

7.8 Results from the Tall Tower Measurement Station for Atmospheric Greenhouse Gases at Bialystok, Poland

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7.8.1 The Bialystok station

The tall tower measurement station near Bialystok, Poland (53°13'N, 23°01'E, 183 masl) was set up in 2005 as part of the tall tower atmospheric measurement network formed under the EU project *CHIOTTO* (Continuous High precision Tall Tower Observations of greenhouse gases) (Vermeulen et al., 2004), and it is presently being operated under the EU project *CarboEurope IP*. The area within a few hundred kilometers around the tower is flat, with a maximal elevation of 250 m above sea level. The land is covered by crops (about 60%), pastures and forest; there is no significant local industry. The nearest town, Bialystok, with ~300000 inhabitants, is situated about 20 km SE of the tower.

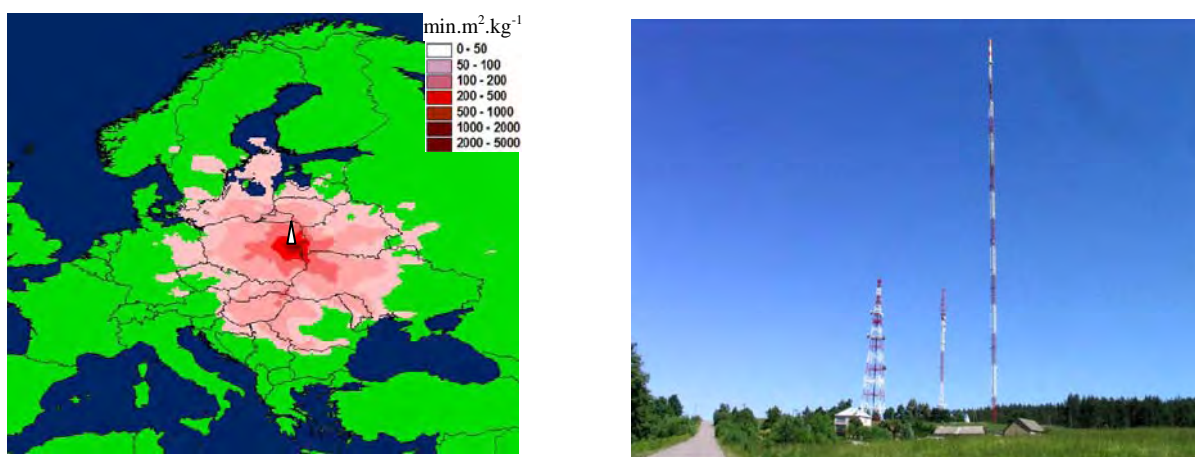


Figure 1. (left) Footprint area of the Bialystok (BIK) tall tower station (level 300 m agl) estimated with the COMET model, for the year 2005 (pers. comm., A. Vermeulen, ECN Netherlands); (right) photo of the BIK tower.

7.8.2 Technical setup

Mole fractions of CO₂, CH₄, CO, N₂O and SF₆ and the O₂/N₂ ratio are measured in-situ, quasi-continuously. The system is designed to measure alternately air sampled from five heights of the tower: 5 m, 30 m, 90 m, 180 m and 300 m. Before being analyzed, the air is first cryogenically dried to a dewpoint of about -80°C. The measurement system is installed inside a temperature controlled laboratory container (±2°C).

CO₂ and O₂ mole fractions are measured successively from the same air sample with a LiCor 7000 non-dispersive infrared (NDIR) CO₂ analyzer and a Sable Systems "Oxzilla" oxygen fuel cell analyzer. The O₂/N₂ ratio is calculated using the measured O₂ mole fraction, taking into account the CO₂ dilution effect. The analyzers are calibrated every 40 hours using air from a set of four high pressure cylinders with concentrations spanning the atmospheric range. Air from a "Target" cylinder is analyzed every few hours to check the stability of the system. The O₂ and CO₂ analyzers are installed inside a thermostated chamber (± 0.1°C) to avoid temperature variations influencing the measurement.

CH₄ and CO mole fractions are measured with an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and a Ni catalyst methanizer, using Molsieve-5A

and Unibeads-1S packed columns. The same chromatograph is equipped with an electron capture detector (ECD) and Hayesep Q columns for the analysis of N_2O and SF_6 . The sample air is measured alternately with a reference gas from a high pressure cylinder, and the ratio between sample and reference peaks is used to compute the sample mole fraction. A calibration takes place every five days using air from a set of four high pressure cylinders, and a “Target” cylinder is analyzed every few hours to check the stability.

Meteorological parameters are measured at different heights on the tower and the data are transmitted to a computer via a CAN-BUS.

Besides quasi-continuous measurement, flask samples are filled regularly and sent for analysis at the Max Planck Institute for Biogeochemistry (MPI-BGC) laboratory in Jena, Germany. These provide the possibility to measure additional species (H_2 , Ar/N_2 ; ^{18}O and ^{13}C in CO_2), and constitute at the same time an important means for quality checking the in-situ measurement.

The measurement system operates unassisted, controlled by a custom written Labview™ program. A computer connection made by Symantec pcAnywhere™ software via ISDN allows remote control of the system and data transfer to MPI-BGC.

7.8.3 Data quality

A detailed evaluation of the measurement performance, including estimation of precision and accuracy, was performed after the first 18 months of operation. We provide here two diagnostics of system performance.

The long-term standard deviation of the Target cylinder measurement is assigned as an average measurement **precision** of the data covering this time period (Figure 2). The precision results, shown in the Figure 2 as standard deviations, and summarized in Table 1, are comparable (for CO_2 , O_2/N_2 and N_2O) or better (for CH_4 , CO and SF_6) than the precision goals of the CHIOTTO project, which have been established taking into account the WMO recommendations (WMO – GAW 161, 2005).

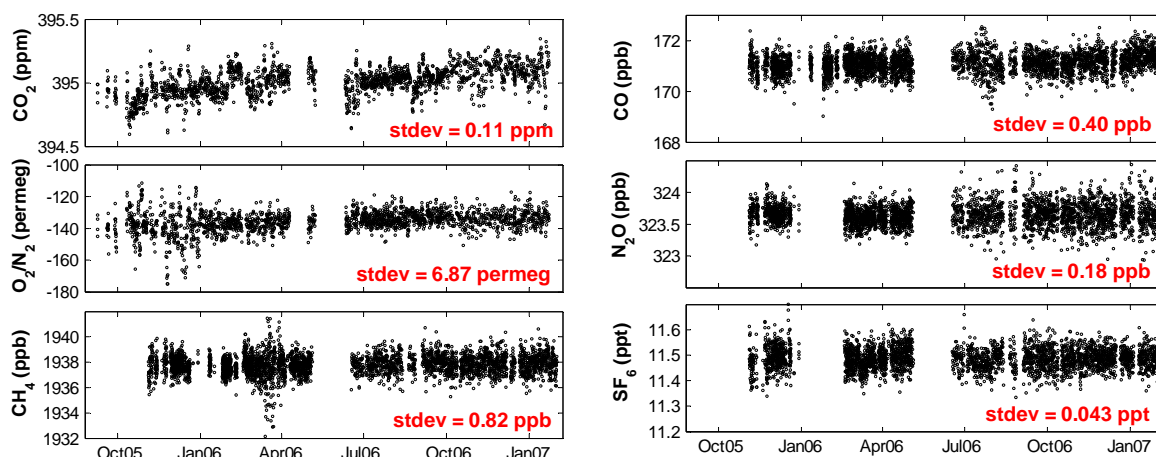


Figure 2. Time series of the Target cylinder measurement at Bialystok tall tower, used as a quality control check on the data.

The comparison between the in-situ measurement and the results of the flask samples analyzed at MPI-BGC GasLab is one of the means employed to verify the **accuracy** of the in-situ measurement. A significant systematic difference of about 10 ppb has been found between the CO mole fraction measured in-situ and the flask sample results, which can be only partly explained by changes in the flask samples during storage. The reason is not a calibration scale difference, since the comparisons with MPI-BGC using high pressure cylinders did not show a similar shift. The suspected reason for the observed difference is a contamination source in the flask sampler,

where the samples are stored with open valves before and after filling, for a significant period of time. For all the other species, no statistically significant differences have been found between the in-situ measurement and the results of flask samples.

Table 1. Average precision of the measurement at Bialystok station, and the precision targets of CHIOTTO project.

Species	BIK average precision (stdev)	CHIOTTO precision goals
CO ₂	0.095 ppm	0.1 ppm
O ₂ /N ₂	4.81 permeg	5 permeg
CH ₄	0.82 ppb	2 ppb
CO	0.40 ppb	1 ppb
N ₂ O	0.18 ppb	0.1 ppb
SF ₆	0.043 ppt	0.1 ppt

7.8.4 Selected results

In order to illustrate the nature of the station we discuss some main features of the data, like diurnal and seasonal variation of the signals.

7.8.4.1 Diurnal variations of CO₂ and O₂/N₂

A particularity of atmospheric oxygen measurements is that the O₂ variations are usually reported as O₂/N₂ ratio and not as mole fraction. The O₂/N₂ ratio is expressed in “per meg”, a relative unit defined by comparison with an arbitrary standard (Keeling & Shertz, 1992).

$$\delta O_2/N_2 (\text{permeg}) = \left(\frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1 \right) \times 10^6$$

The reason for this convention is the “dilution” effect: the mixing ratio of oxygen in air can be altered by variations of other air components (for example CO₂), without the oxygen quantity actually changing. In contrast, the changes in O₂/N₂ ratio can only be due to changes in number of moles of oxygen or nitrogen. In many cases the fluxes of nitrogen in and out of the atmosphere can be neglected, and then the variations of O₂/N₂ ratio represent the changes in the number of moles of oxygen.

During the warm season and under fair weather conditions, the thermally induced atmospheric vertical mixing follows a diurnal periodicity which overlaps with the diurnal cycle of release and uptake of CO₂ due to respiration and photosynthesis of the land biosphere, and with the diurnal cycle of human activity. These effects combine to result in a diurnal evolution of the CO₂ mole fraction and of its vertical gradient.

During night-time, CO₂ released (mainly by land biosphere respiration) accumulates near ground, in the absence of strong vertical mixing. Accordingly, large increases are observed in CO₂ mole fraction near the ground and a build-up of large vertical gradients. During the day, when the net exchange between the biosphere and atmosphere is dominated by photosynthesis, the air is well mixed up to typically 1-3 km. Thus the observed decrease of the CO₂ mole fraction due to photosynthesis is much smaller compared to the night-time increase, due to dilution over the mixed layer of the air column.

The short term variations of atmospheric O₂ are typically linked to the variations of CO₂, because during the processes of respiration, photosynthesis and fossil fuel combustion, O₂ is consumed when CO₂ is produced and vice versa. The diurnal cycle of O₂/N₂ ratio is therefore largely anti-correlated with the diurnal cycle of CO₂.

The dissimilarity in the diurnal signals between the warm and the cold season reflects both differences in sources and sinks and the seasonality of the atmospheric circulation. During the cold season, respiration is reduced and photosynthesis declines to a very low level. According to model simulations (C. Rödenbeck, MPI-BGC Jena, pers. comm.), the anthropogenic emissions and the land biosphere respiration are on the same order of magnitude. Also, the diurnal periodicity of vertical mixing disappears; the air column of a few hundred meters above ground is most of the time well mixed, and temperature inversions appear at non-regular time intervals. As can be observed in Figure 3, the average diurnal variation decreases in amplitude or even becomes indiscernible and independent of height in the cold months.

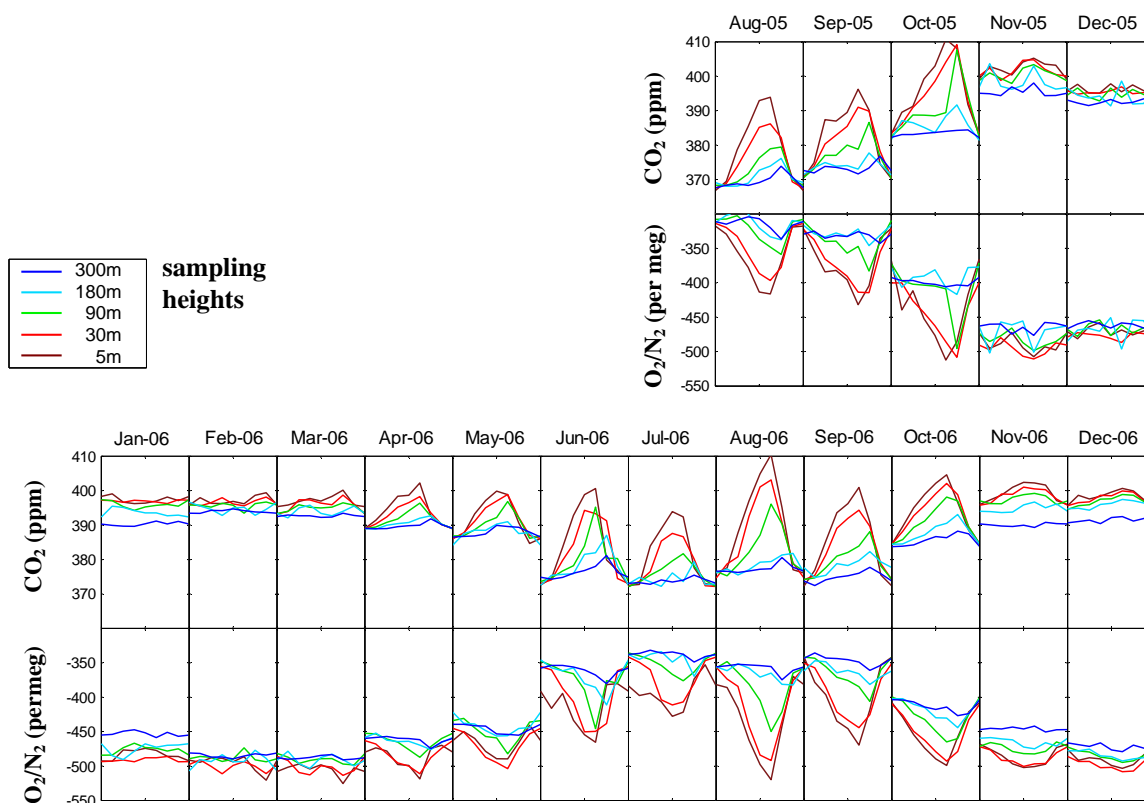


Figure 3. Monthly averaged diurnal cycles of CO₂ and O₂/N₂. The upper panels show CO₂ (ppm) and the lower panels O₂/N₂ (per meg). The colours represent different sampling heights. The x-axis of each plot covers a 24 hours interval, centred on midnight.

7.8.4.2 Observed O₂:CO₂ ratios for the diurnal signals

The correlation between the variations of atmospheric oxygen and carbon dioxide is currently used to distinguish ocean and land uptake of CO₂ on global and regional scales. This utilization relies on the fact that, for land sources and sinks (fossil fuel and land biosphere), the gas exchange of the two species is linked by stoichiometric factors. For the exchange between land biosphere and atmosphere, the presently assumed O₂:CO₂ molar ratio is -1.1 ± 0.05 (Severinghaus, 1995). The global average ratio for fossil fuel burning was estimated to be about 1.4 moles of O₂ consumed per mole of CO₂ produced (Keeling, 1988).

Based on the assumed O₂:CO₂ ratio specific to CO₂ exchange with the land biosphere, a tracer APO has been defined (Stephens et al., 1998), which is essentially unchanged during gas exchange between the land biosphere and atmosphere:

$$APO \text{ (per meg)} = O_2/N_2 \text{ (per meg)} + 1.1 \times 4.8 \times (CO_2 \text{ (ppm)} - 350);$$

where:

- 4.8 is the conversion factor from ppm to per meg-equivalent units for CO₂;
- 1.1 is the stoichiometric ratio for the land biosphere – atmosphere exchange

APO is by definition invariant to land biosphere – atmosphere exchange of CO_2 and O_2 , as long as such exchanges occur in the proportion of -1.1 between O_2 and CO_2 . Thus variations in APO should be only due to air-sea gas exchange of O_2 in the absence of fossil fuel emissions. Therefore APO can give information on the proportion of the oceanic influence in an air parcel. This is only approximately true, as the stoichiometric $\text{O}_2:\text{CO}_2$ ratio during fossil burning is somewhat more negative than the coefficient for land biosphere CO_2 exchange.

We calculated daily $\text{O}_2:\text{CO}_2$ ratios (for each height of the tower separately) for each 24-hours interval of the vegetation period between 12:00 GMT and the same hour the following day, as illustrated in Figure 4. The ratios were computed as slopes of a MODEL-2 least squares fit, minimizing the residuals on both x and y axes and taking into account the estimated uncertainties for both x (CO_2) and y (O_2/N_2) (York et al., 2004).

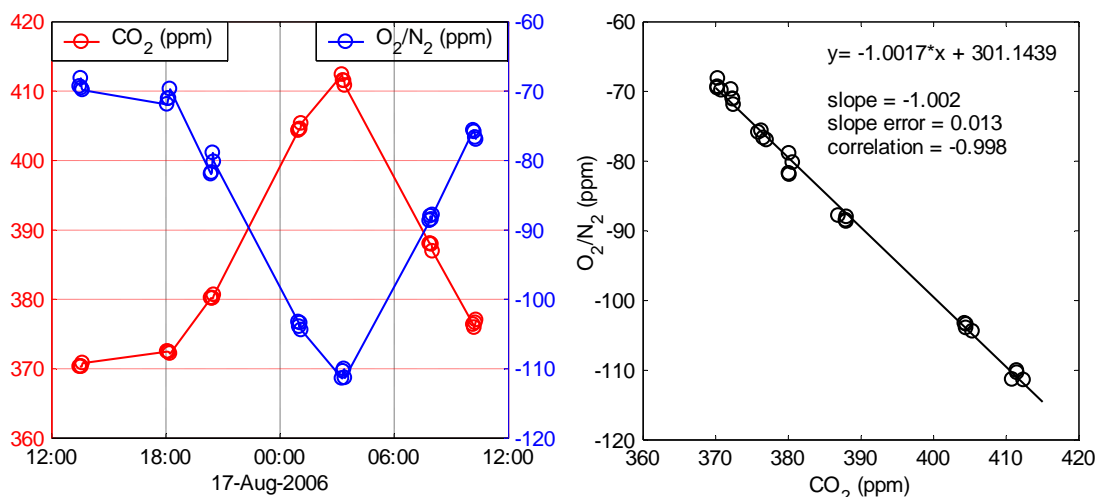


Figure 4. Illustration of CO_2 and O_2/N_2 variations over a 24-hour period (sampling height 30 m) and the corresponding $\text{O}_2:\text{CO}_2$ ratio calculated as slope of a linear fit. The apparent “gaps” are because of sampling from different heights of the tower.

Figure 5 shows the daily $\text{O}_2:\text{CO}_2$ ratio estimates for the signal at 30 m above ground, during the interval Apr – Oct-2006. Each data point represents the ratio calculated for one 24-hour interval (starting at 12:00 GMT) and the error bars represent the estimated error of the slopes.

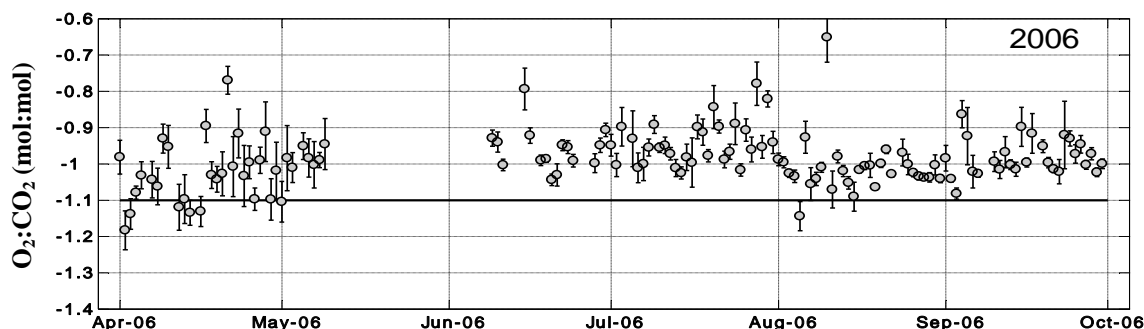


Figure 5. Diurnal $\text{O}_2:\text{CO}_2$ ratio at 30 m height during the vegetation period in 2006. Each point represents the $\text{O}_2:\text{CO}_2$ ratio for one 24-hour interval. The error bars represent the error of the $\text{O}_2:\text{CO}_2$ slopes. The value of -1.1 is marked as a reference.

The largest part of the night-time CO_2 increase observed at Bialystok at 30 m is due to land biospheric respiration. According to model simulations (e.g. Geels et al., 2007) and to estimations based on the $\text{CO}:\text{CO}_2$ ratio, the fossil fuel contribution can be considered smaller than 10% of the

total CO₂ signal. The ocean influence does not significantly contribute to the periodical variations on diurnal time scale. The night-time variations of CO₂ and oxygen represent therefore mainly gas exchange between the local to regional land biosphere and atmosphere. It is thus expected that the O₂:CO₂ ratios should be close to the value of -1.1, slightly more negative due to the contribution of fossil fuel combustion. This is obviously not directly observed (Figure 5), the resultant O₂:CO₂ ratios being significantly less negative than the expected range.

It must be noted, however, that the calculated ratios are mainly those associated with respiration and not the total gas exchange between the land biosphere and atmosphere. This is because, as discussed in the previous section, the atmospheric signature of the gas exchange between the land biosphere and atmosphere (in terms of mole fraction variations) is dominated by respiration, since the photosynthesis signal is strongly diluted by vertical mixing.

We can thus conclude that the variations of atmospheric mole fractions induced by the gas exchange between land biosphere and atmosphere at this particular location and for this particular time interval are not well represented by the generally accepted O₂:CO₂ molar ratio of -1.1.

This result does not necessarily imply that the oxidative ratio of the local land biosphere is lower (in absolute value) than the assumed average, although this is one of the possible causes (e.g. Randerson et al., 2006). Another explanation could be related to the differential transport and storage of CO₂ and O₂ in the forest canopy and in soil.

It is not clear how important this result is for the longer term signals, used to separate air-sea and air-land gas exchange. However it has important implications for the interpretation of short-term APO signals, since APO is defined assuming that there is a constant factor of -1.1 for the O₂ and CO₂ exchange between the land biosphere and atmosphere.

7.8.4.3 Seasonal cycles of CO₂, O₂/N₂ and APO at Shetland Island (SIS) and Bialystok (BIK)

Shetland Island, Scotland (SIS) is a marine flask sampling station (60°10'N, 01°10'E, 30 masl) managed by MPI-BGC. The calculated seasonal cycles of CO₂, O₂/N₂, APO and the residual terrestrial component of the oxygen seasonal cycle (O₂/N₂ (land bio)) at BIK and SIS are shown in Figure 6. The data used to compute the seasonal cycles are weekly flask samples for SIS and robust weekly averages of afternoon values for BIK.

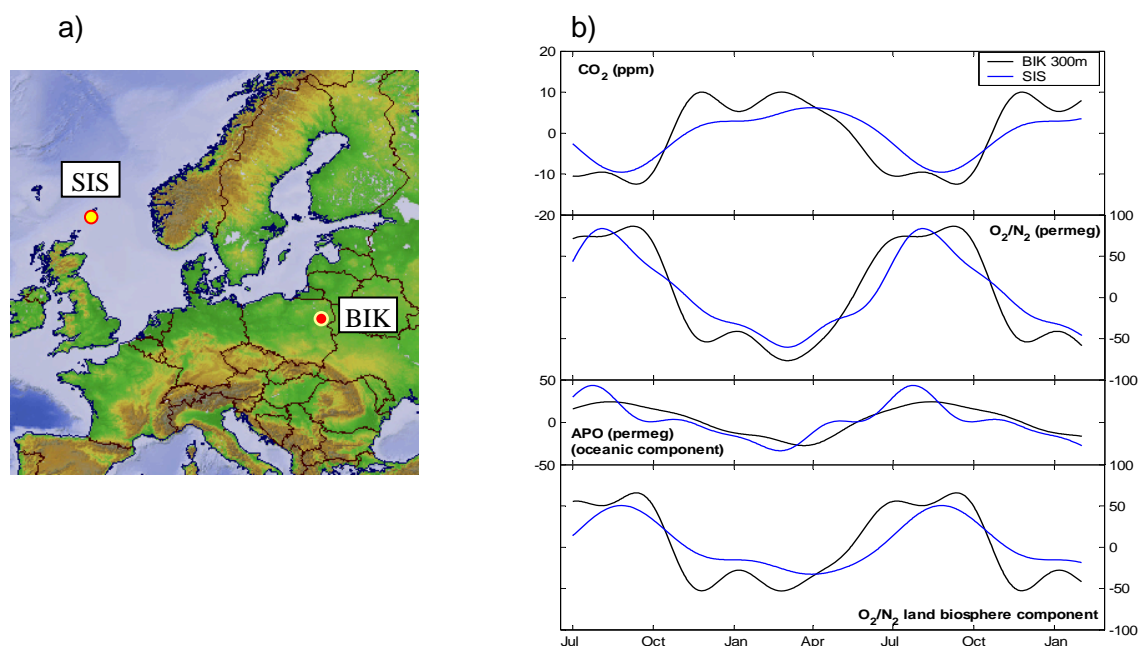


Figure 6. a) Location of sampling stations BIK and SIS; b) Seasonal cycles of CO₂, O₂/N₂, APO and the land biosphere component of O₂/N₂, at BIK (300 m sampling height) and SIS. The 4-harmonic curves are detrended and centred to zero mean. Dataset: Jul-05 to Jan-07.

The CO₂ seasonal cycle, which is mainly due to the land biosphere activity, has smaller amplitude at SIS, and it is delayed compared to BIK by about six weeks, which is on the order of hemispheric mixing time.

In contrast to CO₂, the O₂/N₂ seasonal cycle includes a significant oceanic component. Assuming that APO is conservative to the gas exchange with the land biosphere and it is little influenced by fossil fuel emissions on seasonal time scale, its seasonal cycle can be considered as representing the oceanic contribution to the oxygen seasonal cycle. Consequently, the difference between the O₂/N₂ and APO seasonal cycles represents the land biosphere component of the O₂/N₂ seasonal cycle. By comparing the seasonal cycles of O₂/N₂ and APO at marine and continental stations it is thus possible to estimate the attenuation of oceanic influence over the continent, and to constrain the longitudinal atmospheric transport.

The ocean and the land biosphere have approximately equal contributions to the total O₂/N₂ seasonal cycle at SIS. At BIK the oceanic contribution accounts for about 32% of the total O₂/N₂ seasonal cycle when the 300 m sampling height is considered, and this proportion decreases to about 23% for the 30 m sampling height (not shown). This difference between the sampling heights is consistent with the fact that the higher sampling level has a wider influence area, while the air sampled closer to the ground is more locally influenced. The calculation of these proportions is based on the peak to peak amplitude of the seasonal cycles.

The observed O₂:CO₂ ratio for the seasonal cycle at BIK (Figure 7) does not reproduce the results based on diurnal data in the previous section. An essential difference is the significant contribution of ocean influence in the seasonal variations, which is not present in the daily signal. The O₂:CO₂ ratio of the seasonal variations changes from -1.65 at the SIS marine station to -1.39 at BIK.

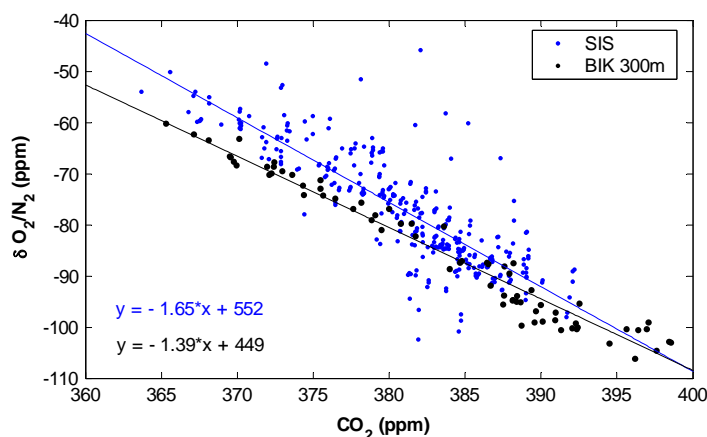


Figure 7. Correlation between the seasonal variations of O₂/N₂ and CO₂ at BIK (300 m) and SIS.

In light of the previous section, we can examine how this result changes if we assume that the O₂:CO₂ ratio specific to gas exchange with the land biosphere is different from the generally used -1.1. Supposing that this O₂:CO₂ factor was -1.0 instead of -1.1, we recalculate APO with this revised ratio. Repeating the seasonal cycle calculation using the new APO definition, the proportion of APO from the total O₂/N₂ seasonal cycle becomes about 39% at BIK at 300 m above ground, compared to the previously calculated 32%. It can be observed that the result differs considerably from the previous calculation. This comparison shows the necessity of expanding the knowledge on the atmospheric O₂:CO₂ signature of the land biosphere – atmosphere gas exchange, and its variability on different spatial and temporal scales.

References

- Geels C., Gloor M., Ciais P., Bousquet P., Peylin P., Vermeulen A.T., Dargaville R., Aalto T., Brandt J., Christensen J.H., Frohn L.M., Haszpra L., Karstens U., Rödenbeck C., Ramonet M., Carboni G. & Santaguida R. (2007). Comparing Atmospheric Transport Models for Future Regional Inversions over Europe - Part 1: Mapping the Atmospheric CO₂ Signals. *Atmos. Chem. Phys.*, 7, 3461-3479.
- Keeling R.F. & Shertz S.R. (1992). Seasonal and Interannual Variations in Atmospheric Oxygen and Implications for the Global Carbon Cycle. *Nature*, 358, 723-727.
- Keeling R. F. (1988). Development of an interferometric oxygen analyzer. Ph.D. thesis, *Harvard University*, Cambridge, Mass., 178pp.
- Randerson J.T., Masiello C.A., Still C.J., Rahn T., Poorter H. & Field C.B. (2006). Is Carbon within the Global Terrestrial Biosphere Becoming More Oxidized? Implications for Trends in Atmospheric O₂. *Global Change Biology*, 12, 260-271.
- Severinghaus J. P. (1995). Studies of the Terrestrial O₂ and Carbon Cycles in Sand Dune Gases and in Biosphere 2. Ph.D. thesis, *Columbia University*, 148 pp.
- Stephens B.B., Keeling R.F., Heimann M., Six K.D., Murnane R. & Caldeira K. (1998). Testing Global Ocean Carbon Cycle Models using Measurements of Atmospheric O₂ and CO₂ Concentration. *Global Biogeochemical Cycles*, 12, 213-230.
- Vermeulen A.T., Hensen A., Gloor M., Manning A.C., Ciais P., Eisma R., van den Bulk W.C.M., Mols J.J. & Erisman J.W. (2004). CHIOTTO - Continuous High-Precision Tall Tower Observations of Greenhouse Gases. In: Inverse Modelling of National and EU Greenhouse Gas Emission Inventories (eds. P. B, Behrend H & Jol A). *JRC Ispra*.
- York D., Evensen N. M., Martinez M. L., and Delgado J. D. (2004). Unified Equations for the Slope, Intercept, and Standard Errors of the Best Straight Line. *American Journal of Physics* 72(3), 367-375.
- WMO/GAW Report No. 161* (2005). 12th WMO/IAEA Meeting of Expert on Carbon Dioxide Concentration and Related Tracers Measurements Techniques (Toronto, Canada, 15-18 September 2003).
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