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Atmospheric CO_2 variation over the Baltic Sea and the impact on air–sea exchange

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The variability in time and space of the atmospheric molar fraction of CO_2 over the Baltic Sea was investigated using data from seven stations from the World Data Center for Greenhouse Gases. The variation on a monthly timescale of CO_2 was divided into a global trend, a regional anthropogenic contribution and a natural seasonal cycle. For the Baltic Sea stations the anthropogenic and terrestrial contributions were largest at the coastal sites in the southern Baltic Sea (an offset of 9 ppm), decreasing towards the north over the Baltic Sea (to about 2 ppm). When calculating the air–sea flux of CO_2 using the difference in partial pressure between air and sea, uncertainties in the atmospheric molar fraction of CO_2 were shown to be of secondary importance as compared with uncertainties in other parameters (< 10%). Realistic uncertainties in the sea surface partial pressure, wind speed or transfer velocity resulted in significantly larger uncertainties in a calculated air–sea flux.

Introduction

Carbon dioxide is one of the most important greenhouse gases in the atmosphere. Already over a century ago Arrhenius (1896) suggested that increased concentration levels of CO_2 in the atmosphere could lead to a warmer climate. To understand and predict future changes in the climate we need to understand the carbon system and its variation in time and space. The concentration levels of CO_2 in the atmosphere have increased continuously since the beginning of the industrialisation in the 19th century. This is due to combustion of fossil fuels and land use change. About half of the anthropogenic emission of CO_2 is stored in the atmosphere, while the other half is absorbed by the oceans and terrestrial biosphere, with the uptake of the two reservoirs being approximately of a similar size (IPCC 2007). The monthly variation of the mixing ratio of atmospheric CO_2 (x_{atm}) is a result of a combination of anthropogenic emissions, uptake and release of growing plants and soil, and seasonal exchange with oceanic waters. The oceans' seasonal cycle is explained by changes in the sea surface temperature (where cooler water in winter has larger dissolvement capacity of CO_2 than the warmer water in summer), as well as a different biological consumption in the ocean surface layer and mixing. The seasonal CO_2 budget for the terrestrial biosphere depends on the consumption of CO_2 in the summer when plants are growing and the release of CO_2 when the plants are beginning to decompose and by the microbial respiration in the soil.

The understanding of the global carbon cycle

has increased during the last decades, but there are still important information missing. According to Sabine *et al.* (2003), research focusing on the regional variability of the carbon cycle is presently needed, even though a number of regional studies already exist. An example is the study by Schmidt *et al.* (2003), in which the mean trend in the CO_2 mixing ratio over the southwest of Germany was found to follow that over the mid-latitudes of the northern hemisphere, in addition to which the monthly-mean mixing ratios were up to 8 ppm higher as compared with those in the marine boundary layer air. Randerson *et al.* (1997) investigated the terrestrial sources and sinks using several stations and models and found that the northern ecosystems were responsible for most of the seasonal variability of the CO_2 mixing ratio. By using trajectories for determining source areas, the impact of horizontal advection and synoptic scale transport has been investigated in several studies for a boreal site in northern Finland, in which relatively large CO_2 mixing ratios and large variability was observed in air transported from continental Europe (Aalto *et al.* 2002, Aalto *et al.* 2003, Eneroth *et al.* 2005). There are, however, few previous studies covering the Baltic Sea region.

The Baltic Sea is a semi-enclosed sea located at relatively high latitudes (Smedman *et al.* 2005). In Rutgersson *et al.* (2008), the atmospheric CO_2 mixing ratio ranged between 365 and 410 ppm for the investigated period (corresponding to partial pressures of 360–405 μatm) at one site in the Baltic Sea, while the CO_2 partial pressure in the sea surface varied between 100 and 800 μatm. The amplitude of the annual cycle of the seawater value of the partial pressure of CO_2 (p_{sea}) varies significantly depending on the region (Schneider *et al.* 2006). The largest seasonal amplitude in p_{sea} (400 μatm) occurs in the northeastern Baltic Proper and the smallest amplitude (120 μatm) is found in the transition areas to the North Sea. The average CO_2 uptake of the Baltic Proper was estimated to be 0.9 mol m^{-2} $year^{-1}$ (Thomas and Schneider 1999).

By using seven stations from the WMO World Data Centre for Greenhouse Gases (WDCGG) located in the Baltic Sea region, we estimated the seasonal and regional variability of x_{atm} over the Baltic Sea. In order to be able to describe the variations with better than a monthly temporal resolution, details about the distribution of sources and sinks of CO_2 are needed as well as detailed information about the synoptic-scale weather systems in the form of numerical weather models or trajectory models. This type of investigation will not be made here — our approach is to evaluate the offset of each station, which we then assume to be the integrated effect of the advected sources of CO_2. For many applications, information on seasonal variations is enough. From estimated values of x_{atm}, together with measured parameters from the Östergarnsholm field station, we will analyse the effect of improved temporal resolution on calculations of air–sea CO_2 exchange over the Baltic Sea. To briefly summarize the aims of this study, we will investigate the variability in time and space of x_{atm} in the Baltic Sea region using a simplified expression describing the variation explained by global trend, anthropogenic effects on a monthly time scale and natural seasonal cycle. We will also investigate the sensitivity of the calculated air–sea flux to uncertainties in x_{atm}.

Data and measurements

WDCGG data

The World Meteorological Organization (WMO) launched the Global Atmospheric Watch (GAW) Programme in 1989 to promote systematic and reliable observations of a number of atmospheric gases. These data are free and available on the internet (http://gaw.kishou.go.jp/wdcgg.html). The data are used for periodical reports on the collected data and for distribution to all kinds of research around the world (WMO 2004). We are focusing on sites in the Baltic Sea region. The stations Zingst, Baltic Sea and Pallas-Sammaltunturi are situated in or relatively close to the water basin, Neuglobsow and Waldhof are more continental stations in Europe, and Westerland faces the North Sea (Fig. 1). The stations span the latitudes from 52°48´N to 67°58´N (Table 1). At two of the stations, measurements are taken at ships about two times per week (Station M and Baltic Sea), whereas at the other stations

Fig. 1. Sites used in the investigation (filled circles). Data from all stations except the Östergarnsholm field station originates at the WDCGG.

measurements are made continuously on fixed towers and integrated over one hour. The altitude of the stations varies from sea surface level to 565 m above mean sea level. The measurement height above the surface is in general between 5 and 30 m. The station Westerland is located on the very coast on an island and is surrounded by dunes, forests and also built-up areas (*see* Levin *et al*. 1995 for a better description of the German stations Westerland and Waldhof). The other coastal station, Zingst, is situated 600 m from the coast and surrounded by meadows and farmlands. At 9-km distance from the station there is a power plant. The Pallas-Sammaltunturi station is placed on a 300-m-high mountain within a chain of mountains in the Pallas–Ounastunturi National Park at 565 m a.s.l. (*see* Aalto *et al*. 2002, Aalto *et al*. 2003, Eneroth *et al*. 2005 for more analysis of this site). The tree line is about 100 m below the station and the vegetation at the top is sparse. The inland station Waldhof is located in a small forest with meadows and farmlands in the surrounding area. At distances larger than 1 km from the station, there are small stationary sources of SO_2 and NO_x. The Neuglobsow station, which is also an inland station, is situated directly on a lake and surrounded by forests and meadows.

Östergarnsholm data

In addition to the WDCGG stations, the field station Östergarnsholm was used. The location of this station is (57°27´N, 18°59´E) (*see* Fig. 1). The site at Östergarnsholm has been running since 1995. It is a land-based, 30-m tower situated on the southern tip of a very small, flat island in the Baltic Sea. For wind directions between 80° and 210°, the data have been shown to represent open sea conditions (Högström *et al*. 2008). The molar fraction of CO_2 in the atmosphere is measured during a 1-minute interval

Table 1. Description of the WDCGG sites. Data frequencies are: m = monthly mean values, w = measurements made on a weekly basis, and h = measurements made every hour. The category includes measurements made on from ship (ship) or from a fixed tower (fixed).

Station	Country	Lat. N	Long. E	Altitude (m a.s.l.)	Data frequency	Category	Data periods
Baltic Sea	Poland	55°21´	17°13´	28 m	m, w	Ship	1993–2005
Station M	Norway	66°00´	2°00´	5 m	m, w	Ship	1993–2005
Neuglobsow	Germany	53°10´	13°02´	6 5m	h	Fixed	1994–1999, 2001–2005
Pallas-Sammaltunturi	Finland	67°58´	24°07´	565 m	h	Fixed	1999–2005
Waldhof	Germany	52°48´	10°46´	74 m	h	Fixed	1993–2002
Westerland	Germany	54°56´	8°19´	1 2m	h	Fixed	1994–2002, 2004
Zingst	Germany	54°26´	12°44´	1 m	h	Fixed	1997–2002

each half hour at 9 m above the tower base using an infrared gas analyser (IRGA, PP-systems). The accuracy of the IRGA is 2–3 ppm and it is calibrated each half hour with a zero gas (N_2) and each fourth hour with a calibration gas (x = 500 ppm). The tower is instrumented with additional measurements of wind speed and temperature (at five levels) and turbulence (at three levels). The sea level varies slightly so that the tower base is 1 ± 0.5 m above the mean sea level. In May 2005 we deployed a SAMI-sensor (submersible autonomous moored instrument, Sunburst Sensors, Missoula, Montana, USA) at a depth of about 4 m, 1 km south-east of the tower. The instrument is designed for continuous measurements of p_{sea}.

Methods

Method of determining seasonal and regional variation

The atmospheric CO_2 budget can be written in different forms where the change in time of the mixing ratio can be expressed as a function of terrestrial and anthropogenic fluxes (Raupach *et al*. 2003). The different fluxes then need to be estimated. We chose to describe the atmospheric CO_2 mixing ratio as a function of different factors acting differently depending on season or region (Perez *et al*. 2001, Åström 2007, Padin *et al*. 2007).

$$x_{atm} = x_{trend} + x_{regional}. \quad (1)$$

Here x_{trend} represents the increasing global mean background concentration of atmospheric CO_2 and $x_{regional}$ are the regional deviations from the global trend. $x_{regional}$ can be divided into two parts:

$$x_{regional} = x_{anthropogenic} + x_{natural}. \quad (2)$$

where $x_{anthropogenic}$ and $x_{natural}$ represents the regional anthropogenic and natural contributions, respectively. These two terms can further be divided into the mean annual offset and seasonal variation:

$$x_\alpha = \overline{x_\alpha} + x'_\alpha, \quad (3)$$

where α refers to either the anthropogenic or the natural components. In order to be able to estimate these terms, we will make the assumption that there is no seasonal variation in the anthropogenic releases of CO_2 ($x'_{anthropogenic} = 0$). This means that $x_{anthropogenic} = \overline{x_{anthropogenic}}$. We will also assume that there is no offset due to the natural cycle, so that the natural effect is zero when averaged over the annual cycle ($\overline{x_{natural}} = 0$), which means that $x_{natural} = x'_{natural}$. These assumptions are of course simplifications as, for example, a part of the seasonal variations (about 10%) have been attributed to the seasonal variation in fossil fuel emissions (Levin *et al*. 1995, Schmidt *et al*. 2003). From the present data it is not possible to estimate the increased anthropogenic emissions during the winter. There is clearly also a natural annual mean difference between the different stations, which is not included here. With these assumptions we can express x_{atm} using the following terms:

$$x_{atm} = x_{trend} + x_{anthropogenic} + x_{natural}. \quad (4)$$

In this study we chose Station M to represent the global background value for the atmosphere in the Baltic Sea region. One can express the terms so that $x_{anthropogenic}$ represents the annual difference to the global trend for the different stations and $x_{natural}$ is the seasonal variation for the different stations. We follow Thoning *et al*. (1989) and several other investigations to fit the seasonal cycle with a number of sinusoidal harmonics. According to Thoning *et al*. (1989), higher-order harmonics (three cycles year^{-1} and higher) are not significant. The annual harmonic (first term on the right-hand side) and a perturbation of the annual harmonic here denoted as the seasonal harmonic (second term on the right-hand side) are described with the following equation (Thoning *et al*. 1989, Padin *et al*. 2007):

$$x_{natural} = A_a \sin[2\pi/365.25(t - \theta_a)] + A_s \sin[4\pi/365.25(t - \theta_s)], \quad (5)$$

where t is the day number, A_a and A_s are the amplitudes of the annual and seasonal harmonics, respectively, and θ_a and θ_s are the annual and seasonal phases (day numbers), respectively.

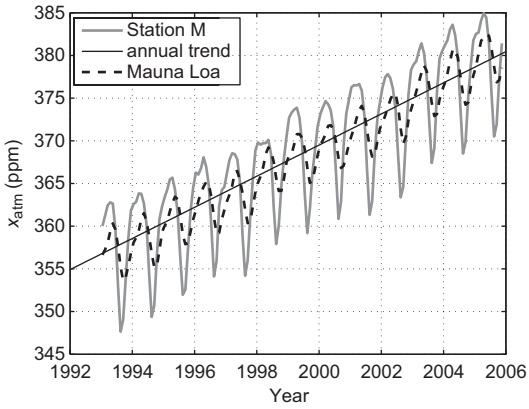

Fig. 2. Monthly concentration of x_{atm} at the Hawaii station Mauna Loa (dashed) and Station M (thick solid) and the annual trend from Eq. 10 (thin solid).

Exchange between the atmosphere and the ocean

The exchange of CO_2 between the ocean and the atmosphere can be calculated from the following equation:

$$F = kK_0\Delta p. \quad (6)$$

Here K_0 is the salinity and temperature dependent CO_2 solubility constant that is calculated by using the empirical formulation from Weiss (1974). Δp is the air – sea difference in partial pressure of CO_2 ($\Delta p = p_{atm} - p_{sea}$, where p_{atm} is the partial pressure in the atmosphere). The value of p_{atm} can be calculated from the molar fraction in dry air:

$$p_{atm} = x_{atm}p \quad (7)$$

where p is the measured total pressure of the dry air. The transfer velocity, k, was computed according to Wanninkhof (1992):

$$k = \left(0.31u_{10}^2\right)\sqrt{\frac{660}{\mathrm{Sc}}}, \quad (8)$$

where u_{10} is the wind speed at 10 m. An alternative expression developed for the Baltic Sea according to Weiss *et al*. (2007) is also used:

$$k = \left(0.365u_{10}^2 + 0.46u_{10}\right)\sqrt{\frac{660}{\mathrm{Sc}}}. \quad (9)$$

The Schmidt number (Sc) is the ratio of the kinematic viscosity of seawater to the diffusion coefficient of the considered gas. For wind speeds greater than 5 m s^{-1} Liss and Merlivat (1986) suggested that k is proportional to $Sc^{-0.5}$.

Results

Global trend

Monthly values of x_{atm} from Station M are shown together with the data from the Mauna Loa station on Hawaii (Keeling and Whorf 2005) for the period 1993 to 2005 (Fig. 2). The amplitude of the seasonal cycle of x_{atm} was larger at Station M than on Hawaii, and both summertime minima and wintertime maxima took place earlier in the year at Station M as compared with those on Hawaii. This can be explained by the differences in the altitude and latitudinal differences. In Thoning *et al*. (1989), a difference in the amplitude and shift in the seasonal cycle was found when comparing measurements at the Mauna Loa station (at 3397 m above mean sea level) with data from the Cape Kumaukhai (also on Hawaii) close to the mean sea level. Latitudinal differences in the amplitude have been shown in other investigations, in which the annual amplitude of x_{atm} have been higher at northern latitudes and decreasing towards the south (Conway *et al*. 1994, WMO 2004). The average annual difference between the Mauna Loa and Station M data was between 0.5 and 1 ppm, with Station M showing slightly higher concentrations.

The global trend representing the global background to the data from the Baltic Sea stations (thin solid line in Fig. 2) from 1993 was derived using data from Station M:

$$x_{trend} = 1.824a + 0.005t - 3278.2. \quad (10)$$

where a is time in unit of years and t is day number for each year.

Annual offset

The annual mean difference (offset) between the different WDCGG stations and Station M were calculated (Table 2). These values represent the

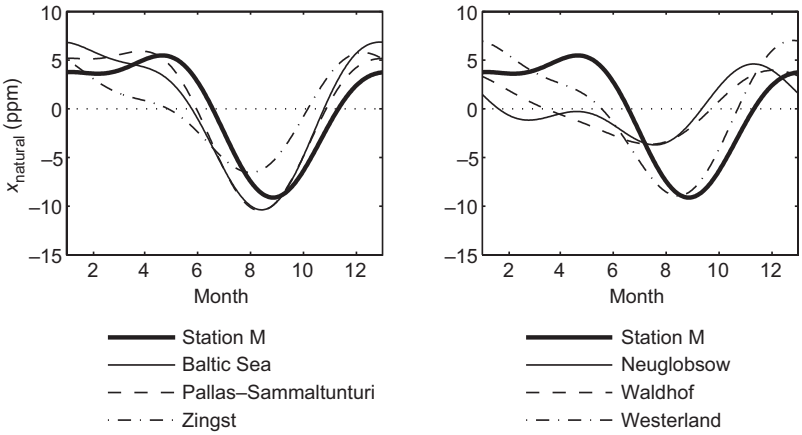

Fig. 3. The seasonal cycle of x_{atm} (i.e. $x_{natural}$) expressed by Eq. 5 for (**a**) Station M, Baltic Sea, Pallas-Sammaltunturi and Zingst and (**b**) Station M, Neuglobsow, Waldhof and Westerland.

regional annual-mean anthropogenic impact (with a natural component) for the different stations, as compared with the regionally relatively undisturbed Station M (i.e. $x_{anthropogenic}$ in Eq. 4). There was a significant difference between the relatively unpolluted station in northern Finland (Pallas-Sammaltunturi) and the more polluted stations in central Europe (Neuglobsow, Waldhof). The annual offset ($x_{anthropogenic}$) over the Baltic Sea had a clear tendency to decrease with the increasing latitude. At the most northern site, Pallas-Sammaltunturi, the offset was 1.7 ppm, whereas the Baltic Sea site, situated in the southern part of the Baltic Sea, had an offset of 4.2 ppm. The coastal sites, Zingst and Westerland, had an even higher offset of around 9 ppm.

Seasonal variations

The mean seasonal cycle (i.e. $x_{natural}$ in Eq. 4) was calculated using Eq. 5 (Fig. 3). Both the increasing global mean background and the annual offset relative to Station M were removed from the data. The coefficients according to Eq. 5 were estimated by regression (Table 3). Equation 5 represented the measured monthly-mean values with good accuracy for all the stations except Waldhof (with a small regression coefficient, *see* Table 3). There was a clear difference in the coefficients of Eq. 5 between the more marine stations and stations significantly influenced by air from continental Europe. The amplitude of the annual harmonic (A_a) was larger for the marine stations as compared with that for the continental stations, and the peak value was also clearly shifted (θ_a). The amplitude of the seasonal harmonic (A_s) was more similar between the stations. The amplitude of the annual harmonic was also reflected by the peak-to-peak amplitude, which was larger for the stations with a larger marine influence. The northern station (Pallas-Sammaltunturi) had the least influence of air from continental Europe and the annual amplitude and phase were more similar to those in the marine stations.

Variability

Standard deviations of the monthly-mean values of $x_{regional}$ were calculated, with the background trend removed (Fig. 4). The standard deviations were calculated using two values every week (every 84th hour). This was the resolution of the data from Station M and Baltic Sea, and here the same resolution of the data was used for all the stations in order to get a comparable variability.

Table 2. Regional anthropogenic contribution ($x_{anthropogenic}$) for the WDCGG-stations.

Station	Annual offset with respect to Station M (ppm CO_2)
Baltic Sea	4.2
Neuglobsow	17.0
Pallas-Sammaltunturi	1.7
Waldhof	14.5
Westerland	9.3
Zingst	8.9

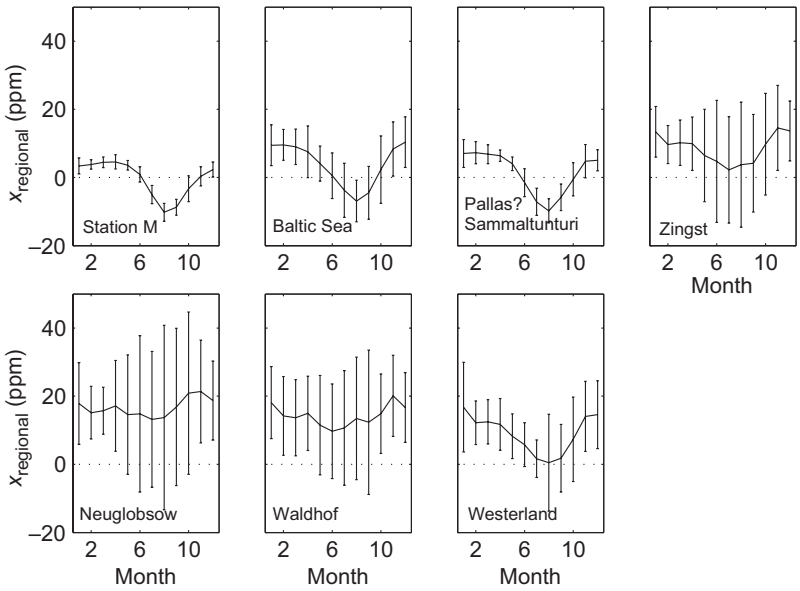

Fig. 4. Monthly mean values and variability of $x_{regional}$ (i.e. the global trend is removed). The error bars show the standard deviations of weekly values, and the solid lines are monthly mean values.

There was a significant difference in the variability of $x_{regional}$ between the stations. The stations with stronger anthropogenic and terrestrial influence had a larger variability than those with a smaller influence. For those terrestrial stations there was a maximum in the variability in the summer and a minimum in the winter. In the summer the terrestrial consumption of CO_2 was more variable than the more homogeneous production of CO_2 during the winter. In the winter also the synoptic forcing of the atmospheric motions was stronger and measurements at the stations were representative of a larger area, so the variability can be expected to be smaller. A connection between the variability of atmospheric CO_2 and large-scale circulation has also been seen by Eneroth *et al*. (2003).

The station Westerland is influenced both by terrestrial and marine areas. There are two distinct sectors where the measurements were mainly influenced by marine conditions for wind directions between 270° and 10° and by continental conditions for wind directions between 100° and 235°. When dividing the data for the different uptake areas with one continental sector and one more marine influenced sector, the variability was found to be larger when there was a large terrestrial and anthropogenic influence (Fig. 5). Furthermore, the annual offsets in relation to Station M were 10.2 and 0.4 ppm for the continental and marine sectors, respectively.

The stations Zingst and Baltic Sea did not have as distinct marine and continental sectors as the station Westerland, but could be divided into a continental and mixed continental/marine sectors. The continental sector represents central Europe (wind directions between 80° and 245°), whereas the mixed sector is basically the sector

Table 3. The coefficients according to Eq. 5 for the WDCGG stations (A_a, A_s, θ_a and θ_s). r^2 is the regression coefficient for the equation, and p-p is the peak-to-peak amplitude.

Station	A_a	A_s	θ_a	θ_s	r^2	p-p
Baltic Sea	7.976	–2.527	–55.85	3.508	0.99	17.0
Station M	6.508	–2.668	–28.91	7.095	0.98	14.3
Neuglobsow	–2.814	–2.046	61.45	–12.98	0.92	8.3
Pallas-Sammaltunturi	7.848	–2.637	–47.35	–5.79	0.99	16.3
Waldhof	–3.533	–0.7768	79.95	–3.579	0.76	7.5
Westerland	7.062	–2.299	–62.4	9.924	0.97	15.8
Zingst	5.211	–1.928	–82.21	–0.4036	0.95	11.9

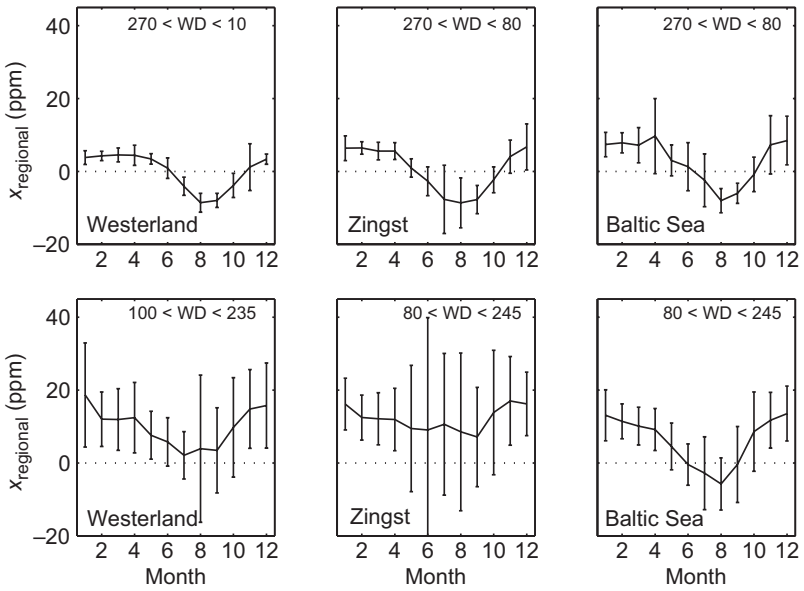

Fig. 5. The variation of $x_{regional}$ when divided the uptake area into a marine and a continental sector. The upper figures are with winds from the marine sector, and the lower from the continental sector.

north of the stations (wind directions between 270° and 80°). For both Zingst and Baltic Sea there was a clear difference in the variability of the CO_2 measurements between the continental and mixed sectors (Fig. 5). The annual offsets in station Zingst with respect to Station M were 12.4 and 0.9 ppm for the continental and mixed sectors, respectively. For the station Baltic Sea the corresponding offsets were 6.4 and 3.2 ppm.

Impact on air–sea exchange

The values of x_{atm} calculated with Eq. 4 (with Eq 10 for the global trend, Table 2 for the annual offset and Eq. 5 for the seasonal cycle) were compared with the measured values of x_{atm} from an independent station (the Östergarnsholm station). The coefficients valid for the Baltic Sea station were used. The monthly mean values from Östergarnsholm agreed relatively well with the values calculated with Eq. 4, except for some months (Fig. 6). During these periods the assumption that the synoptic-scale variability on less than the monthly timescale can be averaged out did not hold and variations due to persistent synoptic-scale systems dominated.

The air–sea fluxes were calculated with Eq. 6. For p_{sea}, data from the SAMI sensor were used, and the transfer velocity was calculated with Eq. 8 with measured hourly winds from the tower at Östergarnsholm. The values of p_{atm} were either calculated from measured values of x_{atm} or from Eq. 4. The difference between results obtained with Eq. 4 and measured x_{atm} for the calculated weekly flux was small (white and light grey bars in Fig. 7). There were, however, larger differences for limited periods. By using a constant annual-mean value of 380 μatm for all data gave a biased seasonal flux, with a too large downward flux in the winter and a too large upward flux in the summer (dark grey bars in Fig. 7). The weekly maximum difference between the two methods was 20 % (or 1.5 mol m^{-2} $year^{-1}$) and the mean absolute difference was smaller than 1 mol m^{-2} $year^{-1}$ for the investigated data. Although there was a non-negligible impact on the air–sea fluxes when using a biased p_{atm}, an error in the atmospheric partial pressure gave a smaller effect on the calculated flux than uncertainties in the values of p_{sea}, or the error in the wind speed used in the calculations (Rutgersson *et al*. 2008). The uncertainty due to the choice of the transfer velocity was significantly larger than uncertainties in the values p_{atm} (Fig. 7: white bars using Eq. 8 and black bars using Eq. 9).

Discussion

Both marine stations (like the Baltic Sea) and more land-influenced stations (like Pallas-Sam-

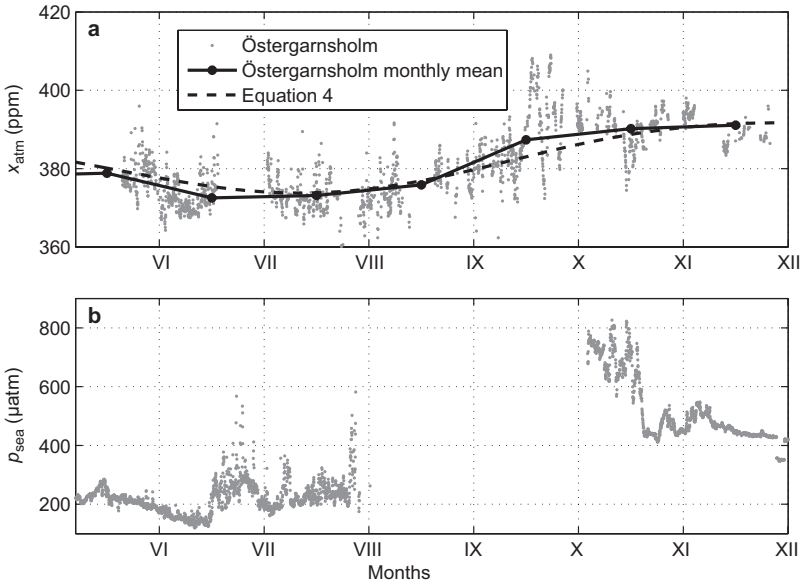

Fig. 6. (**a**) x_{atm} measured at the Östergarnsholm site (dots for hourly values and solid line for monthly mean values) and calculated with Eq. 4. (**b**) p_{sea} measured at the Östergarnsholm site. The period is June–December 2005.

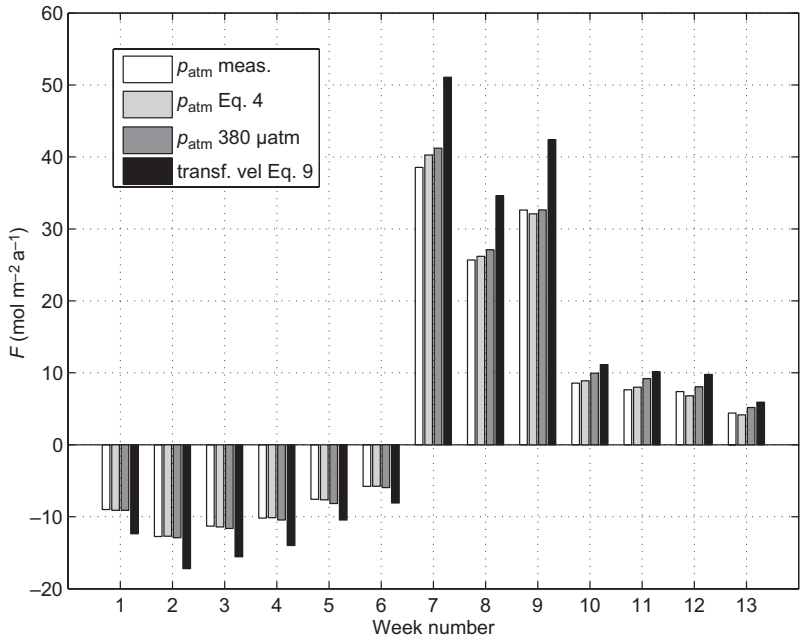

Fig. 7. Calculated weekly air–sea flux of CO_2 (F) using Eq. 6. White bars use measured p_{atm} from the Östergarnsholm site, light grey bars use p_{atm} calculated with Eq. 4 and dark grey bars a constant p_{atm} of 380 µatm. The black bars show the calculated weekly flux using the measured p_{atm} from the Östergarnsholm site calculated with an alternative equation for the transfer velocity (Eq. 9). Week numbers 1–6 are from June–August, week numbers 7–13 from November–December).

maltunturi) showed very distinct seasonal cycles in the mixing ratio of atmospheric CO_2, with a maximum and minimum in winter and summer, respectively (Fig. 3). Sites directly influenced by the terrestrial biosphere would be expected to have larger amplitudes in the seasonal cycle of x_{atm} than sites influenced more by the sea. This was, however, difficult to see in the data. The seasonal cycles were more distinguished, with larger amplitudes of the annual cycle as well as larger peak-to-peak amplitudes, when there was less local anthropogenic influence (Fig. 3). Thus, the land sites (like Neuglobsow and Waldhof) influenced by anthropogenic activities had much smaller amplitudes than the land site with a weaker local anthropogenic influence (like Pallas-Sammaltunturi).

The difference in the phase between the station's seasonal cycles resulted from the influence of the sea and the terrestrial biosphere. As the

terrestrial growing season starts, the consumption of CO_2 increases and the CO_2 concentration consequently decreases. There is also a continuous production of CO_2 by decomposition and respiration. In the autumn the terrestrial production of CO_2 dominates over the consumption, and thus the CO_2 concentration increases. Stations having an early spring and extended growing season (like Zingst, Neuglobsow and Waldhof) had an early-summer CO_2-concentration minimum and a winter maximum. A northern land site with a late spring (like Pallas-Sammaltunturi) had a later minimum and maximum. Marine sites (like Baltic Sea and Westerland) had later minima and maxima. The value of p_{sea} in the surface water was controlled mainly by biological production and mixing, and these processes were influenced by seasonal warming and cooling (e.g. Kuss *et al*. 2006, Schneider *et al*. 2006). The very high values of p_{sea} during the winter were one important explanation for the shift in phase in the marine sites as compared with that in the continental sites.

Some of the sites had a second minimum in the middle of February, which was expressed by the seasonal harmonic (term 2 in Eq. 5). This reflects most likely the impact of the globally-averaged seasonal cycle (represented by the Mauna Loa data). The amplitude of this harmonic was larger for the more sea influenced sites (Station M and Baltic Sea).

Summary and conclusions

The variation on a monthly timescale of the atmospheric CO_2 concentration was divided into a global trend, a regional anthropogenic contribution and a regional natural seasonal cycle. The suggested equation to calculate the monthly-mean molar fraction of CO_2 agreed relatively well with measured data from the Östergarnsholm site. Therefore, if measured data are not available, one can describe relatively well the variation of the CO_2 concentration on a monthly time scale by using the suggested equation. Deviations were explained by unrepresentative synoptic activity, which is not included in the Eq. 4.

Concerning the variation of the CO_2 concentration over the Baltic Sea it was show that:

- The annual offset (mainly explained by an anthropogenic contribution) was largest at the coastal site in the southern Baltic Sea and decreased towards the north over the Baltic Sea (except for the continental stations Neuglobsow and Waldhof, which had a larger offset).
- The amplitude of the seasonal cycle, on the other hand, was smaller for the sites with more terrestrial and anthropogenic inputs. There was also a shift in the season, with a later winter maximum and later summer minimum for the stations located further north.
- It was also clearly shown that the monthly variability was larger for stations having more terrestrial and anthropogenic input. This was especially clear in the summer.

When dividing the data for the near coastal sites into sectors based on the wind direction, the sector with winds from the marine sector showed significantly different properties as compared with the sector with winds coming from the continental sector. These differences included a larger regional terrestrial and anthropogenic influence and larger monthly variability for the continental sector. We can thus conclude that both Zingst and the Baltic Sea stations are partly influenced by regional continental contributions from the central Europe.

If a constant x_{atm} was used (neglecting short and long term variability) in calculating the air–sea flux of CO_2, the difference in the calculated weekly flux when compared with the flux calculated by including the variability of x_{atm} was less than 1 mol m^{-2} $year^{-1}$ (< 10%) for the investigated data. The maximum weekly difference in the flux was almost 20% (or 1.5 mol m^{-2} $year^{-1}$). By not including the seasonal cycle gave too large downward fluxes in the summer and too large upward fluxes in the winter. The impact on the calculated air–sea flux using measured concentration as compared with concentration calculated by Eq. 4 was negligible. The uncertainties in the value of x_{atm} was of minor importance compared with uncertainties in other parameters (p_{sea}, wind speed or transfer velocity) when calculating the air–sea exchange of CO_2.

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References

Aalto T., Hatakka J., Paatero J., Tuovinen, J.-P., Aurelia M., Laurila T., Holmén K., Trivett N. & Viisanen Y. 2002. Tropospheric carbon dioxide concentrations at a northern boreal site in Finland: basic variations and source areas. *Tellus* 54B: 110–126.

Aalto T., Hatakka J. & Viisanen Y. 2003. Influence of air mass source sector on variations in CO_2 mixing ratio at a boreal site in northern Finland. *Boreal Env. Res*. 8: 385–393.

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

Åström G. 2007. *CO_2-variation over the Baltic Sea*. M.Sc. thesis, Department of Earth Sciences, Uppsala University, Uppsala, Sweden.

Conway T.J., Tans P.P., Waterman L.S., Thoning K.W., Kitzis D.R., Masarie K.A. & Zhang N. 1994. Evidence for interannual variability of the carbon cycle from the NOAA/CMDL global air sampling network. *J. Geophys. Res*. 99: 22831–22855.

Eneroth K., Kjellström E. & Holmén K. 2003. A trajectory climatology for Svalbard; investigation how atmospheric flow influence observed tracer concentrations. *Physics and Chemistry of the Earth* 28: 1191–1203.

Eneroth K., Aalto T., Hatakka J., Holmén K., Laurila T. & Viisanen Y. 2005. Atmospheric transport of carbon dioxide to a baseline monitoring station in northern Finland. *Tellus* 57B: 366–374.

Högström U., Sahlée E., Drennan W. M., Kahma K. K., Smedman A.-S., Johansson C., Pettersson H., Rutgersson A., Tuomi L., Zhang F. & Johansson M. 2008. Momentum fluxes and wind gradients in the marine boundary layer — a multi platform study. *Boreal. Env. Res*. 13: 475–502.

IPCC 2007. *Climate change 2007: Impacts, adaptation, and vulnerability. Contribution of Working Group II to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. — Cambridge University Press, Cambridge, United Kingdom.

Keeling C.D. & Whorf T.P. 2005. Atmospheric CO_2 records from sites in the SIO air sampling network. In: *Trends: a compendium of data on global change*, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.

Kuss J., Roeder W., Wlost K.-P. & DeGrandpre M.D. 2006. Time-series of surface water CO_2 and oxygen measurements on a platform in the central Arkona Sea (Baltic Sea): Seasonality of uptake and release. *Marine Chemistry* 101: 220–232.

Levin I., Graul R. & Trivett N.B.A. 1995. Long-term observations of atmospheric CO_2 and carbon isotopes at continental sites in Germany. *Tellus* 47B: 23–34.

Liss P.S. & Merlivat L. 1986. Air–sea gas exchange rates: Introduction and synthesis. In: Buat-Ménard P. (ed.), *The role of air–sea exchange in geochemical cycling*, NATO ASI Series, Series C: Mathematical and Physical Sciences vol. 185, pp. 113–127.

Padin X.A., Vazquez-Rodriguez M., Rios A.F. & Perez F.F. 2007. Atmospheric CO_2 measurements and error analysis on seasonal air–sea fluxes in the Bay of Biscay. *J. Marine Syst*. 66: 285–296.

Perez F.F., Gago J., Alvarez M. & Rios A.F. 2001. Temporal variability of atmospheric CO_2 of the Spanish Atlantic Coast. *Oceanol. Acta* 24: 11–18.

Randerson J.T., Thompson M.V., Conway T.J., Fung I.Y. & Field C.B. 1997. The contribution of terrestrial sources and sinks to trends in the seasonal cycle of atmospheric carbon dioxide. *Global Biogeochem. Cycles* 11: 535–560.

Raupach M.R., Canadell J.G., Bakker D., Ciais P., Sanz M.J., Fang J.Y., Melillo J.M., Lankao P.R., Sathaye J., Schulze E.D., Smith P. & Tschirley J. 2003. Interactions between CO_2 stabilisation pathways and requirements for a sustainable earth system. In: Field C.B. & Raupach M.R. (eds.), *The global carbon cycle: integrating humans, climate, and the natural world*, Island Press, Washington, DC, pp. 131–165.

Rutgersson A., Norman M., Schneider B., Pettersson H. & Sahleé E. 2008. The annual cycle of carbon-dioxide and parameters influencing the air–sea carbon exchange in the Baltic Proper. *J. Marine Syst*. doi:10.1016/j.jmarsys.2008.02.005.

Sabine C.L., Heimann M., Artaxo P., Bakker D., Chen C.-T.A., Field C.B., Gruber N., Le Quéré C. , Prinn R.G., Richey J.E., Lankao P.R., Sathaye J.A. & Valentini R. 2003. Current status and past trends of the global carbon cycle. In: Field C.B. & Raupach M.R. (eds.), *The global carbon cycle: integrating humans, climate, and the natural world*, Island Press, Washington, DC, pp. 17–44.

Schmidt M., Graul R., Sartorius H. & Levin I. 2003 The Schauinsland CO_2 record: 30 years of continental observations and their implications for the variability of the European CO_2 budget, *J. Geophys. Res*. 108: 4619, doi:10.1029/2002JD003085.

Schneider B., Kaitala S. & Maunula P. 2006. Identification and quantification of plankton bloom events in the Baltic Sea by continuous pCO_2 and chlorophyll a measurements on a cargo ship. *J. Mar. Syst*. 59: 238–248.

Smedman A.-S., Gryning S.-E. Bumke, K. Högström U., Rutgersson A., Batchvarova E., Peters G., Hennemuth B., Tammelin B., Hyvönen R., Omstedt A., Michelson D., Andersson T. & Clemens M. 2005. Precipitation and evaporation budgets over the Baltic Proper: observations and modelling. *J. Atm. Ocean Sci*. 10: 163–191.

Thomas H. & Schneider B. 1999. The seasonal cycle of carbon dioxide in Baltic Sea surface waters. *J. Mar. Syst*. 22: 53–67.

Thoning K.W., Tans P.P. & Komhyr W.D. 1989. Atmospheric carbon dioxide at Mauna Loa Observatory: 2. Analysis of the NOAA GMCC data, 1974–1985. *J. Geophys. Res.* 94: 8549–8565.

Wanninkhof R. 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97: 7373–7382.

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

Weiss A., Kuss J., Peters G. & Schneider B. 2007. Evaluating transfer velocity-wind speed relationship using long-term series of direct eddy correlation CO_2 flux measurements. *J. Mar. Syst.* 66: 130–139.

WMO 2004. *Word Data Centre for Greenhouse Gases (WDCGG) data summary*. WDCGG No. 30.