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Sensitivity of the air–sea CO_2 exchange in the Baltic Sea and Danish inner waters to atmospheric short term variability

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Abstract

Minimising the uncertainties in estimates of air–sea CO_2 exchange is an important step toward increasing the confidence in assessments of the CO_2 cycle. Using an atmospheric transport model makes it possible to investigate the direct impact of atmospheric parameters on the air–sea CO_2 flux along with its sensitivity to e.g. short-term temporal variability in wind speed, atmospheric mixing height and the atmospheric CO_2 concentration. With this study the importance of high spatiotemporal resolution of atmospheric parameters for the air–sea CO_2 flux is assessed for six sub-basins within the Baltic Sea and Danish inner waters. A new climatology of surface water partial pressure of CO_2 ($p$$CO_2$) has been developed for this coastal area based on available data from monitoring stations and underway $p$$CO_2$ measuring systems. Parameterisations depending on wind speed were applied for the transfer velocity to calculate the air–sea CO_2 flux. Two model simulations were conducted – one including short term variability in atmospheric CO_2 (VAT), and one where it was not included (CAT).

A seasonal cycle in the air–sea CO_2 flux was found for both simulations for all sub-basins with uptake of CO_2 in summer and release of CO_2 to the atmosphere in winter. During the simulated period 2005–2010 the average annual net uptake of atmospheric CO_2 for the Baltic Sea, Danish Straits and Kattegat was 287 and 471 $Gg\,C\,yr^{-1}$ for the VAT and CAT simulations, respectively. The obtained difference of 184 $Gg\,C\,yr^{-1}$ was found to be significant, and thus ignoring short term variability in atmospheric CO_2 does have a sizeable effect on the air–sea CO_2 exchange. The combination of the atmospheric model and the new $p$$CO_2$ fields has also made it possible to make an estimate of the marine part of the Danish CO_2 budget for the first time. A net annual uptake of 2613 $Gg\,C\,yr^{-1}$ was found for the Danish waters.

A large uncertainty is connected to the air–sea CO_2 flux in particular caused by the transfer velocity parameterisation and the applied $p$$CO_2$ climatology. However, the present study underlines the importance of including short term variability in the atmo-

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spheric CO_2 concentration in future model studies of the air–sea exchange in order to minimise the uncertainty.

1 Introduction

The capacity of ocean and land to take up and re-emit atmospheric CO_2 has a dominating effect on the greenhouse gas balance, and hence changes in climate. Currently, the land areas and the global oceans are estimated to take up about 27 and 28 %, respectively, of the CO_2 emitted by anthropogenic sources (Le Quéré et al., 2013).

In recent years the biogeochemical active coastal seas have been given increased attention (Borges et al., 2006; Chen et al., 2013; Mørk et al., 2014). Although such coastal waters only amount to 7 % of the global oceans, high inputs, production, degradation and export of organic matter might result in coastal air–sea CO_2 fluxes contributing a great deal more than 7 % to the global air–sea flux (Gattuso et al., 1998). Due to the high heterogeneity of these areas, coastal CO_2 fluxes are prone to large uncertainties. Several studies agree that continental shelves, in general, act as sinks, while estuaries act as sources of CO_2 to the atmosphere. However, global estimates vary in size according to applied methodology, with oceanic uptake in shelf areas between 0.21 and 0.40 $\mathrm{Pg\,C\,yr^{-1}}$, and release from estuaries in the range of 0.10 to 0.50 $\mathrm{Pg\,C\,yr^{-1}}$ (Cai, 2011; Chen et al., 2013; Chen and Borges, 2009; Laruelle et al., 2010). The poor coverage of observations in both space and time makes validation of these global estimates difficult.

In order to better quantify the impact of coastal regions on the global carbon budget, detailed studies of the processes at the regional scale are necessary (Kulinski and Pempkowiak, 2011). A coastal region that has been well studied is the Baltic Sea. The Baltic Sea is a high latitude inner shelf sea connected to the North Sea though the shallow transition zone of the Danish Straits, and enclosed by land with various terrestrial ecosystems and densely populated areas. Seasonal amplitudes of up to 400 µatm are observed in the partial pressure of CO_2 ($p\mathrm{CO_2}$) in the Baltic Sea (Thomas and Schnei-

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der, 1999) with maximum values of pCO_2 found in winter and minimum during summer. Since the difference between the pCO_2 level in the ocean and the atmosphere controls the direction of the air–sea CO_2 flux, this is an indication of the pronounced seasonal variation of the flux in the Baltic Sea, with outgassing of CO_2 to the atmosphere during winter and uptake during summer (Thomas et al., 2004; Thomas and Schneider, 1999). Despite numerous studies, it is still uncertain, whether the Baltic Sea currently acts as a net sink or source of atmospheric CO_2, as previous studies have given ambiguous results varying from -4.3 to $2.7\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ for the entire Baltic Sea region (Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011; Norman et al., 2013). Thereby, it is also difficult to project how the Baltic Sea will contribute to the global carbon budget in the future. Moreover, the region may possibly have changed from being a net source to a net sink of atmospheric CO_2, due to the industrialization and the enormous input of nutrients (Omstedt et al., 2009). These inputs will, however, likely change in the future due to changes in climate and anthropogenic activities (Geels et al., 2012; Langner et al., 2009).

As the Baltic Sea is bordered by land areas, the atmospheric CO_2 concentration found here will be directly affected by continental air leading to a greater temporal and spatial variability in the CO_2 level, than what is found over open oceans. The impact of temporal variations in atmospheric CO_2 on the air–sea CO_2 exchange has been discussed by Rutgersson et al. (2008, 2009). They show an overestimation in the amplitude of the seasonal cycle for calculated air–sea CO_2 fluxes, when using a constant annual mean value of atmospheric CO_2 concentration instead of daily levels of the atmospheric concentration. Annually, the difference was less than 10 % between the two cases, but weekly flux deviations of 20 % were obtained. This indicates how synoptic variability in the atmosphere not always can be ignored (Rutgersson et al., 2009). Further, Rutgersson et al. (2008) note that the uncertainties connected with the transfer velocity are much greater. However, it is still worthwhile to minimise the bias in the estimation of the flux by including detailed information of the atmospheric CO_2 concentration. The short term variability (hourly) of both meteorology and atmospheric

CO_2 concentrations is not always accounted for or has not been discussed in previous estimates of the air–sea CO_2 fluxes in the Baltic Sea (Algesten et al., 2006; Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011; Loffler et al., 2012; Norman et al., 2013; Wesslander et al., 2010).

To enlighten this matter, the present study aims to determine the importance of the short-term variability in atmospheric CO_2 concentrations for the net air–sea CO_2 flux. The Baltic Sea and Danish inner waters (consisting of Kattegat and the Danish straits; Øresund and the Belt Seas) are chosen as focus areas for the present study. A modelling approach is applied, which includes both short-term (hourly to synoptic) and long-term (seasonal to inter-annual) variability in the atmospheric CO_2 concentrations. The analysis is carried out by constructing a meso-scale model framework based on an atmospheric transport model covering the study region with high resolutions in both space and time. The model includes a new spatial $p$$CO_2$ climatology developed especially for the investigated marine area, as existing climatologies do not cover this area. The advantages of the present study are that the same and consistent method is applied to the entire Baltic Sea and Danish inner waters, and that the impact of spatial and temporal short term variability in atmospheric parameters will be investigated in more details than in the previous studies of this region.

Recently, national CO_2 budgets that include both anthropogenic and natural components have been estimated in various countries (Meesters et al., 2012; Smallman et al., 2014). The present study is likewise part of a national project: Ecosystem Surface Exchange of Greenhouse Gases in an Environment of Changing Anthropogenic and Climate forcing (ECOCLIM) that is to determine the CO_2 budget for Denmark. For that reason the present study will also estimate the marine component of the Danish CO_2 budget.

In Sect. 2 the study area, the applied surface fields of $p$$CO_2$ and the model frame work are described. Results are presented in Sect. 3, leading to a discussion in Sect. 4, and concluding remarks in Sect. 5.

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2 Study setup

2.1 Study area

The marine areas investigated in this study comprise of the Baltic Sea, Kattegat and the Danish Straits, with the two latter also referred to as the Danish inner waters (see Fig. 1). In the following a short introduction to these heterogeneous marine areas is given, as well as a description of the overall atmospheric CO_2 field in the region.

The Baltic Sea is a semi-enclosed continental shelf sea area with a large volume of river runoff adding a substantial amount of nutrients and terrestrial carbon to the Baltic Sea (Kulinski and Pempkowiak, 2011). The circulation in the Baltic Sea is influenced by a relative large runoff from the surrounding drainage areas, and this causes a low-saline outflowing surface water mass from the area. The Baltic Sea can, therefore, be considered as a large estuary. Inflow of high-saline water from the North Sea ventilates the bottom waters of the Baltic Sea, and the exchange between these water masses occurs through the shallow North Sea/Baltic Sea transition zone centred around the Danish Straits (Bendtsen et al., 2009). Ice coverage is observed in the northern part of Baltic Sea during winter (Loffler et al., 2012), which has implications for the air–sea exchange of CO_2.

Atmospheric concentrations of CO_2 in the Baltic region have a greater seasonal amplitude than at e.g. Mauna Loa, Hawaii, which often is referred to as a global reference for the atmospheric CO_2 background, due to the remoteness of the site. The larger seasonal amplitude over the Baltic can be explained by the difference in latitude between the studied area (54–66° N) and Mauna Loa (20° N), and the undisturbed air at the high altitude site of Mauna Loa compared to the semi-enclosed Baltic Sea (Rutgersson et al., 2009). The study by Rutgersson and colleagues also showed that the atmospheric CO_2 concentration in the southern part of the Baltic Sea is more affected by regional anthropogenic and terrestrial sources and sinks, than the more remote northern part of the Baltic Sea area.

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2.2 Surface water pCO_2 climatology

Model calculations of the surface air–sea gas exchange of CO_2 are parameterised in terms of the difference in partial pressure of CO_2 (i.e. ΔpCO_2) between the atmosphere and the ocean surface. The global climatology of oceanic surface pCO_2 by Takahashi et al. (2009) is commonly used in atmospheric transport models of CO_2 (e.g. Geels et al., 2007; Sarrat et al., 2009), and is also applied here for areas outside the Baltic Sea and the Danish inner waters. However, this climatology does not cover the Baltic Sea area, and therefore, a new Baltic Sea climatology has been created and merged with the climatology of Takahashi et al. (2009) in the model domain towards the North Sea and the Northern North Atlantic.

Available pCO_2 surface measurements and water chemistry data from the Baltic Sea and the Danish inner waters are combined in six sub-domains of the Baltic Sea to provide monthly averaged pCO_2 values for this new climatology. The sub-domains cover Skagerrak, Kattegat and the Belt Sea (henceforth referred to just as Kattegat), the Western Baltic Sea, the Baltic Proper, the Gulf of Finland, the Bothnain Sea and the Bothnian Bay. Two data sets are analysed; one from marine stations (stationary) and the other obtained from ships (underway). All available data collected since year 2000 is included in the analysis (Fig. 1). From the two data sets monthly mean values for each sub-domain are determined.

Surface measurements of salinity, temperature, alkalinity and pH from six marine measuring stations (operated by the Swedish Meteorological and Hydrological Institute, SMHI; Shark Data Base, 2013) are applied to calculate the surface pCO_2 values by a similar approach as described in Wesslander et al. (2010). The six stations are located from the central Skagerrak to the Bothnian Bay (Fig. 1), but no measurements are available from the Gulf of Finland. A relatively high frequency of observations is obtained at the six monitoring stations with the number of observations in each month ranging between 4–8 at station A17, 15–36 at station Anholt E, 6–18 at station BY5, 7–17 at station BY15, 1–5 at station C3 (but no data representing November) and 2–10 at station F9 (but no data representing January, February and November).

Surface levels of pCO_2 from the central Baltic Sea (Schneider and Sadkowiak, 2012) have been measured by underway-pCO_2 systems (Körtzinget et al., 1996; Schneider et al., 2006) from cargo and research ships. In particular, a route between Germany (Kiel) and Finland (Helsinki) has regularly been monitored from cargo-ships, whereas no measurements are available in the northern part of the Baltic Sea, the Danish straits, Kattegat and Skagerrak. Good data coverage of underway pCO_2 measurements is obtained in the sub-domain of the Western Baltic Sea, with the number of observations in each month ranging between 9000 and 55 000, and in the Baltic Proper, where the corresponding number of observations ranges from 20 000 to 116 000. In the Bothnian Sea the number of observations ranges from 2000 to 77 000, but there are no observations in December. Only a single month (March) is represented in the Bothnian Bay with about 5000 observations. The Gulf of Finland is represented with observations ranging from 3000 and 18 000 each month.

The stationary data from the monitoring stations and the underway data have been combined in such a manner that if underway data exists for a sub-domain, these data is used for the pCO_2 fields in the given subdomain. Otherwise, measurements from the monitoring stations are used to calculate the pCO_2 fields. Thus, pCO_2 fields for Skagerrak, Kattegat, and the Bothnain Bay are calculated solely based on data from the SMHI stations. The pCO_2 fields for the Western Baltic Sea, the Baltic Proper, the Gulf of Finland and the Bothnian Sea are obtained from the underway measurements of pCO_2, except for December in the Bothnian Sea, which is represented by the monitoring station C3. The data used to obtain the monthly averages of surface pCO_2 in each sub-domain have all been normalised to year 2000 using an annual increase in CO_2 of 1.9 µatm yr^{-1} found for the central Baltic Sea (Wesslander et al., 2010).

The resulting pCO_2 climatology for the Baltic Sea and Danish inner waters is combined with the global open ocean pCO_2 climatology from Takahashi et al. (2009). This climatology is calculated for a global oceanic grid with a horizontal resolution of $5^{\circ} \times 4^{\circ}$ in

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longitude and latitude, respectively. Consequently, this field has an even coarser spatial resolution than the sub-domains defined in the Baltic Sea area. The global climatology is by Takahashi and co-workers referenced to the year 2000 with an annual trend of 1.5 $\mu atm\,yr^{-1}$. This trend is also used to extrapolate the global data for year 2000 to the proceeding years covered in this study. Note that the trend used for the Baltic Sea and Danish inner waters is 1.9 $\mu atm\,yr^{-1}$, as this trend is shown to match this particular area. However, the difference in annual trends between the two climatologies is so small compared to the absolute pCO_2 values, thus it is reasonable to assume that the impact on the current results will be insignificant.

The monthly averaged pCO_2 values show a characteristic seasonal pattern at all monitoring stations and for the underway pCO_2 data (Fig. 2, Table S1 in the Supplement). The surface pCO_2 is under-saturated during spring and summer and super-saturated during fall and winter (Fig. 3a). However, there is a large spatial gradient in the seasonal amplitude from Skagerrak and into the Baltic Sea. A seasonal amplitude of about 140 µatm characterises the variation in Skagerrak and Kattegat, where the pCO_2 varies between 275 and 420 µatm, and the surface water is only slightly super-saturated during the winter months. In the Baltic Sea a relatively large seasonal amplitude of up to 400 µatm is observed, as primary production during the growing season, i.e. spring and summer, causes a large uptake of total dissolved inorganic carbon in the surface layer and contributes to lowering the surface pCO_2 values. The data shows how biological uptake causes a reduction of surface pCO_2, despite the general warming during the summer month, which normally tends to increase the pCO_2 in the surface water. During fall and winter, the surface pCO_2 value increase, because subsurface waters enriched in total dissolved inorganic carbon from remineralisation of organic matter during the summer are mixed into the surface layer. In the areas northeast of the Western Baltic Sea in particularly, this allows for high monthly averaged surface pCO_2 values of 460–530 µatm during winter with the largest average winter values observed in the Gulf of Finland.

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In general a good accordance between the pCO_2 values calculated from the monitoring stations and underway pCO_2 data from the sub-domains exists. The underway pCO_2 data includes both temporal and spatial variability within each sub-domain during the period since 2000. Therefore, their standard deviations (SD) are larger than the SDs from the monitoring stations, which mainly arise due to inter-annual variability in the period. Two sub-domains, the Western Baltic Sea and the Baltic Proper, have good data coverage from both the monitoring stations and underway pCO_2 data. The stations, BY5 and BY15, that represent the Western Baltic Sea and the Baltic Proper, respectively, have lower surface pCO_2 values during the summer period than the underway pCO_2 data, but the difference between the two data sets are within their SD.

2.3 Model framework

The model framework is based upon the Danish Eulerian Hemispheric Model (DEHM) – a well validated three dimensional large scale atmospheric chemical transport model (Brandt et al., 2012; Christensen, 1997). DEHM is based on the equation of continuity and use terrain following sigma levels as vertical coordinates. Here, 29 vertical levels are distributed between the surface and 100 hPa with a higher density of vertical levels in the lower part of the atmosphere. The main domain of DEHM covers the Northern Hemisphere with a horizontal grid resolution of 150 km × 150 km using a polar stereographic projection true at 60° N. Furthermore, DEHM has nesting capabilities allowing for a nest over Europe with a resolution of 50 km × 50 km, a nest of Northern Europe with an approximate resolution of 16.7 km × 16.7 km, and a 5.6 km × 5.6 km nest covering Denmark. In order to cover the Baltic Sea and the Danish marine areas in focus, a setup with two nests is applied in the current study (the European and the Northern European nests). The main domain and the nests each comprise of 96 × 96 grid points. This study uses a modified version of DEHM solely simulating transport and exchange of CO_2 (Geels et al., 2002, 2004, 2007), but in the present study with an updated description of the surface exchange of CO_2 (described in Sect. 2.2.1).

DEHM is driven by meteorological data from the meteorological model MM5v3.7 (Grell et al., 1995) using National Centers for Environmental Prediction, NCEP, data as input.

2.3.1 Model inputs

To accurately simulate the atmospheric content of CO_2, a number of CO_2 sources and sinks within the model domain as well as inflow at the lateral boundaries are required together with a background concentration. The atmospheric concentration of CO_2 (X_{atm}) can be described by

$$X_{atm} = X_{ff} + X_{bio} + X_{fire} + X_{ocn} + X_{background} \tag{1}$$

where X_{ff} is the contribution of CO_2 from fossil fuel emissions, X_{fire} from vegetation fires, and X_{bio} and X_{ocn} are the contribution to the atmospheric concentration from exchange of CO_2 with the terrestrial biosphere and ocean, respectively. $X_{background}$ is the atmospheric background of CO_2.

Fossil Fuel (X_{ff})

Fossil fuel emissions for the domain covering the Northern Hemisphere are implemented in DEHM from the Carbon Tracker (hereafter referred to as CT) simulation system (CarbonTracker CT2011_oi, 2013; Peters et al., 2007). This emission map has a three hourly temporal resolution on a 1° × 1° grid.

CT is for the European area substituted by a fossil fuel emission inventory with a higher spatiotemporal resolution (hourly, 10 km × 10 km) developed by the Institute of Energy Economics and the Rational Use of Energy (Pregger et al., 2007).

For the area of Denmark, emissions with an even finer spatial resolution of 1 km × 1 km are applied obtained from the Department of Environmental Science, Aarhus University. These are based on the Danish national inventory submitted yearly to UNFCCC (United Nations Framework Convention on Climate Change) and constructed from

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energy statistics, point source and statistic sub-models (Plejdrup and Gyldenkærne, 2011).

As the European and Danish emission inventories are for the years 2005 and 2011, respectively, these inventories are scaled to total yearly national estimates of carbon emissions from fossil fuel consumption conducted by the Carbon Dioxide Information Analysis Center, CDIAC, in order to account for the year to year change in emissions (Boden et al., 2013).

Biosphere (X_{bio})

Terrestrial biosphere fluxes from the CT system, with a spatial resolution of $1^\circ \times 1^\circ$ and a temporal resolution of three hours, are applied in DEHM. In the CT assimilation system the Carnegie-Ames Stanford Approach (CASA) biogeochemical model is used for prior fluxes (Giglio et al., 2006; van der Werf et al., 2006). The prior terrestrial biosphere fluxes are optimised in the CT assimilation system by atmospheric observations of CO_2. Via this atmospheric inversion a best guess of surface fluxes is obtained, and the optimised fluxes are implemented in DEHM.

Fires (X_{fire})

CO_2 emissions due to vegetation fires are obtained from the CT fire module and applied in DEHM. The CT fire module is based on the Global Fire Emission Database, GFEDv3.1, and CASA, while the burned area from GFED is based on MODIS satellite observations of fire counts. The resolution is likewise three hourly on a $1^\circ \times 1^\circ$ grid.

Ocean (X_{ocn})

The CO_2 flux (F) at the air–sea interface is calculated using the relation: $F = k\alpha\Delta pCO_2$, where, k is the exchange coefficient, α is the gas solubility and ΔpCO_2 is the difference in partial pressure of CO_2 between the surface water and the overlying air. The gas solubility of CO_2 is determined from Weiss (1974) and depends on the

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water temperature and salinity. A $0.25^{\circ} \times 0.25^{\circ}$ salinity map is implemented in DEHM for the calculation of CO_2 solubility (Boyer et al., 2005). To calculate ΔpCO_2 the surface pCO_2 fields described in Sect. 2.2 are applied together with the concentration of CO_2 in the lowest atmospheric layer in DEHM.

No standardised parameterisation of the transfer velocity, k, exists, but k is most often parameterised as a power function of the wind speed (Garbe et al., 2014; Rutgersson et al., 2008) normalised to the Schmidt's number (Sc) according to Wanninkhof (1992). In the present study we use the parameterisation of Wanninkhof (1992) (hereafter referred to as W92), which is the parameterisation most frequently applied. This transfer velocity is a function of the wind speed at 10 m above the surface (u_{10}) and when normalised to Sc at 20 °C in salt water it has the form:

$$k_{660} = \left(0.31 u_{10}^2\right) \sqrt{\frac{660}{Sc}} \tag{2}$$

However, a few additional parameterisations that could be more representative for the study area are also tested. One is Nightingale et al. (2000), who estimate a transfer velocity based on tracer gas measurements in the North Sea of:

$$k_{660} = \left(0.333 u_{10} + 0.222 u_{10}^2\right) \sqrt{\frac{660}{Sc}} \tag{3}$$

Another is by Weiss et al. (2007), who have carried out measurements using eddy covariance techniques in the Arkona basin located within the Baltic Sea to estimate an accurate k for this particular area. This parameterisation takes the form:

$$k_{660} = \left(0.365 u_{10}^2 + 0.46 u_{10}\right) \sqrt{\frac{660}{Sc}} \tag{4}$$

Sea ice coverage is in DEHM obtained from NCEP. The sea ice coverage is implemented in the calculations of the air–sea CO_2 exchange, such that the flux in a grid cell is reduced by the fraction of sea ice. If the fraction of sea ice coverage is 1, the entire grid cell will be covered with ice, and no exchange of CO_2 will take place between the ocean and atmosphere. Recent studies have shown that CO_2 exchange between ice-covered sea and the atmosphere does take place, but to what extent has not yet been quantified (Parmentier et al., 2013; Sørensen et al., 2014). For that reason the exchange over sea ice is not accounted for here.

k_{660}, α and ΔpCO_2 are calculated at each time step of the model simulation (the time step of the model varies between ca. 3–20 min depending of e.g. the nest). Consequently, the air–sea CO_2 flux has the same temporal resolution as the simulated atmospheric CO_2.

Atmospheric background ($X_{\text{background}}$)

The level of atmospheric CO_2 has been increasing since pre-industrial times. It is not feasible to simulate this entire time period with the model system as to replicate this build-up. Therefore, an atmospheric background of CO_2 is needed. The atmospheric background of CO_2 is established on the basis of the NOAA ESRL GLOBALVIEW-CO2 data product using observations from the Baltic Station, BAL (lat = 55°35′ N, lon = 17°22′ E) (GLOBALVIEW-CO2, 2013). BAL lies within the area of interest, but far from local sources and sinks. It can therefore be assumed to represent the atmospheric background level in the study area. The atmospheric background of CO_2 is calculated based on the following equation:

$$X_{\text{background}} = X_{CO_2\,2000} + 1.91(\text{year} - 2000) + 0.16\text{month} \tag{5}$$

Here $X_{CO_2\,2000} = 370.15$ ppm is the mean CO_2 concentration at the station in 2000, year and month is the simulated year and month, and 1.91 and 0.16 represent the yearly and monthly trend of atmospheric CO_2. The trends are based on the times series at BAL for the period 2000–2010, in order to get a representative overall trend for the period in focus here (2005–2010).

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Boundary conditions

DEHM only covers the Northern Hemisphere; hence boundary conditions for the main domain are needed at the lateral boundaries towards the Southern Hemisphere, as to account for inflow from the Southern Hemisphere. Three dimensional atmospheric mole fractions of CO_2 from the CT system are applied at these boundaries.

3 Results

3.1 Model evaluation

The period 2005–2010 is simulated by DEHM with setup and fluxes as described in Sect. 2. The performance of the model for this period is evaluated by comparing simulated atmospheric CO_2 concentrations against observed. The comparison is made at six stations within the study area, where both remote continental (PAL), marine (F3, MHD, OST, WES) and anthropogenic (LUT) influenced stations are represented.

Measured and simulated atmospheric CO_2 from the marine site Östergarnsholm, Sweden (OST, 57°27′ N, 18°59′ E) and the anthropogenic continental site Lutjewad, the Netherlands (LUT, 53°40′ N, 6°31′ E) (van der Laan et al., 2009) are shown for year 2007 in Fig. 4. The Östergarnsholm marine micrometeorological field station has been running semi-continuously since 1995, measuring atmospheric CO_2 since 2005. The site has been shown to represent marine conditions and is describe further in Rutgersson et al. (2008) and Högström et al. (2008). The site at Lutjewad is on the other hand both influenced by background air from the North Sea and polluted air from the continent, depending on the wind direction. Hourly mean concentrations are plotted for simulated and measured atmospheric CO_2, and at both sites a large diurnal variability is seen in the observations. The model is not able to capture the large amplitude in the diurnal cycle, but correlations of 0.75 and 0.71 are obtained for LUT and OST, respectively. The root mean square errors, RMSE, are 9.6 and 8.8 ppm, respectively.

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These high RMSEs are linked to the underestimation of the diurnal cycle in the model. Earlier model studies have shown the same tendency to underestimate the observed variability (e.g. Geels et al., 2007). The underestimation of the diurnal cycle by DEHM is most likely caused by the coarse spatial resolution of the biosphere fluxes. Further, weekly averages are made for both observed and modelled concentrations of atmospheric CO_2 (see Fig. 4). Improvements are obtained in both correlation and RMSE to 0.89 and 5.3 ppm for LUT, and 0.91 and 5.6 ppm for OST. Synoptic scale variability is seen in the atmospheric CO_2 concentration in both the simulated and observed time-series. Especially at LUT large positive spikes are seen due to the influence of air from densely populated and industrialised regions.

Flask measurements of CO_2 at F3, the Netherlands (54°51′ N, 4°44′ E) (van der Laan-Luijkx et al., 2010) are compared to hourly modelled averages (Fig. 5) during the six year simulated period. This results in a correlation of 0.64, and a RMSE of 5.7 ppm. F3 is positioned on an oil platform in the North Sea, where local sources can influence the measured CO_2 concentration under certain wind conditions. Consequently, the most extreme outliers were filtered out with the help of simultaneous CH_4 and CO measurements, when the influence from the local source was obvious. As to examine the model performance on a longer time scale, weekly averages are made for the three remaining stations Mace Head, Ireland (MHD, 53°20′ N, 9°54′ W) (Biraud et al., 2000), Pallas-Sammaltunturi, Finland (PAL, 67°58′ N, 24°07′ E) (FMI, 2013) and Westerland, Germany (WES, 54°56′ N, 8°19′ E) (UBA, 2014) for the six year period (Fig. 5). In general a reasonable correspondence between model and observations is seen during this period with correlations of 0.96, 0.98 and 0.89, and RMSEs of 1.8, 1.9 and 3.8 ppm for MHD, PAL and WES, respectively. The ability of the model to capture the seasonal cycle is contributing to the very high correlation, but the model is also capable of capturing weekly variability and transport events especially during winter.

To conclude, this evaluation shows that the DEHM model captures the overall CO_2 pattern across the marine region in focus in the current study.

3.2 Air–sea CO_2 fluxes

In order to investigate the effect on the air–sea CO_2 flux from variations in the atmospheric CO_2 concentration at the Baltic Sea and Danish inner waters, two different model simulations are conducted. One model simulation has atmospheric CO_2 concentrations that vary from time step to time step according to the fluxes and atmospheric transport in DEHM. This is in the following referred to as the VAT ("Variable ATmosphere") simulation. The other simulation contains at each time step and grid cell the monthly mean CO_2 concentration for the given month. This is in the following referred to as CAT ("Constant ATmosphere"). All other settings are identical in the two simulations. The simulations are made for the period 2005 to 2010 using the transfer velocity parameterisation by W92.

First, the results of atmospheric CO_2 concentrations and air–sea CO_2 fluxes from the VAT simulation will be presented. These results can be used to get an understanding of how the atmospheric CO_2 concentrations vary, and of how the air–sea CO_2 fluxes behave in terms of size and direction in the different sub-basins of the Baltic Sea and Danish inner waters. This will be followed by the comparison of the VAT and CAT simulation.

3.2.1 Variable atmospheric CO_2 concentration

The variability of atmospheric CO_2 in the Baltic area is illustrated in Fig. 6, which shows a few examples of the hourly simulated surface concentration. The top panel shows the variability in February 2007, where synoptic scale variability influence transport of CO_2, and hence the surface concentrations. On 1 February 2007 at 4:00 GMT, a low pressure system has during the last days moved through Southern Scandinavia and is now located over Poland. This system has rotated continental air with high levels of CO_2 from east towards the Baltic Sea. On 3 February 2007, the prevailing winds are now westerly, where marine air masses with lower CO_2 concentrations are transported towards the Baltic Sea. The lower panel of Fig. 6 shows the diurnal variability on 14

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July 2007. At 2:00 GMT, air masses with high CO_2 concentrations are transported from land towards the marine areas – most evident in near-coastal areas. The same is the case at 14:00 GMT, but with lower concentrations due to the uptake of CO_2 by the terrestrial biosphere at this time of the day. These examples show that large spatial gradients of up to 20 ppm can develop across the Baltic Sea during summer.

The seasonal averaged air–sea CO_2 fluxes estimated by DEHM in the VAT simulation are shown in Fig. 3b. In winter, a gradient is seen from the North Sea through the Danish inner Straits towards the Baltic Sea, indicating a large release of CO_2 to the atmosphere in the Baltic, and uptake in the North Sea. Progressing to spring, the gradient towards the Baltic ceases and all areas now have marine uptake of atmospheric CO_2, which continues throughout the summer. In fall, the gradient starts to build up again, and the Baltic Sea becomes a source of CO_2 to the atmosphere.

The monthly mean 2005–2010 sub-basin averaged fluxes likewise depict this seasonality (Fig. 7). The highest seasonal amplitudes are found in the Baltic Sea area stretching from the Baltic Proper and northwards with the greatest seasonal amplitude of 12 $\mathrm{g\,C\,m^{-2}\,month^{-1}}$ found in the Bothnain Sea. Less seasonal variation in the CO_2 flux is obtained for Kattegat and the Danish Straits, which yearly experiencse a variability of just 4.3 $\mathrm{g\,C\,m^{-2}\,month^{-1}}$.

The total sub-basin monthly mean fluxes of CO_2 between the atmosphere and ocean also show a seasonal variation for all areas with release in winter and uptake of atmospheric CO_2 in summer (Table 1). The entire area comprising of the six sub-basins has for the period 2005–2010 an average annual net uptake of atmospheric CO_2 of 287 $\mathrm{Gg\,C\,yr^{-1}}$. However, the net exchange varies greatly from sub-basin to sub-basin. Kattegat, the Western Baltic Sea and the Baltic Proper all have annual net uptake of atmospheric CO_2 averaged over 2005 to 2010, while the remaining three sub-basins release CO_2 to the atmosphere. The Baltic Proper contributes the most to the total annual averaged flux with an uptake of 254 $\mathrm{g\,C\,yr^{-1}}$, but during the individual months the fluxes in the Baltic Proper are even larger (up to 900 $\mathrm{g\,C\,month^{-1}}$). Monthly fluxes of this considerable size are not obtained in any of the other sub-domains. This is of

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course related to the fact that the Baltic Proper has the greatest spatial extent of all the six sub-basins.

To estimate the marine contribution in the Danish national CO_2 budget, the air–sea CO_2 flux in the Danish Exclusive Economic Zone (EEZ) is calculated. The EEZ is a zone adjacent to the territorial waters extending up to 200 nautical mile off shore, and in the EEZ the coastal state has the right to explore, exploit and manage all resources within this area (United Nations Chapter XXI Law of the Sea, 1984). The Danish EEZ has an area of approximately 105 000 km^2 (Fig. S2 in the Supplement). During the six years simulated an average annual uptake in the Danish EEZ of 2613 $Gg\,C\,yr^{-1}$ is obtained. The main part of the uptake in the Danish EEZ occurs in the North Sea. The North Sea has the largest extent in the Danish EEZ and combined with a small seasonal amplitude in pCO_2, this results in a constant uptake throughout the year. The other sub-basins within the Danish EEZ all release CO_2 in winter and take up CO_2 during summer. Compared to the Danish national emissions of anthropogenic CO_2, the marine uptake by the Danish EEZ corresponds to 18 % per year of these emissions (Table 2). For the six year period investigated, the annual mean inventory in CO_2 excluding land use and land use change is 14.6 Tg C (Nielsen et al., 2013).

3.2.2 Constant atmospheric CO_2 concentration

The impact of variations in the atmospheric CO_2 concentration is analysed in the following by comparing the results of the net annual averaged air–sea CO_2 fluxes for the VAT and CAT simulations in the six sub-basins. A total annual difference of 184 $Gg\,C\,yr^{-1}$ is obtained, which corresponds to a 64 % difference (calculated with VAT as the reference). CAT gives a total annual uptake of 471 $Gg\,C\,yr^{-1}$, while VAT only has an annual uptake of 287 $Gg\,C\,yr^{-1}$. The seasonal difference between VAT and CAT across the study area is seen in Fig. 8. The monthly fluxes in the sub-basins maintain the same direction in both VAT and CAT. However, for months where the different sub-basins experience outgassing, the outgassing is reduced in the CAT simulation as compared

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to in the VAT simulation. For months with uptake of CO_2 in the individual sub-basins, a higher uptake is simulated with the CAT setup than with the VAT setup.

In order to further analyse the difference between the VAT and the CAT simulations, times series of the driving parameters are compared. Examples of the atmospheric pCO_2 (pCO_2^a) in the lowest model layer in the VAT and CAT simulations are shown for a coastal site south of Sweden (55°18′ N, 13°55′ E) in Figs. 9 and 10 for February and July 2007, respectively. February represents a case of outgassing, and July a case of marine uptake of atmospheric CO_2. Time series of wind velocity at 10 m, u_{10}, and the atmospheric mixing height, h_{mix}, are also plotted. Further, the differences in the atmospheric partial pressure of CO_2 (ΔpCO_2^a) and in the air–sea CO_2 flux (ΔF_{CO_2}) between the two simulations are shown (calculated as VAT − CAT). Differences in the pCO_2^a in the two simulations determines the difference in ΔpCO_2 between the two simulations, as the partial pressure of CO_2 in the water is the same in the two simulations. pCO_2^a is the only variable allowed to vary in the air–sea CO_2 flux calculations between VAT and CAT, and is thus responsible for the obtained flux differences.

For both months pCO_2^a_VAT fluctuates around the constant pCO_2^a_CAT. During the first half of February, a period of anti-correlation between pCO_2^a_VAT and u_{10} is seen. This anti-correlation is greatest during the second week with a weekly correlation coefficient (r) equal to −0.69. During the last week of February, a positive correlation of $r = 0.62$ between the two is obtained with wind speeds above 10 m s^{-1} and high pCO_2^a levels in the atmosphere. In February no clear diurnal cycle is seen in the mixing height, but it seems to follow the pattern of the wind speed with decreases in h_{mix} during periods with low wind speeds and increases in h_{mix} during high wind speeds. The correlation between these two parameters in February is $r = 0.72$.

In July a clear diurnal variability is seen in pCO_2^a_VAT, and an anti-correlation between h_{mix} and pCO_2^a_VAT is evident throughout the month with the highest anti-correlation during the last week (with $r = -0.72$). In the VAT simulation the so-called diurnal rectifier effect is modelled. The collaboration between terrestrial ecosystems and boundary layer dynamics that act towards lowering pCO_2^a during the day and increase it during night is known as the rectifier effect. In particularly during the growing season the rectifier effect is apparent (Denning et al., 1996).

An anti-correlation between $\Delta p\mathrm{CO}_2^\mathrm{a}$ and ΔF_{CO_2} is seen in both February and July, which will be discussed in more detail in Sect. 4.3. During winter the largest difference in the air–sea CO_2 flux between VAT and CAT coincides with high wind speeds or large differences in the atmospheric CO_2 concentrations (hence large $\Delta p\mathrm{CO}_2^\mathrm{a}$ values). In summer the diurnal cycle in the atmospheric CO_2 levels are translated into the flux difference.

Vertical profiles of atmospheric CO_2 at the site south of Sweden have been plotted together with h_{mix} in Fig. 11. Note that the unit in Fig. 11 is ppm and not µatm. The variability of CO_2 is also evident in the vertical profile, where air masses with low or high CO_2 concentrations are being transported to and from the site (55°18′ N, 13°55′ E). Continental air is represented by high levels of CO_2 that extend up to 2 km into the atmosphere, while marine air masses have lower levels of CO_2 corresponding to the levels above 2 km. The shift between the two types of air masses is clearly seen in the vertical profile e.g. on 2 February. Here higher wind speed leads to transport of marine air masses to the site (see Fig. 9). Like Fig. 9, the vertical profile in February shows no clear connection between surface concentrations of CO_2 and h_{mix}. In July, the vertical profile depicts the rectifier effect. Low surface values of CO_2 coincide with the greatest boundary layer heights found during the day time, and high surface levels of CO_2 concur during night time with the nocturnal boundary layer. It is remarkable how the vertical profile during July 2007 represents a much more mixed atmosphere as compared to February 2007, where the marine and continental air masses clearly are distinguished from each other.

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4 Discussion

4.1 Surface water pCO_2 climatology

A representative map of surface pCO_2 has been created for Skagerrak and six sub-domains in the Baltic using two data sets, one obtained from monitoring stations and one using underway measurements of surface pCO_2 (see Sect. 2.2).

Previous estimates of pCO_2 at two positions within the Baltic Sea have shown an inter-annual variability of up to 25 % in winter and almost 140 % in summer (Wesslander et al., 2010). Likewise, large short term variability has been measured in different coastal systems (Dai et al., 2009; Leinweber et al., 2009; Wesslander et al., 2011). The representation of surface pCO_2 values in the sub-domains by a monthly averaged value does not account for the temporal variability during each month and the spatial variability in the relatively large areas. Also, the inter-annual variability is not accounted for by the average values. However, the simplified description of the conditions in the Baltic Sea in a number of sub-domains is currently the best solution in order to obtain a surface field of pCO_2 that spatially covers the whole model domain for this study. The estimated surface fields of pCO_2 are based on relatively few observations, and therefore, it has not been possible to include neither spatial, nor short-term or inter-annual variability. Although, underway pCO_2 measurements (Schneider and Sadkowiak, 2012) have increased the data coverage in the central Baltic Sea significantly in the most recent years.

4.2 Air–sea CO_2 fluxes

The atmospheric CO_2 concentration is seen to vary greatly within the study area (Figs. 6 and 11). The dynamics of the fluxes and the atmospheric transport and mixing lead to short-term variations and spatial gradients in the atmospheric CO_2 level across the marine areas in focus here. Pressure systems move through the region transporting air masses with different characteristics and CO_2 levels to and from the Baltic and the

Danish inner waters. In the growing season, the effect from the terrestrial biosphere is apparent with a clear diurnal cycle in the atmospheric CO_2 caused by respiration during night time and photosynthesis during the day. Even these short term variations in atmospheric CO_2 concentrations over land can be transported to marine areas, indicating why atmospheric short term variability is important to include in the air–sea flux estimations.

For the six year period an annual average uptake of 287 $Gg\,C\,yr^{-1}$ is obtained with the VAT-setup as a total for the six sub-basins. A statistical analysis of the simulated fluxes shows that Kattegat and the Western Baltic Sea are annual sinks (at a significance level of 0.05), while the Gulf of Finland and the Bothnian Bay are annual sources of atmospheric CO_2. In the transition zone between these areas, i.e. the Baltic Proper and the Bothnian Sea, large variations in the annual flux are seen in this study. During the six years simulated, these sub-domains change annually between being sources and sinks of CO_2 to the atmosphere. This also affects the total flux for the entire investigated area, which also shifts between being an annual source and sink. A significant test (student's t test with a significance level of 0.05) show that the variability from year to year is so large that we cannot conclude that the area is a net sink, despite the estimated averaged uptake of 287 $Gg\,C\,yr^{-1}$.

The air–sea CO_2 fluxes obtained from the VAT simulation for six sub-basins are compared to previous results from the area as to assess the consistency. Previous studies of the air–sea CO_2 flux in the Baltic Sea area are ambiguous as to the Baltic Sea's role in the carbon cycle. This is partly caused by the various techniques used, ranging from in-situ measurements using eddy covariance method to model simulations (Kulinski and Pempkowiak, 2011; Rutgersson et al., 2009; Weiss et al., 2007; Wesslander et al., 2010), and partly by the different spatial areas investigated. Some of the previous studies are site specific (Algesten et al., 2006; Kuss et al., 2006; Loffler et al., 2012; Rutgersson et al., 2008; Wesslander et al., 2010), and other studies cover the entire area (Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011; Norman et al., 2013). None of the previous regional studies have based their estimates of the air–sea CO_2

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flux on results from an atmospheric transport model capable of combining large spatial coverage with high spatiotemporal resolution of the entire Baltic region as in the present study. Results from previous studies and the present study have been converted to the same unit of $g\,C\,m^{-2}\,yr^{-1}$, as to allow for a direct comparison (Table 3).

Table 3 reveals that in terms of the direction of the flux, the present study corresponds well with some of the previous studies while contradicts others. As the results obtained from the VAT simulation lie within in the range of previous estimates, it seems reasonable to use the current model setup for sensitivity analysis of the air–sea CO_2 flux in the region. Additional, it can be concluded that the obtained results from the VAT simulation together with recent studies converge towards the Baltic Sea and the Danish inner waters being annual sinks of atmospheric CO_2.

4.3 Impact of atmospheric short term variability

The difference of $184\,Gg\,C\,yr^{-1}$ between the annual air–sea flux in the CAT and VAT simulations was tested to be significantly different from zero at a 0.05 significance level. Therefore, it can be concluded that using a constant level of atmospheric CO_2 has a significant impact on the estimated annual air–sea CO_2 flux. The greatest differences are found in winter and fall in the Baltic Sea area (Fig. 8). But large differences are also found over open water areas in spite of a less variable atmospheric CO_2 concentration here. The generally higher wind speeds over open water might lead to the large flux difference here.

The deviation between the two simulations in the study region is mainly caused by a reduction in the winter uptake in the CAT simulation. An optimal situation where higher uptake during winter occurs in the VAT simulation is seen, when high wind speeds coincide with lower pCO_2^a in the VAT than the CAT simulation. Thereby, ΔpCO_2 is greater in the VAT simulation than in the CAT simulation. In combination with the non-linearity of the wind speed in the parameterisation of the transfer velocity, this leads to a larger outgassing of CO_2 in the VAT simulation. Such a situation is seen at the coastal site south of Sweden (55°18′ N, 13°55′ E) in Fig. 9, where episodes with high

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wind speeds in the beginning of the month transport air masses with lower CO_2 levels to the site and increase the flux in VAT as compared to CAT (i.e. a positive ΔF_{CO_2}).

The higher marine CO_2 uptake in summer by the CAT simulation is a result of diurnal boundary layer dynamics and the diurnal cycle or lack of it in the atmospheric CO_2 concentrations. The rectifier effect is not accounted for in the CAT simulation, and the constant pCO_2^a in CAT is higher during the day and lower during the night than in the VAT simulation. This allows for a greater air–sea ΔpCO_2 in the CAT simulation during day, which together with a tendency of higher wind speeds during day time increases the oceanic uptake in CAT. This is illustrated by ΔF_{CO_2}, where positive values indicate how the flux is numerical larger in CAT than VAT (see Fig. 10). As described in Sect. 3.1, the diurnal cycle of atmospheric CO_2 is generally underestimated by the DEHM model. Due to this underestimation the difference between the VAT and CAT simulations found during the growing season is likely a conservative estimate.

While Rutgersson et al. (2008) find a slightly overestimated seasonal amplitude, when using a constant atmospheric CO_2 concentration, the present study finds that the seasonal cycle of the CAT simulation is displaced downwards as compared to the VAT simulation. This displacement results in a greater annual uptake in the CAT simulation.

4.4 Uncertainties

The estimated air–sea CO_2 flux is controlled by several parameters in the applied model setup: choice of transfer velocity parameterisation, wind speed, temperature, salinity, atmospheric CO_2 concentration and marine pCO_2 surface values. Each of these is connected with some uncertainty and errors.

Takahashi et al. (2009) estimate the combined precision on the global air–sea flux to be on the order of ±60 %, when including a possible climatology bias due to interpolation and under-sampling. The uncertainty might be higher in the current study, as the climatology for the pCO_2 in surface waters used here covers arears, where the spatiotemporal variability in the measured pCO_2 is higher than in open waters. The natural

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variability within the sub-domains is represented by the SDs in Fig. 2 and it reflects both the spatial and temporal variation in the domains during the period of sampling, i.e. the last decade. The Baltic Sea domains (i.e. except the Kattegat sub-domain) are all characterised by a significant under-saturation of the surface water during spring and summer. During winter these stations are in general supersaturated with respect to the atmospheric $p\mathrm{CO_2}$. Thus, the sign of the CO_2 flux during the seasons is assumed to be well-determined in the Baltic Sea sub-domains due to the large seasonal amplitudes. However, during the seasonal change between summer and winter, where typical SDs in the climatology of 50 ppm are seen, we estimate that the uncertainty due to the ocean surface $p\mathrm{CO_2}$-values is in the order of 50 % in the Baltic Sea. The uncertainty in the Kattegat sub-domain is estimated to be up to 50–100 % because of the relatively small seasonal amplitude.

Atmospheric CO_2, wind speed and temperature all vary in each model time step and grid cell. The uncertainties of wind speed and temperature are small compared to the uncertainties of the $p\mathrm{CO_2}$ fields. Figures 4 and 5 show how well the DEHM model captures the weekly and seasonal variability in the atmospheric CO_2 concentrations. However, some problems arise in capturing the variability on shorter time scales (e.g. diurnal). The diurnal cycle is under-estimated in this model setup, which is related to the coarse resolution of the biosphere fluxes, and of the model itself.

Short term variability does not only exist in the atmospheric concentration of CO_2, it has also been detected in the $p\mathrm{CO_2}$ of surface water (Dai et al., 2009; Leinweber et al., 2009; Rutgersson et al., 2008; Wesslander et al., 2011). The magnitude of the short term variability is site dependent with smallest variability found in open oceans (Dai et al., 2009) and greatest at near-coastal sites (Leinweber et al., 2009; Wesslander et al., 2011). Off the Californian coast, Leinweber et al. (2009) find a diurnal cycle of $p\mathrm{CO_2}$ with an average amplitude of 20 µatm – a diurnal amplitude double of what they find in the atmosphere. Short term variability of marine $p\mathrm{CO_2}$, could potentially alter the annual estimate of the coastal air–sea CO_2 flux. Thus, in the present study the fluxes at the near-coastal areas within the sub-domains could be affected by this short term variability and could possibly modify the total flux for the sub-domains. However, the short term variability in marine pCO_2 is not included in this study, and it is therefore difficult to estimate how this might affect the estimated flux. Further, the short term variability in the air and water might be correlated, thus it is not possible to make a deduction of the combined effect in the present model study.

The largest uncertainty connected to the estimated air–sea flux is related to the choice of transfer velocity. The results from the VAT simulation presented here were calculated using the parameterisation by Wanninkhof (1992), but model simulations using parameterisation of Nightingale et al. (2000) and Weiss et al. (2007) have also been conducted. With these parameterisations the annual flux for the study area is changed to -667 and $-858\,\mathrm{Gg\,C\,yr^{-1}}$, respectively. The present study supports the findings briefly touched upon by Rutgersson et al. (2009), who conclude that the uncertainty due to the value of atmospheric CO_2 is small compared to uncertainty in transfer velocity. We, however, stress that ignoring short term variability in marine and atmospheric pCO_2 introduces a bias in the estimates of the air–sea CO_2 flux.

5 Conclusion

Using an atmospheric CO_2 model with a relatively high spatial and temporal resolution we have estimated the air–sea flux of CO_2 in the Danish inner waters and the Baltic Sea region. More specifically we have made a detailed analysis of the sensitivity to temporal variability in atmospheric CO_2 and the related impact of driving parameters like wind speed and atmospheric mixing height.

In the process of this study new monthly marine pCO_2 fields have been developed for the region combining existing data from monitoring stations and measurements from ships. Due to the sparseness of these data, only seasonal variations are included in the pCO_2 fields.

The atmospheric concentration of CO_2 is often assumed to be constant or only vary by season in many marine model studies, but according to this novel sensitivity analy-

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sis, neglecting e.g. the diurnal variability in atmospheric CO_2 concentrations could lead to a systematic bias in the annual net air–sea flux. Previous studies have looked at the entire Baltic region (Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011; Norman et al., 2013; Thomas and Schneider, 1999), but not with the same approach as in the present study.

In all the included sub-basins a seasonal cycle was detected in the air–sea CO_2 flux with release of CO_2 during winter and fall, and uptake of atmospheric CO_2 in the remaining months. An annual flux for the study area of $-287\,\mathrm{Gg\,C\,yr^{-1}}$ ($-0.7\,\mathrm{g\,C\,m^2\,yr^{-1}}$) was obtained for the six years simulated. This agrees with the previous findings of Norman et al. (2013) and Gustafsson et al. (2014), who estimate annual air–sea CO_2 fluxes of -2.6 and $-4.3\,\mathrm{g\,C\,m^2\,yr^{-1}}$, respectively. Significant testing of the flux for the study area shows that for the six years simulated here, we cannot conclude that the total Baltic Sea region is an annual sink. Instead our results indicate that the region alternates between being an annual source and sink. If examining the results at sub-basin scale, this alternation is caused by two sub-basins: the Baltic Proper and the Bothnian Sea. Furthermore, our results suggest that Kattegat and the Western Baltic Sea act as annual sinks of atmospheric CO_2, and the Gulf of Finland and the Bothnian Bay act as sources.

In order to test the importance of short term (hourly) variations in the atmospheric CO_2 in relation to the yearly air–sea flux, two different model simulations have been made. The first simulation includes the short-term variations (the VAT simulation), while the other simulation includes a monthly constant atmospheric CO_2 concentration (the CAT simulation). A significant difference of $184\,\mathrm{Gg\,C\,yr^{-1}}$ (corresponding to 67 %) was obtained for the air–sea CO_2 flux for the Baltic Sea and Danish inner waters between the two model simulations. The seasonal amplitude of the air–sea CO_2 flux was in the CAT simulation shifted downwards as compared to the VAT simulation, resulting in a reduced winter release of CO_2 in the CAT simulation and an increased summer uptake. The difference occurs solely due to the difference in the atmospheric CO_2 concentrations.

As a part of the Danish project ECOCLIM with focus on the Danish CO_2 budget, the natural marine annual flux of CO_2 was for the first time estimated by the present study. The Danish waters – in this context defined as the Danish Exclusive Economic Zone – is according to our simulations taking up 2613 $Gg\,C\,yr^{-1}$ with the majority taken up in the North Sea. This is comparable to approximately 18 % of the Danish anthropogenic CO_2 emissions.

The uncertainty in estimating the air–sea CO_2 exchange has many contributions. The largest is found to be the parameterisation of the transfer velocity, which supports previous findings. The present study, however, underlines the importance of including short term variability in the atmospheric CO_2 in order to minimise the uncertainties in the air–sea CO_2 flux. This further leads to the deduction that also short term variability in pCO$_2$ of the water, in particular of coastal areas, needs to be included, as short term variability in near coastal surface water pCO$_2$ potentially is greater than in the atmosphere.

To conclude, we recommend that future studies of the air–sea CO_2 exchange include short term variability of CO_2 in the atmosphere. Thereby, the uncertainty related to estimating the marine part of the carbon budget at regional to global scales can be reduced.

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Table 1. Monthly mean fluxes for the period 2005–2010 depicting seasonal variation of the air–sea CO_2 exchange. Unit is in Gg C per sub-basin. Positive sign indicates release of CO_2 from the ocean to the atmosphere, negative sign indicates uptake of atmospheric CO_2 by the ocean. This sign convention is used throughout the paper.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann
Kattegat	29	−21	−98	−42	−25	−28	−26	−33	−33	−15	14	43	−235
Western Baltic	125	31	−113	−226	−206	−142	−153	−92	60	137	236	140	−203
Baltic Proper	804	365	92	−654	−808	−718	−844	−784	−178	481	995	993	−254
Gulf of Finland	49	60	8	−61	−92	−68	−74	−67	1	78	151	117	102
Bothnian Sea	207	120	83	−253	−383	−325	−355	−284	−22	439	529	412	167
Bothnian Bay	31	23	10	−7	−50	−91	−118	−18	48	205	94	9	137

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Table 2. The top row shows the annual Danish CO_2 emissions as reported to UNFCCC. The middle row contains the annual uptake of CO_2 in the marine area defined as the Danish Exclusive Economic Zone as estimated in this study. The bottom rows give this uptake as a percentage of the Danish anthropogenic CO_2 emissions.

	2005	2006	2007	2008	2009	2010	6 yr avg.
DK CO_2 (Tg C)	14.3	16.5	15.2	14.3	13.6	13.7	14.6
Total Uptake – EEZ (Tg C)	−2.6	−2.4	−2.8	−2.6	−2.6	−2.7	−2.6
Percentage of CO_2	18	14	18	18	19	20	18

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Table 3. Present study compared to previous results within the different sub-domains. Study type indicates the type of previous study (Mod. – model based, MBA – mass balance approach, Meas. – measurement based, Cru. – cruise based) and its spatial extend (s-b – sub-basins, s-s – site specific). All shown results are in $g\,C\,m^2\,yr^{-1}$.

	Previous results	Study	Study type	Presents Study
Kattegat	−40.0	Gustafsson et al. (2014)	Mod., s-b	−7.0
	19.0	Norman et al. (2013)	Mod., s-b	
	−13.9	Wesslander et al. (2010)	Meas., s-s	
Western Baltic	−34	Gustafsson et al. (2014)	Mod., s-b	−3.1
	−36.0	Kuss et al. (2006)	Meas., s-s	
	−14.4 to 17.9	Norman et al. (2013)	Mod., s-b	
	28.1	Wesslander et al. (2010)	Meas., s-s	
Baltic Proper	−4.2 to −4.3	Norman et al. (2013)	Mod., s-b	−1.5
	−10.8	Schneider and Thomas(1999)	Cru., s-b	
	19.7	Wesslander et al. (2010)	Meas., s-s	
Bothnian Sea	2.2	Gustafsson et al. (2014)	Mod., s-b	2.2
	−8.8	Löffler et al. (2012)	Cru., s-b	
	−0.6	Norman et al. (2013)	Mod., s-b	
Bothnian Bay	12.0	Gustafsson et al. (2014)	Mod., s-b	3.8
	1.7	Löffler et al. (2012)	Cru., s-b	
	4.3	Norman et al. (2013)	Mod., s-b	
Gulf of Finland	7.4	Norman et al. (2013)	Mod., s-b	4.3
Total Baltic Sea	2.7	Kulinski and Pempkowiak (2010)	MBA, s-b	−0.7
	−4.3	Gustafsson et al. (2014)	Mod., s-b	
	−2.6	Norman et al. (2013)	Mod., s-b	

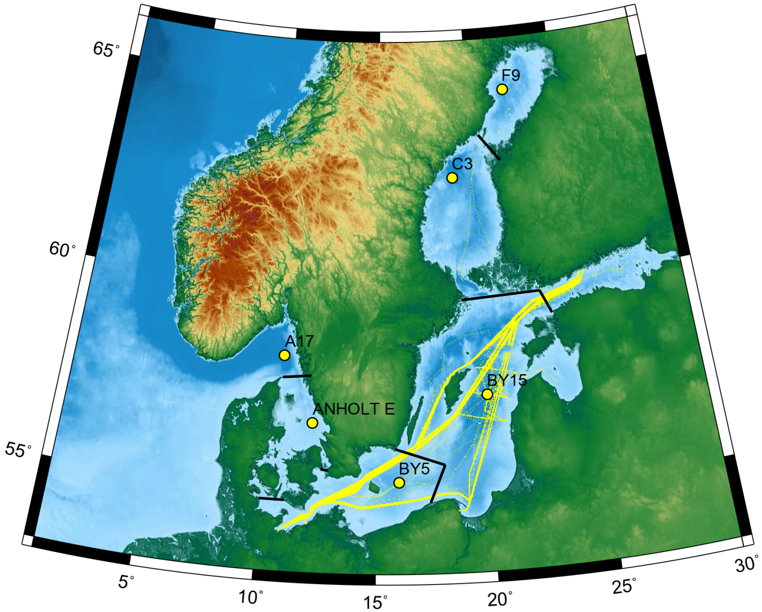

Figure 1. The locations of the six monitoring stations in the Baltic Sea, where surface pCO_2 values are calculated (Shark Data Base, 2013). The stations are located in Skagerrak (A17), Kattegat and the Danish straits (Anholt E), the Western Baltic Sea (BY5), Baltic proper (BY15), the Bothian Sea (C3) and the Bothnian Bay (F9). Data from underway measurements of surface pCO_2 is shown with yellow and covers in particular the area between Kiel and Helsinki. The division of the six sub-domains is indicated with black lines.

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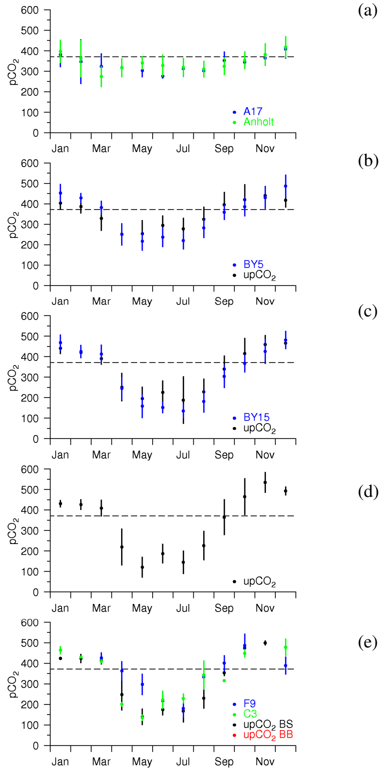

Figure 2. Monthly averaged surface pCO_2 values from the six monitoring stations and from underway pCO_2 data in the sub-domains in the study region. Monthly averaged values are shown with bullets together with the SDs. **(a)** Values from monitoring stations in Skagerrak (A17, blue) and Kattegat (Anholt E, green), **(b)** station BY5 (blue) and underway pCO_2 in the Western Baltic Sea (black), **(c)** station BY15 (blue) and underway pCO_2 from the Baltic Proper (black), **(d)** underway pCO_2 data from the Gulf of Finland and **(e)** station F9 (blue), C3 (green) and underway pCO_2 data from the Bothnian Sea (black) and underway pCO_2 from March in the Bothnian Bay (red).

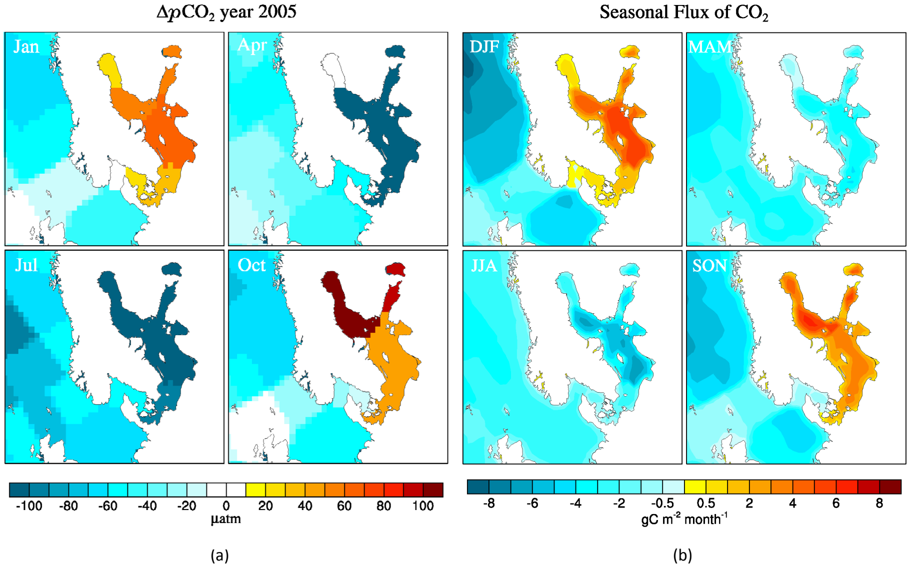

Figure 3. (a) ΔpCO_2 for selected months during 2005. For the calculations of ΔpCO_2 the combined surface map of the global pCO_2 climatology by Takahashi et al. (2009) and the climatology for the Baltic Sea constructed in this study is used. The coarse resolution of the global climatology is clearly visible along the west coast of Norway. Periods of under and over-saturation are seen which indicates the direction of the air–sea CO_2 flux (positive ΔpCO_2 indicates release of CO_2 to atmosphere, negative values indicate uptake of atmospheric CO_2). **(b)** The mean seasonal air–sea CO_2 flux for the years 2005 to 2010 in $\mathrm{g\,C\,m^{-2}\,month^{-1}}$. Positive sign indicates release of CO_2 from the ocean to the atmosphere, negative sign indicates uptake of atmospheric CO_2 by the ocean. This sign convention is used throughout the paper.

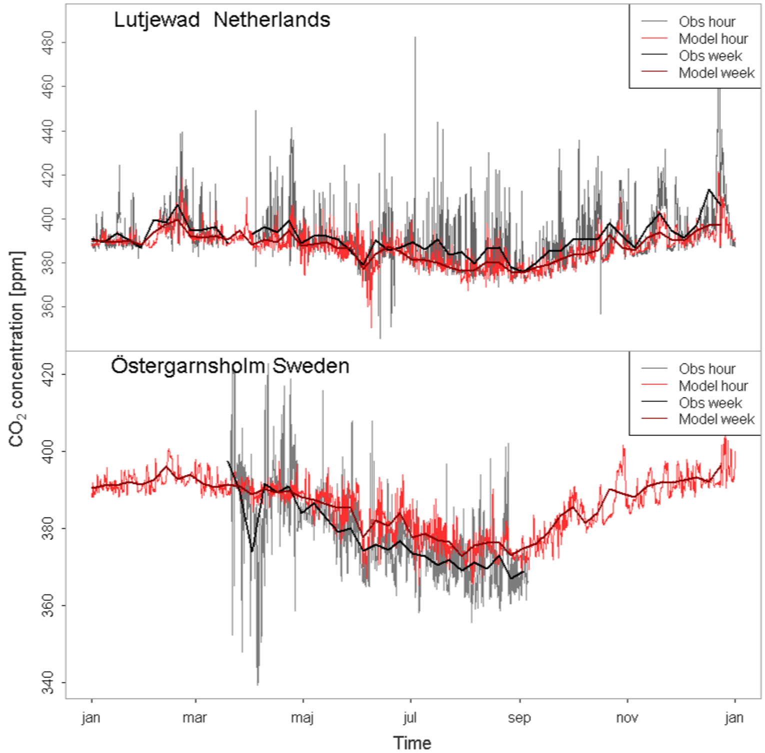

Figure 4. One hour averages of modelled and continuously measured atmospheric CO_2 concentrations in 2007. Also weekly averages of both modelled and measured CO_2 concentrations are shown.

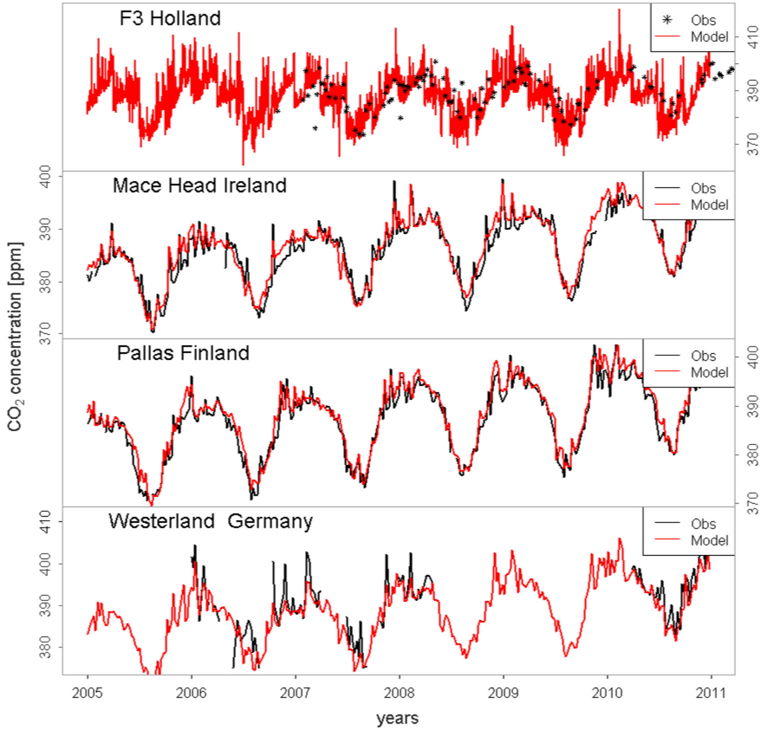

Figure 5. Top panel shows hourly averages of modelled atmospheric CO_2 concentrations compared to flask measurement at F3. The three panels below include comparisons of weekly averages of modelled and continuous measurements of CO_2 at MHD, PAL and WES for the period 2005–2011.

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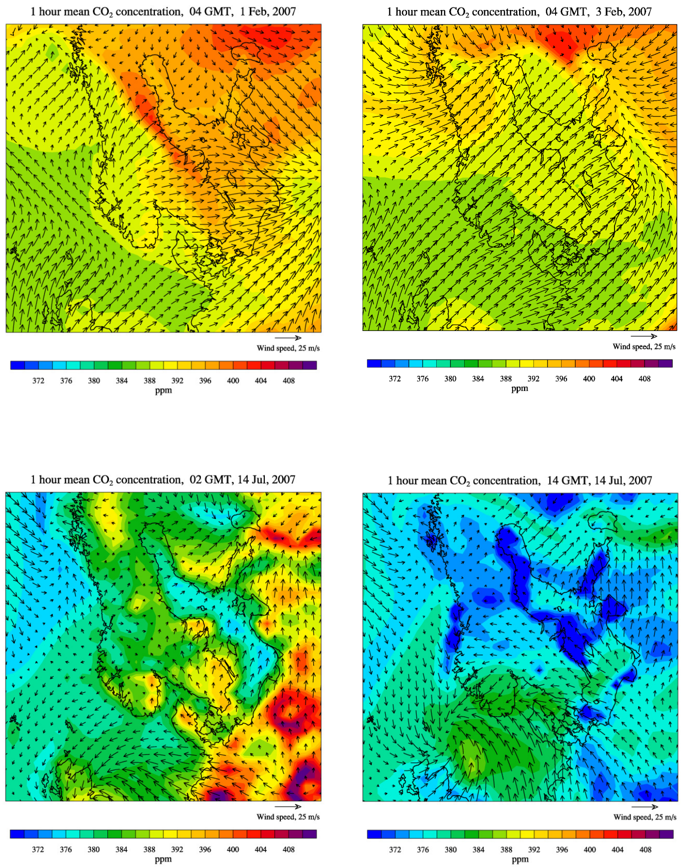

Figure 6. Examples of the simulated variability of atmospheric CO_2 in the study area shown here as extracted from the European domain in DEHM with a 50 km × 50 km resolution. Top panel: two situations for February 2007. Continental air masses cover the Baltic region on 1 February, while marine air masses are dominating on 3 February. Bottom panel: the diurnal variability on 14 July 2007 (night time (left) and day time (right)).

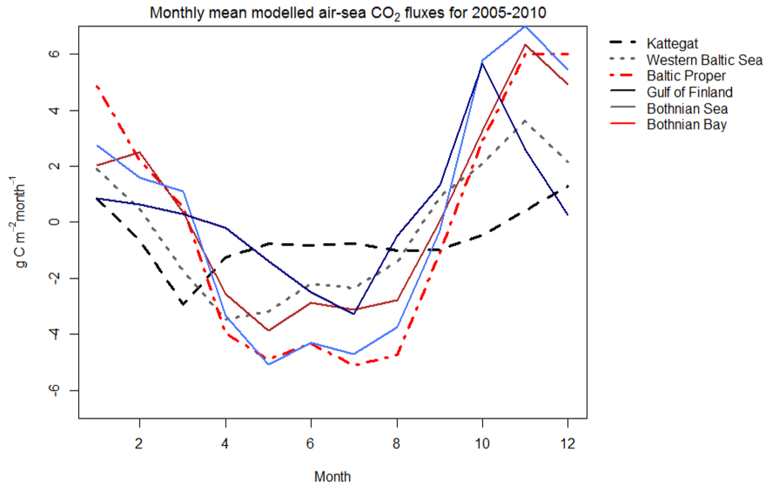

Figure 7. The monthly mean air–sea CO_2 flux for the years 2005 to 2010 in the six sub-basins in $g\,C\,m^2\,month^{-1}$.

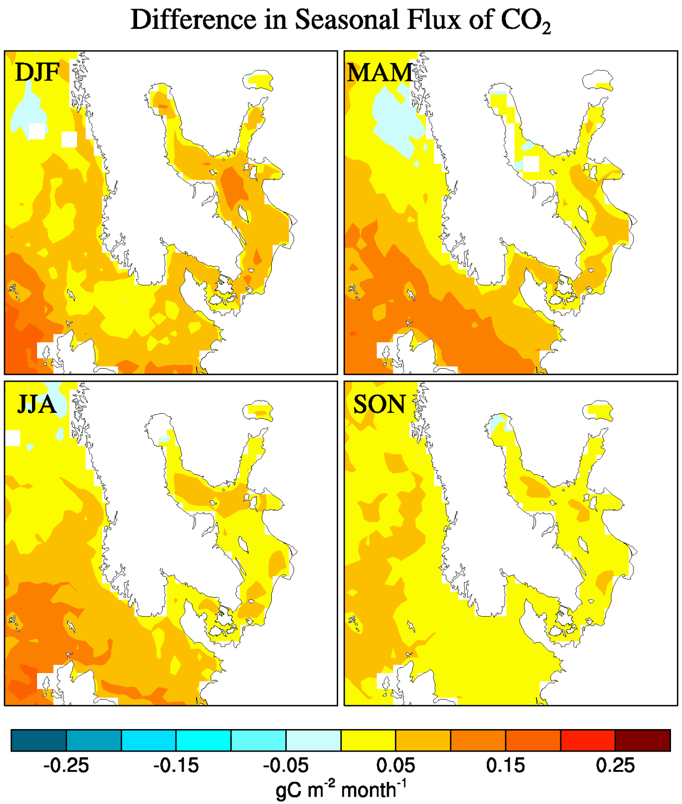

Figure 8. The seasonal flux difference between the VAT and CAT simulations for the period 2005 to 2010 in g C m^2 month^{-1} calculated as VAT – CAT.

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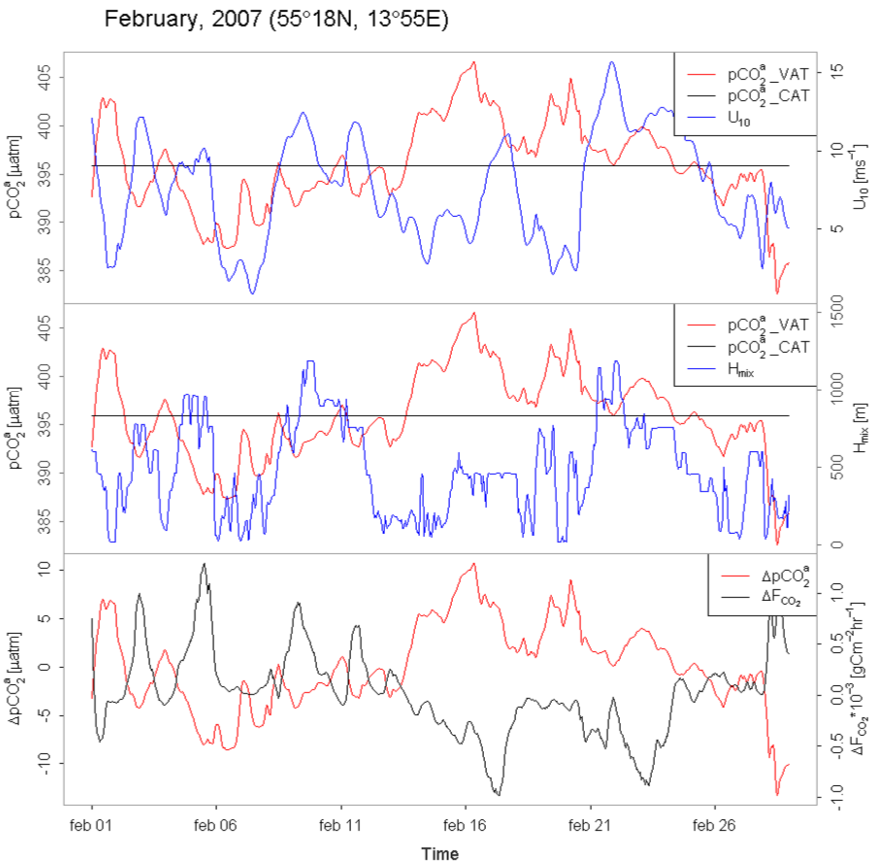

Figure 9. Time series of driving parameters as extracted from the simulations at the site south of Sweden (55°18′ N, 13°55′ E) February 2007. Top panel: $p\mathrm{CO}_2^a$ for VAT and CAT together with u_{10}. Middle panel: $p\mathrm{CO}_2^a$ for VAT and CAT together with h_{mix}. Bottom panel: difference in $p\mathrm{CO}_2^a$ ($\Delta p\mathrm{CO}_2^a$) and F_{CO_2} (ΔF_{CO_2}) between VAT and CAT.

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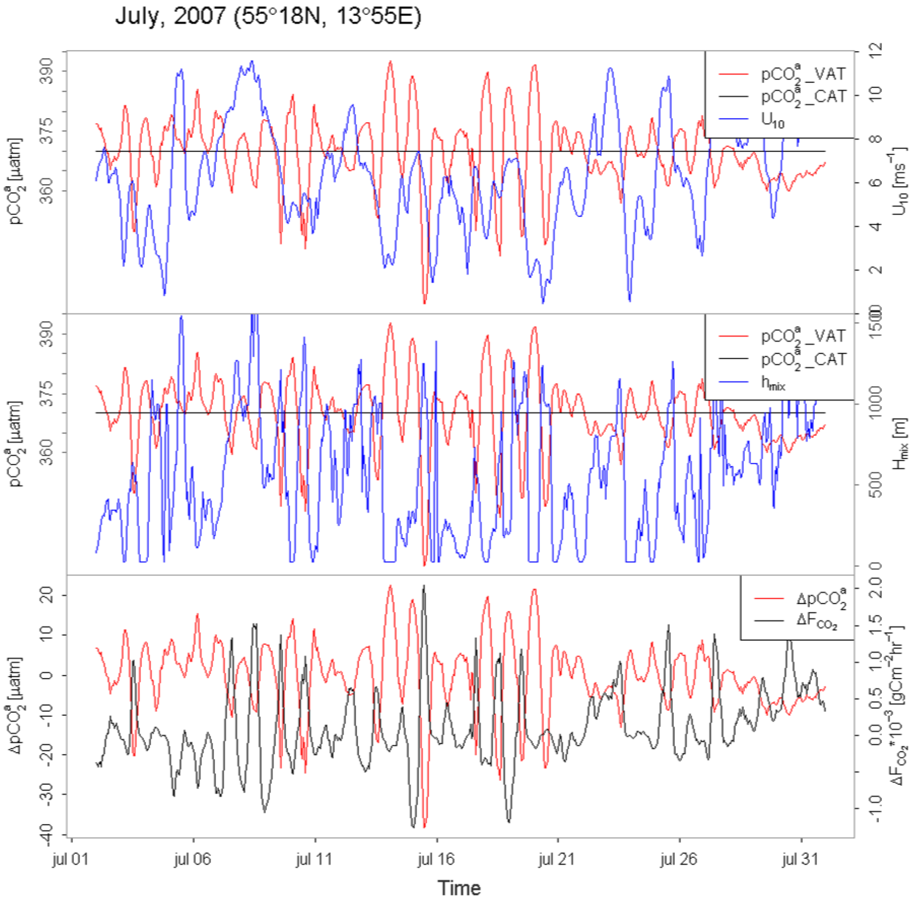

Figure 10. Simulated parameters as in Fig. 9 at the site south of Sweden (55°18′ N, 13°55′ E), but for July 2007. Top panel: pCO_2^a for VAT and CAT together with u_{10}. Middle panel: pCO_2^a for VAT and CAT together with h_{mix}. Bottom panel: difference in pCO_2^a (ΔpCO_2^a) and F_{CO_2} (ΔF_{CO_2}) between VAT and CAT.

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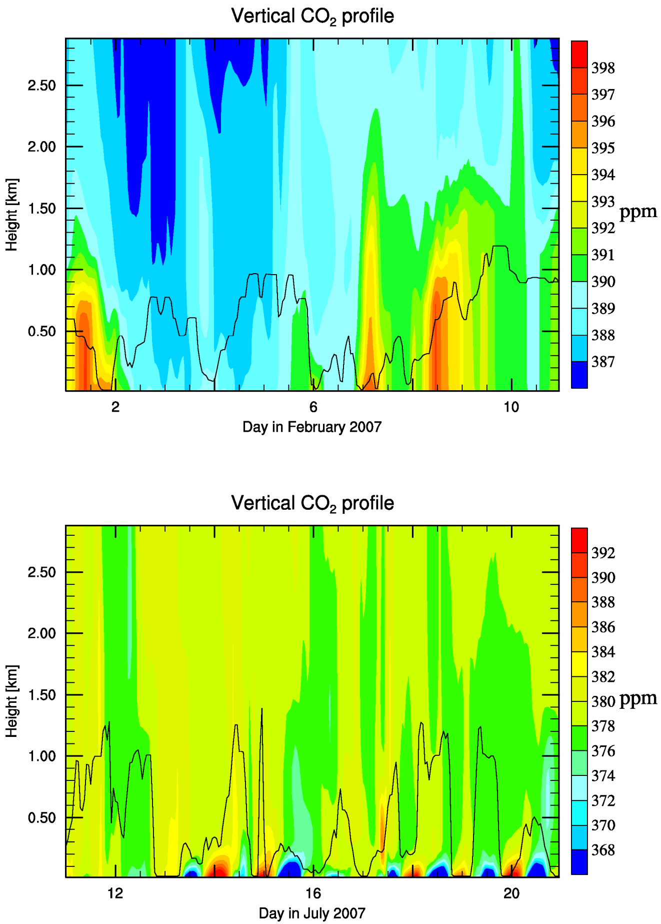

Figure 11. Simulated vertical profiles of atmospheric CO_2 at the site south of Sweden (55°18′ N, 13°55′ E) in units of ppm. Top panel: 1–10 February 2007. Bottom panel: 11–20 July 2007. The black line represents the mixing height in km. Note the different scales used in the two plots.

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