Atmospheric oxygen and the global carbon cycle. Observations from the new F3 North Sea platform monitoring station and 6 additional locations in Europe and Siberia
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Chapter 6
Conclusion and Outlook
The work presented in this thesis forms a significant extension to the global network of atmospheric O$_2$ measurements. The amount of sites worldwide measuring atmospheric O$_2$ is increasing gradually and this PhD project has contributed to that. Chapter 3 has shown that it is possible to measure atmospheric O$_2$ concurrently with CO$_2$ in a remote place like the gas and oil platform F3 in the Dutch part of the North Sea. Despite the challenging logistic situation, the monitoring station has been running since 2006, initially with flask sampling only, but later with continuous O$_2$ and CO$_2$ measurements as well. The platform is for persons only accessible by helicopter and materials and parts can only be delivered by supply ships which frequent the platform every two weeks. The operation of the monitoring station is therefore successful only thanks to the high degree of automation, the extended remote control options and, last but not least, to the highly appreciated cooperation of the platform’s staff.

The F3 North Sea platform is a unique location for atmospheric O$_2$ measurements; it is the first fixed sea-based monitoring station in the world. The North Sea is an ideal location since the carbon cycle processes in coastal waters are currently poorly understood. Furthermore it is close to anthropogenic influences, while remote enough to not experience direct disturbances on the measurements. The first data series from the continuous O$_2$ and CO$_2$ measurements as presented in chapter 3 show clearly that the signal is practically free of nightly inversions, which leads to a direct background signal for the coastal north western part of Europe. On short timescales the observations show interesting signals such as large and fast changing negative atmospheric O$_2$ excursions without an accompanying change in the CO$_2$ signal, which most likely indicate marine O$_2$ uptake.

Running continuous atmospheric O$_2$ measurements is challenging in itself, regardless of the location, which was explained in detail in the previous chapters. The obtained combined uncertainty for the continuous O$_2$ measurements was found to be $\pm 8$ per meg, which is based on the average of the measurements of a target cylinder during a period of 2 months. Measurement of the atmospheric CO$_2$ concentration is not straightforward either, as the required precision for the measurements is hard to achieve. In chapter 3 it was demonstrated that relatively simple and inexpensive CO$_2$ analyzers can be used to measure atmospheric CO$_2$ concentrations to a fairly good combined uncertainty of $\pm 0.3$ ppm. In comparison to (far more expensive) state-of-the-art instruments such as gas-chromatography, larger non-dispersive
infrared analyzers, laser-technology etc., the precision of the Vaisala Carbo-
Caps is robust but modest. The main parameter of interest throughout this
PhD project is, however, the atmospheric potential oxygen (APO). There-
fore, the CO\textsubscript{2} precision is adequate, as the combined uncertainty of the APO
measurements is completely dominated by the O\textsubscript{2} measurement precision.
For new setups including O\textsubscript{2} measurements using the Oxzilla, other CO\textsubscript{2} in-
struments are recommended (e.g. LiCor LI-820).

Chapter 3 includes several possibilities for improvement of the continu-
ous measurement system in section 3.4.1. The measurements do already give
good information on the seasonal amplitude and the yearly trend can also be
estimated quite well with the current precision. However, improvements are
necessary to obtain a better time resolution and thereby improve precision
for the short scale phenomena like the O\textsubscript{2} decreases as presented in chapter
3. The major improvements in the continuous measurement system can be
found in decreasing the volume of the drying system and increasing the used
flow rates. Both measures will decrease the flushing time of the fuel cells and
especially the Vaisala CarboCaps, which have a large internal volume. The
calibration procedure can be improved by including additional calibration
cylinders. It is then even more essential that the flushing time of the (drying)
system is decreased, since the calibration procedure takes up already (too)
much time during which no ambient measurements can be performed. Fur-
thermore, the air inlet design and the Nafion pre-dryer have to be studied to
find possible improvements in those parts of the measurement setup.

Besides the continuous O\textsubscript{2} and CO\textsubscript{2} measurements at the F3 platform as
presented in chapter 3, this thesis includes in chapter 4 and 5 the analyses of
the measurements of atmospheric O\textsubscript{2} and CO\textsubscript{2} from flask samples. The
challenges related to the continuous O\textsubscript{2} measurements are the reason that
these are not performed in many different stations across the globe. Flask
samples are easier to obtain and can therefore be used in more locations in-
cluding those that are difficult to reach or on moving platforms such as air-
craft. The appendix of this thesis gives details about the calibration of the O\textsubscript{2}
measurements performed by the mass spectrometer that was used for the
analysis of the flask samples in this thesis. Chapter 3 and 4 show the com-
bined results for the continuous measurements and the flask sample meas-
urements for O\textsubscript{2} and CO\textsubscript{2}. Unfortunately the overlapping period for the
flasks and continuous measurements for the F3 platform includes only 6
flask samples: too short for a useful intercomparison.
The measurement quality of the mass spectrometer has improved significantly over the past years. The use of extra cylinders for the calibration has had benefits for the sample measurements. To maintain the current precision and accuracy it is required to always measure at least three cylinders for the calibration procedure and include these in the routine when measuring the Scripps cylinders which define the scale. Furthermore the procedure should include a target cylinder, which is measured less frequently than the calibration cylinders, to provide an independent measure for the stability of the instrument. The stability of the O₂ measurements by the air optima was between ±6 and ±17 per meg over the years, depending on the measurement period (defined by the machine gas). This precision is obtained from the precision of the local reference gases in the specific machine gas period representing a flask sample measurement (i.e. a repetition of two measurements per sample). The measurements in the later machine gas periods are more stable than the earlier periods.

The flask sample data have been presented in Chapters 4 and 5. The amplitudes of the seasonal cycles and the long term trends of atmospheric O₂ and CO₂ for Lutjewad, Mace Head and F3 have been presented in Chapter 4. That chapter also contains the analysis of the gradients between Lutjewad and Mace Head for both O₂ and CO₂. Between 2001 and 2008 the CO₂ gradient between both stations increased by 0.5 ppm. For O₂ the gradient also increased (which means it became more negative) by 20 per meg. The CO₂ gradient fits well to the results of a study of the CO₂ gradients between Mace Head and other European stations (Ramonet et al., 2010). The addition of the O₂ gradient is an important result from the work presented in this thesis. From the combination of the two gradients, increased oceanic CO₂ uptake can be ruled out as a cause for the increasing CO₂ gradient. The other two causes suggested by Ramonet et al. (2010), namely a shallower boundary layer height and regional changes in emissions, can still be explained with the obtained O₂ gradient. The large difference between the observed increasing O₂ gradient and the expected increase based on the CO₂ gradient—in case the increase is based on a higher fossil fuel consumption—implies another major contribution to the increasing δO₂/N₂ gradient. An increasing share of natural gas in the fossil fuel mix in the continent is suggested in chapter 4 as an explanation for a possible contributing factor.
A basic estimate of the global average marine CO$_2$ uptake can be made using a single atmospheric monitoring station, as was presented in chapter 4. The required parameters for this estimate are the long term trends in the atmospheric CO$_2$ and O$_2$ concentrations which are combined to form the trend in the atmospheric potential oxygen. Using the APO time series between 1998 - 2009 from the flasks sampled at Mace Head (during restricted baseline conditions) and information on the net oceanic O$_2$ exchange, the global oceanic CO$_2$ uptake is estimated at 1.8 ± 0.8 PgC/year. Within the error bars this agrees with the recent study of Manning and Keeling (2006). The resulting ocean CO$_2$ uptake from the Mace Head time series in comparison to this study suggests that the oceanic CO$_2$ sink is decreasing, although the errors in the estimate are too large to confirm this. Samples from Mace Head cover mainly the Atlantic Ocean which –by means of oceanographic studies– has been proposed to be taking up variable or lower amounts of CO$_2$ (e.g. Corbière et al., 2007; Schuster and Watson, 2007; Watson et al., 2009). Based on the APO trend from Lutjewad (2000 - 2009), the estimate of the oceanic uptake would be higher: 2.7 ± 0.8 PgC/year.

Longer data series will further improve the quality of the annual trends and the oceanic uptake. Using long-term observations of multiple locations in the region will further improve the APO trend estimation and thereby improve the accuracy of the marine CO$_2$ uptake estimate of the Atlantic Ocean and the differences with the North Sea region. For this purpose, the correction of APO with the actual fossil fuel oxidative ratio (OR) is required. It is therefore essential that model efforts focus on independently transporting CO$_2$ and O$_2$ (instead of APO) yielding model based OR estimates for longer time periods (as well as more insight into the seasonal cycles). Furthermore, the observations presented in this thesis can be used in model efforts (both forward and inverse) to provide additional insights into the carbon cycle, also in a quantitative sense.

Most of the data series presented in this thesis will be continued and thereby extended in the future. The continuous measurements on the F3 platform will be continued together with the flask sampling. By means of this longer time series, flask samples are expected to coincide with the continuous measurements more frequently, thereby enabling a better comparison between both systems. The data analysis software developed during this PhD project will provide semi-real time provisionally calibrated O$_2$ and CO$_2$ data, which can be published online within a maximum of 10 hours after the ac-
tual measurements. This will allow the possibility to collect flask samples during episodes with huge $O_2$ decreases, as presented in chapter 3. The analysis of the additional concentrations and isotopes will possibly contribute to an improved explanation of these events.

The time series of the $O_2$ measurements at Lutjewad currently comprises of almost 10 years. The flask sampling will be continued in the future as well as for Mace Head. The Lutjewad atmospheric monitoring station will be extended by a setup for continuous measurements of $O_2$ and $CO_2$ identical to that presented in chapter 3, in the near future. For Mace Head, continuous measurements of atmospheric $O_2$ are planned by the group of A.C. Manning of the University of East Anglia.

The aircraft flask sampling program over Russia has unfortunately run out of (European) funding. Therefore, there are currently no plans to continue the data series as presented in chapter 5.

At the F3 platform the atmospheric $O_2$ and $CO_2$ measurements will hopefully be extended with semi-continuous in-situ measurements of the $O_2$ and $CO_2$ concentrations in the seawater (as the partial pressure $pO_2$ and $pCO_2$). By means of simultaneous atmospheric and marine $CO_2$ and $\delta O_2/N_2$ measurements over several years, the $CO_2$ uptake by the North Sea region, and its variability, can be estimated.

References


