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 5
Atmospheric oxygen and carbon dioxide concentrations from aircraft flask samples collected over Russia

Abstract
In this chapter we present atmospheric CO$_2$ concentration and δO$_2$/N$_2$ records for four locations in Russia. Flask samples were taken onboard an aircraft at two different altitudes, 3000 m and 100 m, representing the free troposphere and local influences, respectively. Flasks were sampled irregularly between 1998 and 2008 at Fyodorovskoye (56°27'N, 32°55'E), Syktyvkar (61°23'N, 52°17'E), Zotino (60°44'N, 89°09'E) and Ubs Nur (51°29'N, 95°13'E), thereby representing a large part of Russia, including Siberia. The amplitudes of the seasonal cycles of CO$_2$ and δO$_2$/N$_2$ increase from west to east over the continent, due to a larger influence by the continental biosphere. The long term CO$_2$ and δO$_2$/N$_2$ trends from Fyodorovskoye—which has the longest record— are comparable to those from the marine sector atmospheric sampling station Mace Head in Ireland and the coastal site Lutjewad in the Netherlands. The Atmospheric Potential Oxygen (APO) is also presented in this chapter, and is compared to the APO simulations with the atmospheric transport model TM3.

This chapter has been submitted to Tellus B as:
5.1. Introduction

Rising global fossil fuel consumption patterns continue to increase the atmospheric CO₂ concentration (e.g. Forster et al., 2007). The interaction between the different carbon reservoirs on earth—atmosphere, land biosphere and oceans—determines the fraction of CO₂ remaining in the atmosphere, as the rest is taken up by the other two compartments. Recent research has shown that the fraction of the remaining atmospheric CO₂ has increased each year, since the carbon sinks are decreasing due to changing climate conditions (e.g. Le Quere et al., 2009). The size of the carbon sinks in the continental ecosystems in the northern hemisphere is significant (e.g. Tans et al., 1990; Bousquet et al., 2000), however the uncertainty in the sizes and region of the continental and marine carbon sinks is still rather high.

The European project EuroSiberian CarbonFlux and its follow-up project Terrestrial Carbon Observation System (TCOS) Siberia aimed at improving the knowledge on the net carbon balance of Russia and Siberia and its variability both by an ecological bottom up approach (e.g. Lloyd et al., 2002b; Milyukova et al., 2002; Shibistova et al., 2002) and by atmospheric measurements, both ground based and from aircraft for top down carbon balance information. Earlier work by Levin et al. (2002), Ramonet et al. (2002) and Lloyd et al. (2002a) presented the atmospheric CO₂ records from aircraft samples during the first phase of the project. Other projects have also increased the knowledge of the carbon balance and atmospheric CO₂ concentrations in Siberia, e.g. a tall tower setup for continuous measurements of atmospheric trace gases and O₂ (Kozlova and Manning, 2009) and additional transcontinental aircraft campaigns (e.g. Nakazawa et al., 1997; Paris et al., 2008). In this chapter we will contribute δO₂/N₂ records together with the extended CO₂ records up to 2008 from aircraft flask samples over four locations in Russia. We will first describe the sampling routines and measurement techniques. After that we address the four sampling locations and finally we present the CO₂ and O₂ records together with the Atmospheric Potential Oxygen (APO) from these flask samples.
5.2. Sampling locations and methods

5.2.1. Aircraft flask sampling
Flasks were filled with sample air irregularly between 1998 and 2008 using a manually operated set-up from a Antonov AN2 biplane aircraft. The air inlet of the flask sampler was mounted on the steel wires between the wings of the aircraft on the opposite side of the exhaust pipe. The sampling setup furthermore included around 10 m of 1/4” Synflex 1300 tubing and a KNF Neuberger membrane pump (N86). The air was dried using Magnesiumperchlorate drying agent in a v-shaped tube. The flasks were filled to a standard target pressure of 1 bar. The used flasks are 2.5 litre glass flasks with two glass valves (Louwers, Hapert, the Netherlands) with viton o-rings and ball and cup joint connections (Rotulex). Most of the flask samples were taken in duplicate, when logistics was not permitting these were single samples. Flask sampling only took place in the daytime during weather conditions suitable for flying. The standard sampling heights were 100 m and 3000 m. The height of the atmospheric boundary layer changes from 300-500 m in winter to 1500-2800 in summer (Levin et al., 2002; Lloyd et al., 2002a; Ramonet et al., 2002; Sidorov et al., 2002). Samples taken at 3000 m therefore remain unaffected by regional short term processes and represent the free troposphere (i.e. the larger-scale background situation).

5.2.2. δO₂/N₂ and CO₂ measurements
The flasks were analyzed in the CIO laboratory for the concentrations of CO₂, CH₄ and CO, as well as for δO₂/N₂, δ¹³CO₂ and δCO¹⁸O. The δO₂/N₂ is measured using a Micromass Optima, which is a dual inlet isotope ratio mass spectrometer (DI-IRMS), similar to that developed by Bender et al. (1994). The atmospheric O₂ concentration is measured as the ratio of O₂ versus N₂. Since the atmospheric N₂ concentration is much less variable, the changes in the O₂/N₂ ratio mainly represent the changes in the O₂ concentration. The O₂/N₂ ratio is insensitive to changes in other atmospheric gases (e.g. CO₂). The changes in the O₂/N₂ ratio of a sample are expressed as the ratio versus the O₂/N₂ ratio of a known reference gas, as shown in equation 5.1 (Keeling and Shertz, 1992). For natural air the δO₂/N₂ values are relatively small and therefore multiplied with 10⁶ and expressed in per meg.

\[
\delta(O_2 / N_2) = \frac{(O_2 / N_2)_{\text{sample}}}{(O_2 / N_2)_{\text{reference}}} - 1
\]  
(5.1)
The δO₂/N₂ measurements of our mass spectrometer are calibrated using three primary cylinders spanning from -805 to -258 per meg purchased from the Scripps Institution of Oceanography (SIO). The mass spectrometer measures each sample twice against a machine reference gas (i.e. the reference in equation 4.1). Besides the samples, working gas cylinders were measured following an identical procedure as for the samples. Each measurement gives the difference between the sample or working gas and the machine reference gas. The calibration procedure included a drift correction of this difference based on the measurements of a suite of working cylinders against the machine reference gas. The amount of working gas cylinders used has increased during the operational period of our mass spectrometer –from 1998 onwards– from one cylinder to four, which makes the latest data more accurate than the earlier data. During the start-up phase of the measurements, the machine reference gas has been changed several times, requiring a scale conversion for each change. The SIO primary cylinders were measured only against the current machine reference gas, which makes the data of samples measured (i.e. not necessarily sampled) after 2006 the most accurate. The combined uncertainty in the measurements of the flask samples varies between 6 per meg for the latest measurements to 15 per meg in the initial measurement periods. The used procedures and further details on each measurement period are extensively described in the appendix of this thesis.

Next to the δO₂/N₂ measurements, the concentrations of CO₂, CH₄ and CO are measured using a Hewlett-Packard gas chromatograph (GC) model 6890, comparable to the setup described by Worthy et al. (2003). Each flask is measured at least two times on the GC to enhance the measurement precision. A working standard is measured after every second sample measurement, and the measurement sequence includes a target cylinder for quality control. The GC measurements are calibrated with a suite of standards purchased from the Earth System Research Laboratory (ESRL) of the National Oceanic and Atmospheric Administration (NOAA). The final CO₂ concentrations of the flask samples is expressed in ppm on the World Meteorological Organization (WMO) X2007 scale. More details on both measurement instruments are presented by Sirignano et al. (2010) and more extensively in the appendix of this thesis.
5.2.3. Atmospheric Potential Oxygen

Stephens et al. (1998) have defined the tracer Atmospheric Potential Oxygen (APO), as shown in equation 5.2.

$$\delta\text{APO} = \delta\text{O}_2/\text{N}_2 + \frac{1.1 \cdot (\text{CO}_2 - 350)}{\text{S}_\text{O}_2} \text{ (per meg)}$$ (5.2)

APO is the sum of $\delta\text{O}_2/\text{N}_2$ plus 1.1 times the $\text{CO}_2$ concentration, with 1.1 being the global average stoichiometric ratio between $\text{O}_2$ and $\text{CO}_2$ in photosynthesis and respiration processes (Severinghaus, 1995). $\text{S}_\text{O}_2$ is the standard mole fraction of $\text{O}_2$ in air. An arbitrary reference of 350 ppm is subtracted from the $\text{CO}_2$ concentration, as used on the SIO per meg scale for APO (Manning and Keeling, 2006). The definition implies that APO is unaffected by activity of land biota and is therefore sensitive principally to ocean-atmosphere exchange of $\text{O}_2$ and $\text{CO}_2$, but also still partly to fossil fuel combustion and its specific oxidation ratio ($\text{OR} = \text{O}_2 : \text{CO}_2$). The global average OR for fossil fuel is 1.4 (Keeling, 1988). Therefore the APO on average still includes 0.3 times the fossil fuel combustion contribution.
5.2.4. Sampling locations

The flasks were sampled from an aircraft over four different locations in Russia, which are shown in figure 5.1. The Central Forest Reserve of Fyodorovskoye (56°27'N, 32°55'E) is situated in the Tver region, around 300 km northwest of Moscow. The forest mainly consists of spruce and birch and the hilly landscape ranges between 220 and 280 m a.s.l. The city of Syktyvkar is located in northern Russia and is the capital of the Komi republic. The flights were performed 100 km south east of the city of Syktyvkar, around 400 km west of the Ural mountains (61°23’N, 52°17’E). The area is part of the northern European taiga and the vegetation consists mainly of pine forest. Zotino (60°44’N, 89°09’E) is located 600 km north of Krasnoyarsk on the west bank of the Yenisei river, which is part of the central Siberian boreal coniferous forest taiga region. More detailed information on these three sampling locations is presented by e.g. Schulze et al. (2002), Levin et al. (2002), Ramonet et al. (2002) and Lloyd et al. (2002a). The sampling site Ubs Nur (51°29’N, 95°13’E) is situated in the Tuva republic in a mountainous area consisting of Mongolian semi-deserts and dry steppes and Siberian larch taiga and highland tundra.

Figure 5.1: The four locations where the flasks have been sampled from an aircraft.
5.3. Results

5.3.1. CO$_2$ and $\delta$O$_2$/N$_2$

Flasks have been sampled over Russia between 1998 and 2008. Due to logistic and financial reasons the four locations as mentioned in the previous section have not been sampled regularly. Fyodorovskoye has been sampled most frequently, from 1998 to 2008, with a gap between mid 2001 and mid 2003. Flask samples have been sampled at Syktyvkar in 2000, 2003 and 2004. Zotino and Ubs Nur have been taken only shortly, end 1998 to beginning 2001 and mid 2003 through 2005 respectively.

Flask samples included in the subsequent analysis were selected based on the absence of contamination in the air samples, which was identified using the CO concentration. As the major source of local contamination related to the flask sampling is the aircraft exhaust, a high CO is a good proxy for the amount of contamination. A high CO concentration can also be a sign of a possible disturbance by fires. Flask samples with a CO concentration higher than 300 ppb, were excluded from the analysis. The amount of samples excluded based on a high CO concentration varied between 4% for Fyodorovskoye, 10% for Syktyvkar and Ubs Nur and 17% for Zotino (for Zotino mainly samples after 2000).

The CO$_2$ and $\delta$O$_2$/N$_2$ records from the four locations were fitted with a linear combination of a linear trend and a single or double harmonic function. For the CO$_2$ records from all sites, we have used a double harmonic function, as the amount of data points was not sufficient for a three harmonic function, as used by e.g. Keeling and Shertz (1992). For the $\delta$O$_2$/N$_2$ from Fyodorovskoye a double harmonic function was used too. For the other three locations, the sampling periods were short and furthermore the scatter in the data points was large, which did not provide sufficient information for a double harmonic function. Therefore we have used a single harmonic function for those three $\delta$O$_2$/N$_2$ records.

The fits were used to exclude additional data points from the records, to identify outliers, i.e. samples not representing the seasonal signal at the respective locations. Samples for which the residuals of the fits were larger than 2.5 times the standard deviation of the average of the residuals were excluded from the data series. This process was iterated until all outliers were removed. In total, between 10 and 20% of the data were considered outliers.
Table 5.1: CO$_2$, δO$_2$/N$_2$ and APO trend and seasonality at two different heights (3000 m and 100 m) from four aircraft sampling locations: Fyodorovskoye, Syktyvkar, Zotino and Ubs Nur (this work) together with Zotino tall tower measurements (Kozlova et al., 2008) and flask samples from Mace Head and Lutjewad (van der Laan-Luijkx et al., 2010).

<table>
<thead>
<tr>
<th>Location</th>
<th>CO$_2$ trend (per year) (ppm)</th>
<th>APO amplitude (per meg)</th>
<th>CO$_2$ amplitude (maximum day, minimum day) (ppm)</th>
<th>O$_2$/$N_2$ trend (per year) (ppm)</th>
<th>APO amplitude (maximum day, minimum day) (per meg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fyodorovskoye</td>
<td>1.77±0.05 -16.4±1.1 -6.3±1.3</td>
<td>12.3±0.4 (103, 237)</td>
<td>22.7±1.1 (67, 216)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
<tr>
<td>Syktyvkar</td>
<td>1.58±0.09 -13.4±2.2</td>
<td>26±2 (105, 239)</td>
<td>14.8±1.1 (87, 214)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
<tr>
<td>Ubs Nur</td>
<td>1.58±0.09 -13.4±2.2</td>
<td>26±2 (105, 239)</td>
<td>14.8±1.1 (87, 214)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
<tr>
<td>Zotino</td>
<td>1.58±0.09 -13.4±2.2</td>
<td>26±2 (105, 239)</td>
<td>14.8±1.1 (87, 214)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
<tr>
<td>Mace Head</td>
<td>1.90±0.04 -18.5±0.7 -8.4±0.7</td>
<td>26±2 (105, 239)</td>
<td>14.8±1.1 (87, 214)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
<tr>
<td>Lutjewad</td>
<td>1.97±0.07 -21.0±0.9 -10.6±0.7</td>
<td>26±2 (105, 239)</td>
<td>14.8±1.1 (87, 214)</td>
<td>1.86±0.12 -17.5±1.9 -8.0±1.5</td>
<td>165±12 (234, 52)</td>
</tr>
</tbody>
</table>

References:
- 1998-2008 (F) (this work)
- 1998-2008 (F) (this work)
- 1999-2005 (F) (this work)
- 2003-2005 (F) (this work)
- 2005-2007 (C) (Kozlova et al., 2008)
- 1998-2009 (F) (Chapter 4)
- 2000-2009 (F) (Chapter 4)
The results for the four locations for CO$_2$ and δO$_2$/N$_2$ are presented in figure 5.2a through 5.2d. Flask samples from 3000 m are represented with dark symbols and those from 100 m are represented by lighter symbols. The fits through the data are also included in the figure, a solid line for 3000 m and a dashed line for 100 m. As expected, there is clear difference between the records from the two different heights, even at those locations with only a short record. The samples taken within the boundary layer at 100 m are highly influenced by the local biosphere, whereas the samples from 3000 m represent the free troposphere. This results in a larger seasonal amplitude at 100 m for both CO$_2$ and δO$_2$/N$_2$. The parameters obtained by the fits are given in table 5.1. The table includes the seasonal amplitudes (given as peak-trough amplitudes of the harmonic fit) and the long term annual trend. In those cases where the record is too short to obtain reliable information, the numbers have not been included in the table. The number of flasks sampled at 100 m is generally much lower than at 3000 m, mostly due to logistic reasons. The seasonal amplitudes as well as the long term annual trend are therefore less well defined for the records from 100 m. For Zotino, flasks were only collected at 3000 m. When comparing the seasonal amplitudes from the CO$_2$ records at 3000 m over the four locations, the amplitudes are increasing from west to east. As the two most eastern sites, Zotino and Ubs Nur, are situated deeper into the continent, the amplitudes are likely to increase, as any oceanic influence is more dampened, which leads to a more pronounced terrestrial biospheric seasonal pattern.

From figure 5.2 an absolute offset between Zotino and e.g. Fyodorovskoye can be seen. For the other locations a possible offset is not observed within the uncertainties in the measurements, however the existence of an offset cannot be excluded directly. The offset between Zotino and Fyodorovskoye is estimated at about 100 per meg, which cannot be caused by natural variations; it would correspond to an offset in CO$_2$ of about 20 ppm, which is more than the seasonal variation. A possible explanation for this offset might by fractionation effects on the air inlets. In principle, the air inlets are identical for each aircraft set up, however, (differences in) fractionation might occur by variations in the positioning onto the aircraft (see e.g. Langenfelds, 2002) which was not well-known during the initial sampling period. As these differences cannot be ruled out for our observations, it is not possible to give a valid estimate of the absolute gradients between the four locations for δO$_2$/N$_2$. 
Figure 5.2: Observations of the atmospheric O$_2$ (circles) and CO$_2$ (squares) concentrations at four locations in Russia: Fyodorovskoye (a) Syktyvkar (b), Zotino (c) and Ubs Nur (d) between 1998-2008. The concentrations are measurements of aircraft flask samples from two heights: 3000 m (dark symbols) and 100 m (lighter symbols). The fits through the data points are a linear combination of a linear trend and a harmonic function: double harmonics for all CO$_2$ data series and δO$_2$/N$_2$ from Fyodorovskoye and a single harmonic function for δO$_2$/N$_2$ from Syktyvkar, Ubs Nur and Zotino.
Atmospheric $O_2$ and $CO_2$ concentrations from aircraft samples

Figure 5.2 continued.
5.3.2. Comparison to other measurements in Europe

The seasonal amplitude at Zotino from continuous tall tower measurements was also presented by Kozlova et al. (2008). They found an amplitude of 26.6 ppm for CO$_2$ and 134 per meg for $\delta$O$_2$/N$_2$ measured at 52 m. Their obtained amplitudes are higher than those we obtained from the aircraft flasks samples at 3000 m, in accordance with expectations as 52 m is highly influenced by the local terrestrial biosphere.

The seasonal amplitude of CO$_2$ aircraft flask samples collected over Russia has also been presented in earlier work. Ramonet et al. (2002) obtained seasonal amplitudes for Fyodorovskoye: 14.8 ppm and 26.5 ppm for the free troposphere (FT) and the atmospheric boundary layer (ABL) respectively. Sidorov et al. (2002) obtained amplitudes for Syktyvkar, they found amplitudes of 14.0 ppm (FT) and 22.1 ppm (ABL). Lloyd et al. (2002a) presented the seasonal amplitude for Zotino, these were 15 ppm (FT) and 25 ppm (ABL). Combined data is presented by Levin et al. (2002) who show amplitudes for 3000 m at Syktyvkar and Zotino to be 12.4 ppm and 13.06 ppm respectively. The values presented by Levin et al. (2002) are slightly lower than the other two studies, because these represent the average of the FT and the combined study gives the amplitudes for 3000 m. The differences in the seasonal amplitudes between the ABL and the FT that we have obtained from our flask samples are quite similar. There are, however, some differences to this earlier work. Our amplitudes at Fyodorovskoye are lower for both the ABL and the FT. Compared to the combined data from Levin et al. (2002), our obtained amplitudes for the FT samples at Syktyvkar and Zotino are also lower. However, the trend of the amplitudes to increase from west to east is also present in our data. Using the amplitude of the FT for Fyodorovskoye of 12.3 ppm and comparing this to the average FT amplitude of Ubs Nur and Zotino (since both records are only short) of 14.8 ppm, this gives a significant increase in the seasonal amplitude from east to west of 20% ($\pm$ 7%).
Atmospheric O$_2$ and CO$_2$ concentrations from aircraft samples

Figure 5.3: The trend (a and b) and seasonal cycles fits of CO$_2$ and δO$_2$/N$_2$ (b) of the longest record from the aircraft samples, Fyodorovskoye, in comparison to trend and seasonal cycles fits from the observations of Mace Head, Ireland and Lutjewad, the Netherlands (van der Laan-Luijkx et al., 2010) and the marine background reference from the Globalview-CO$_2$ database at 53°N (GLOBALVIEW-CO$_2$, 2008).
Figure 5.3 shows a comparison of the trend fits of CO$_2$ (a), δO$_2$/N$_2$ (b) and the seasonal cycles (c) of the longest record from the aircraft samples (Fyodorovskoye) in comparison to the trend fits from the observations of Mace Head, Ireland (53°20’N, 9°54’W) and Lutjewad, the Netherlands (53°24’N, 6°21’E) (van der Laan-Luijkx et al., 2010) and the marine background reference from the Globalview-CO$_2$ database at 53°N (GLOBALVIEW-CO$_2$, 2008). The flask samples at Mace Head and Lutjewad are sampled from 35 m and 60 m respectively. The long term annual trend at Fyodorovskoye at 100 m for CO$_2$ is therefore better comparable than that from 3000 m. The CO$_2$ concentration increases at Fyodorovskoye with 1.86 ± 0.12 ppm/year and at Mace Head and Lutjewad with 1.90 ± 0.04 ppm/year and 1.97 ± 0.07 ppm/year respectively. For the δO$_2$/N$_2$ trend this is -17.5 ± 1.9 per meg/year for Fyodorovskoye, -18.5 ± 0.7 per meg/year for Mace Head and -21.0 ± 0.9 per meg/year for Lutjewad. For CO$_2$ the trends at these three stations are the same within the uncertainties. For δO$_2$/N$_2$ Fyodorovskoye and Mace Head agree, whereas Lutjewad has a trend that is just significantly more negative. The comparison of the seasonal patterns in figure 5.3c shows clearly the difference between the continental signal from Fyodorovskoye at 100 m and the other signals. The gradient in the summer –the growing season of the terrestrial biosphere– between Fyodorovskoye at 100 m and Mace Head is about 6 ppm, comparable to the summertime gradient found by Kozlova et al. (2008) between Zotino and the Shetland Islands, which was 7 ppm.

Ramonet et al. (2010) show that the CO$_2$ gradients between Mace Head and several other continental European sites is increasing and attribute this partly to increasing fossil fuel emissions and to a decreasing boundary layer height. Van der Laan-Luijkx et al. (2010) show a combination of increasing CO$_2$ and δO$_2$/N$_2$ gradients between Mace Head and Lutjewad and connect this to the influence of local fossil fuel use with a larger oxidative ratio. The data presented in this work suggest a decrease in both the CO$_2$ and the δO$_2$/N$_2$ gradient between Mace Head and Fyodorovskoye. The uncertainty in the trend fits, especially for Fyodorovskoye, are however too large to deduce the size of the possible change in the gradient.
5.3.3. Atmospheric Potential Oxygen

We have calculated APO for each of our four locations. The same (single harmonic) fit procedure has been applied to the data to exclude outliers from the record. The obtained fit parameters on the trend and the seasonality are included in table 5.1. As the records from Syktyvkar, Zotino and Ubs Nur contain only few data points, we show only the record for Fyodorovskoye in figure 5.4. The seasonal amplitudes are mostly half of that of δO2/N2, as expected from the definition of APO. The APO long term trend at Fyodorovskoye is found to be -6.3 ± 1.3 per meg/year for 3000 m and -8.0 ± 1.5 per meg/year for 100 m. The latter is the same within the uncertainties as the trends obtained at Mace Head and Lutjewad, which are -8.4 ± 0.7 per meg/year and -10.6 ± 0.7 per meg/year, respectively.

The seasonal amplitude of APO at Zotino as obtained by Kozlova et al. (2008), is 51 per meg. Although for CO2 and δO2/N2 we found lower seasonal amplitudes at 3000 m than Kozlova et al. (2008) for 52 m, our amplitude for APO, which is 54 per meg, is the same for the two different heights. The terrestrial biospheric component clearly causes the major part of the difference in amplitudes between the boundary layer and the free troposphere, and this is nicely demonstrated by the correspondence of APO at 52 and 3000 m: APO removes the terrestrial biosphere component, the remainder is the seasonal oceanic signal (and a residual fossil fuel seasonality).

![Figure 5.4: Observations of the Atmospheric Potential Oxygen (APO) at Fyodorovskoye between 1998-2008. The aircraft flask samples are taken from two heights: 3000 m (dark symbols) and 100 m (lighter symbols). The fits through the data points are a linear combination of a linear trend and a single harmonic function.]
5.3.4. **APO comparison to TM3 simulations**

In this section we show a comparison of the APO observations with model simulations. Although the scatter in the presented data of the flask samples is large and the records consist of few data points, they can be used as a test case to improve model outcomes on the source and sink estimates. As the APO record from Fyodorovskoye is the only record out of the collected four which contains sufficient data to estimate the trend fit, we used that record for the comparison. We used the atmospheric transport model TM3 (Rödenbeck et al., 2008) to obtain the simulated APO record for Fyodorovskoye at both 3000 and 100 m. The model was driven by surface fluxes from Rödenbeck et al. (2008, updated) which have been optimized as to match APO observations at 7 sites from the Scripps atmospheric network (Manning and Keeling, 2006). Figure 5.5 shows the model-simulation comparison for both heights for Fyodorovskoye during 1998-2008 (a) and for the detrended seasonal cycles (b). Since the terrestrial biospheric component is removed from APO by definition, the APO trend and seasonal amplitudes are expected to be the same for both altitudes, which is both confirmed by the model results and –within the error bars– by the observations. The seasonal cycle model-observation comparison in figure 5.5b shows that the magnitude of the seasonal amplitude is best obtained from the Fyodorovskoye record at 100 m, while the timing of the APO seasonality is represented better by the record from 3000 m. It is, however, also clear from the scatter of the data points that the observational seasonal cycles contain a high degree of uncertainty. The decreasing APO trend from the model simulations in figure 5.5a is estimated at \(-10.3 \pm 0.1\) per meg/year for both 3000 m and 100 m during this period. The trend obtained from the observations is lower than that from the simulation. This difference can have several causes. First of all the quality of our observations might have lead to a too low estimate for the trend. On the other hand, the APO trend of the model simulations could be too high due to a too large oceanic sink or a transport problem. More observation-simulation comparisons are required in order to verify the reason for the difference in the APO trend and to obtain better estimates on the APO trends and variability. Improvements can also be found in independent modelling of \(\delta O_2/N_2\) and \(CO_2\) instead of transporting APO directly.
Figure 5.5: The APO time series at Fyodorovskoye between 1998-2008 based on observations in comparison to TM3 model simulations for 3000 m and 100 m (a) and a comparison of the seasonal cycles (b).
5.4. Discussion and Conclusion

In this chapter we have presented the CO$_2$, δO$_2$/N$_2$ and APO records from four locations in Russia between 1998 and 2008. In spite of the fragmentary data, it is possible to obtain the seasonal and annual trends from these four data sets. The amount of locations where atmospheric δO$_2$/N$_2$ is sampled is increasing gradually, however, the vast continental land masses remain relatively under-sampled. The aircraft flask sampling campaigns over Russia (including Siberia) during the past decades have reduced the lack of information on the CO$_2$ balance and related components to some extent. Continuous concurrent observations of atmospheric CO$_2$ and δO$_2$/N$_2$ like the Zotino tall tower observatory (Kozlova et al., 2008) should however be extended, as this area is highly interesting in light of the global and Eurasian carbon budget.

Unfortunately, O$_2$ gradients between these Russian locations could not be determined, due to insufficient data availability for some of the sites and because the differences in the air inlets of the flask sampler on board the different aircrafts have a systematic influence (caused by e.g. fractionation) on the O$_2$ concentration of the collected air samples which is larger than the expected gradients between the locations.

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