numerical models when turbulent fluxes from a surface are to be determined. Numerous studies have been performed in order to determine these universal functions, from the early 50s until today. The non-dimensional gradient functions for momentum ($\phi_M$) and heat ($\phi_H$) have been validated by several investigators (e.g. Dyer & Hicks 1970; Businger et al. 1971; Högström 1988), while the non-dimensional gradient function for water vapor ($\phi_q$) has not been sufficiently validated. However, studies have suggested that $\phi_q$ could be described with the same relationships as those for heat (e.g. Dyer 1967). Also non-dimensional gradient functions of other trace gases, e.g. CO$_2$, can be assumed to be described in the same way (Arya 2001). Park et al. (2009) showed however a dissimilarity between heat and water vapor and suggested two different relationships for these two quantities. Owing to this it is of great interest to study the non-dimensional gradient functions for water vapor and CO$_2$, especially over the ocean due to the lack of knowledge within the marine boundary layer.

1.2 Purpose

The main objective of this study is to determine the non-dimensional gradient functions for water vapor ($\phi_q$) and CO$_2$ ($\phi_c$) in the marine boundary layer using data from the marine site Östergarnsholm located in the Baltic Sea. This is especially interesting since the Department of Earth Sciences at Uppsala University never before has analysed the $\phi$-functions of these quantities at this marine site. The purpose
is also to evaluate the quality of the instrumentation used in the analysis. The normalized standard deviations of water vapor ($\sigma_q/|q_\ast|$) and CO$_2$ ($\sigma_{c_\ast}/|c_\ast|$) will also be briefly investigated.

2 Theory

2.1 The atmospheric boundary layer

The atmospheric boundary layer (ABL) represents the lowest part of the atmosphere and is directly influenced by the underlying surface. The thickness of the ABL may range from just some several tens of meters up to a few kilometers, depending on the characteristics of the underlying surface such as topography and roughness, the rate of heating or cooling of the surface, the wind strength and mesoscale processes, just to mention a few factors. The ABL depth is also relatively variable in time and show a strong diurnal cycle due to its response to the heating and cooling of the underlying surface (Arya 2001). The boundary layer over the ocean, the marine boundary layer, differs from that over land and exhibits small variations both in time and space. The reason is that the ocean has a large heat capacity, in combination with good mixing properties in the upper parts of the ocean. This results in small temperature changes at the ocean surface and therefore also a small diurnal variation of the ABL depth over the ocean (Stull 1988). The marine boundary layer also differs from the boundary layer over land due to the presence of surface waves. If a phenomenon called swell, i.e. when the waves are travelling faster than the wind (Smedman et al. 1999), is prevailing the turbulence characteristics can be affected and deviations from what is predicted by the Monin-Obukhov similarity theory might occur.

2.2 Monin-Obukhov similarity theory

Turbulent fluxes may be hard to properly describe due to sometimes insufficient knowledge of the physical processes that take place in the boundary layer, or because of too complex physics. However, since observations in the boundary layer show similar characteristics a similarity theory is a good tool to describe a certain feature. A similarity theory is an empirical method aiming at establish a universal relationship between the variables of interest by dimensional analysis. With help of appropriate scaling parameters the variables of interest are made non-dimensional (Stull 1988).

Turbulent fluxes in the surface layer are described with the Monin-Obukhov similarity theory (henceforth referred to as MOST). The surface layer is the bottom part of the boundary layer where the variation of turbulent fluxes is less than 10 % of their magnitude with height, i.e. it can be assumed to be a constant flux layer (Stull 1988). According to MOST (see e.g. Monin & Obukhov 1954), which is only applicable under the assumption that the flow in the surface layer is horizontally homogeneous and stationary, in addition to the constant flux assumption, a universal relationship for turbulent fluxes in the surface layer could be establish with help of four relevant variables: the height above the surface, $z \ (m)$; the friction velocity, $u_\ast = (\overline{u'w'^2})^{1/4} (ms^{-1})$, where $\overline{u'w'}$ and $\overline{v'w'}$ are the kinematic momentum fluxes in the x- and y-direction, respectively ($m^2 s^{-2}$); the kinematic heat flux, $\overline{w'\theta'} (ms^{-1}K)$; and the buoyancy parameter, $g/T_0$, where $g$ is the acceleration of gravity ($ms^{-2}$) and $T_0$ is the mean temperature of the surface layer ($K$). Characteristic scales, or in other words scaling parameters of length, wind and temperature can be defined with help of the four variables. The vertical gradients of momentum, heat, water vapor and CO$_2$, as well as other quantities, can then be made non-dimensional with help of the scaling
parameters and according to MOST the non-dimensional gradients should all be unique functions of $z/L$ (a parameter describing the atmospheric stability) only. The non-dimensional gradients of water vapor, $\phi_q$, and $CO_2$, $\phi_c$, can be expressed as:

$$\phi_q(z/L) = \frac{\kappa z}{q_\ast} \frac{\partial Q}{\partial z}$$  \hspace{1cm} (1)

$$\phi_c(z/L) = \frac{\kappa z}{c_\ast} \frac{\partial C}{\partial z}$$  \hspace{1cm} (2)

where $Q$ and $C$ are the mean specific humidity ($kgkg^{-1}$) and the mean concentration of $CO_2$ (ppm), respectively, $q_\ast = -\overline{w'q'/u_\ast}$ is the scaling parameter for water vapor where $\overline{w'q'}$ is the turbulent flux of water vapor ($ms^{-1}kgkg^{-1}$), $c_\ast = -\overline{w'c'/u_\ast}$ is the scaling parameter for $CO_2$ where $\overline{w'c'}$ is the turbulent flux of $CO_2$ ($ms^{-1}ppm$), $z$ is the height above the surface ($m$), and $\kappa$ is the von Karman constant, equal to 0.4. $L$ is the Obukhov length ($m$), defined as:

$$L = -\frac{u_\ast^3 T_0}{g \overline{w'\theta'_v}}$$  \hspace{1cm} (3)

where $\overline{w'\theta'_v}$ is the vertical flux of virtual potential temperature ($ms^{-1}K$). In a physical sense the Obukhov length represents the height above the surface where wind shear effects dominates over buoyancy effects (Arya 2001; Stull 1988). The sign of $L$ is dependent on the stability of the atmosphere. When the atmosphere is stable stratified, $\overline{w'\theta'_v} < 0$, giving $L > 0$; when the atmosphere is unstable stratified, $\overline{w'\theta'_v} > 0$, giving $L < 0$; and when the atmosphere is neutral stratified, $\overline{w'\theta'_v} = 0$, giving $L \rightarrow \pm \infty$.

Expressions for the non-dimensional $\phi$-functions can only be determined from accurate measurements since the forms of the functions are not given by MOST. However, if MOST is valid the $\phi$-functions should be universal. This means that the empirical relationships can be used to describe a turbulent quantity in the surface layer all the time (Högström & Smedman 1989).

As mention earlier the non-dimensional gradient functions for water vapor and $CO_2$ are commonly described with the expressions for heat. Although there exist different suggestions on the exact expressions for heat the generally recommended forms of the functions are those obtained by Dyer and Hicks (1970):

$$\phi_H = 1 + 5 \frac{z}{L}, \text{ for } z/L > 0 \text{ (stable conditions)}$$  \hspace{1cm} (4)

$$\phi_H = (1 - 16 \frac{z}{L})^{-1/2}, \text{ for } z/L < 0 \text{ (unstable conditions)}$$  \hspace{1cm} (5)

and the expressions obtained by Högström (1988) (actually re-formulated expressions of those found by Businger et al. (1971), who used 0.35 as a value of the von Karman constant instead of its nowadays recommended value of 0.4):

$$\phi_H = 0.95 + 7.8 \frac{z}{L}, \text{ for } 0 < z/L \leq 0.5$$  \hspace{1cm} (6)

$$\phi_H = 0.95(1 - 11.6 \frac{z}{L})^{-1/2}, \text{ for } z/L < 0$$  \hspace{1cm} (7)

According to Dyer and Hicks (1970), Eqs. 4 and 5 are also valid for water vapor.

Previous studies have been done in order to determine the non-dimensional gradient function for
water vapor. Smedman and Högström (1973) carried out micro-meteorological field measurements over a two-year period at the agricultural site Marsta, located about 10 km north of Uppsala in Sweden. From the humidity measurements following empirical expression for $\phi_q$ was obtained:

$$\phi_q = (1 - 9 \frac{z}{L})^{-1/2}, \text{ for } z/L < 0$$

(8)

Another relationship for $\phi_q$ was obtained by Park et al. (2009), determined from the Cooperative Atmosphere-Surface Exchange Study-1999 (CASES-99) field experiment conducted on a flat and grassy field in southeastern Kansas, USA, in October 1999. The obtained $\phi_q$-functions by these authors are as follows:

$$\phi_q = 1.21(1 + 60.4 \frac{z}{L})^{1/3}, \text{ for } z/L > 0$$

(9)

$$\phi_q = 1.21(1 - 13.1 \frac{z}{L})^{-1/2}, \text{ for } z/L < 0$$

(10)

Edson et al. (2004) determined the $\phi_q$-function over the open ocean using measurements from two field experiments: the 2000 Fluxes, Air-Sea Interaction, and Remote Sensing (FAIRS) that took place aboard the R/P FLIP (research vessel) in the northeastern Pacific Ocean in September and October 2000, and the 2001 GasEx experiments that took place aboard the National Oceanic and Atmospheric Administration (NOAA) R/V Ronald H. Brown (research vessel) in the equatorial Pacific Ocean in February 2001. From the experiments, following relationship for $\phi_q$ was considered to be the best fit to the data:

$$\phi_q = 1(1 - 13.4 \frac{z}{L})^{-1/2}, \text{ for } z/L < 0$$

(11)

Important to mention is that although Eq. 11 was considered to be the best fit the authors got 1.11(±0.22) as a mean value for the coefficient in front of the parenthesis in Eq. 11.

Also normalized standard deviations of turbulence quantities, e.g. $\sigma_q/q$, $\sigma_c/c$, $\sigma_T/T_e$ etc., should be universal functions of $z/L$ according to MOST (Högström & Smedman 1989).

### 2.3 The eddy covariance technique

The eddy covariance (or correlation) technique is a measurement technique used to directly measure turbulent fluxes within the atmosphere. First, the Reynolds decomposition need to be applied on a given time series of a measured quantity, e.g. the vertical wind component $w$. This is done by separating the wind component into a mean part, $\overline{w}$, and a part that represents the deviation from the mean (simply the turbulence), $w'$:

$$w = \overline{w} + w'$$

(12)

By multiplying the vertical component with another quantity decomposed in the same manner, e.g. the potential temperature $\theta$, averaging the product and simplify with help of Reynolds averaging rules, see e.g. Stull (1988), yields:

$$\overline{w\theta} = \overline{w'\theta'} + \overline{w\theta}$$

(13)
The first term on the right-hand side represent the kinematic heat flux and the second term the transport due to the mean flow. Since the mean vertical velocity is small over a flat surface like the ocean the second term is often neglected (Sahlée 2007), why Eq. 13 could be written as:

\[
\overline{w\theta} = \overline{w'\theta'}
\] (14)

Thus by measuring the vertical wind component together with quantities such as the temperature, water vapor, CO\textsubscript{2} and other trace gases, vertical turbulent fluxes can be calculated with this kind of measurement technique.

2.4 Air-sea flux estimations of CO\textsubscript{2}

The flux of CO\textsubscript{2} between the ocean and atmosphere is driven by the air-sea difference in partial pressure of CO\textsubscript{2} (\(pCO_2\)) and can be calculated with the following bulk formula (Wanninkhof & McGillis 1999):

\[
F_{CO_2} = kK_0 \Delta pCO_2
\] (15)

where \(k\) is the transfer velocity of CO\textsubscript{2} (\(ms^{-1}\)), \(K_0\) is the solubility constant (\(molm^{-3}atm^{-1}\)) and \(\Delta pCO_2 = pCO_{2water} - pCO_{2atmosphere}\) is the difference in partial pressure between the ocean and atmosphere (\(\mu atm\)). The solubility constant is dependent on the sea surface temperature (SST) and salinity and is calculated with the expression proposed by Weiss (1974). The transfer velocity \(k\) can be calculated in different ways. Wanninkhof (1992) and Wanninkhof and McGillis (1999) have suggested the following equations:

\[
k = 0.31u_{10}^2 \sqrt{\frac{660}{Sc}}
\] (16)

\[
k = 0.0283u_{10}^3 \sqrt{\frac{660}{Sc}}
\] (17)

where \(u_{10}\) is the wind speed at 10 m height (\(ms^{-1}\)) and \(Sc\) is the Schmidt number (ratio of the kinematic viscosity of the water and the molecular diffusivity of the gas in water).
3 Site, measurements and methodology

3.1 The Östergarnsholm site

Data is taken from the air-sea interaction station at Östergarnsholm, a small and flat island located in the Baltic Sea 4 km east of Gotland, see Fig. 1. A 30 m high measurement tower is situated at the southernmost tip of the island. Due to variations of the sea level, mainly caused by synoptic weather conditions, the height between the instrumentation on the tower and the sea level also varies, usually ±0.5 m (Sahlée 2007). The actual height to the instrumentation have been calculated with help of sea level measurements at Visby harbour on the west coast of Gotland, provided by the Swedish Meteorological and Hydrological Institute (SMHI).

It has been shown by Högström et al. (2008) that the tower measurements represent open sea conditions when the winds are coming from the sector 80° − 210°. According to the same study the site also represent open sea conditions for wind directions between 50° − 80°, but only in the absence of swell. For other wind directions the measurements are disturbed or influenced by the tower itself or the Gotland island.

Figure 1: Map of Östergarnsholm and the surrounding area. The tower and the SAMI-CO₂ sensor are marked with arrows. Source: Modified from Rutgersson et al. (2008)
3.2 Instrumentation

The tower is equipped with both slow response instruments and instruments measuring rapid turbulent fluctuations. Profile measurements of wind speed, wind direction and temperature are recorded at 1 Hz with slow response sensors placed at five levels on the tower: 6.9, 11.9, 14.3, 20.2 and 28.8 m above the tower base. Relative humidity is also measured with a slow response sensor, placed at 7 m above the tower base.

Turbulence measurements of temperature and the three wind components are recorded at 20 Hz with CSAT3 3-D sonic anemometers (Campbell Scientific, Inc., Logan, Utah, USA) at three levels on the tower: 9, 16.5 and 25 m above the tower base. From the sea level measurements the mean height of the tower base above the sea level was 1.3 m during the investigation period. This gave mean heights of 10.3, 17.8 and 26.3 above the sea level for the turbulence measurements. These heights will henceforth in the text be referred to as 10, 18 and 26 m. Note however that the daily actual values of the heights have been used in the calculations. A LI-COR LI-7500 open-path gas analyser (LI-COR Inc., Lincoln, Nebraska, USA) is placed at 10 and 26 m, while a LI-COR LI-7200 closed-path gas analyser is placed at 18 m, giving density measurements of water vapor and $CO_2$ in the atmosphere. Combined with sonic anemometers at the same heights turbulent fluxes of humidity and $CO_2$ are obtained. The Webb correction, see section 3.2.1, have been applied to the turbulent fluxes of humidity and $CO_2$ at 10 and 26 m in the post processing.

The eddy covariance technique is used to measure and calculate the turbulent fluxes, explained in the theory section. Prior to the flux calculations (i.e. calculations of the variances and covariances) a high-pass filter based on a 10-minute running average is applied on the turbulence time series in order to remove possible trends. Corrections for cross-wind effects on the sonic data also need to be applied, but the reader are here referred to Sahlée (2007) for a detailed description of the procedure.

Recently, new instrumentation have been installed on the tower for measurements of concentrations of water vapor and $CO_2$: an AP200 $CO_2$/H$_2$O atmospheric profile system (Campbell Scientific, Inc., Logan, Utah, USA), see Fig. 2. The instrumentation measures atmospheric water vapor and $CO_2$ concentrations from four up to eight intake assemblies. Each intake is connected to an AP200 system enclosure through cables and the intakes are usually mounted along the height of a tower in order to give a vertical profile of water vapor or $CO_2$ in the air. A LI-COR LI-840A analyser (LI-COR Inc., Lincoln, Nebraska, USA) is installed within the AP200 system enclosure and is used for the measurements (Campbell Scientific, Inc. 2012).

At Östergarnsholm, intake assemblies are placed at four levels on the tower: 6.9, 11.9, 20.2 and 28.8 m above the tower base. The mean heights for the AP200 instrumentation was 8.2, 13.2, 21.5 and 30.1 m due to the sea level variation.

When investigating the quality of the LICOR instruments with respect to the $CO_2$ data measurements from a SAMI-$CO_2$ sensor (Submersible Autonomous Moored Instrument, Sunburst Sensors, LLC, Missoula, Montana, USA) located at 4 m depth 1 km southeast of Östergarnsholm has been used, see Fig. 1. The SAMI-$CO_2$ sensor measures both SST and $pCO_2$ at an hourly temporal resolution.
3.2.1 The Webb correction

Density fluctuations of water vapor and CO$_2$ measured by the LI-7500 instrument does not take into account fluctuations of temperature, humidity and pressure of the ambient air (in contrast to the LI-7200 instrument), i.e. density fluctuations of the ambient air, which in turn will affect the measured density fluxes of water vapor and CO$_2$. Correct density fluxes are obtained by applying the Webb correction to the measured density fluxes, developed by Webb et al. (1980):

$$F_v = (1 + \frac{1}{\varepsilon} \frac{\overline{\rho}_v}{\overline{\rho}_a})(\overline{w'}\overline{\rho}'_v + \frac{\overline{\rho}_v}{\overline{T}}\overline{w'T'})$$  \hspace{2cm} (18)

$$F_c = \overline{w'}\overline{\rho}'_c + \frac{1}{\varepsilon} \frac{\overline{\rho}_c}{\overline{\rho}_a}\overline{w'}\overline{\rho}'_v + (1 + \frac{1}{\varepsilon} \frac{\overline{\rho}_v}{\overline{\rho}_a})\frac{\overline{\rho}_c}{\overline{T}}\overline{w'T'}$$  \hspace{2cm} (19)

where $F_v$ and $F_c$ are corrected density fluxes of water vapor respectively CO$_2$ (mmol m$^{-2}$s$^{-1}$), $\overline{w'}\overline{\rho}'_v$ and $\overline{w'}\overline{\rho}'_c$ are uncorrected density fluxes, $\overline{\rho}_v$, $\overline{\rho}_c$ and $\overline{\rho}_a$ are densities of water vapor, CO$_2$ and the ambient air, respectively (mmol m$^{-3}$), $\overline{T}$ is the air temperature (K), $\overline{w'T'}$ is the kinematic heat flux (ms$^{-1}$K) and $\varepsilon \approx 0.62198$.

3.3 Data selection

In this study two different data sets have been used: one for water vapor and one for CO$_2$. Both data sets contained measurements averaged over 60 minutes periods. The two data sets comprised a total of 2904 60-minutes data from the profile, turbulence and AP200 measurements, ranging from end of June to end of October 2014. However, since the data have been chosen after the criteria described below the data sets do not cover the whole period. The common selected criteria for both water vapor and CO$_2$ are as follows:

1) Wind direction between 80° – 210°. As mention previously it has been shown by Högström et al. (2008) that the tower measurements represent open sea conditions when the winds are coming from this sector.
2) The variance of the relative signal strength indicator (RSSI\textsuperscript{1}), $r'/r' < 0.01$. This value was chosen to ensure a good quality of the measurements, without excluding to many measurements.

3) $\overline{w^2} < 0 \text{ m}^2 \text{s}^{-2}$. To have situations where the wind forces the water.

Point 4-6 and 7-8 below are additional criteria for the water vapor and CO\textsubscript{2} data set, respectively:

4) Latent heat flux $\geq 3 \text{ W/m}^2$. To remove cases with low signal-to-noise ratio.

5) Sensible heat flux $\geq 5 \text{ W/m}^2$. Same reason as for point 4).

6) The fourth moment error $q'' < 0.1 \text{ kg}^4 \text{ kg}^{-4}$. A large value indicates a large error in the measurements and give large scatter in the measurements.

7) $\overline{w^2c^2} \geq 2 \cdot 10^{-4} \text{ ms}^{-1} \text{ ppm}$. Same reason as for point 4).

8) The fourth moment error $c'' < 0.01 \text{ ppm}^4$. Same reason as for point 6).

Totally, 214 60-minutes measurements passed the criteria for the water vapor data set and 207 measurements for the CO\textsubscript{2} data set. Unless otherwise stated in the report the above criteria have been used in the analysis for the respective data set. However, at 18 m the turbulence measurements are only good until the 20th of September since some instrumentation error occurred after this date. Therefore only measurements taken before this date were included in the analysis at 18 m.

Additional analysis for the water vapor data set have been done when using different criteria on the wind direction. Also the normalized standard deviations of water vapor and CO\textsubscript{2} have been investigated during unstable conditions.

In the investigation of the instrumentation quality with respect to the CO\textsubscript{2} data SST- and $p$CO\textsubscript{2}-data from the SAMI-CO\textsubscript{2} sensor have also been used in the analysis. Same criteria as the ones described above for the CO\textsubscript{2} data set have been used, except that the winds had to come from the wind sector $80^\circ - 160^\circ$. This is due to that the SAMI-CO\textsubscript{2} sensor is in the footprint area\textsuperscript{2} of the fluxes measured by the tower for this wind sector, i.e. the tower and the SAMI-CO\textsubscript{2} sensor is ”seeing” the same area (Rutgersson et al. 2008).

### 3.4 Methodology

#### 3.4.1 Determination of vertical gradients

The vertical gradients of water vapor and CO\textsubscript{2} (used in the calculations of $\phi_q$ and $\phi_c$ in Eqs. 1 and 2, respectively) were evaluated at 10, 18 and 26 m and were calculated using two different methods. First, the vertical profiles were fitted to second-order polynomials in ln(z):

$$X(z) = A \ln^2(z) + B \ln(z) + C$$ (20)

where $X(z)$ is the fitted value of water vapor or CO\textsubscript{2} at height $z$. This fitting method was chosen since vertical profiles of water vapor and CO\textsubscript{2} (and other quantities such as temperature and wind) are expected

\textsuperscript{1}A measure of the quality of the measurements. The RSSI value represents the cleanness of the windows/mirrors on the LICOR instrument where a high value (in percent) indicates a good signal.

\textsuperscript{2}An upwind area where the turbulent fluxes measured by an instrument are generated.
to vary logarithmic with height in neutral conditions. The coefficients $A$, $B$ and $C$ were determined from profile measurements of water vapor and $CO_2$ from the AP200 profile system by the method of least squares. Differentiating each side of Eq. 20 with respect to $z$ gives the water vapor or $CO_2$ gradient at height $z$, i.e:

$$\frac{\partial X}{\partial z} = 2A \frac{ln(z)}{z} + \frac{B}{z}$$

(21)

The second-order polynomials, together with the profile data, were plotted for each hour to see whether the given fit were acceptable or not. The polynomials that did not fit the profile data very well were rejected in the further analysis.

Second, the vertical gradients were locally determined using a linear approximation (the vertical gradients are approximated with finite differences), i.e:

$$\frac{\partial X}{\partial z} \approx \frac{\Delta X}{\Delta z}$$

(22)

For example, the vertical gradients at 10 m were calculated with help of the profile measurements at 8.1 and 13.2 m. This method was chosen because it does not require more than two heights for profile measurements.

The reason for using two different methods was to see whether $\phi_q$ was affected by the choice of fitting method or not. This is important to know since the more simple linear approximation only requires measurements at two heights and is therefore not as expensive as the logarithmic approximation which requires measurements at several heights.

### 3.4.2 Determination of the non-dimensional gradient functions

For the unstable case empirical expressions for the non-dimensional gradient functions were formulated on the form (according to e.g. Dyer & Hicks 1970; Smedman & Högström 1973; Högström 1988; Park et al. 2009):

$$\phi_x(z/L) = A_x(1 - B_x \frac{z}{L})^{-C_x}$$

(23)

where $x$ represents water vapor or $CO_2$ and $A_x$, $B_x$ and $C_x$ are empirical coefficients to be determined. The coefficient $C_x$ was put equal to 1/2 since it has been shown from several previous studies that $C_x$ is expected to take this value during unstable conditions (e.g. Dyer & Hicks 1970; Smedman & Högström 1973; Park et al. 2009). When it comes to determine the coefficient $A_x$ different methods have been applied in previous studies. Park et al. (2009) determined the $A_x$-coefficient by performing a linear regression through the $\phi$-values in near-neutral conditions (with the definition that $|z/L| \leq 0.05$). The coefficient was obtained at $z/L = 0$ since $\phi_x$ in Eq. 23 is equal to $A_x$ in neutral conditions, i.e. when $z/L \to 0$. However, in this study same approach as one of the methods used in the study performed by Edson et al. (2004) was used. Both the $A_x$- and $B_x$-coefficient was varied in order to minimize the mean squared error between the $\phi_x$-values calculated with Eq. 1 or Eq. 2 (i.e. the data) and the $\phi_x$-values calculated with the empirical expression formulated on the form given by Eq. 23.
error is defined as:

\[ MSE = \frac{1}{n} \sum_{i=1}^{n} (\hat{\phi}_x - \phi_x)^2 \]  

(24)

where \( n \) is number of data, \( \hat{\phi}_x \) is a vector of all the estimated values and \( \phi_x \) is a vector of all the true values (i.e. the data). Note that only the negative values of the parameter \( z/L \) and the corresponding values of \( \phi_x \) were used in order to determine the \( \phi_x \)-function during unstable conditions.

During stable conditions it is expected that the \( \phi_x \)-function has linear dependence of \( z/L \) according to several studies (see e.g. Dyer & Hicks 1970; Högström 1988). Thus, for the stable case the expression was formulated on the form:

\[ \phi_x(z/L) = A_x + B_x \frac{z}{L} \]  

(25)

The expression for the \( \phi_x \)-function was obtained by linear regression, where the \( A_x \)-coefficient represents the \( y \)-intercept and the \( B_x \)-coefficient represents the slope of the regression line. As was the case in the determination of the \( \phi_x \)-function during unstable conditions only positive values of \( z/L \) and the corresponding values of \( \phi_x \) were used when determining the function during stable conditions.
4 Results

4.1 Water vapor

Fig. 3a-c shows time series of the specific humidity, sensible heat flux and latent heat flux during the investigation period. The sensible heat flux together with the specific humidity follow each other well at all heights and shows a good agreement. However, regarding the latent heat flux, the measured fluxes at 18 m deviate compared to the latent heat fluxes at 10 and 26 m. It thus seems like it is something wrong with the LICOR LI-7200 instrument at this level. This error affects the $\phi_q$-values calculated with Eq. 1 since the specific humidity scale, $q^*$, is included in the calculations, which in turn is dependent on the latent heat flux (or in other words the vertical flux of water vapor, $\overline{w'q'}$). Thus, due to the instrumentation error the calculated $\phi_q$-values at 18 m are considered to be wrong and are therefore not included in the report. Other intermediate results related to the 18 m height are not included in the report from now on either.

![Time series graphs](image)

**Figure 3**: Time series of a) specific humidity, b) sensible heat flux and c) latent heat flux during the investigation period.

4.1.1 Vertical gradients of water vapor

To see whether the non-dimensional gradient of water vapor is affected by the choice of fitting method or not the sensitivities of the vertical gradients to the different fitting methods were investigated. Fig. 4
shows the ratio between gradients obtained using the linear approximation and gradients obtained using the logarithmic approximation at 10 and 26 m. As shown in the figure the gradients are not that sensitive to the fitting methods at 10 m, Fig. 4a, but at 26 m, Fig. 4b, large differences are seen. The median ratio at 26 m is 1.20, compared to 1.03 at 10 m. Thus at 26 m the uncertainty of the vertical gradients increases. Similar results were found in the study made by Park et al. (2009) who fitted the vertical gradients to a first-, second- and third-order polynomial in ln(z), respectively.

Examples of water vapor profiles obtained by the logarithmic approximation are shown in Fig. 5 with a logarithmic scale on the y-axis. As seen in the figure the second-order fits to the measurements do not always give a good result. The polynomial in Fig. 5a has a very good fit, while the polynomial in Fig. 5b has an acceptable fit although the line does not go through all the measurement points. Polynomials with a similar appearance like those in Figs. 5a and 5b have been used in the calculation of $\phi_q$. Fig. 5c shows a polynomial with a bad fit and polynomials with a similar look have been excluded in the calculations. Of the original 214 water vapor profiles 203 profiles were left after excluding badly fitted profiles.

Figure 4: Ratio of vertical gradients of water vapor between gradients obtained using the linear and the logarithmic approximation at a) 10 m and b) 26 m. The red line represent the 1:1 relationship.

Figure 5: Examples of water vapor profiles plotted against ln(z) with a) a good fit, b) a moderate fit and c) a bad fit. Dots are the measurements and the lines are the fitted second-order polynomials in ln(z).
4.1.2 Non-dimensional gradient function for water vapor

Fig. 6 shows bin-averages of $\phi_q$ plotted as a function of the stability parameter $z/L$ (where $L$ has been calculated with Eq. 3) at 10 and 26 m for the two different fitting methods. In general there is a good agreement between the two methods, although there is a larger difference, but still small, at 26 m compared to the result at 10 m. However, on the stable side, i.e. when $z/L > 0$, larger differences are seen at both heights between the two methods.

In the further analysis, only the outcome when using the logarithmic approximation to the vertical gradients will be presented and discussed. This is because the vertical profiles of water vapor are expected to vary logarithmic with height in neutral conditions, as mentioned in section 3.4.1, and is therefore considered to be a more preferable and sophisticated method than the linear approximation.

![Figure 6: Bin-averages of $\phi_q$ plotted against $z/L$ at a) 10 m and b) 26 m for the two different fitting methods. The error bars represent the standard deviation within each bin for the linear and the logarithmic approximation, respectively. Each bin has the size $\Delta(z/L) = 0.2$.](image)

In Figs. 7 and 8 $\phi_q$ is plotted as a function of $z/L$ over the entire stability range at 10 and 26 m, respectively. Most measurements are obtained during unstable conditions: 145 compared to 58 measurements during stable conditions at 10 m, and 142 respectively 61 measurements during unstable and stable conditions, respectively, at 26 m. In neutral conditions, i.e. when $z/L = 0$, $\phi_q$ at 10 m is larger than $\phi_q$ at 26 m, about 2 compared to about 1 at 26 m. According to MOST and previous findings it is expected that $\phi=1$ at neutral conditions, regardless of which turbulent quantity (e.g. water vapor, heat, momentum etc.) that is investigated. $\phi_q$ at 26 m thus seems to follow what is predicted by MOST.

The scatter in the data are less in unstable than stable conditions at both heights. Additionally, less scatter are observed at 10 m compared to 26 m during stable conditions.
Figure 7: $\phi_q$ plotted against $z/L$ at 10 m over the entire stability range. The red error bars represent the standard deviation within each bin. Each bin has the size $\Delta(z/L) = 0.2$.

Figure 8: $\phi_q$ plotted against $z/L$ at 26 m over the entire stability range. The red error bars represent the standard deviation within each bin. Each bin has the size $\Delta(z/L) = 0.2$.

Owing to less scatter in the data during unstable conditions at both heights empirical expressions on the form given by Eq. 23 can be established during these conditions. Fig. 9 shows $\phi_q$ at 10 m as a function of $z/L$ during unstable conditions. The minimum mean squared error between the calculated $\phi_q$-values (i.e. the data) and the $\phi_q$-values estimated with the empirical expression (Eq. 23) is reached when $A_x = 2$ and $B_x = 18$. This gives the following empirical expression for $\phi_q$ at 10 m (black curve...
in Fig. 9):

\[ \phi_q(z/L) = 2(1 - 18 \frac{z}{L})^{-1/2} \quad \text{for } z/L < 0 \]  

(26)

As a reference the empirical expressions obtained by Smedman and Högström (1973), Eq. 8, Park et al. (2009), Eqs. 9 and 10, and Edson et al. (2004), Eq. 11, are inserted in the figure, represented by the blue, red and black dashed curve, respectively. The data points show significantly higher values compared to the expressions given by the above mentioned authors. Nevertheless, the measurements collapse reasonably well onto a curve-shaped form and the scatter is relatively small.

Figure 9: Non-dimensional water vapor gradient \( \phi_q \) plotted against \( z/L \) at 10 m during unstable conditions.

In Fig. 10 \( \phi_q \) at 26 m is shown as a function of \( z/L \) during unstable conditions. Even here the above mentioned reference functions are inserted in the figure. Unlike the result at 10 m the scatter is more pronounced at 26 m, but contrary to \( \phi_q \) at 10 m \( A_x \) in neutral conditions is estimated to be 1.2. This is in agreement with the study of Park et al. (2009). This value is also close to the \( A_x \)-coefficients reported by Smedman and Högström (1973) and Edson et al. (2004). With \( A_x = 1.2 \) and \( B_x = 14 \) the minimum mean squared error is reached, which gives the following empirical expression for \( \phi_q \) at 26 m (black curve in Fig. 10):

\[ \phi_q(z/L) = 1.2(1 - 14 \frac{z}{L})^{-1/2} \quad \text{for } z/L < 0 \]  

(27)

This expression resembles those given by Eqs. 10 and 11. Even though there is a small difference between the \( B_x \)-coefficient obtained in this study and the one obtained by Smedman and Högström (1973), the curves are located close to each other, see Fig 10.
Figure 10: Non-dimensional water vapor gradient $\phi_q$ plotted against $z/L$ at 26 m during unstable conditions.

4.1.3 Variation of $\phi_q$ with wind direction

As shown in Fig. 8 a large spread of the data is observed on the stable side, thus an empirical expression for the $\phi_q$-function is hard to establish under these conditions. However, if different criteria on the wind directions are used there might be a possibility to determine an empirical expression for $\phi_q$ during stable conditions. To see if this is the case $\phi_q$ is plotted as a function of $z/L$ for different criteria on the wind directions over the entire stability range. This is only done for the measurements at 26 m and the results are shown in Figs. 11 and 12. Note that only the criterion on the wind direction is changed. Other criteria defined in section 3.3 are the same.

In Fig. 11 the original wind sector $80^\circ - 210^\circ$ has been subdivided into two new wind sectors: $80^\circ - 160^\circ$ and $160^\circ - 210^\circ$, respectively. The most interesting results are found on the stable side where $\phi_q$ for the two different wind sectors are clearly grouped separately from each other. When the winds are coming from the sector $80^\circ - 160^\circ$ $\phi_q$ show less scatter on the stable side and follow a linear relationship. An empirical expression of the form given by Eq. 25 is formulated for these wind directions for $0 < z/L < 1$, where the regression line is forced to pass through $A_x = 1.2$ (i.e. the y-intercept of Eq. 25) when $z/L = 0$. This gives the following empirical expression for $\phi_q$ at 26 m (blue line in Fig. 11):

$$\phi_q = 1.2 + 10.7 \frac{z}{L}, \text{ for } 0 < z/L < 1 \text{ and } 80^\circ < WD < 160^\circ \quad (28)$$

Also inserted are the $\phi_q$-function at 26 m proposed in this study, Eq. 27, and the expressions suggested by Högström (1988), Eqs. 6 and 7, and Park et al. (2009), Eqs. 9 and 10. (Note that even though the $\phi_H$-function of Högström was suggested to be valid only for stabilities up to $z/L \leq 0.5$ the function has been plotted for larger stabilities in Figs. 11 and 12.

For winds coming from the other sector, i.e. $160^\circ - 210^\circ$, larger scatter are seen on the stable side.
compared to the $80^\circ - 160^\circ$ wind sector. Due to this it is hard to determine whether $\phi_q$ has an entirely linear or non-linear dependence of $z/L$, wherefore an empirical expression for these wind directions is not established. However, it seems like the non-linear relationship suggested by Park et al. (2009), Eq. 9, is more appropriate to describe $\phi_q$ for the given wind directions than the $\phi_H$-function obtained by Högström (1988), Eq. 6, during stable conditions.

As mention in section 3.1, the sector $50^\circ - 80^\circ$ represents open sea conditions in the absence of swell. It is therefore of interest to study $\phi_q$ as a function of stability for these wind directions, shown in Fig. 12. The figure also shows the same reference functions as those in Fig. 11. As seen in the figure $\phi_q$ show little scatter during both stable and unstable conditions. However, during near-neutral conditions on the unstable side the data points are diverging upwards from the curve given by Eq. 27. For stable conditions the data clearly show a linear dependence of $z/L$. An empirical expression of the form given by Eq. 25 is formulated for these wind directions for $0 < z/L < 1.5$. Following expression is obtained through linear regression (blue line in Fig. 12):

$$\phi_q = 1.8 + 7.1 \frac{z}{L}, \text{ for } 0 < z/L < 1.5 \text{ and } 50^\circ < WD < 80^\circ$$

This expression should be compared with the expression obtained by Högström (1988), Eq. 6, where the coefficient in front of $z/L$ is close to the value obtained by Högström.
4.1.4 Normalized standard deviation of water vapor

Another way to investigate if MOST is valid in the surface layer is to look at the normalized standard deviations of the turbulence. If MOST is valid, these quantities should also be unique functions of $z/L$.

Fig. 13 shows the normalized standard deviation of water vapor, $\sigma_q/|q_*|$, in a log-log representation during unstable conditions at 10 and 26 m, i.e. $\sigma_q/|q_*|$ is plotted as a function of $-z/L$. Since $q_*$ can take both positive and negative values, depending on the sign of $w'q'$, the absolute value of $q_*$ is used.

During free convection Högström and Smedman (1974) suggested following expression for $\sigma_q/|q_*|$ over land (black solid line in Fig. 13):

$$\sigma_q/|q_*| = 1.04(-\frac{z}{L})^{-1/3} \quad (30)$$

In this study, the limit of free convection has been defined as $-z/L > 0.2$, wherefore Eq. 30 only is plotted for these stabilities. Also inserted in the figure is the expression obtained over land by Chen et al. (2014) for unstable conditions (black dashed curve in Fig. 13):

$$\sigma_q/|q_*| = 2.1(1-8.2\frac{z}{L})^{-1/3} \quad (31)$$

As seen in the figure the measurements at 10 and 26 m fall below the two expressions, but the measurements follow the shape of the curve and the line, respectively.
Figure 13: Normalized standard deviation of water vapor, $\sigma_q/|q_*|$, plotted against $-z/L$ during unstable conditions at 10 and 26 m.
4.2 \textit{CO}_2

Fig. 14a-b shows time series of the concentration and the vertical flux of \textit{CO}_2 during the investigation period. The concentration of \textit{CO}_2 follow each other well at all heights and shows a good agreement. The vertical flux of \textit{CO}_2 shows, however, not a satisfactory result. As seen in Fig. 14b the flux shows a relatively bad agreement between the heights during the whole period, which in theory should be approximately height constant.

![Time series of concentration and vertical flux of CO2](image)

\textbf{Figure 14:} Time series of a) concentration and b) vertical flux of \textit{CO}_2 during the investigation period.

4.2.1 Vertical gradients of \textit{CO}_2

In the analysis of water vapor a comparison between the gradients obtained with the logarithmic and the linear approximation was done. However, in the analysis of \textit{CO}_2 a similar comparison will not be done since both methods give poor results when calculating the non-dimensional gradients of \textit{CO}_2 with Eq. 2. For this reason only the outcome when using the logarithmic approximation will be presented and discussed.

In Fig. 15 examples of \textit{CO}_2 profiles obtained by the logarithmic approximation are shown with a logarithmic scale on the y-axis. As seen in the figure, and as was the case for the vertical profiles of water vapor, the second-order fits to the measurements do not always give a good result. Fig. 15a shows a polynomial with a good fit, Fig. 15b a polynomial with an acceptable fit and Fig. 15c a polynomial with a bad fit. The polynomials were selected in the same manner as for water vapor in order to exclude...
badly fitted profiles. After the procedure 121 CO$_2$ profiles of the original 207 were left for the further analysis.

**Figure 15:** Examples of CO$_2$ profiles plotted against ln(z) with a) a good fit, b) a moderate fit and c) a bad fit. Dots are the measurements and the lines are the fitted second-order polynomials in ln(z).
4.2.2 Non-dimensional gradient function for $CO_2$

Fig. 16a-c shows $\phi_c$ at 10, 18 and 26 m, respectively, as a function of $z/L$ for both unstable and stable conditions. As a reference the $\phi_H$-functions obtained by Högström (1988), Eqs. 6 and 7, are also inserted. The data points are widely scattered, although less pronounced at 10 m, and do not seem to show any Monin-Obukhov similarity behaviour.

Figure 16: Non-dimensional $CO_2$ gradient $\phi_c$ plotted against $z/L$ at a) 10 m, b) 18 m and c) at 26 m over the entire stability range.
4.2.3 Normalized standard deviation of $CO_2$

Fig. 17 shows the normalized standard deviation of $CO_2$, $\sigma_c/|c_\ast|$, during unstable conditions at 10, 18 and 26 m, i.e. $\sigma_c/|c_\ast|$ is plotted as a function of $-z/L$. As a reference the expressions obtained by Högström and Smedman (1974), Eq. 30, and Chen et al. (2014), Eq. 31, are inserted. The data show a high degree of scatter and $\sigma_c/|c_\ast|$ do not seem to show any Monin-Obukhov similarity behaviour.

![Figure 17: Normalized standard deviation of $CO_2$, $\sigma_c/|c_\ast|$, plotted against $-z/L$ during unstable conditions at 10, 18 and 26 m.](image)

4.2.4 Comparison between measured and calculated $CO_2$-fluxes

Due to the large degree of scatter in the $\phi_c$-data it is of interest to try to figure out a possible reason for that. One way to do this is to compare the vertical flux of $CO_2$, i.e. $w'c'$, measured directly with the eddy covariance technique with the LICOR instruments and calculated with the bulk formula, Eq. 15, see Fig. 18. The fluxes have been calculated both using the squared and the cubic dependence of the wind speed in the transfer velocity, Eqs. 16 and 17. As seen in the figure the agreement between the measured and calculated fluxes are low during most of the time at all heights. Actually, the fluxes have opposite directions during a large part of the period, which will be discussed in the following section.
5 Discussion

The main objective of this study was to determine the non-dimensional gradient functions for water vapor ($\phi_q$) and $CO_2$ ($\phi_c$) in the marine boundary layer in order to get a better understanding of the air-sea exchange processes taking place there. The aim was also to evaluate the quality of the instrumentation used in the study and briefly study the normalized standard deviations of water vapor ($\sigma_q/|q_\ast|$) and $CO_2$ ($\sigma_c/|c_\ast|$). The study is mainly based on meteorological data taken from the air-sea interaction station Östergarnsholm located in the Baltic Sea. The discussion part is divided into two separate sections: one for water vapor and one for $CO_2$.

5.1 Water vapor

First, the vertical gradients obtained with the logarithmic and the linear approximation were compared in order to see whether the non-dimensional gradients of water vapor were affected by the choice of fitting method or not. Even if larger differences between the two methods were found at the highest level (26 m) than at the lowest level (10 m) the results show that $\phi_q$ at the two heights is not influenced so much by the choice of fitting method during unstable conditions, while $\phi_q$ during stable conditions is more sensitive to the choice of fitting method. This indicates that even if only two heights are available for profile measurements for this type of investigations the $\phi$-function for any turbulent quantity should not be significantly different compared to when several heights are available for profile measurements (i.e. there is a possibility to do a second-order approximation). A possible reason for the larger uncertainty
between the two fitting methods at the highest level compared to the lowest one has however not been established.

The empirical expression obtained for $\phi_q$ at 26 m during unstable conditions is in good agreement with the expression obtained over land by Park et al. (2009) and the expression obtained over ocean by Edson et al. (2004). The expression is also relatively consistent with the $\phi_q$-function obtained over land by Smedman and Högström (1973), even if the coefficient in front of $z/L$ shows a larger value in this study. The result in this study indicates that the non-dimensional gradient function for water vapor obtained over land could be used to describe the flux of water vapor over the ocean, and vice versa.

At the 10 m level, on the contrary, $\phi_q$ shows significantly higher values compared to the 26 m level and the suggested empirical expression during unstable conditions does not resemble those given by the previous mentioned authors. This might depends on some error in the turbulence measurements at this level. One way to test this is to measure the turbulence at same heights with the LICOR instrument located at 10 and 26 m and, if necessary, do new calibrations between the two instruments. Another reason why $\phi_q$ at 10 and 26 does not show the same values is the uncertainty connected to determination of the exact height between the instrumentation on the tower and the sea level. The actual heights are calculated with help of sea level measurements at Visby harbour, which is located on the west side of Gotland, but it is not known how good they actually correlate with the sea levels at Östergarnsholm. The 10 m level is more sensitive to errors in the height determination compared to the 26 m level\(^3\), which could explain the difference in the results between the two heights. Furthermore, the size of the footprint areas are also different between the 10 and 26 m level, i.e. different turbulent properties might be represented at the two heights.

During stable conditions higher degree of scatter could be observed at both heights, although more pronounced at 26 m compared to the 10 m level. Larger scatter during stable conditions could be due to that turbulent motions are suppressed in these conditions, resulting in a more small-scale turbulence (i.e. smaller fluxes) which might lead to uncertainties in the eddy covariance measurements of the vertical flux of water vapor, i.e. $w'q'$. To see if this might be the case a comparison of the magnitude of $w'q'$ during stable and unstable conditions was done (not shown in the report). From the comparison it was clearly seen that the fluxes were smaller during stable compared to unstable conditions. The small fluxes during stable conditions might thus lead to an increasing uncertainty when calculating the values of $\phi_q$, resulting in more scatter. An explanation of why $\phi_q$ at 26 suffers from more scatter compared to the 10 m height could again be due to instrumentation errors or that the two heights might "see" somewhat different footprint areas.

Even though empirical expressions for $\phi_q$ have been formulated in this study, of which the expression at 26 m is similar to the ones found by other authors, there is an uncertainty connected to them. In addition to the uncertainty connected to the measurements few measurements were found during neutral and stable conditions, wherefore the estimated value of $\phi_q$ at neutral condition, i.e. when $z/L = 0$, is uncertain. Measurements that extend over the entire stability range are required in order to reduce the uncertainty in the estimation of $\phi_q$ at neutral condition. If more data had been available it would have been possible to obtain the $\phi_q$-value in neutral condition through linear regression, as was done in the study by Park et al. (2009), which probably would have increased the accuracy of the value. Still, due to the relatively good result of $\phi_q$ it seems like both the LICOR instruments and the AP200 profile system

\(^3\)For instance: An error of 0.5 m in the height gives a relative error of 5% at the 10 m level compared to around 2% at the 26 m level.
are working fine for the measurements of water vapor.

When analysing the behaviour of $\phi_q$ for different wind directions at the 26 m level $\phi_q$ is clearly grouped separately from each other during stable conditions for different wind sectors. During stable conditions, in the range $0 < z/L < 1$, $\phi_q$ can be described with a linear relationship for winds coming from the sector $80^\circ - 160^\circ$. However, no resemblance with the non-linear $\phi_q$-function suggested by Park et al. (2009) during stable conditions can be seen for this wind sector. The relationship also differs somewhat from the linear $\phi_H$-function obtained by Högström (1988). This might depend on that the expression of Högström are valid over land but it might also be an indication that there actually are dissimilarities between heat and water vapor.

For the wind sector $160^\circ - 210^\circ$ $\phi_q$ seems to follow the $\phi_q$-function from Park et al. (2009) during stable conditions, rather than a linear relationship like the one suggested by Högström (1988). The relatively large scatter makes this conclusion somewhat uncertain.

Another interesting result is that $\phi_q$ in the wind sector $50^\circ - 80^\circ$, which only represents open sea conditions in the absence of swell, seems to follow MOST, although higher values of $\phi_q$ than predicted by the theory is observed close to neutral conditions. Swell was probably not present during the time of these measurements and the sector thus truly represents open sea conditions in this case. The coefficient in front of $z/L$ during stable conditions is close to the value obtained by Högström (1988), but the estimated $\phi_q$-function should be regarded with caution due to rather few measurements in the $50^\circ - 80^\circ$ wind sector. Thus, more measurements are needed to confirm the behaviour of $\phi_q$ within this wind sector.

The normalized standard deviations of water vapor were only investigated during unstable conditions but show lower values at both 10 and 26 m compared to the functions obtained by Högström and Smedman (1974) and Chen et al. (2014). This difference might depend on that the functions from these authors are derived over land. Still, $\sigma_q/|q_s|$ follows the same shape of the reference functions, thus it seems that the normalized standard deviation of water vapor follows MOST.

A data set covering a larger time period than the relatively short time period used in this study would be of advantage to use in further studies in order to get more reliable results. Additionally, if the vertical fluxes of water vapor are not allowed to vary more than for e.g. $\pm 10\%$ with height (i.e. the assumption of a constant flux layer is taken into account) the results might also get more reliable. However, this criterion was not used in the study due to a significantly smaller data set compared to when not using this criterion. Furthermore, wave measurements could give information about the state of the waves, i.e. if swell is present or not, and therefore increase our knowledge of how $\phi_q$ behaves in the marine boundary layer. Unfortunately this type of data was not available during the investigation period. Previous studies performed at Östergarnsholm (e.g. Johansson et al. 2001) have also shown that the non-dimensional gradient functions for heat and momentum also can be described as a function of $z_i/L$, where $z_i$ is the boundary layer height, besides its dependence of $z/L$. Thus, there might be a possibility that also $\phi_q$ could be described as a function of $z_i/L$ wherefore data about the boundary layer height could be of importance to include in further studies.

### 5.2 $CO_2$

The non-dimensional gradients of $CO_2$ are widely scattered at all heights and do not seem to show any Monin-Obukhov similarity behaviour. Therefore empirical expressions could not be formulated for $\phi_c$. The normalized standard deviations of $CO_2$ do not seem to follow MOST either. The results indicate
that there probably are measurement problems with the LICOR instruments or the AP200 profile system. In order to find a possible reason for the bad result a comparison of the vertical flux of $CO_2$, i.e. $w'\ell'$, measured with the LICOR instruments and calculated with the bulk formula was done. Unfortunately, the correlation between these two methods is low and from Fig. 18 it is not possible to determine whether it is the LICOR instruments or the bulk formula that show the most correct values of the fluxes since there are uncertainties connected to both the measurements and the calculations. As proposed by Rutgersson et al. (2008) the greatest uncertainty in the calculations originate from the transfer velocity in the bulk formula since there exists several different parametrizations of this parameter. Another reason for the bad agreement between the two methods, which is important to keep in mind, is that the $CO_2$-flux measured with the LICOR instruments and the $CO_2$-flux calculated with the bulk formula represent fluxes originating from different source areas. The LICOR measurements represent fluxes originating from a larger footprint area, determined by the measurement heights, wind speed, wind direction and atmospheric stability, whereas the fluxes calculated with the bulk formula represent a point source. Thus, the flux can vary between the tower and the SAMI-$CO_2$ sensor, although they are in the same footprint area for winds coming from the sector $80^\circ - 160^\circ$ and in theory should "see" the same area.

One of the greatest uncertainties connected to the LICOR instruments are the measurements of the vertical flux of $CO_2$. The low agreement of the fluxes between the heights is probably due to the smallness of the magnitude of $w'\ell'$ which makes the flux measurements of $CO_2$ more uncertain. This will of course increase the uncertainty in the calculations of $\phi_c$, which is reflected in the high degree of scatter in $\phi_c$. Although all the above mentioned uncertainties are taken into account the low agreement of the $CO_2$-fluxes between the two methods is an indication that there are measurement problems with the LICOR instruments regarding the measurements of the $CO_2$-flux.

The results indicate that it might would be desirable to perform a new calibration of the LICOR instruments in order to get more reliable results of $\phi_c$. However, the results are based on rather few data wherefore more investigations of the $CO_2$-fluxes based on a larger data set than the one used in this study have to be done before a definite conclusion can be drawn about the quality of the LICOR instruments used in this study. Additionally, more studies are also needed in order to draw a conclusion about the quality of the profile measurements of $CO_2$ measured with the AP200 profile system. Moreover, as mentioned in the discussion of water vapor, the results might also get more reliable if the assumption of a constant flux layer is taken into account. However, as was the case for the water vapor data set, few data were left after introducing this criterion.
6 Conclusions

From this study, following conclusions can be drawn:

- Calculations of the non-dimensional gradients of water vapor, $\phi_q$, show similar results when using a logarithmic and linear fit of the vertical gradients.

- $\phi_q$ can during unstable conditions be described with the relationships $\phi_q = 2(1 - 18z/L)^{-1/2}$ and $\phi_q = 1.2(1 - 14z/L)^{-1/2}$ at 10 and 26 m, respectively.

- No unique relationship could be established for $\phi_q$ during stable conditions due to a high degree of scatter in the data.

- $\phi_q$ at 26 m shows a dependence of wind directions and can for the wind directions $80^\circ - 160^\circ$ be described with the relationship $\phi_q = 1.2 + 10.7z/L$ for stabilities $0 < z/L < 1$, while $\phi_q$ for the wind directions $50^\circ - 80^\circ$ can be described with $\phi_q = 1.8 + 7.1z/L$ for $0 < z/L < 1.5$.

- The normalized standard deviations of water vapor, $\sigma_q/|q|$, at 10 and 26 m show lower values compared to the empirical expression for $\sigma_q/|q|$ obtained by Högström and Smedman (1974) and Chen et al. (2014).

- The non-dimensional gradients of $CO_2$, $\phi_c$, do not seem to show any Monin-Obukhov similarity behaviour at any of the heights, nor do the normalized standard deviations of $CO_2$, $\sigma_c/|c|$.

- More studies of $CO_2$-flux measurements are needed in order to draw a firm conclusion about the quality of the LICOR instruments used in this study.

- The AP200 profile system seems to work fine, in particular for the profile measurements of water vapor, but no firm conclusion can be drawn concerning the quality of the profile measurements of $CO_2$.

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