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**Measurements of  
greenhouse gases  
and related tracers at  
BIK tall tower**

M. E. Popa et al.

# Measurements of greenhouse gases and related tracers at Bialystok tall tower station in Poland

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## Abstract

Quasi-continuous, in-situ measurements of atmospheric CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, and SF<sub>6</sub> have been performed since August 2005 at the tall tower station near Białystok, in Eastern Poland, from five heights up to 300 m. Besides the in-situ measurements, flask samples are filled approximately weekly and measured at Max-Planck Institute for Biogeochemistry for the same species and, in addition, for H<sub>2</sub>, Ar/N<sub>2</sub> and the stable isotopes <sup>13</sup>C and <sup>18</sup>O in CO<sub>2</sub>. The in-situ measurement system was build based on commercially available analysers: a LiCor 7000 for CO<sub>2</sub>, a Sable Systems "Oxzilla" FC-2 for O<sub>2</sub>, and an Agilent 6890 gas chromatograph for CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>. The system was optimized to run continuously with very little maintenance and to fulfill the precision requirements of the CHIOTTO project. The O<sub>2</sub> measurements in particular required special attention in terms of technical setup and quality assurance. The evaluation of the performance after more than three years of operation gave overall satisfactory results, proving that this setup is suitable for long term remote operation with little maintenance. The precision achieved for all species is within or close to the project requirements. The comparison between the in-situ and flask sample results, used to verify the accuracy of the in-situ measurements, showed no significant difference for CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, and a very small difference for SF<sub>6</sub>. The same comparison however revealed a statistically significant difference for CO, of about 6.5 ppb, for which the cause could not be fully explained at the moment.

From more than three years of data, the main features at Białystok have been characterized in terms of variability, trends, and seasonal and diurnal variations. CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> show large short term variability, and large diurnal signals during the warm seasons, which attenuate with the increase of sampling height. The trends calculated from this dataset, over the period August 2005 to December 2008, are 2.02±0.46 ppm/year for CO<sub>2</sub> and -23.2±2.5 per meg/year for O<sub>2</sub>/N<sub>2</sub>. CH<sub>4</sub>, CO and N<sub>2</sub>O show also higher variability at the lower sampling levels, which in the case of CO is strongly seasonal. Diurnal variations in CH<sub>4</sub>, CO and N<sub>2</sub>O mole fractions can be observed during the

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warm season, due to the periodicity of vertical mixing combined with the diurnal cycle of anthropogenic emissions. We calculated increase rates of  $10.1 \pm 4.4$  ppb/year for  $\text{CH}_4$ ,  $(-8.3) \pm 5.3$  ppb/year for CO and  $0.67 \pm 0.08$  ppb/year for  $\text{N}_2\text{O}$ .  $\text{SF}_6$  shows only few events, and generally no vertical gradients, which suggests that there are no significant local sources. A weak  $\text{SF}_6$  seasonal cycle has been detected, which most probably is due to the seasonality of atmospheric circulation.  $\text{SF}_6$  increased during the time of our measurement at an average rate of  $0.29 \pm 0.01$  ppt/year.

## 1 Introduction

Atmospheric measurements are a tool to quantify greenhouse gas fluxes into and out of the atmosphere, and to understand the underlying processes. Traditionally, most of the atmospheric measurement stations were remotely located. Continental stations were avoided because the large concentration variability in the vicinity of strong sources makes the data difficult to interpret.

Tans (1991) proposed a strategy to address the need of continental measurements, overcoming the main problems associated with them, by measuring  $\text{CO}_2$  and other gas species on tall towers. To infer fluxes at regional level, it is useful to sample close to the earth surface (in the planetary boundary layer), where the proximity to sources and sinks results in large signals with high temporal resolution. If the gases are measured at sufficient height above ground (ideally a few hundred meters to avoid local influences), the signal integrates fluxes over a footprint on the order of 500 to 1000 km around (Gloor et al., 2001). Sampling continuously from different heights above ground allows one to separate the local from regional signals (Gloor et al., 2000).

Following this strategy, in 1992 NOAA-CMDL (now NOAA-ESRL GMD) started a measurement program in North-America using 300–500 m tall towers (Bakwin et al., 1995, 1998). Also in 1992, measurements from a tall tower at Tsukuba, Japan (Inoue and Matsueda, 2001) were started. In Europe first tall tower measurements were brought into operation at Cabauw, Netherlands in 1992 (Vermeulen et al., 1997),

Hegyhátsál, Hungary in 1994 (Haszpra et al., 2001), and Norunda, Sweden in 1994 (Lundin et al., 1999).

The need to better determine the distribution of sources and sinks of greenhouse gases became more imperative following the ratification of the Kyoto Protocol. Inverse modeling studies identified the lack of continental stations as a strong limitation in resolving the longitudinal fluxes distribution (Fan et al., 1998; Prentice et al., 2000; Schimel et al., 2001; Gloor et al., 2000).

In this context, the EU-funded project CHIOTTO (Continuous High-precision Tall Tower Observations of Greenhouse Gases in Europe, EVK2-CT-2002-00163) was launched in 2002, with the mission to build a coherent infrastructure for continuous monitoring of greenhouse gas concentrations across Europe above the surface layer (Vermeulen et al., 2004). The approach of the project was to measure continuously the mole fractions of CO<sub>2</sub>, and other greenhouse gases or species related to the carbon cycle like CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>, at different heights in the boundary layer, using tall towers. The mole fraction data coupled with information about atmospheric transport (inverse modeling technique) are used to obtain regionally representative greenhouse gas flux estimates for Europe. One of the strengths of the CHIOTTO project was to create a harmonized monitoring network, for which partial standardization of the equipment and of the measurement procedures was required. The target precision of the measurements was common for all partners and was established taking into account the WMO recommendations (WMO – GAW 161, 2005). CHIOTTO incorporated the already existing European tall tower stations and added new ones (Moncrieff et al., 2009; Vermeulen et al., 2009; Thompson et al., 2009; Haszpra et al., 2001). Another tall tower station was set up in Siberia (Kozlova et al., 2009), which, although not part of the CHIOTTO network, had many similarities in terms of technical design to the CHIOTTO towers.

MPI-BGC (Max Planck Institute for Biogeochemistry, Jena, Germany) was responsible for setting up two of the CHIOTTO tall tower monitoring stations, one at Ochsenkopf, Germany (Thompson et al., 2009), and one near Bialystok, in Eastern Poland, the

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subject of this paper. For the new station at Bialystok, an analysis system for quasi-continuous, in-situ measurements of CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> mole fractions and O<sub>2</sub>/N<sub>2</sub> ratio was designed and built based on commercially available analyzers. The challenge was to obtain a reliable automatic system that can run continuously with very little maintenance, and at the same time fulfil the high precision requirements for all the measured species. The tall tower station Bialystok (BIK) became operational in August 2005, continuing to the present. The system measures air sampled from five heights of the tower, between 5 and 300 m above ground. The measurement instruments are: an Oxzilla FC-2 O<sub>2</sub> fuel cell analyzer, a LiCor 7000 NDIR (non-dispersive infrared) CO<sub>2</sub> analyzer and an Agilent 6890 gas chromatograph set up for CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> analysis.

A comprehensive description of the measurement setup can be found in Popa (2008). In this paper we present the main technical aspects, which can be helpful for interpreting the measurement data and for comparing them with data from other stations. We describe the instrumental setup, the measurement and calibration procedures, and the quality check means employed. We also present the time series of the in-situ measurements during the period 2005–2008, and discuss the typical variability patterns.

## 2 Methods

### 2.1 The Bialystok station

The BIK measurement station was set up at a pre-existing television tower owned by TP EmiTel in Eastern Poland (53°13′ N, 23°01′ E, 183 m a.s.l.). The neighbouring area within a few hundreds of kilometres around the tower is flat, with an elevation above sea level of about 150 m. The land is mostly covered by crops and grasslands, with patches of forest and wetlands. The nearest town, Bialystok, with about 300 000 inhabitants, is situated about 20 km SE of the tower; the metropolitan area of Warsaw lies more than

160 km SW of the tower. Excluding Bialystok, the mean population density within a 50 km radius around the tower is below 60 inhabitants/km<sup>2</sup>. Also there is no significant industry in the neighbouring vicinity. According to Henne et al. (2008), BIK is classified as a rural background site.

5 The climate is continental, with large differences between summer and winter temperatures. The movement of air masses is not altered by high obstacles (e.g. mountains) thus it follows the general average west-east pattern of this latitude. The average influence area for the air sampled at Bialystok tower at 300 m above ground, as calculated for the year 2005 using the COMET transport model (Vermeulen et al., 2006), is  
10 illustrated in Fig. 1.

## 2.2 Measurement setup

Mole fractions of CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> and the O<sub>2</sub>/N<sub>2</sub> ratio are measured in-situ, quasi-continuously, meaning a sample point every 3 min for CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>,  
15 and every 14 min for the GC species. The main part of the measurement system is installed at the base of the tower, inside a thermally controlled laboratory container ( $\pm 2^\circ\text{C}$ ). There are two almost independent modules; one of them measures CO<sub>2</sub> mole fraction and O<sub>2</sub>/N<sub>2</sub> ratio, and the other measures the mole fractions of CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> by a gas chromatographic method. The connection between the two modules consists in sharing some of the calibration gases, which requires partial coordination.

20 The system is designed to measure alternately air sampled from five heights of the tower: 5, 30, 90, 180 and 300 m. The air inlets are fixed on the tower at these heights, and atmospheric air is collected continuously by pumps installed inside the measurement container. From each sampling height, there are dedicated inlet lines for each of the two measurement modules. Only one sampling height is selected at a time, independently for each of the two measurement systems, but the air flow is continuously  
25 maintained through all the lines. The air from the selected height is cryogenically dried to a dewpoint of about  $-80^\circ\text{C}$ , before being directed to the gas analysers.

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## 2.2.1 CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> measurement

The CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> measurement system has been developed having as starting point the technique introduced by Stephens et al. (2001, 2007) and the further experience achieved from the first setup of the tall tower station at Ochsenkopf, Germany. The gas flow diagram of the CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> measurement system is shown in Fig. 2. CO<sub>2</sub> and O<sub>2</sub> mole fractions are measured successively from the same air sample with a LiCor 7000 non-dispersive infrared (NDIR) CO<sub>2</sub> analyzer and an Oxzilla FC-2 (Sable Systems) oxygen fuel cell analyzer.

A peculiarity of atmospheric oxygen measurements is that the results are reported as O<sub>2</sub>/N<sub>2</sub> ratio and not as mole fraction, because the O<sub>2</sub> mole fraction will be significantly influenced by variations in other species (notably CO<sub>2</sub>), possibly leading to erroneous conclusions about O<sub>2</sub> fluxes. O<sub>2</sub>/N<sub>2</sub> variations, in contrast, reflect better the fluxes of oxygen in and out of the atmosphere (Keeling and Shertz, 1992). The variations in O<sub>2</sub>/N<sub>2</sub> are expressed in “per meg”, a relative unit defined by comparison with an arbitrary standard (Manning and Keeling, 2006):

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

In our setup, the O<sub>2</sub>/N<sub>2</sub> ratio is calculated using the measured O<sub>2</sub> mole fraction, and corrected for the CO<sub>2</sub> dilution effect using measured CO<sub>2</sub>, according to the following formula:

$$\delta O_2/N_2(\text{per meg}) = \frac{\Delta X_{O_2}(\text{ppm}) + (CO_2 - CO_{2\text{ref}}) \times X_{O_2}^0}{X_{O_2}^0 \times (1 - X_{O_2}^0)} \quad (2)$$

where  $\Delta X_{O_2}$  (ppm) is the measured O<sub>2</sub> mole fraction, relative to a scale specific reference;  $X_{O_2}^0 = 0.20946$  (reference mole fraction of oxygen in air);  $CO_{2\text{ref}} = 363.29$  ppm (specific to SIO scale).

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The measurement for both CO<sub>2</sub> and O<sub>2</sub> is differential, which means that the sample is measured in parallel with a reference gas from a high pressure cylinder (“Working tank”) and the difference between the sample and the reference is used to compute the mole fractions. The sample and reference lines are maintained at the same pressure by a differential pressure controller (MKS 250E) coupled with a differential pressure sensor (MKS 223BD) and a solenoid valve (MKS 248A). The O<sub>2</sub> and CO<sub>2</sub> analyzers are installed inside a thermostated chamber (±0.1°C) to avoid temperature variations influencing the measurement.

A routine calibration takes place every 40 h using air from a set of four high pressure cylinders with mole fractions spanning the atmospheric range. The values for the calibration gases were assigned by MPI-BGC laboratories, and are traceable to the NOAA-ESRL GMD X2005 scale for CO<sub>2</sub> and to the Scripps Institution of Oceanography (SIO) scale for O<sub>2</sub>/N<sub>2</sub>. Only for CO<sub>2</sub>, there is a more frequent “Zero” calibration, which corrects for possible short term drifts in the baseline response. The name of this gas does not mean that it has zero CO<sub>2</sub> mole fraction (actually the Zero calibration gas has a CO<sub>2</sub> mole fraction in the normal atmospheric range), but that it is being used to correct the zero term of the analyser’s response function (in our case, a quadratic fit). Air from a “Target” cylinder is analyzed every few hours to check the stability of the system. All high pressure air cylinders used are Luxfer type P2806Z, made from Aluminium alloy, with a volume of 50 L. We use cylinder valves Rotarex-Ceodeux type D20030163 (brass, PCTFE seat) and cylinder pressure regulators Scott Specialty Gases type 51-14C (high purity, two stages, Ni-platted brass, SS diaphragm).

Oxygen measurements are particularly sensitive because the oxygen content can be altered inside the measurement system by various fractionation phenomena (Keeling et al., 1998a, 2007; Manning, 2001; Sturm et al., 2006). For example, oxygen tends to accumulate in regions with lower temperature, higher humidity or higher pressure. The measurement strategy had therefore to be adapted to minimize oxygen fractionation effects and to make possible their monitoring. For example, the calibration cylinders are stored horizontally inside a thermally insulated box, in order to minimise gravimetric and

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thermal oxygen fractionation phenomena inside the cylinders. The pressure, flow and temperature gradients which cannot be avoided are maintained as much as possible stationary in time. No plastic is used within the gas flow paths, because the  $O_2/N_2$  ratio could change due to differential permeation. In order to monitor possible fractionation inside the tee-junctions of the main sampling lines (Manning, 2001), additional “control” sampling lines without tee-junctions have been installed at two heights of the tower (30 m and 300 m) for comparison with the main sampling lines.

## 2.2.2 Gas chromatographic measurement

The gas chromatographic measurement of  $CH_4$ ,  $CO$ ,  $N_2O$  and  $SF_6$  has as starting point the method implemented by Worthy et al. (2003) at the Canadian baseline stations, and the initial setup of the measurement at Ochsenkopf tall tower station (Jordan et al., 2005).  $CH_4$  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 scheme of the gas chromatograph is shown in Fig. 3, and Table 1 lists the main parameters of the setup. Appendix 1 contains a detailed description of the chromatographic method, allowing to reproduce the measurement.

The sample air is measured alternately with a reference gas from a high pressure cylinder, and the ratio between the sample peak and the bracketing reference peaks is used to compute the sample mole fraction. This procedure corrects most of the sensitivity variations on time scales longer than a few minutes. The best precision for mole fraction calculations in the case of  $CH_4$  and  $N_2O$  is obtained when using the peak area, whilst for  $CO$  and  $SF_6$  the calculation using the peak height leads to better results (Popa, 2008).

A calibration takes place every five days using air from a set of four high pressure cylinders covering the atmospheric range, and a “Target” cylinder is analyzed every few hours to check the stability. The values for the calibration gases were assigned by MPI-

BGC laboratories, and are traceable to internationally recognized scales maintained by NOAA/ESRL GMD. The gas cylinders, cylinder valves and cylinder pressure regulators are the same types as the ones used for the CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> measurements.

The support gases used are as follows. H<sub>2</sub> (for the FID flame) is supplied from a high pressure cylinder (purity 99.999%) and is purified using Molsieve 13X. Zero air (for the FID flame) is produced by a Parker 75-83 zero air generator, and purified using a self-made purifier containing Molsieve 13X and Sofnocat. N<sub>2</sub> (carrier gas for the FID) is produced by a Parker UHP 76-94 generator, and purified by a NuPure<sup>®</sup> Eliminator<sup>®</sup> CG purifier (00040-CG-VR4-PF). ArCH<sub>4</sub> (carrier gas for ECD) is supplied from a high pressure cylinder (5% CH<sub>4</sub> in Ar, ECD quality) and purified by a NuPure<sup>®</sup> Eliminator<sup>®</sup> CA purifier (00040-CA-VR4-PF).

### 2.2.3 Meteorological measurement

Meteorological parameters are measured at different levels on the tower and the data are transmitted to the main Labview™ program (see below) by a CAN-Bus system. The meteorological data are registered in the data files every 90 s, together with the CO<sub>2</sub> and O<sub>2</sub> data. The measured parameters are:

- wind speed and direction at 75 m, 300 m
- atmospheric pressure at 30 m, 300 m
- atmospheric temperature at 5 m, 30 m, 90 m, 180 m, 300 m
- atmospheric humidity at 30 m, 300 m

### 2.2.4 Software

The measurement system operates unassisted, controlled by a custom written Labview™ program. The program controls the valve switching according to the preset

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measurement sequence, acquires data from the analysers and the system diagnostic parameters (flows, pressures, temperatures), and calculates in real time the CO<sub>2</sub> mole fraction and O<sub>2</sub>/N<sub>2</sub> ratio. The Labview™ program also performs a first level quality check and writes the measurement result files. The gas chromatograph has its own software (Agilent Chemstation) which controls the measurement according to the pre-defined method, and computes the area and height of the peaks. The reports created by Chemstation are read into the Labview™ software which computes the final calibrated mole fraction results. A computer connection made by Symantec pcAnywhere™ software via ISDN allows remote control of the system and data transfer to MPI-BGC.

### 2.2.5 Flask sampling

Besides the quasi-continuous measurement, flask samples are filled regularly and sent for analysis at the MPI-BGC laboratory. This provides the possibility to measure additional species (H<sub>2</sub>, Ar/N<sub>2</sub>; <sup>18</sup>O and <sup>13</sup>C in CO<sub>2</sub>), and constitutes at the same time an important means for quality checking the in-situ measurement. The automated flask sampling apparatus (National Institute of Water & Atmospheric Research, New Zealand) is fully independent from the main in-situ measurement system. Air is sampled via dedicated air inlet lines from 30 and 300 m, and dried cryogenically to a dew-point of about -80°C. We use 1 L glass flasks equipped with two PCTFE sealed valves (Normag, Ilmenau, Germany), preconditioned with dried air at 1.8 bar in MPI-BGC laboratory. The flasks are filled in pairs, to an absolute pressure of 1.6–1.8 bar. Regular sampling takes place about once per week, at 15:00 local time, from the 300 m height. Samples from the 30 m height are only filled during special events.

### 2.2.6 Quality check means

A series of quality check means have been implemented for both real-time monitoring and posterior processing. First, a large number of system parameters are recorded every 90 s, together with the raw analyzers' data: the signals from 55 pressure sen-

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sors, 5 temperature sensors and 2 flow sensors, additional diagnostic information from analysers, and the status of the electronic valves. These parameters are used by the Labview™ software to take decisions for the real-time calibration, and used further for the final quality check.

5 The “Target” measurements are used to signal possible problems and to evaluate the long term performance of the measurement system in terms of precision and stability. The estimation of analytical precision based on the target measurements is presented in Sect. 3.1.2. Intercomparisons using flask samples analysed at MPI-BGC and analyses from “round-robin” high pressure cylinders are used to monitor measurement  
10 accuracy; some results of these intercomparisons are presented in Sect. 3.1.3.

There are other means to check specific issues as follows. (i) Air sampled via the “control” lines (see Sect. 2.2.1) is measured every few hours and the results are compared with the ones corresponding to the main sampling lines from the same heights. This comparison has a double purpose: it may indicate an eventual problem (e.g. a  
15 broken sampling tubing) and it is a way to detect eventual oxygen fractionation. (ii) The measurement from each sampling height or gas cylinder is performed a few times in succession, in order to detect incomplete flushing of the common gas paths. (iii) The Working tank mole fractions of oxygen, computed after every calibration, are monitored in order to detect eventual evolution of oxygen inside cylinders.

## 20 **3 Results and discussion**

### **3.1 Data coverage and quality**

#### **3.1.1 Data coverage**

The in-situ measurements of CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> were started in August 2005 and they have continued to the present, with two gaps (of about one  
25 month each) in 2006 due to technical problems. Between March and November 2008,

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the CH<sub>4</sub> measurements from all sampling levels except for the 5 m one were affected by a presumed leak in the system and were flagged during post-processing as “bad”. The O<sub>2</sub>/N<sub>2</sub> data between June and November 2008 show large noise probably due to an instrumental problem; they were not eliminated during the quality check but their potential use is limited by the large noise. The flask sampling was started in November 2005 and had one major interruption of about four months during the summer of 2008.

### 3.1.2 Precision

The long term reproducibility of the Target cylinder measurement is used as a quantitative estimator of the average analytical precision. Table 2 summarizes the standard deviations of the Target measurements, over the whole measurement interval 2005–2008, for each gas species. For O<sub>2</sub>/N<sub>2</sub>, the average precision was estimated excluding the time interval between June and November 2008. The average precisions at Białystok are comparable with the precision goals of the CHIOTTO project.

The measurement precision compared with the typical signal amplitude, which can be considered as a signal to noise ratio, can be more suggestive than the absolute value of precision. This is illustrated in Fig. 4, where we compare the measurement of air from the sampling height with the lowest natural variability (300 m) with the measurement of the target gas. In the case of CO<sub>2</sub>, CH<sub>4</sub> and CO, the target variability is insignificant compared to the atmospheric short term signals. For N<sub>2</sub>O and SF<sub>6</sub>, the target variability and the atmospheric signals are on the same order of magnitude most of the time, because the atmospheric variability is relatively small. This suggests that an improved analytical precision for these two species would be useful at this specific measurement location, if we want to distinguish better the short term signals.

### 3.1.3 Comparisons between in-situ measurement and flask samples

The comparison of in-situ measurements with flask samples filled at the same location and analyzed at the MPI-BGC laboratory is a valuable tool to estimate the accuracy

of the in-situ measurement. Because the flask sampling is not synchronized with the in-situ measurement, a direct quantitative comparison of discrete results is not appropriate. Therefore a statistical approach, using a large number of samples, is necessary.

The comparison procedure employed was as follows. Only those flasks were selected for which the nearest in-situ measurement sampling time from 300 m height was different by at most 2 h (for CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>) or 3 h (for CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>). Corresponding in-situ values were obtained by linear interpolation at the flask collection times, and the differences were computed between these interpolated values and the flask sample results. For each species, a t-test was performed to check if the average difference is significantly different from zero at a confidence level of 95%.

Table 3 shows for each species the mean difference between in-situ and flask results and its 95% confidence intervals (“CI 95%”), the standard error of the mean differences, and the result of the t-test. The standard error of the mean difference (“Difference error” in Table 3) was calculated as the standard deviation of the differences, divided by the square root of the number of flasks. The intervals for a 95% confidence level are given by the standard error of the mean multiplied by 1.96.

For CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, the mean differences between the in-situ and flask results were not statistically significant. The CH<sub>4</sub> difference of 0.82 ppb is however consistent with the results of intercomparisons of high pressure cylinder measurements, within the CarboEurope “Cucumber” programme. The average difference between the cylinder measurements made at BIK (analyses in 2007 and 2008) and at MPI-BGC laboratory was 0.92 ppb (Manning et al., 2009). This similarity between flasks and cylinders comparisons indicates a possible BIK CH<sub>4</sub> calibration scale offset, and necessitates further investigation.

The CO mean difference of  $-6.54 \pm 1.98$  ppb was found to be statistically significant. Comparisons made using the previously mentioned high pressure “Cucumber” cylinders showed a much smaller difference, of about  $-1.3$  ppb, thus a calibration scale bias cannot explain most of the difference observed from the comparison with flask samples. An increase of the CO mole fraction in stored flasks could be the reason. Such an

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increase, of about 0.047 ppb/day, has been observed in the same type of flasks, during storage tests performed at MPI-BGC. The flasks sampled at Bialystok were stored on average  $80.8 \pm 46.7$  days, which could explain a difference of about  $3.8 \pm 2.2$  ppb. However, more tests are necessary in order to definitely exclude any problem within the air sampling sub-system of the in-situ measurement.

According to the t-test, the SF<sub>6</sub> mean difference between the in-situ measurement and flask samples is also statistically significant. However, this difference is very small ( $-0.02$  ppt), therefore will not represent a problem for interpreting the measurement data.

For each species, the differences between in-situ measurements and flask samples were tested for possible dependence on mole fraction, but no significant correlations were found.

## 3.2 General characteristics of the time series

### 3.2.1 CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>

Variations of atmospheric CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> are largely anti-correlated, because during the processes of respiration, photosynthesis and fossil fuel combustion O<sub>2</sub> is consumed when CO<sub>2</sub> is produced and vice versa. Therefore they will be discussed together in what follows.

The CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> records (Fig. 5) show anti-correlated trends and seasonal cycles, and superimposed short term (diurnal and synoptic scale) variations which are also largely anticorrelated. The patterns and amplitude of short term variations depend on season and sampling height. During the warm seasons, the diurnal cycles with amplitude of up to 70 ppm for CO<sub>2</sub> and 300–400 per meg for O<sub>2</sub>/N<sub>2</sub> clearly dominate the variability at the sampling levels close to the ground. The amplitude of the diurnal signal gradually decreases with the sampling height, so that at 300 m above ground level it is comparable with the amplitude of the synoptic scale variations. During the cold season, the synoptic scale events become the dominant type of variability

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at all sampling heights. The synoptic events (which dominate the variability of the mole fractions in the air sampled at 300 m) have the same order of magnitude throughout the year; therefore the short term variability of the data series from 300 m does not show large seasonal differences. Vertical gradients are largest in summer time, but do appear in all seasons. During summer, the vertical gradients follow a daily cycle, whilst during winter they do not have a regular evolution.

The relatively high variability of the CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> data series is characteristic of continental measurements, due to the proximity of strong sources and sinks. The nocturnal enhancements of CO<sub>2</sub> at the lower sampling levels indicate strong local and regional sources.

### 3.2.2 CH<sub>4</sub>

The CH<sub>4</sub> record (Fig. 5) is characterized by high short term variability, on the order of 200–300 ppb. Strong diurnal signals dominate the variability at low sampling levels during summer. The synoptic signals are stronger during winter than during summer. The difference between the seasons consists mainly in differences in the data variability and in the vertical gradients. The large vertical gradients, with generally higher mole fractions at lower sampling levels, suggest the existence of strong local to regional sources.

### 3.2.3 CO

CO (Fig. 5) has a seasonally varying atmospheric lifetime primarily caused by seasonality in OH radical, the main CO sink. This is reflected in the observed mole fractions at BIK. The seasonality is mostly manifested as difference in variability, although a difference in “baseline” can also be observed. During summer, the diurnal variations and the synoptic signal have comparable amplitudes. This is unlike the behaviour of CO<sub>2</sub> and CH<sub>4</sub> mole fractions, for which during summer the diurnal variations are dominant. The strong winter time CO signals, often above 600 ppb, are likely due to increased anthro-



pogenic emissions combined with a longer CO lifetime during the cold season. Vertical gradients with higher mole fraction at lower sampling levels are apparent throughout the year but the differences between the sampling levels are usually small compared to the general data variability. This indicates that the main CO sources are not local, but distributed over a wider area.

### 3.2.4 N<sub>2</sub>O

The N<sub>2</sub>O time series is shown in Fig. 5. The summer time variability of N<sub>2</sub>O is dominated by the diurnal signal, similarly to CO<sub>2</sub> and CH<sub>4</sub>. Vertical gradients with higher mole fractions at lower sampling levels show the existence of local to regional sources. The variability is relatively small, with typical signals of a few ppb above the background, and slightly larger during the warm seasons.

### 3.2.5 SF<sub>6</sub>

The SF<sub>6</sub> time series (Fig. 5) has little short term variability, with only few “events” reaching a few ppt above the background mole fraction. Unlike the other species measured at Bialystok, during most of the pollution events observed, the vertical gradient was either absent or reversed, that is, the highest sampling height showed the largest signal. These features, together with the general absence of a discernible vertical gradient, suggest that there are no significant SF<sub>6</sub> sources in the vicinity of the station.

## 3.3 Trends and seasonal cycles

### 3.3.1 Data processing

In order to derive the long-term trends and seasonal amplitudes, the Bialystok data have been processed as follows. Only the afternoon data have been selected, that is, between 11:00 and 16:00 GMT, which means 13:00–18:00 local time (during summer). Weekly trimmed averages are calculated from the selected data excluding the highest

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and the lowest 10% of the data. The function shown below, consisting of a linear trend and a three harmonics seasonal cycle is fitted to the weekly averages by a linear least squares method.

$$f(x) = a_0 + a_1x + \sum_{n=1}^3 \left( b_n \sin \left( \frac{2\pi}{365} nx \right) + c_n \cos \left( \frac{2\pi}{365} nx \right) \right) \quad (3)$$

where  $x$  is the time in days since the start of the measurements;  $a_0$ ,  $a_1$ ,  $b_n$  and  $c_n$  are the fitted coefficients.

The trend for each species is calculated by fitting the function described above to the data from 300 m height, which has the lowest short term variability. For the trend estimation we use a robust linear least squares method (which reduces the weight of outliers using bisquare weights; Matlab Curve Fitting Tool 1.2). The time series of different sampling heights are then de-trended using the trend previously calculated, and the harmonic function is fitted (non-robust) in order to obtain the seasonal curves. In Figs. 6 and 7, the seasonal cycles are plotted normalized to the mean of one “reference” sampling height, in order to preserve the relative position of the curves corresponding to different heights. The uncertainties specified below for the trend values are given by the 95% confidence intervals.

### 3.3.2 Trends and seasonal cycles of CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>

The CO<sub>2</sub> average growth rate between July 2005 and December 2008, estimated from the Bialystok record, was 2.02±0.46 ppm/year. This result is consistent with the recent World Meteorological Organization (WMO) estimates of the global CO<sub>2</sub> increase during 2007 (1.9 ppm) and over the last ten years (2 ppm/year) (WMO Greenhouse Gas Bulletin No. 4, 2008). O<sub>2</sub>/N<sub>2</sub> decreased during the same period with an average rate of 23.2±2.5 per meg/year. For comparison, Thompson et al. (2009) observed at another European station (Ochsenkopf, Germany) a smaller O<sub>2</sub>/N<sub>2</sub> decrease rate of 16.3±3.1 per meg/year (using data covering a partly different time interval, July 2006

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to July 2008). Another study (Kozlova et al., 2008), using data from Shetland Islands, United Kingdom (SIS), estimated an  $O_2/N_2$  decrease of 18.6 per meg/year over the period 2004 to 2008.

There are several large scale processes which involve absorption or emission of  $CO_2$  and  $O_2$  and which are characterized by seasonal variability: the land and ocean biosphere activity, the thermally induced variations of solubility in ocean water, and the seasonal patterns of atmospheric circulation. The seasonal variability of anthropogenic emissions is very small compared to the processes listed before. There is, however, an essential difference between the two species regarding the gas exchange between ocean and atmosphere. For  $CO_2$ , this exchange is buffered by chemical reactions in sea water, while oxygen is not affected. This translates into a large difference in equilibration time between the ocean and atmosphere for the two species: about one year for  $CO_2$  and about three weeks for oxygen (Broecker and Peng, 1982). As a consequence, the activity of the ocean biosphere and the thermally induced variations of solubility do not affect significantly the seasonal cycle of the atmospheric  $CO_2$ , while having a significant effect on the  $O_2$  seasonal cycle. The seasonal variation of atmospheric  $CO_2$  therefore is mainly due to the land biosphere and to the seasonal pattern of atmospheric circulation, while the seasonal variation of  $O_2/N_2$  has, in addition, an important oceanic component.

The oceanic component of the  $O_2/N_2$  seasonal cycle has been computed in previous works (e.g. Keeling et al., 1998b) by subtracting the land biosphere component from the total oxygen seasonal cycle. The land biosphere component is calculated based on the seasonal cycle of  $CO_2$ , assuming an average molar ratio between the oxygen and  $CO_2$  variations due to the land biosphere of  $-1.1$  (Severinghaus, 1995). The oceanic component of the oxygen signal calculated in this way is referred to as APO (Atmospheric Potential Oxygen) defined by Stephens et al. (1998). The simplified definition of APO (ignoring very minor influences from  $CH_4$  and  $CO$ ) is:

$$APO(\text{per meg}) = O_2/N_2(\text{per meg}) + 1.1 \times (CO_2(\text{ppm}) - 350) / 0.20946 \quad (4)$$

where 0.20964 is the standard mole fraction of  $O_2$  in air; 350 is an arbitrary reference

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CO<sub>2</sub> mole fraction (Stephens et al., 1998).

Figure 6 shows the three-harmonic seasonal cycles of CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and APO, corresponding to two sampling heights: 30 m and 300 m above ground level. Table 4 lists the trends and the characteristics of the seasonal cycles of all species measured in-situ at

5 Bialystok, and of APO.

CO<sub>2</sub> exhibits a seasonal cycle with a peak to peak amplitude of about 20 ppm for measurements from the 300 m level (blue line in Fig. 6), the amplitude increasing for lower sampling heights, up to about 25 ppm at 30 m (red line in Fig. 6). The lower sampling heights have higher seasonal amplitude due to the stronger influence from local CO<sub>2</sub> emissions during winter and from the CO<sub>2</sub> biosphere uptake during summer. The largest difference between the sampling heights can be seen during the cold season, but this could be due to our data processing method (only afternoon data have been considered, i.e. the time when the vertical mixing is strong, especially during summer). The minimum of the CO<sub>2</sub> seasonal cycle is in August, and there is a double maximum in December and in February-March. A possible explanation for the first maximum is enhanced heterotrophic respiration in autumn after the leaf fall, when the available quantity of fresh organic matter is higher. The second maximum could be due to an increase of gas exchange with the soil after the snow melted.

The O<sub>2</sub>/N<sub>2</sub> seasonal cycle is to a large degree anti-correlated with the seasonal cycle of CO<sub>2</sub>, even to the point of exhibiting corresponding double minima, the main drivers being processes which involve both species. The correlation is not perfect, due to the oceanic component of the O<sub>2</sub>/N<sub>2</sub> cycle which has no equivalent for CO<sub>2</sub>. The peak to peak amplitude of the O<sub>2</sub>/N<sub>2</sub> seasonal cycle is about 156 per meg (corresponding to 29.5 ppm in CO<sub>2</sub>) at 300 m, and 161 per meg (30.5 ppm CO<sub>2</sub>) at 30 m above ground. The timing of the O<sub>2</sub>/N<sub>2</sub> maximum and minima mirrors those of CO<sub>2</sub>.

The APO seasonal cycle has a peak to peak amplitude of 49 per meg at 300 m, and 43 per meg at 30 m. Compared to the total amplitude of the O<sub>2</sub>/N<sub>2</sub> seasonal variation, the oceanic component represents 31% (at 300 m) and 27% (at 30 m). The APO minimum is in March, and the maximum in August–September.

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### 3.3.3 Trends and seasonal cycles of CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>

Figure 7 shows the three-harmonic seasonal cycles of CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> from different sampling heights.

For CH<sub>4</sub>, in contrast to the other species, the trend was calculated using the data from the lowest sampling height, because for a large part of 2008 the data for the other sampling heights are missing. The average increase rate over the whole period (1 August 2005–31 December 2008) is  $10.1 \pm 4.4$  ppb/year. It is evident from the large uncertainty that the calculated trend for CH<sub>4</sub> is not very well defined, which is due to the shortness of the data series combined with the relatively large variability. The CH<sub>4</sub> trend calculated at Bialystok is very close to the results from another recent study (Thompson et al., 2009), which estimated the increase rate at two other European locations (Ochsenkopf, Germany, OXK, and Shetland Islands, United Kingdom, SIS). Thompson et al. (2009) calculated an increase rate of 9.8 ppb/yr and 10.4 ppb/yr for OXK respectively SIS, using data covering partly the time interval of this work. Both our results and those of Thompson et al. (2009) are higher than the recent global increase of about 6 ppb/year, estimated from WMO-GAW global greenhouse gas monitoring network (WMO, 2008).

The peak to peak amplitude of the CH<sub>4</sub> seasonal cycle ranges from 64 ppb at 300 m to about 88 ppb at 30 m above ground, with the maximum in December and a relatively sharp minimum in May–June. The curve corresponding to the 300 m sampling height has a different shape compared to the other heights, having the absolute maximum in November followed by a slow decrease and a secondary maximum in March. In comparison to the other species, CH<sub>4</sub> starts rising earlier after the spring minimum, a fact which can likely be attributed to temperature enhanced emissions from wetlands and to burning of agricultural residues during summer and autumn. The large differences between the sampling heights, especially during winter, indicate the existence of significant regional sources.

The CO trend calculated from this data set is  $(-8.3 \pm 5.3)$  ppb/year. Considering the

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large intra- and inter-annual variability of CO and the shortness of the data series, this decreasing trend result might be not representative.

The CO seasonal cycle has an amplitude of about 130 ppb at 300 m, and increases to about 200 ppb at lower sampling heights. The maximum is in January, slightly delayed compared to the maximum of CH<sub>4</sub>. In autumn CO starts increasing later than CH<sub>4</sub>, the low CO mole fraction level season is longer, and the minimum of the seasonal cycle is about two months delayed in comparison with CH<sub>4</sub>. The CO seasonal cycle reflects the seasonality of its main sink, the reaction with OH radical (which is in greater abundance in the summer). As with CH<sub>4</sub>, the winter time large differences between the sampling heights indicate significant local sources.

N<sub>2</sub>O increased during our measurement period with an average rate of 0.67±0.08 ppb/year, a value lower than other recent estimates. The global increase estimated from the WMO-GAW global greenhouse gas monitoring network was 0.8 ppb in 2007, and 0.77 ppb when averaged over the last ten years (WMO, 2008). Thompson et al. (2009), estimated increase rates of 0.99 ppb/year and 0.95 ppb/yr for OXK and SIS, respectively. We suspect that the difference between the estimates at Bialystok and other sites is partly due to the irregular variability combined with the shortness of the data set.

The N<sub>2</sub>O seasonal cycle at Bialystok has a relatively small amplitude of about 0.7 ppb at 300 m, which increases to 0.8 ppb at 30 m. The different sampling heights have different shapes, but the tendency is to have a double minimum in June and September, and a double maximum in November and March. This feature is most visible at the highest sampling height. The rather complicated seasonal cycle is due to interfering influences of different sources and sinks, some of the potential control factors being the soil freezing-thawing cycle and the intermittent use of fertilizers in agriculture. Besides these, N<sub>2</sub>O seasonal cycle includes most probably a component due to atmospheric (including stratospheric) circulation (Levin et al., 2002) and possibly a component due to the seasonality of the oceanic source (Nevison et al., 2004). A striking feature is the offset between the lowest sampling height (5 m) and the others, quite constant

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through the year. This offset suggests a strong and relatively constant source in the near vicinity, possibly from the agricultural areas.

SF<sub>6</sub> increased constantly during the time of our measurement, with an average rate of 0.29±0.01 ppt/year. SF<sub>6</sub> shows a weak but statistically significant seasonal cycle.

5 The SF<sub>6</sub> seasonal cycle is bimodal, with an absolute maximum in November and a secondary maximum in March, and minima in May–June and September. The amplitude varies between 0.09 and 0.14 ppb for different sampling heights, but the differences between the sampling heights are not statistically significant. SF<sub>6</sub> has no known seasonally varying sources, thus the observed seasonal cycle most probably  
10 reflects the seasonal evolution of atmospheric circulation. If we compare the shape of the SF<sub>6</sub> seasonal cycle with the other species, we can observe some similarities. The CH<sub>4</sub> and N<sub>2</sub>O seasonal shape at 300 m reproduce somewhat attenuated the location of the three “peaks” from the SF<sub>6</sub> curve. This suggests atmospheric circulation as one of the factors influencing the shape of the seasonal cycles, especially at the highest  
15 sampling height. Our result is consistent to the findings of Levin et al. (2002). Using aircraft measurements across the Eurasian continent, Levin et al. (2002) observed correlated seasonal cycles in SF<sub>6</sub> and N<sub>2</sub>O, and indicated atmospheric transport patterns as probable cause, with a significant contribution from stratosphere-troposphere exchange.

## 20 3.4 Diurnal variations

### 3.4.1 Diurnal variations of CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>

The average summer-time diurnal variation of CO<sub>2</sub>, calculated for the year 2006, is shown in Fig. 8a. During the warm season, atmospheric vertical mixing follows a diurnal periodicity, which overlaps with the diurnal cycle of the release and uptake of CO<sub>2</sub>  
25 by respiration and photosynthesis of the biosphere, and with the diurnal cycle of the human activity. During 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.

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Thus the decrease in mole fraction due to photosynthesis is relatively minor, due to dilution in the air column. During night, photosynthesis stops and vertical mixing is weak, while respiration continues. The  $\text{CO}_2$  emitted by respiration accumulates near ground level. Thus strong increases of the mole fraction near the ground and also strong vertical gradients can be observed. Anthropogenic emissions also add a small contribution to the observed  $\text{CO}_2$  summer night-time increase.

The variations of atmospheric oxygen are directly linked to the variations of  $\text{CO}_2$ , because oxygen is consumed when  $\text{CO}_2$  is produced (and vice versa) by respiration and photosynthesis, or when fossil fuels are burned. The diurnal cycle of  $\text{O}_2/\text{N}_2$  ratio is therefore largely anti-correlated with the diurnal cycle of  $\text{CO}_2$ .

In the cold season respiration is reduced and photosynthesis declines to non-significant level. Anthropogenic emissions and land biosphere respiration are of 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. Figure 9 shows the evolution over the year of the monthly averaged diurnal cycles of  $\text{CO}_2$  and  $\text{O}_2/\text{N}_2$ . It can be observed that the average diurnal variation decreases in amplitude or even becomes indistinguishable during the cold months.

### 3.4.2 Diurnal variations of $\text{CH}_4$ , $\text{CO}$ , $\text{N}_2\text{O}$ and $\text{SF}_6$

Figure 8b–e presents the average summer-time diurnal cycles of  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\text{SF}_6$ . At the first view, the mole fractions of  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  follow a temporal pattern similar to  $\text{CO}_2$ . During day the vertical gradient is reduced by the strong vertical mixing of the air column. During night the vertical gradient increases and there is a strong accumulation at levels close to the ground.

There are however dissimilarities of the diurnal variations of different species, which reflect the differences in sources and sinks. The weak vertical gradient during day is opposite in sign for  $\text{CO}_2$  compared to  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$ . During day the net  $\text{CO}_2$  flux into the atmosphere is negative due to photosynthesis. Thus the air sampled closer to



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the ground (where photosynthesis occur) is depleted in  $\text{CO}_2$  compared to the higher levels. On the other hand,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  are being emitted near the ground level, which results into higher mole fractions at sampling heights closer to the ground, as can be observed in Fig. 8. Related to this is the night time evolution of mole fractions at 300 m sampling height. After the vertical mixing has diminished, the mole fraction of  $\text{CO}_2$  at 300 m shows a slight increase, because the input of air depleted in  $\text{CO}_2$  by photosynthesis declined. In the same time, the mole fractions of  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  at 300 m decrease because the upwards transport of the gases emitted near ground level drastically reduced.

A midnight (=02:00 local time) partial minimum can be observed in the  $\text{CO}$  mole fraction at the sampling levels close to the ground, bracketed by evening and morning maxima. This evolution is consistent with the temporal variation of human activities. The decrease of the accumulation rate of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  near the ground around midnight can also probably be related to the decrease of the anthropogenic emissions. Around 06:00 (=08:00 local time) the  $\text{CO}_2$  mole fraction near the ground decrease due to the joint effect of vertical mixing and photosynthesis onset. The morning decrease of the mole fraction of the other species is delayed because the decrease due to vertical mixing is partly counteracted by an increase of anthropogenic emissions.

Although part of the  $\text{CO}_2$  accumulated by night is due to anthropogenic emissions, the land biosphere respiration is the main  $\text{CO}_2$  source during summer. A rough estimation of the proportion of the anthropogenic  $\text{CO}_2$  in the total night time accumulation can be done by comparing the amplitudes of the vertical profiles of  $\text{CO}$  and  $\text{CO}_2$ . The  $\text{CO}:\text{CO}_2$  ratio specific to anthropogenic emissions, estimated by different authors (e.g. Gamnitzer et al., 2006; Bakwin et al., 1998), ranges usually between 10 and 25 ppb:ppm for rural areas. Thus the lower limit of the average  $\text{CO}:\text{CO}_2$  ratio specific to anthropogenic emissions in this region can be reasonably assumed to be about 10 ppb:ppm. The maximum  $\text{CO}$  accumulation between 5 m and 300 m heights is about 25 ppb. This means that the anthropogenic  $\text{CO}_2$  accounts for up to 2.5 ppm from the maximum night time vertical gradient of about 25 ppm. Assuming a higher average

CO:CO<sub>2</sub> ratio for the anthropogenic emissions, for example 25 ppb:ppm, leads to an even smaller proportion of anthropogenic CO<sub>2</sub> from the total of 1 ppm, which is 4% from the total CO<sub>2</sub> accumulation.

An interesting feature visible in Fig. 8 is the strong correlation between the diurnal cycles of CH<sub>4</sub> and N<sub>2</sub>O, which suggest that the largest sources are either common or have a similar diurnal variation pattern. The CH<sub>4</sub>:N<sub>2</sub>O ratio calculated for different sampling heights varies between 32 (for 5 m) and 40.3 (for 300 m) and the correlation coefficients are higher than 0.96. Common sources for CH<sub>4</sub> and N<sub>2</sub>O could be industry and biomass burning. Sources with similar average diurnal pattern could be temperature dependent emissions from soil (N<sub>2</sub>O) and wetlands (CH<sub>4</sub>).

SF<sub>6</sub> shows a very weak diurnal variation and no accumulation during night, which supports the idea mentioned before, that there are no significant local SF<sub>6</sub> sources.

#### 4 Summary and concluding remarks

The Bialystok tall tower station for atmospheric measurements of greenhouse gases and related tracers has been running since 2005. The system is designed to measure in-situ, quasi-continuously CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> in air sampled at five heights of the tower, between 5 and 300 m above ground level. The gas analysers used are: a LiCor 7000 for CO<sub>2</sub>, an Oxzilla FC-2 for oxygen, and an Agilent 6890 gas chromatograph with FID and ECD detectors for CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>. Besides the in-situ measurements, flask samples are filled regularly and measured at Max-Planck Institute for Biogeochemistry for the same species and, in addition, for H<sub>2</sub>, Ar/N<sub>2</sub> and stable isotopes <sup>13</sup>C and <sup>18</sup>O in CO<sub>2</sub>.

In order to achieve the required precision while running unattended, the measurement system required careful optimization of gas handling and measurement procedures, as well as thorough quality check means. Some of the most important quality check means employed are: the system diagnostic parameters registered together with the mole fraction data, the measurements of the Target gases, and the inter-

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comparisons using flask samples and high pressure cylinders.

The evaluation of the measurement performance after more than three years led to overall satisfactory results. For example, the precision, estimated as the long term reproducibility of the Target measurements, is within or close to the project targets. The comparison between the in-situ and the flask sample results, used to check the accuracy of the in-situ measurements, revealed no statistical significant differences between the in-situ and the flask sample results for CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, and only a very small difference of 0.02 ppt for SF<sub>6</sub>. The same comparison, however, revealed a significant difference of about 6.5 ppb between the in-situ and the flask sample CO results. The suspected main cause for this difference is the evolution of CO in flask samples, but an error within the in-situ measurement system cannot be excluded without further investigation.

This measurement setup proved to be suitable for long term unattended running at a relatively remote station. For an even more remote location, however, the large demand of high pressure gas cylinders, the requirements for laboratory temperature stability, and the relatively high power consumption could be inconvenient.

From the record covering more than three years, it was possible to characterize the typical variability features of the species measured. Generally, CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub> and CO show large short term variability on diurnal and synoptic time scales. During summer, large diurnal variations dominate the variability at lower sampling levels. Synoptic variations are present at all sampling levels through the year, and are stronger during winter in case of CO. Large vertical gradients develop during all seasons, and follow a diurnal periodicity during warm seasons. N<sub>2</sub>O shows the same features as the species above, but its variability is relatively small, with typical signals of only few ppb above the background. During the warm seasons, the CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> short term variability at Bialystok is due mainly to the land biosphere photosynthesis and respiration, with a small contribution from fossil fuel burning. In case of CH<sub>4</sub>, CO and N<sub>2</sub>O, the diurnal pattern with morning and evening maxima correlated with the peaks of human activity suggests that anthropogenic emissions have an important contribution. SF<sub>6</sub>

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record shows only few signals, generally no vertical gradients and no accumulation near ground during stable nights. These features suggest that there are no significant SF<sub>6</sub> sources in the vicinity of the station.

Seasonal variations could be observed at Bialystok in all in-situ measured species.

5 The seasonal cycles of CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> are mainly due to the land biosphere activity, with an oceanic component contributing to the O<sub>2</sub>/N<sub>2</sub> cycle. CO seasonal cycle is strongly influenced by the seasonally variation of its main sink, the reaction with OH radical. CH<sub>4</sub> and N<sub>2</sub>O seasonal cycles suffer possibly multiple influences from land management, biomass burning and soil freezing/thawing cycles. SF<sub>6</sub> has not known  
10 seasonally varying sources, thus its seasonal cycle reflects probably the seasonality of atmospheric circulation.

As estimated from this dataset covering the period August 2005 to December 2008, the CO<sub>2</sub> increased with an average of 2.02±0.46 ppm/year while O<sub>2</sub>/N<sub>2</sub> decreased with an average of -23.2±2.5 per meg/year. The increase rate of CH<sub>4</sub> of 10.1±4.4 ppb/year  
15 is higher than recent estimates of the global CH<sub>4</sub> increase, but consistent with other results in Europe. The CO trend estimated from this dataset is (-8.3)±5.3 ppb/year, result which might not be significant considering the large variability combined with the shortness of the time series. N<sub>2</sub>O increased with a rate of 0.67±0.08 ppb/year, which is smaller than other estimates. SF<sub>6</sub> increased during the time of this measurement  
20 with an average rate of 0.29±0.01 ppt/year.

The measurement system at Bialystok contributes to the general expertise in the field of high precision atmospheric measurements. In particular, Bialystok is one of the few stations worldwide which include in-situ, quasi-continuous measurements of atmospheric oxygen. The knowledge about the measurement setup and quality, and  
25 about the specifics of the data at this sampling station will be useful for data users, for example when selecting data according to representativity for a specific study.

The measurement station at Bialystok is meant to be operated on long term, as part of the European atmospheric monitoring network. The mole fraction data, coupled with inverse models, will be used to derive regional and continental fluxes of greenhouse

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gases. Besides this long-term purpose, the quasi-continuous data offer the possibility to study processes occurring of various time scales. The large local biospheric signals will permit observing the evolution of the land biosphere, for example the reaction to extreme weather events or the response to global warming. On the other hand, the location on the Eastern limit of the highly populated area of Western Europe gives the opportunity to observe regional anthropogenic emissions. The presence of well-defined vertical gradients can help to distinguish between signals from the different influence areas of the different sampling heights. The flat surrounding area results in a relatively simple atmospheric circulation, which makes the model simulations for this site less difficult.

## Appendix A

### Description of the gas chromatographic method-170206.M

GC oven temperature (ECD columns): 76°C

Auxiliary oven temperature (FID columns): 60°C

Run time: 7.02 min

FRONT DETECTOR (FID)

Temperature: 175°C (On)

Hydrogen flow: 50.0 mL/min (On)

Air flow: 320.0 mL/min (On)

Mode: Constant makeup flow

Makeup flow: 5.0 mL/min (On)

Makeup Gas Type: Nitrogen

Flame: On

Lit offset: 1.0

BACK DETECTOR (ECD)

Temperature: 385°C (On)

Anode purge flow: 6.0 mL/min (On)

Mode: Constant makeup flow

Makeup flow: 5.0 mL/min (On)

Makeup Gas Type: Nitrogen

Adjust offset: 60.00

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AUX PRESSURE 3  
Gas Type: Nitrogen  
Initial pressure: 1.000 bar (On)

AUX PRESSURE 4  
Gas Type: Argon methane 5%  
Initial pressure: 3.000 bar (On)

AUX PRESSURE 5  
Gas Type: Argon methane 5%  
Initial pressure: 4.200 bar (On)

METHANISER  
Temperature: 385°C (On)

The remainder of the method, including the description of the valves, the time table and the integration parameters, is presented in Tables A1–A4.

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**Table 1.** GC measurement specifications.

	CH <sub>4</sub> and CO	N <sub>2</sub> O and SF <sub>6</sub>
Detector type and characteristics	FID, 175°C	ECD, 385°C
Oven temperature	Ni catalyst, 385°C H <sub>2</sub> flow 50 ml/min Air flow 320 ml/min 60°	76°C
Sample loop volume	15 ml	25 ml
Precolumn	SS, 4 ft, 1/8" O.D., Molsieve 5A, 80–100 mesh	SS, 6 ft, 3/16" O.D., Hayesep Q, 80–100 mesh
Column	SS, 4 ft, 1/8" O.D., Unibeads 1S, 60–80 mesh	SS, 12 ft, 3/16" O.D., Hayesep Q, 80–100 mesh
Carrier gas	N <sub>2</sub>	P5 (5% CH <sub>4</sub> in Ar)
Run time	7 min	7 min

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**Table 2.** Average precision of the measurement at Bialystok station, and the precision targets of CHIOTTO project.

Species	BIK average reproducibility (stdev)	CHIOTTO precision goal
CO <sub>2</sub>	0.08 ppm	0.05 ppm
O <sub>2</sub> /N <sub>2</sub>	4.8 per meg	5 per meg
CH <sub>4</sub>	1.7 ppb	2 ppb
CO	0.9 ppb	1 ppb
N <sub>2</sub> O	0.2 ppb	0.1 ppb
SF <sub>6</sub>	0.03 ppt	0.1 ppt

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**Table 3.** Results of the comparison between in-situ and flask sample results. Differences are in-situ minus flasks.

Species (unit)	No. flasks	Mean difference BIK-MPI	Difference error	CI 95%	t-test result
CO <sub>2</sub> (ppm)	211	0.02	0.06	−0.09...0.13	0
O <sub>2</sub> /N <sub>2</sub> (per meg)	154	1.59	1.52	−1.41...4.60	0
CH <sub>4</sub> (ppb)	148	0.82	0.65	−0.47...2.11	0
<b>CO(ppb)</b>	<b>168</b>	<b>−6.54</b>	<b>1.00</b>	<b>−8.52...−4.55</b>	<b>1</b>
N <sub>2</sub> O (ppb)	182	−0.003	0.028	−0.059...0.053	0
<b>SF<sub>6</sub> (ppt)</b>	<b>168</b>	<b>−0.020</b>	<b>0.004</b>	<b>−0.027...−0.014</b>	<b>1</b>

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**Table 4.** Trends and seasonal amplitudes for the species measured in-situ at Bialystok.

Species (unit)	Average growth rate	Seasonal ampl. at 300 m	Seasonal ampl. at 30 m	Data period
CO <sub>2</sub> (ppm)	2.02±0.46	20	25	Aug 2005–Jun 2008
O <sub>2</sub> /N <sub>2</sub> (per meg)	−23.2±2.5	156	161	Aug 2005–Jun 2008
APO (per meg)	−12.2±0.9	49	43	Aug 2005–Jun 2008
CH <sub>4</sub> (ppb)	10.1±4.4	64	88	Aug 2005–Dec 2008
CO (ppb)	−8.3±5.3	132	201	Aug 2005–Dec 2008
N <sub>2</sub> O (ppb)	0.67±0.08	0.69	0.79	Aug 2005–Dec 2008
SF <sub>6</sub> (ppt)	0.29±0.01	0.11	0.14	Aug 2005–Dec 2008

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**Table A1.** Valves table.

Valve	Type	Description	Initial position	OFF	ON
1	switching	FID injection	OFF	Sample load	Sample inject
2	switching	ECD injection	OFF	Sample load	Sample inject
3	switching	FID methaniser bypass	OFF	no bypass	bypass
4	switching	ECD bypass	OFF	bypass	no bypass
5	switching	signal to Labview	OFF	0	1
6	switching	between sample loops	ON	closed	open
7	switching	MFC valve control	OFF	closed	open
8	switching	Sample inlet	ON	closed	open

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**Table A2.** Time table.

Time	Specifier	Parameter and Setpoint	Detector	Comment
0.01	Aux 3 Pressure	0.00 bar	FID	pressure decrease needed for Valve 3 switching, otherwise the FID flame is blown off
0.01	Valve 5	On		start signal to Labview program
0.01	Valve 6	On	FID, ECD	start sample load
0.01	Valve 8	On	FID, ECD	start sample load
0.02	Valve 7	On	FID, ECD	start sample load
0.50	Valve 3	On	FID	methaniser bypassed
0.50	Valve 5	Off		stop signal to Labview program
0.55	Aux 3 Pressure	3.80 bar	FID	back to work pressure after Valve 3 switch
1.00	Valve 8	Off	FID, ECD	end sample injection
1.15	Aux 4 Pressure	0.15 bar	ECD	pressure adjustment according to valves position
1.20	Valve 1	On	FID	FID sample injection
1.20	Valve 2	On	ECD	ECD sample injection
3.30	Valve 3	Off	FID	sample through methaniser for CO detection
4.48	Valve 1	Off	FID	FID pre-column back-flushing
4.48	Valve 6	Off	FID, ECD	separate FID and ECD sample loops
4.50	Aux 3 Pressure	4.00 bar	FID	pressure adjustment according to valves position
4.50	Aux 4 Pressure	3.00 bar	ECD	pressure adjustment according to valves position
4.50	Aux 5 Pressure	4.80 bar	ECD	pressure adjustment according to valves position
4.50	Valve 2	Off	ECD	ECD pre-column back-flushing
4.50	Valve 4	On	ECD	lead sample to ECD, after the oxygen was flushed outside
4.80	Valve 6	On	FID, ECD	start sample load for next run
5.00	Valve 8	On	FID, ECD	start sample load for next run
7.00	Aux 5 Pressure	4.20 bar	ECD	pressure adjustment according to valves position
7.00	Valve 4	Off	ECD	ECD bypass
7.00	Valve 7	Off	FID, ECD	MFC valve closed

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**Table A3.** FID integration events.

Event	Value	Time
Initial Slope Sensitivity	0.900	Initial
Initial Peak Width	0.220	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	0.100	Initial
Initial Shoulders	OFF	Initial
Integration	OFF	0.000
Integration	ON	2.200
Integration	OFF	3.200
Integration	ON	3.450
Slope Sensitivity	0.600	3.500
Fixed Peak Width	0.400	3.500
Integration	OFF	4.450

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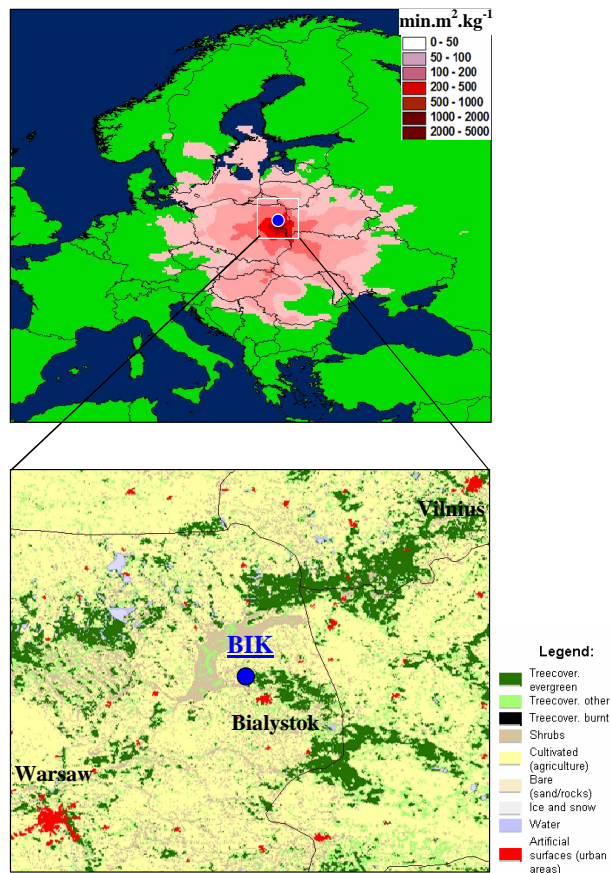
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**Table A4.** ECD integration events.

Event	Value	Time
Initial Slope Sensitivity	0.800	Initial
Initial Peak Width	0.400	Initial
Initial Area Reject	3.915	Initial
Initial Height Reject	0.190	Initial
Initial Shoulders	OFF	Initial
Integration	OFF	0.000
Integration	ON	4.600
Baseline Now		4.650
Baseline Now		5.750
Integration	OFF	6.800

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**Fig. 1.** (a) Footprint area of the Bialystok tall tower station (level 300 m a.g.l.), for the year 2005, estimated for CO<sub>2</sub> with the COMET model (figure courtesy A. Vermeulen, ECN Netherlands); (b) Land cover in the surroundings of the station. Map from Globalis.gvu.unu.edu (data source: GLC2000 – European Commission, Joint Research Centre, 2003).

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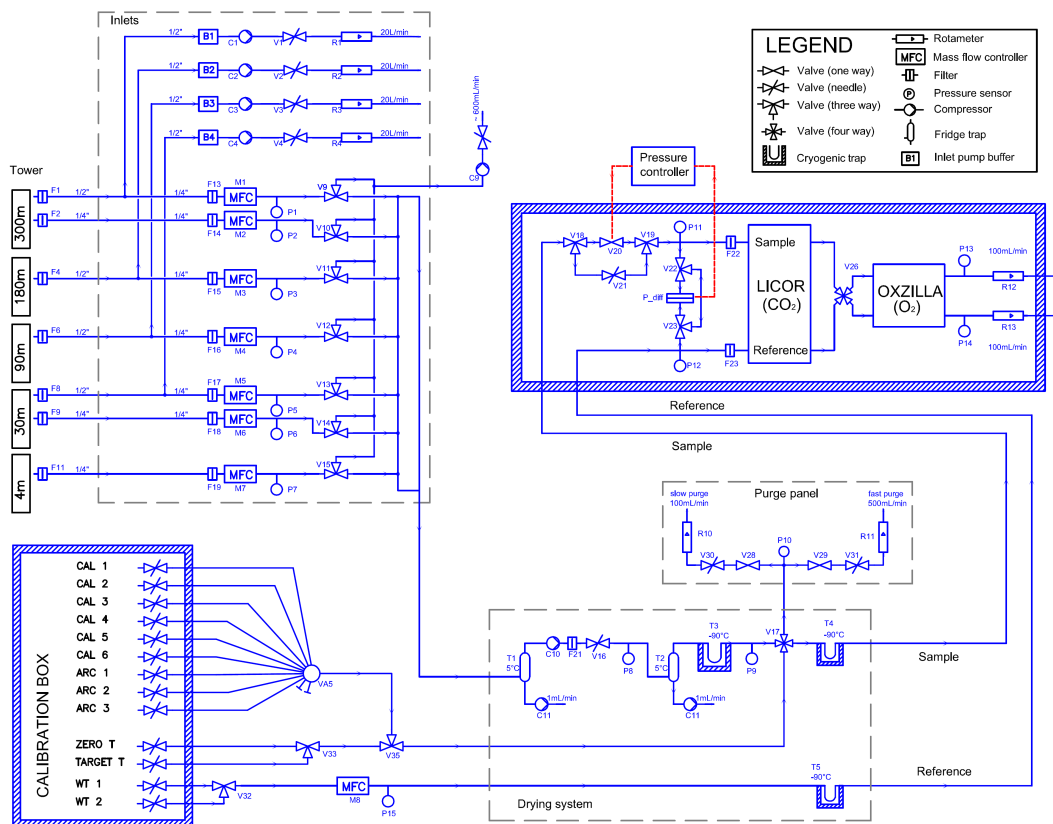


Fig. 2. Flow diagram of the CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> measurement system.

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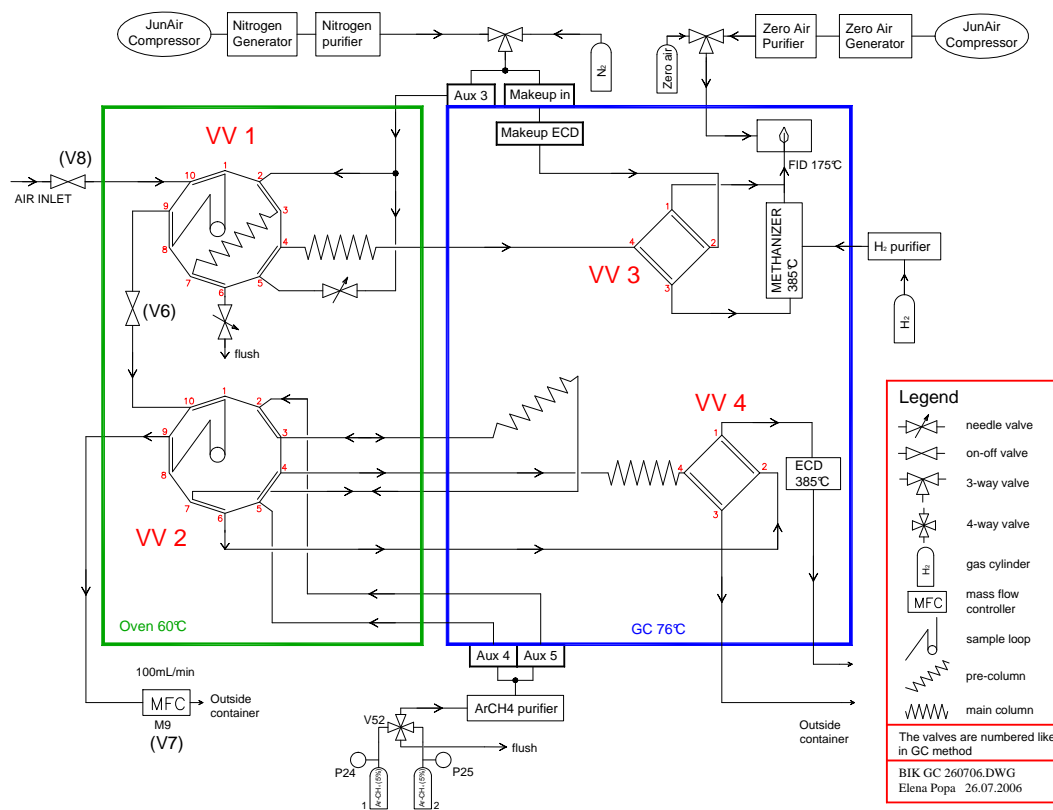


Fig. 3. The GC system diagram – LOAD position.

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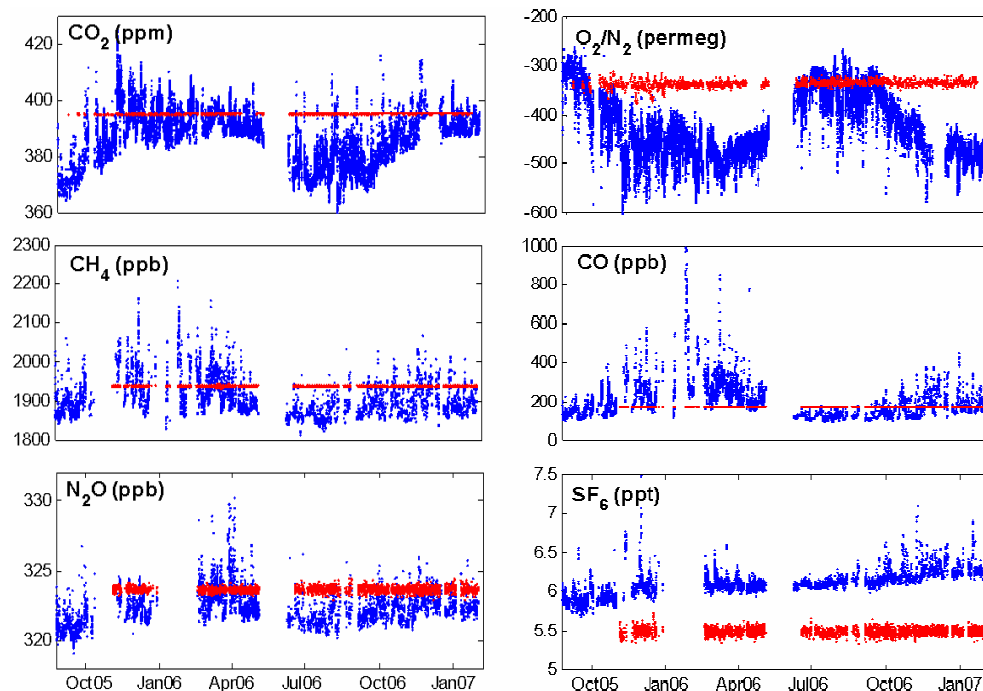
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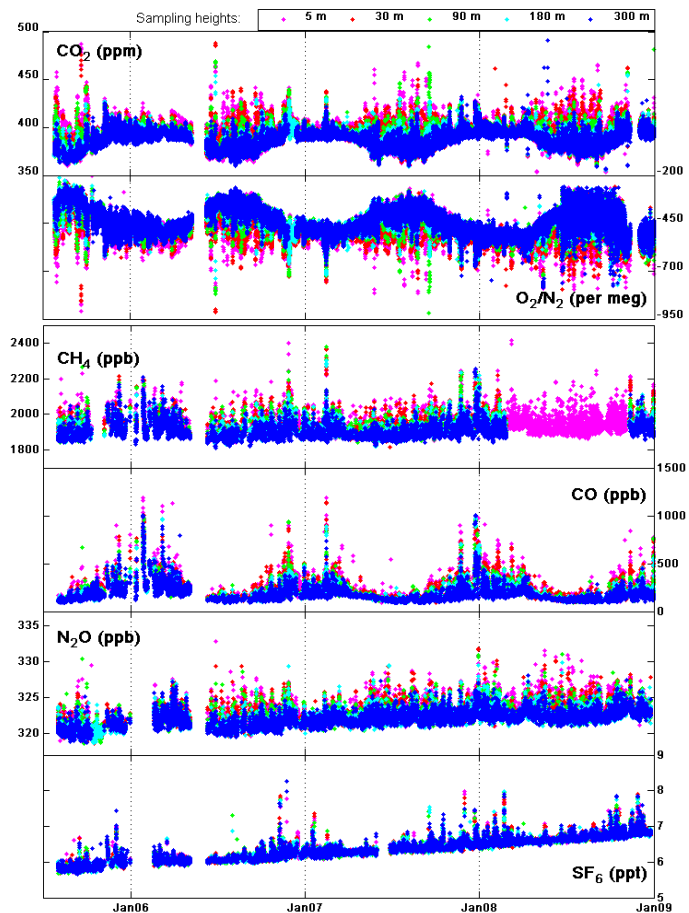


**Fig. 4.** Comparison between the noise of the Target measurement (red) and the atmospheric variability at 300 m above ground (blue). In order to use the same y-scale for both air and Target results, the values of  $\text{O}_2/\text{N}_2$  Target measurement have been adjusted with  $-200$  permeg and the values of  $\text{SF}_6$  Target measurement with  $-6$  ppt.

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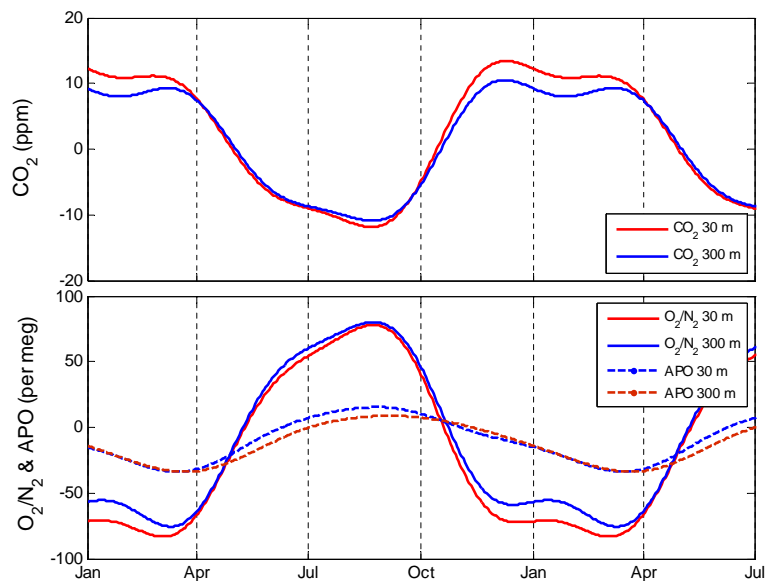


**Fig. 5.** Time series of  $\text{CO}_2$ ,  $\text{O}_2/\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\text{SF}_6$ , from different sampling heights.  $\text{CH}_4$  data between March and November 2008, except for the 5 m height, were excluded following quality check.

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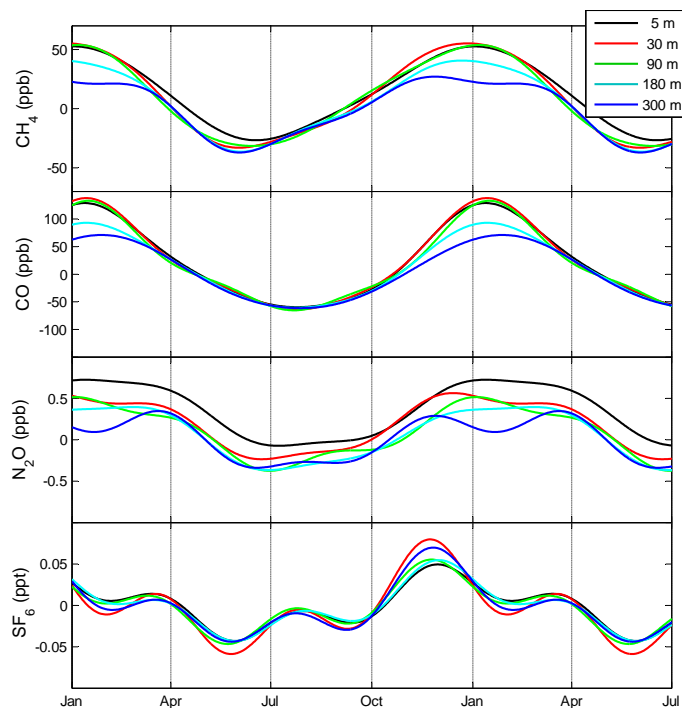
**Fig. 6.** Seasonal cycles of  $\text{CO}_2$ ,  $\text{O}_2/\text{N}_2$  and APO, at two sampling heights.

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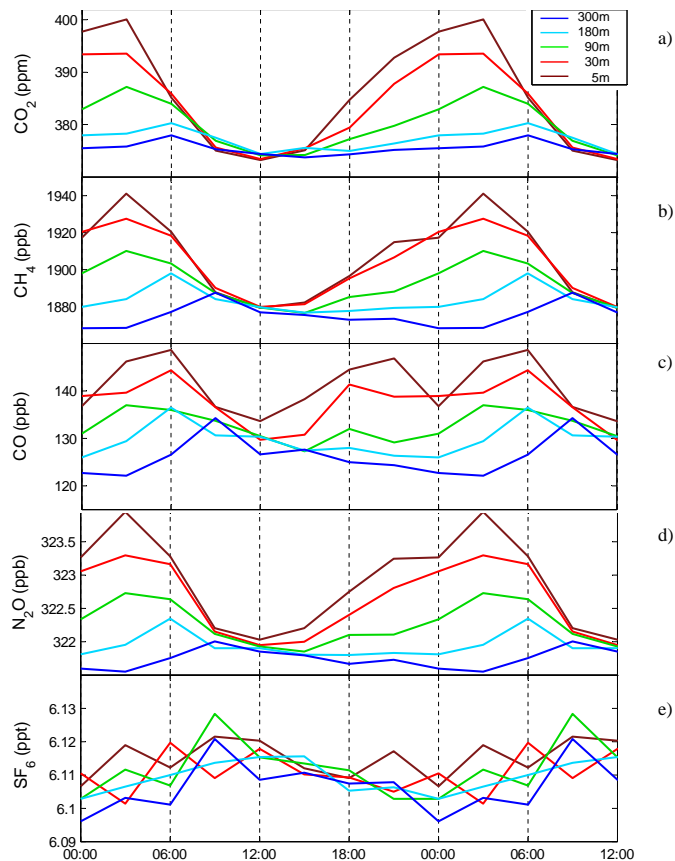


**Fig. 7.** Seasonal cycles of CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub>. The colours represent different sampling heights.

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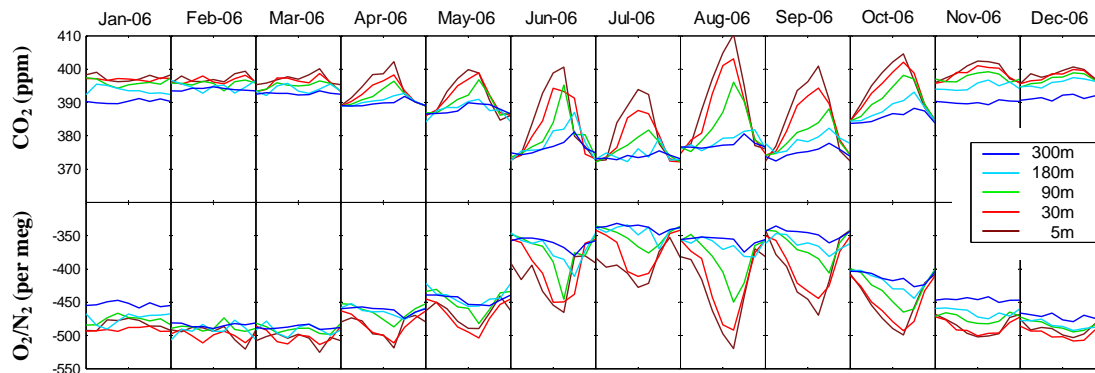


**Fig. 8.** Average diurnal variation of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\text{SF}_6$  for the period June–September 2006. X-axis represents GMT time (= local time-2 h). The colours represent different sampling heights. The averages for 3-h bins are calculated using a robust method, the lowest and the highest 5% of the data being dismissed. The first half of day was repeated for visual clarity.

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**Fig. 9.** Monthly averaged diurnal cycles of  $\text{CO}_2$  and  $\text{O}_2/\text{N}_2$  for the year 2006. The upper panels show  $\text{CO}_2$  and the lower panels  $\text{O}_2/\text{N}_2$ . The colours represent different sampling heights. The x-axis of each sub-plot covers a 24 h interval, centered on midnight.

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