**Atmospheric
Measurement
Techniques**

Methodology and calibration for continuous measurements of biogeochemical trace gas and O_2 concentrations from a 300-m tall tower in central Siberia

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Abstract. We present an integrated system for measuring atmospheric concentrations of CO_2, O_2, CH_4, CO, and N_2O in central Siberia. Our project aims to demonstrate the feasibility of establishing long-term, continuous, high precision atmospheric measurements to elucidate greenhouse gas processes from a very remote, mid-continental boreal environment. Air is sampled from five heights on a custom-built 300-m tower. Common features to all species' measurements include air intakes, an air drying system, flushing procedures, and data processing methods. Calibration standards are shared among all five measured species by extending and optimising a proven methodology for long-term O_2 calibration. Our system achieves the precision and accuracy requirements specified by the European Union's "CarboEurope" and "ICOS" (Integrated Carbon Observing System) programmes in the case of CO_2, O_2, and CH_4, while CO and N_2O require some further improvements. It was found that it is not possible to achieve these high precision measurements without skilled technical assistance on-site, primarily because of 2–3 month delays in access to data and diagnostic information. We present results on the stability of reference standards in high pressure cylinders. It was also found that some previous methods do not mitigate fractionation of O_2 in a sample airstream to a satisfactory level.

1 Introduction

The major driver of recent climatic changes on Earth is the increasing concentration of infrared-active gases (so-called greenhouse gases, GHGs). Despite a large number of studies, there remain significant "gaps" in our current observational capacity, for example, in the high latitudes of the Northern Hemisphere, particularly Siberia. This region is currently experiencing some of the fastest temperature increases globally (Chapin et al., 2005), and contains vast amounts of carbon stored in soils, wetlands, and the world's largest forest. While a warming climate promotes longer seasonal vegetation periods and thus increased CO_2 uptake (Myneni et al., 1997), it could also stimulate more intensive microbial decomposition of soil carbon, and release of CO_2 and CH_4 from wetlands.

Continental ecosystems are generally under-represented in current global observation networks (e.g. Tans, 1993). On the one hand there exist "background" air mixing ratio measurements made at coastal and mountain sites providing data on a hemispheric scale, and on the other hand eddy covariance flux measurements providing "bottom-up" information over local areas up to $1\,km^2$. The large spatial gap between these two types of measurements can be partially filled with aircraft measurements, but they suffer from prohibitive costs and non-continuity. Thus "tall tower" measurements, with footprints up to $10^6\,km^2$ (Gloor et al., 2001), have been identified as a means to fill this geographic and spatial scale gap, allowing us to examine "background" behaviour of GHGs in continental interiors.

It is with this motivation that we have established the 300-m Zotino Tall Tower Observatory (ZOTTO) in central Siberia (60.80° N, 89.35° E). The tower site is located in a relatively homogeneous, undisturbed continental boreal ecosystem, close to the southern border of discontinuous permafrost. The natural vegetation type is coniferous forest with significant areas of wetlands. The remoteness of the site leads to low anthropogenic influences, which, together with the homogeneity of the ecosystems and topography, allow for a large tower footprint area.

In the USA, the use of pre-existing tall towers has been made into an advanced measurement approach with towers in Wisconsin and North Carolina (Bakwin et al., 1995, 1997, 1998; Hurst et al., 1997). The main advantage of tall tower measurements is the ability to probe a well-mixed part of the atmosphere, which, for example, in central Siberia extends from about 200 m up to 2000 m in summer (Styles et al., 2002). In the surface layer (from 0 to 200 m), air masses are significantly influenced by diurnal changes in photosynthetic and respiration activities in the local ecosystems, as well as possible surface heterogeneity. Tall tower measurements, being somewhat removed from these relatively large source/sink patterns in the surface layer, allow gradual long-term changes in the background atmospheric composition to be observed and quantified. In addition, such measurements allow observations of vertical profiles of the measured gas species.

Outside of North America, GHG-related tall tower measurements have previously been made only in Hungary (CO_2) (Haszpra et al., 2001) and in The Netherlands (CO_2 and CH_4) (Vermeulen et al., 2006). In parallel to the ZOTTO project, the European Commission-funded "CHIOTTO" (Continuous HIgh precisiOn Tall Tower Observations of greenhouse gases) project (Vermeulen et al., 2004) was launched, initiating air measurements from eight pre-existing tall towers in Europe. Contrasts with the ZOTTO tower site include the facts that there is almost no primary forest remaining in central and western Europe, that almost all of Europe has been intensively used for agriculture and industry over the last few centuries, and that climatic variations are less extreme than in central Siberia.

There are several key approaches to our tall tower methodology. First, our measurements are made on a semi-continuous basis (one data point every 12–16 min), allowing relatively high frequency processes and events to be observed, and providing a dense dataset which facilitates more accurate long-term observations. The second approach is the multi-species nature of our measurements, including the major biogeochemical gases: carbon dioxide (CO_2), oxygen (O_2), methane (CH_4), carbon monoxide (CO), and nitrous oxide (N_2O). Third, and unique in continuous GHG observations, our analytical measurement system is built as an integrated cohesive unit, rather than a suite of independent analysers measuring different species. Finally, regular collection of air samples in glass flasks allows for isotopic composition

analyses ($\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2). Taken together, these approaches provide us with an invaluable, multi-functional strategy for observing large-scale regional biogeochemical processes and their response to climate change in Siberia.

The second section of this paper is devoted to the methodology of our measurements, system setup, and gas handling procedures, which are prerequisites for high-precision continuous measurements. The third section discusses and presents results from our calibration methodology. The fourth section presents data evaluation results on the repeatability and comparability of our measurements, and brief findings on O_2 fractionation issues. The fist data and analyses from our concentration measurements at ZOTTO covering the period November 2005 to June 2007 have been presented in Kozlova et al. (2008).

2 Analytical measurement system

The ZOTTO tall tower measurement system consists of 6 subsystems, all shown in Fig. 1, and described in the following sub-sections and Sect. 3.

2.1 Air intake subsystem

Air is sampled from five heights on the tower: 300, 227, 92, 52 and 4 m. At all platforms except 4 m, air intakes employ 12 mm outside diameter (OD) sampling lines (Saint-Gobain Performance Plastics Corp., Synflex 1300 tubing) for O_2 and CO_2, and GC species (CH_4, CO and N_2O). At 4 m, 1/4″ OD Synflex lines are used. Additionally, at 300 and 52 m, 1/4″ OD lines for O_2 and CO_2 measurements are used to check for possible O_2 fractionation effects. Air is pulled into each 12 mm line by a dedicated pump (Thomas Industries, model 607CD32) at a flowrate of 5 L/min (for example, pumps OXC7 and GCC5, Fig. 1). Since the analytical system is designed for a flowrate of 150 mL/min, a tee-junction (kept at constant temperature inside the laboratory, thus reducing the potential for fractionation) allows the excess air (4.85 L/min) to be purged, while also purging all non-selected lines. For the 12 mm O_2 and CO_2 lines, cylindrical buffer volumes (3.1 L) were installed between the tees and the purge pumps to minimise pressure pulsations from the pump at the tee, which have been shown to cause fractionation (Manning, 2001). The 1/4″ OD sampling lines are not equipped with purge pumps or tees and have flowrates of 150 mL/min from the tower inlets. Comparisons of O_2 concentration data from both "fast" and "slow" flowrate lines will be helpful in evaluating the fractionation contribution in continuous O_2 measurements (see Sect. 4.2.). O_2 fractionation has also been observed at air inlets under relatively slow flowrates (Manning, 2001), caused by ambient temperature variations and, especially, under the influence of direct sunlight (Blaine et al., 2006). To minimise these effects, aspirated radiation shields (R. M. Young Co., model 43408) were
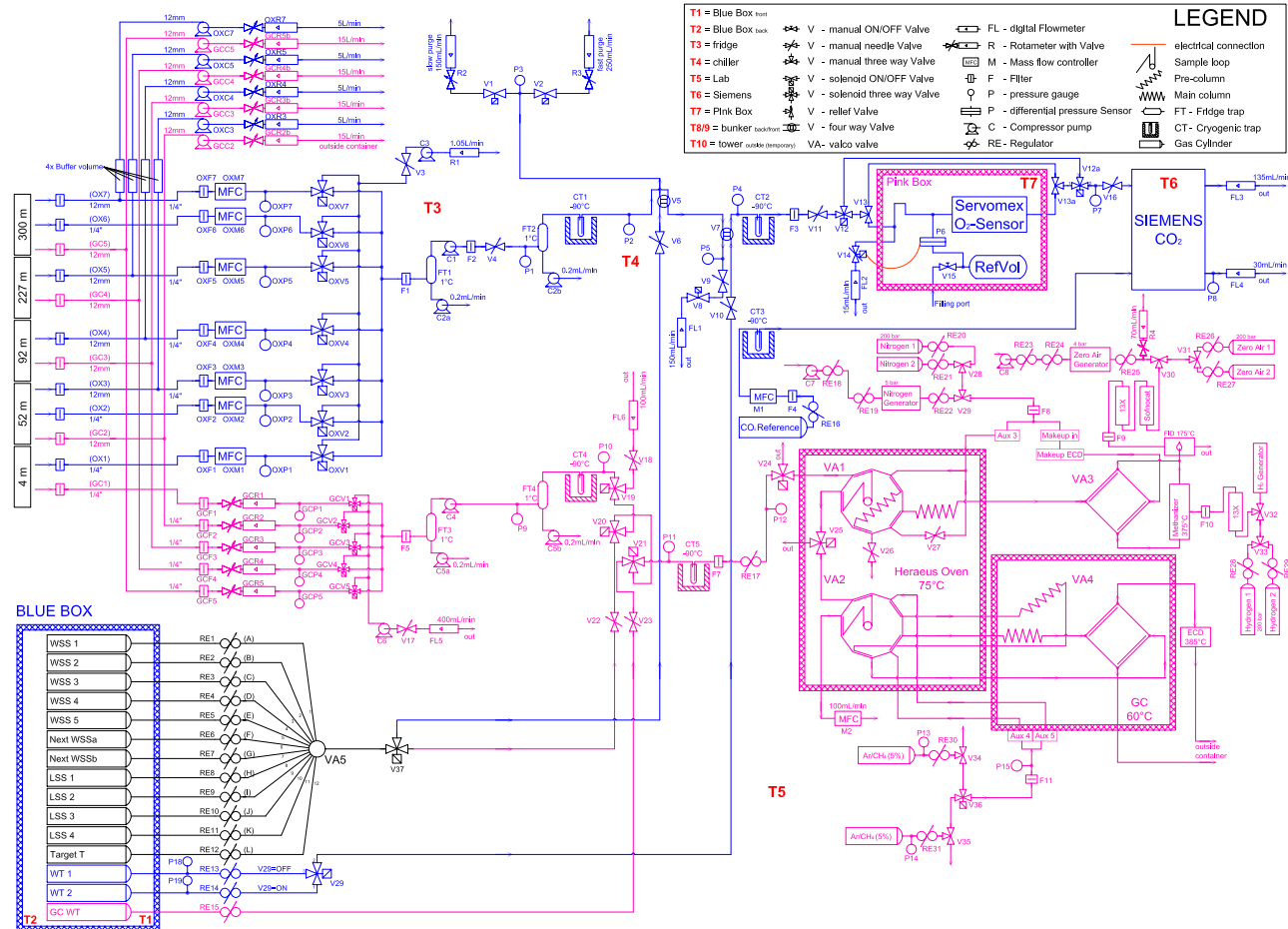
Fig. 1. Gas-handling schematic for atmospheric measurements of O$_2$ and CO$_2$ (shown in blue), and CH$_4$, CO and N$_2$O (shown in pink). As schematically represented, there appear to be dead volumes downstream of 3-way valves OXV1-7 and GCV1-5, however, in reality they are mounted in a manifold arrangement with zero dead volume.

installed at the inlets on all 1/4″ OD O$_2$ and CO$_2$ sampling lines following Blaine et al. (2006). For the higher flowrate 12 mm lines, inlets were designed as simple, inverted metal shielding for protection from snow/rainfall, in some cases using inverted metal coffee cups. All sampling lines are protected from dirt and particulate matter with replaceable stainless steel 40 μ filters installed immediately after the inlets on the tower (shown unlabelled in Fig. 1, Swagelok, TF series).

At the base of the tower, all sampling lines incorporate a nylon union, to protect the analytical equipment from possible lightning strikes on the tower. For O$_2$ and CO$_2$ measurements, the desired flowrate (150 mL/min) is achieved by mass flow controllers (MFC, OXM1-7 in Fig. 1, MKS Instruments Inc., model 1179B). Three-way manifold-mounted solenoid valves (OXV1-7 and GCV1-5 in Fig. 1, Numatics Inc., S-series) allow selection of sampling lines for analysis; air from the selected lines travels to the analysers while air from all non-selected lines is constantly purged by pumps C3 and C6 (Thomas Industries, 107CCD18) to minimise the ef-

fects of pressure distortions and flushing times (if the air is static, then there could be a significant flushing time needed to purge it out) upon switching lines. The GC inlet sampling lines are of similar design as those for O$_2$ and CO$_2$ with the only difference being that the analytical flowrate of 100 mL/min is set manually by rotameters with integrated needle valves (GCR1-5, Cole Parmer). This design is more economical than MFCs while still functional, since the GC measurements are not as sensitive to flowrate variations as O$_2$ measurements.

For each airstream selected for analysis, a diaphragm compressor pump (C1 and C4, for the O$_2$ and CO$_2$, and GC systems, respectively, KNF Neuberger, model N05-ATI) draws the air into the system.

2.2 Air drying subsystem

Sample air is pre-dried by passing through two glass traps in the O$_2$ and CO$_2$ (FT1 and FT2), and GC (FT3 and FT4) measurement subsystems. These traps are installed in a

commercial refrigerator maintained at about +1–2°C to remove the bulk water content from the air. The traps are filled with borosilicate glass beads (Sigma Aldrich, 4 mm diameter) both to reduce the internal volume of each trap (from 61 to 36 mL), as well as to provide additional surface area for water vapour to condense. The condensed water is removed at a flowrate of 0.2 mL/min by a peristaltic pump (C2a,b and C5a,b, for O_2 and CO_2, and GC systems, respectively) where "a" and "b" indicate two pump heads attached to the same pump motor (Cole Parmer, L/S® Fixed-Speed Economy Drive). Further drying occurs by passing the air through cryogenic, electro-polished, stainless steel traps (CT1 and CT4) immersed in an ethanol bath at −90°C (FTS Systems Inc., 8 litre Vapor Trap). On the assumption that the sample air has sufficient time to equilibrate with the cryogenic trap temperature, the water content of the air would then be about 0.06 ppm. Direct measurements with an identical setup in the laboratory gave a water content of less than 0.4 ppm (the limit of the dew point meter used; M. Patecki, personal communication, 2005). To mitigate the analysers' "sweep out" time (because of a large trap volume) we filled the cryogenic traps with 4 mm diameter borosilicate glass beads, reducing their total volume by a factor of two (from 105 to 45 mL). The system also employs smaller cryogenic traps (CT2, CT3 and CT5), used to dry cylinder air to the same dew point as sample air, improving the reproducibility of the measurements. The "small" traps, also filled with glass beads (3 mm diameter), have a total volume of 7.6 mL (with beads). To eliminate the need to remove the built up ice from the cryogenic traps manually, we make use of the excess unused air from the GC purge pumps to dry the traps (when the traps are not online).

2.3 O_2 and CO_2 measurements subsystem

The "Paramagnetic Oxygen Sensor, Paramax 101" from Columbus Instruments International Corp. was improved by adding high precision temperature and pressure control systems, and making fine-tuning adjustments similar to those described in Manning et al. (1999) and Manning (2001). The O_2 sensor inside the analyser is a "PM1155" (Servomex Company Inc.) which exploits the paramagnetic properties of O_2 (Kocache, 1986). Initially we received an analyser with an "upgraded" PM1158 sensor, which showed very poor performance. A second PM1158 had similar poor performance, so finally, in October 2006, we installed a now obsolete PM1155 model, loaned to us by Ralph Keeling (Scripps Institution of Oceanography, USA). Fortunately, our O_2 data prior to October 2006 do not appear to be compromised. Although the short-term precision of the PM1158 was almost three times worse than the PM1155, means calculated on hourly or greater timescales do not appear to be significantly affected. CO_2 measurements are made with a commercially available NDIR CO_2 analyser (Siemens AG, Ultramat 6F).

To improve the analysers' precision by minimising the influence of temperature-induced baseline drift, measurements of a reference standard with known O_2 and CO_2 concentrations (referred to as "Working Tank", WT) always bracket each sample air measurement (Sect. 3). A four-way valve (V7, Swagelok, 40 Series ball valve) with pneumatic actuator is programmed to alternately switch every 8 min between sample air and WT air. To maintain pressure and flow equilibrium in all tubing and equipment, air from the line which is not being analysed is flushed through a solenoid valve V8 (Numatics, S-series). This procedure is particularly important to achieve good O_2 concentration results. In the case of the WT, in order to save air, we only start flushing through V8 4 min before its next measurement. An identical four-way valve, V5, selects between either calibration standard or sample air lines.

The Servomex O_2 sensor is known to be extremely sensitive to flow, pressure and temperature variations (Manning, 2001). To ensure a very stable temperature environment we built a well-insulated box (referred to as "Pink Box" in Fig. 1) enclosing the Servomex O_2 sensor, a differential pressure gauge (P6, MKS Instruments Inc., Baratron 223B; ±1 mbar full scale range) and a pressure reference volume. Six surface-mount heating elements (Omega Engineering Inc., Kapton Flexible Heaters), thoroughly cover all interior walls, bottom, and lid of the box. Together with two fans (RS Components Ltd., Micronel Fan), an active temperature controller (Omega Engineering Inc., CN4800 Series Logic controller), and custom electronic circuitry, we are able to keep the inside temperature both homogeneous and stable to ±0.006°C (typical 1σ standard deviation of an hourly average) with an absolute value of about 36°C. This very high temperature stability was found to be necessary to achieve the required O_2 precision.

Valves V13 and V13a are manual 3-way valves used to isolate the Servomex sensor manually during testing and start-up procedures. Precise pressure-compensating needle valves (Brooks Instrument, model 8504) were installed upstream (V11) and downstream (V16) of the O_2 analyser to fine-tune the pressure in the sample line. Pressure control in the O_2 sensor is achieved with the differential pressure gauge P6, a controlling solenoid valve (V14, MKS Instruments Inc, 248A) and an electronic controller (MKS Instruments Inc., 250E). By adjusting the solenoid, the controller maintains zero differential pressure (with ±0.0005 mbar short-term precision) between the sensor and the reference volume (filled to 1270 mbar). To avoid any potential leakage, the reference volume was soldered to the differential pressure gauge (P6). Adjustable bypass flow through the control valve, V14, allows both pressure and flowrate to be kept highly constant at the inlet of the sensor (Manning et al., 1999), so that any variations in flowrate or pressure upstream of the analyser will affect solely the bypass flowrate (about 15 mL/min), maintaining constant flow through the analyser (135 mL/min).

Table 1. Settings and specifications for CH_4, CO and N_2O measurements on the Agilent 6890A GC.

Setting or specification	FID (CH_4 and CO)	ECD (N_2O)
Sample loop volume	15 mL	25 mL
Pre-column	SS 1/8″ OD, 4 ft long, Molsieve 5A, Mesh 80–100	SS 3/16″ OD, 6 ft long, Haysep-Q, 80–100 Mesh
Analytical column	SS 1/8″ OD, 4 ft long, Unibeads 1S, Mesh 60–80	SS 3/16″ OD, 6 ft long, Haysep-Q, 80–100 Mesh
Carrier gas flow rate	N_2 at 100 mL/min	Ar-CH_4 (5%) at 190 mL/min
Back-flush flowrate	N_2 at 100 mL/min	Ar-CH_4 (5%) at 360 mL/min
Oven temperature	75°C	60°C
Detector and catalyst temperature and fuel gas flowrate	175°C NiO Catalyst: 375°C H_2: 70 mL/min Zero Air: 300 mL/min	385°C
Run time	6.0 min	6.0 min

After the airstream has been analysed for O_2 mole fraction, it enters the sample cell of the Siemens CO_2 analyser. Unlike the O_2 analyser, the CO_2 analyser operates in a "differential" mode, measuring the difference in CO_2 mole fraction between sample and reference cells, and therefore requires a constant reference cell air flow, provided by a dedicated cylinder ("CO_2 Reference"). The CO_2 Reference flowrate is set to 30 mL/min by a mass flow controller (M1, MKS Instruments Inc., 1179B). The outlets of both sample and reference cells are vented to the atmosphere.

2.4 Gas chromatographic (GC) measurements subsystem

The GC measurement subsystem consists of a GC (Agilent Technologies, 6890A) equipped with a Flame Ionization Detector (FID) with a methaniser, used for CH_4 and CO measurements, and an Electron Capture Detector (ECD) for N_2O measurements. An isothermal ($\pm 0.1°C$) oven (Heraeus Holding GmbH, model T6), sample loops, and packed columns are integrated with both detectors (Table 1). Our GC analytical system is similar to that described in Worthy et al. (2003) and Jordan et al. (2005). To ensure that air enters the sample loops at constant pressure we use a forward pressure regulator (RE17, Porter Instrument Company Inc., model 8286) set to approximately 1280 mbar. Two 3-way solenoid valves (V24 and V25) downstream of RE17 simultaneously switch to their "on" positions to allow air to flush through the sample loops. A constant flowrate of 100 mL/min through the sample loops is ensured with a MFC (M2) downstream. The loops are flushed for 1 min at the beginning and the end (with the subsequent sample) of each analysis, resulting in a total flushing time of 2 min for each sample. After flushing, V24 and V25 switch to their "off" positions (vented to the room) and the system pauses for 30 s, allowing the air in the sample loops to equilibrate with oven temperature and atmospheric pressure (Worthy et al., 2003),

and preventing CH_4 (which comprises 5% of the ECD carrier gas) contamination of the FID sample loop.

Two 10-port, 2-position injection valves (VA1 and VA2, Valco Instruments Co. Inc., UW Type with electric actuators) switch simultaneously to pass the air in the sample loops onto the respective pre-columns and analytical columns (Table 1). Both injection valves switch again (at different times) to the pre-column backflush position as soon as the gas species of interest have passed onto the analytical columns, both to reduce the measurement time as well as to avoid contaminants entering the analytical columns. Since passing O_2 through an ECD is known to cause baseline drift and deterioration of the detector (Jordan et al., 2005), the O_2 in the sample air is vented outside, bypassing the detector. This is made possible by incorporating a 4-port, 2-position valve (VA4, Valco Instruments Co. Inc., W Type with micro-electric actuator). Similarly, another valve of the same configuration (VA3) is used to bypass O_2 away from the methaniser (nickel oxide catalyst) to avoid the degrading influence of O_2 on its efficiency. VA3 switches back to the methaniser pathway as soon as CH_4 elutes from the analytical column, so that CO can be reduced to CH_4 and detected by the FID.

2.5 GC peripherals subsystem

The GC peripherals consist of gas generators combined with the optional use of high pressure gas cylinders. Due to the remoteness of the site, the use of gas generators is particularly preferable. In addition, use of generators helps to avoid gas purity variability from one cylinder to another.

2.5.1 Nitrogen generating and purifying component

To provide a constant source of high purity (99.9999%) gaseous nitrogen (N_2) for the FID, we use a N_2 generator (Parker Balston, model UHPN$_2$-1100). Pressurised air for the generator is supplied by an air compressor (C7, Jun-Air,

model OF302-25B). To reduce the influence of pressure pulsations from the compressor on the performance of the generator, a two-stage regulator (RE19, Parker Balston, model 425) was installed upstream of the generator. The stability of the delivery pressure of N_2 (5.4 bar) to the GC is ensured by a two-stage regulator (RE22, same model as RE19) downstream of the generator. In case of maintenance work or generator failure we have the option to use N_2 from high pressure (200 bar) cylinders. A manual valve (V29, Swagelok, 40 Series Ball valve) allows selection of either the generator or a cylinder, while a second identical valve (V28) selects between one of two N_2 cylinders. This system allows for rapid selection between cylinders and the generator, without introducing any contaminants into the GC.

2.5.2 Synthetic air generating and purifying component

High-purity synthetic air (so-called "Zero Air") is produced by a Zero Air generator (Parker Balston, model 75-83). The setup is similar to that of the N_2 generator described above, with pressurised air supplied by an identical compressor (C8), which is also used as a source of compressed air for the pneumatic air actuators of the 4-way valves in the O_2 and CO_2 system (V5 and V7). Identical regulators (RE24 and RE25) are used to provide stable pressure to the generator and GC, respectively, and a manual system for selecting between the generator or high pressure cylinders is similarly provided by valves V30 and V31. The Zero Air from either the generator or from cylinders is purified in two stages. A Sofnocat (Molecular Products Ltd, product number 423) trap (0.1 L) removes any residual CO from the incoming air stream by oxidising it to CO_2. The second stage consists of a 13X molecular sieve trap (0.2 L), where any CO_2 formed in the first trap and any residual water vapour are removed.

2.5.3 Hydrogen generating and purifying component

Hydrogen fuel gas for the FID is supplied to the GC by a H_2 generator (Parker Balston, model H_2-150). The design again allows for easily selecting between the generator or H_2 gas cylinders via valves V32 and V33. High purity (5 meg-ohm) deionised water is required for the H_2 generator. We use a Hydrogen Mate™ deionised water system (Parker Balston, model 72-230, not shown in Fig. 1). To further purify the H_2 from the generator or cylinders we use a purifying trap filled with 13X molecular sieve (0.2 L).

2.5.4 Argon-methane component

An argon (95%) and methane (5%) mixture (Ar-CH_4) (Westfalen, Germany) is used as ECD carrier gas and is supplied from two high pressure cylinders (200 bar) installed on the system. Switching between the two cylinders is achieved by a 3-way computer-controlled solenoid valve, V36 (Parker, Series 9), programmed to switch when the pressure in the

cylinder in use drops below 15 bar (cylinder pressure is monitored by pressure transducers; P13 and P14, PMA, model P30). In addition, to prevent the possibility of both cylinders being depleted which could damage the ECD, a controller independent from our computers is employed, setting off audible and flashing alarms in the house, if the summed pressure in both cylinders drops below 40 bar. To flush the regulator of a newly installed Ar-CH_4 cylinder (to eliminate the possibility of O_2 contaminating the ECD), we employ manual 3-way valves installed at the outlet of the regulators (V34 and V35, Swagelok, 40 Series Ball valve).

2.6 Data acquisition procedures

In addition to the analysers' response signals, our computers acquire data from 29 pressure sensors, 6 digital flowmeters, 10 temperature sensors, and 9 MFCs, all shown in Fig. 1. These parameters are all displayed on the computer monitor in real-time, and all data from these sensors are sent to output files every 30 s. These data provide information about system performance, and assist in interpreting data quality and troubleshooting. Figure 2 shows an example of results from some of our diagnostic parameters, showing pressures at 17 different positions in the O_2 and CO_2 system. Patterns can be seen in these parameters which, if all is running well, should correspond with our sampling protocols. For example, approximately once per day a calibration cycle is run for several hours, illustrated most notably in Fig. 2 (top panel) by the relatively high pressure in OXP7 and relatively low pressure in P03. The Figure also shows (bottom panel) that one WT cylinder is at full pressure (160 bar) and ready to be implemented when the current online WT cylinder, showing a steadily decreasing pressure, is exhausted. Other important system parameters, for example, the stability of O_2 and CO_2 line pressures (second from the top panel) and the pressure inside the Servomex sensor (third from the top panel) can be easily monitored when using this semi-automated data evaluation tool.

However, even such diagnostic information could not be released to project scientists without pre-approval from the Russian Gostech Commission (a 2-month process), thus our diagnostic parameters have been reduced to retrospective "flagging" of data and long-term preventative maintenance, rather than near-real-time system troubleshooting and correction, as done at other atmospheric monitoring stations.

The overall ZOTTO measurement system is controlled by a custom-written LabVIEW™ (National Instruments Corp.) program running on our primary computer. The GC is controlled by a second, dedicated computer using ChemStation™ software (version B.01.03, Agilent Technologies) with which all GC parameters and chromatography integration procedures are set. Our LabVIEW™ program automatically transfers the GC integration results to our primary computer, processes these results, and creates all GC data output files.
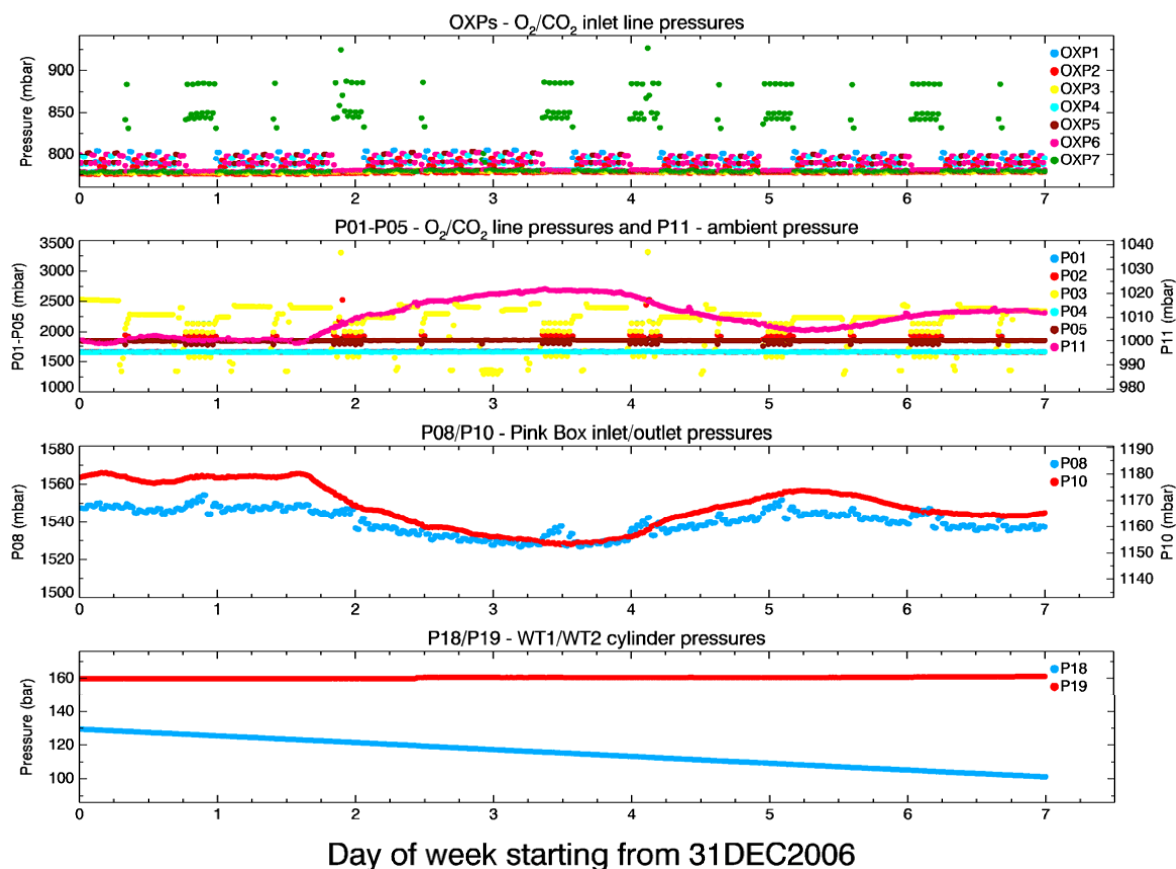
Fig. 2. Example of diagnostic parameters, showing all pressures relevant to the O_2 and CO_2 system over a one-week period starting from 31 December 2006. Each data point in the figure is a 16 min average (for all parameters). The labels in the legends correspond with those shown in Fig. 1.

The O_2 and CO_2, and GC subsystems function as an integrated whole, sharing equipment such as the cryogenic cooler, refrigerator, calibration standards and the "Target Tank" (defined in Sect. 4.), and having separate but identical air intakes, pumps and tubing. Our LabVIEW™ program integrates the analytical procedures of all subsystems into a cohesive unit, and creates standardised data output files for all species. The most "raw" files collect unprocessed data every second, whereas the most processed files incorporate all of our calibration results to provide data in concentration units on the "S1" calibration scales (defined in Sect. 3). The philosophy of our programming is to calculate species' concentrations in real-time, significantly reducing the need for post-processing of data. An important component of this philosophy is automated data quality indicators, so-called "flags". These flags are raised for a variety of conditions ranging from unacceptable diagnostic parameters, to "impossible" concentrations or calibration coefficients. As an example, if a calibration is declared by the system as "bad", then ambient air concentrations will continue to be calculated with the previous "good" calibration coefficients (with a note in the data files). If two consecutive calibrations are declared as bad, a

flashing message appears on the computer monitor, alerting the on-site technician of a possible system problem.

3 Calibration methodology and results

Our calibration methodology is similar to that for O_2 and CO_2 measurements described in Keeling et al. (1998), except that we use it for continuous rather than flask-based measurements, and we have extended the methodology to GC measurements. A similar methodology was also outlined in Manning (2005) for use in the EU CHIOTTO project. Calibrations are achieved using a suite of 50 L, 46 L, and 29 L aluminium cylinders (Luxfer Gas Cylinders Inc.) containing high pressure air with known concentrations of the relevant species. Concentrations of all measured species in our calibration cylinders have been pre-defined at the Max Planck Institute for Biogeochemistry (MPI-BGC), measured against primary standards obtained from the Scripps Institution of Oceanography, in the case of O_2, and from the WMO Central Calibration Laboratory (CCL; at NOAA/ESRL/GMD, formerly NOAA/CMDL), in the case of all other species.
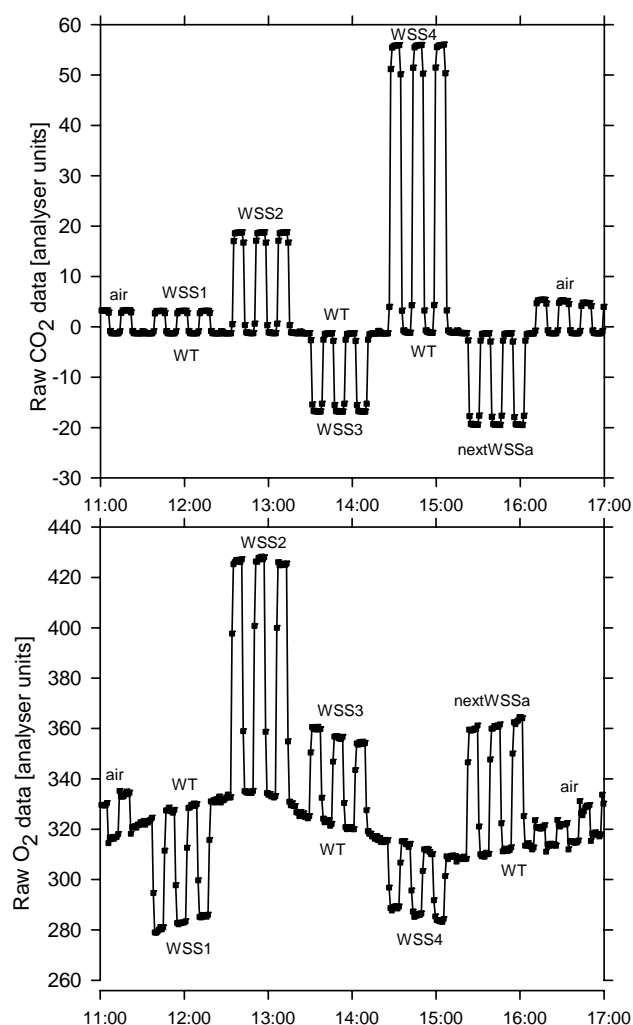
Fig. 3. Example of a WSS calibration cycle, for O_2 and CO_2, run on 3 March 2007. Data are shown in uncalibrated analyser units and each symbol is a 30 s average of 1 s data. Four standards (WSS1-4) were used to define calibration curves for both O_2 and CO_2 on the S1 calibration scales. The fifth standard (nextWSSa) was being analysed for 2–3 months before it replaced the existing WSS1 (see Sect. 3 for more details). As shown, we switch frequently between a given calibration standard and Working Tank (WT) to minimise the influence of the temperature induced baseline drift on the measurements, which can be clearly seen in the O_2 analyser signal.

All calibration cylinders are placed horizontally in the thermally insulated enclosure (referred to as the "Blue Box" in the O_2 measurement community and elsewhere in this paper) (Fig. 1). In the case of O_2 measurements, such horizontal orientation is a requirement, and it has also been shown to improve the long-term accuracy of CO_2 measurements (Keeling et al., 2007). Two-stage cylinder regulators (RE1-RE12 in Fig. 1; Scott Specialty Gases, model 51-14C) are mounted on a manifold on top of the Blue Box, connected to the cylinders via 1/16″ OD nickel tubing (Valco Instruments Co. Inc.,

"Nickel 200" TNI140). Installing the regulators on a manifold rather than directly on the cylinders, results in much less frequent opening of the Blue Box, allowing a more stable thermal environment. A multi-position valve (VA5, Valco Instruments Co. Inc., MW/SD-type with micro-electric actuator) selects a given calibration cylinder to be analysed.

We employ three hierarchical levels of calibration: (1) all sample air derived from the tower is directly measured against a reference standard ("Working Tank" (WT1 or WT2 in Fig. 1) for O_2 and CO_2 analyses, and "GCWT" for GC analyses); (2) WT and GCWT are both calibrated on a regular basis using four Working Secondary Standards (WSSes); (3) long-term stability of the WSSes is assessed by periodic (3–4 times/year) analysis of a suite of Long-term Secondary Standards (LSSes). Following Keeling et al. (1998), we define the calibration scales resulting from the frequent WSS analyses as the "S1" scales, and any changes to these scales deemed necessary from the LSS analyses result in corrected "S2" calibration scales.

In the case of O_2 and CO_2 measurements, we analyse air from a given height on the tower for 8 min, referred to as an "air jog", and bracket it with 8 min "WT jogs" both before and after the air jog. For both air and WT jogs, we discard the first 4 min owing to a long sweep-out time of the Siemens CO_2 analyser cell (88 mL volume), and average the last 4 min. A linear interpolation of the two WT jog averages is then subtracted from the 4 min jog average of air data. This procedure results in one tower air measurement (differenced from the WT) every 16 min.

Calibration curves for both O_2 and CO_2 analysers are also defined relative to WT values (giving (WSS-WT) differences), thus the (tower air – WT) differences can easily be converted into concentration units. This procedure of frequent analyses of WT is necessarily employed owing to the relatively variable baseline behaviour of the Servomex O_2 sensor mainly caused by temperature variations (Fig. 3). As a by-product, however, we achieve very good CO_2 repeatability (Table 2). For CO_2, the function of our WT is similar to the "Zero Tank" commonly used in high precision CO_2 measurements (Manning, 2005; Trivett and Koehler, 2000), except that our WT analyses are much more frequent, and some other methodologies do not incorporate an interpolation between successive Zero Tank analyses.

Analyses of CH_4, CO, and N_2O on the GC follow a similar philosophy as that for O_2 and CO_2, in that every tower air jog is bracketed by GCWT jogs. For each GC analysis the sample loops are flushed in series for 2 min before injecting the sample aliquots. The resultant chromatographic peaks are integrated using ChemStation™ software, and the heights of these peaks (for all measured species) are used as proxies for concentrations. We divide the tower air peak measurement by the average of the two bracketing GCWT peak measurements. As with the O_2 and CO_2 system, when GCWT is being analysed, we continue to flush the tower air lines, through V18 and V19 (Fig. 1). In contrast to the O_2 and CO_2 system,

Table 2. Repeatability and comparability goals and achievements for all gas analysers.

Gas species	Repeatability			Comparability	
	Goal	Achieved from Target Tanks[b]	Achieved from air lines[c]	Goal	Achieved from Target Tanks[d]
CO_2 (ppm)	±0.05	±0.0032±0.0007	±0.03	±0.10[e]	0.06±0.08
O_2 (per meg)[a]	±5	±1.5±0.2	±1.2	±10	−6.3±6.0
CH_4 (ppb)	±1.0	±0.6±0.4	±0.7	±2.0[e]	0.1±0.5
CO (ppb)	±1.0	±1.7±1.3	±1.4	±2.0[e]	−3.3±3.3
N_2O (ppb)	±0.1	±0.3±0.2	±0.3	±0.2	−0.6±0.4

[a] From an analytical perspective, our Servomex sensor measures O_2 mole fractions, and we express these throughout the paper in "ppmEquiv" units. However, the O_2 mole fraction can be influenced by variations in other species, notably CO_2. Thus from a scientific perspective, there is the danger of misinterpreting changes in O_2 mole fraction as an O_2 flux. For this reason, the scientific community typically reports changes in O_2 as changes in the O_2/N_2 ratio, given in "per meg" units (Keeling and Shertz, 1992). For comparison purposes, 6.04 per meg can be considered equal to a 1 ppmEquiv change in O_2 mole fraction, assuming no variability in any other species. We use "ppmEquiv" rather than 'ppm' to indicate that one can not always consider O_2 values given in mole fraction units in the same way as trace gas concentrations.

[b] Mean standard deviations of the average of two consecutive measurements from a given cylinder ("Target Tank" (TT)), determined from over 500 TT measurements collected over a 6 month period from November 2006 to May 2007 for CO_2 and O_2, and from over 250 TT measurements over a 4 month period from February to June 2007 for CH_4, CO, and N_2O. Uncertainties are given on these mean standard deviations, illustrating the fact that analytical repeatability varies over time.

[c] Typical standard deviations of two successive sample air measurements from the tower, during selected periods when ambient concentrations were relatively stable. These values, which incorporate both ambient variability and analytical imprecision, are used to validate the repeatability results achieved from the TT analyses. Data from all 5 heights were used to compute the values shown, using a period in May 2007 for GC results, and two periods in December 2006 and April 2007 for O_2 and CO_2 results.

[d] Mean differences between our determinations of TT, and the "declared" values determined at MPI-BGC against primary calibration standards before the cylinder was shipped to ZOTTO. These data were computed over the same time periods as given in [b], and the uncertainties represent the 1σ standard deviations of the (ZOTTO – MPI-BGC) average differences. The MPI-BGC primary standards have been obtained from Scripps Institution of Oceanography, in the case of O_2, and from the WMO Central Calibration Laboratory (NOAA/ESRL/GMD, formerly NOAA/CMDL), in the case of all other species.

[e] These values are the same as the WMO-specified inter-laboratory comparability goals (Expert Group Recommendations Miller, 2007). In the case of O_2 and N_2O, the WMO goals (1 per meg and 0.1 ppb, respectively) are not achievable by any pair of laboratories, therefore we have set slightly less stringent goals (equivalent to the CarboEurope goals).

however, when tower air is being analysed, we do not flush GCWT. This was found not to be necessary, because the relative precisions required for the GC species are much less than that for O_2 (approximately 65 times lower relative precision for the most challenging GC species, N_2O). Calibration curves for the GC species are also defined as ratios relative to the GCWT, giving (WSS/GCWT) values. The total run-time for a single GC analysis is 6 min, thus we achieve one tower air measurement every 12 min for CH_4, CO, and N_2O.

Using four WSS cylinders, we calibrate the O_2 and CO_2 analysers every 26 h, and the GC once every ∼7 days. We do not calibrate with multiples of exactly 24 h to prevent possible aliasing of the calibration results. The WSS cylinders span ranges of concentration for each species that are greater than those expected from ambient air taking into account diurnal and seasonal variability. It was not possible to prepare appropriate ranges for all five species in only four cylinders, thus we use a total of five WSS cylinders (shown in Fig. 1), three of which are shared. Each WSS is analysed three times

in succession for the O_2 and CO_2 calibration, and five times in succession for the GC calibration (to obtain more precise measurements of the GC species). Prior to the first analysis (jog), we purge the cylinder regulator and tubing for 8 min at 250 mL/min (through valve V2 via the second outlet on the four-way valve, V5; Fig. 1) followed by 8 min at 150 mL/min (through valve V1 via V5; identical to the analysis flowrate) for the O_2 and CO_2 system, and for 4 min at 250 mL/min for the GC system (through valve V2). Typically, this purging is still not sufficient, thus we discard the first WSS jog, and average the remaining jogs to define the analysers' response to the given WSS. For the O_2 and CO_2 system, we additionally flush the WSS through V8 (via the second outlet on the four-way valve, V7) during all WT jogs to maintain pressure and flow equilibrium, as discussed above. For the analyses of LSSes our software allows for a longer purging time (total of 24 min prior to the analyses of each cylinder) as these cylinders are analysed much less frequently. This has been shown to be necessary by Manning (2001). Figure 3 shows

a typical WSS calibration for O_2 and CO_2. GC calibrations look essentially identical, except with 5 jogs of each WSS instead of 3.

Using these averaged WSS data and the pre-defined concentrations for these cylinders from MPI-BGC, we can compute calibration curves. For all species, we fit linear least squares fits to the averaged (WSS-WT) or (WSS/GCWT) values, using a linear fit for O_2, CH_4, and CO, and a quadratic fit for CO_2 and N_2O. Thus, we are able to report tower air measurements in concentration units, and we refer to these values as being on the "S1" calibration scales. Each time a calibration cycle is completed, the new calibration curve coefficients are automatically updated in the LabVIEW™ program, provided that they are considered within acceptable tolerances.

The WSSes are consumed relatively rapidly (∼2 years), thus it is important to have a methodology for replacing them. We follow the same procedures given in Keeling et al. (1998), extended to our five measured species, allowing the S1 scales to be propagated indefinitely into the future with high internal consistency. Two to three months before a WSS cylinder requires replacement an additional fifth (and sometimes sixth) cylinder is analysed immediately after the four WSSes, following identical analytical procedures. The calibration curve coefficients are determined as per usual with the four WSSes, while the additional cylinders' (called "Next WSSa" and "Next WSSb" in the Blue Box) concentrations are determined based on these calibration coefficients. After 2–3 months of measurements, results for the new cylinder are averaged, and "declared" concentrations (on the S1 scale) are defined for the cylinder, after which the cylinder takes the place of one of the four WSSes in all future calibration cycles. Because of differences in the frequency of WSS calibrations between the O_2 and CO_2, and GC systems, our Lab-VIEW™ program has been made versatile so that either (or both) systems can be in a transition stage of analysing 1 or 2 next WSSes, and the transition stage for the GC system is necessarily made longer, owing to less frequent GC WSS calibration cycles. We also never replace two WSSes at the same time, so that any unexpected calibration scale shifts upon WSS replacement can immediately be attributed to a given cylinder.

Although being internally consistent by strictly following the above procedures, it is nevertheless possible that the S1 scales may drift over time. We examine and correct for such possible drift by periodic (3–4 times/year) analyses of an additional suite of cylinders named LSSes, again following procedures similar to Keeling et al. (1998). Any corrections deemed necessary result in revised "S2" calibration scales, and these scale corrections are applied retrospectively to all tower air measurements. Thus far, we have not applied any S2 scale corrections, because no LSS cylinders were available at ZOTTO until October 2006.

Examining our WSS calibration results, the curve fits gave average "r-squared" values of 0.989, 0.9999, 0.99999, 0.9991, and 0.995 for O_2, CO_2, CH_4, CO, and N_2O, respectively (103 calibrations for O_2 and CO_2 and 16 calibrations for all GC species, collected over 4 months from February to June 2007). In 2008, we learnt that the MPI-BGC declared values for O_2 for two of the WSS cylinders were incorrect by ∼50 per meg, which explained the poor r-squared result for O_2. The calibration curve coefficients for CO and N_2O were relatively variable in February/March 2007, and more stable in April/May. This shows that both the ECD and methaniser required many weeks to stabilise after modifications were made to the GC setup in early February.

Regarding the frequency of WSS calibration, the variation of our N_2O calibration coefficients, even under the most stable conditions, clearly demonstrated the need to calibrate more frequently than once every 7 days (which we plan to implement in future). For all other species, the existing frequency appears to be sufficient. For O_2 and CO_2, we calculated that a decrease in calibration frequency by a factor of two (to once every 52 h) would introduce additional inaccuracies of only 0.1±0.8 ppmEquiv and 0.006±0.005 ppm, respectively. Thus, in an effort to reduce the rate of depletion of our calibration standards, such a change should be considered. (See Table 2, footnote a for an explanation of per meg and ppmEquiv O_2 units.)

3.1 Stability of WT concentrations

A secondary result from the WSS calibrations is that we obtain information about the stability of the measured gas species in our WT and GCWT cylinders. Figure 4 shows these results from 2007 for O_2 and CO_2. For O_2, we observe that the WTs become slightly depleted as the cylinder pressure decreases. This effect has been observed previously (Manning, 2001), and is most likely owing to preferential desorption of N_2 relative to O_2 from the cylinders' interior walls. The average O_2 depletion over the lifetime of the WT cylinders (excluding ND21972) was about 5 ppmEquiv, which is about 5 times greater than that observed by Manning (2001) and M. Patecki (personal communication, 2008). Possible reasons for this faster depletion rate include: (1) a 50% higher WT flowrate in our system (150 mL/min compared to 100 mL/min); (2) our cylinders were new, and thus may have been undergoing interior wall "conditioning" processes such as corrosion or other surface reactions; and (3) relatively "wet" cylinders prepared by MPI-BGC possibly resulting in enhanced reaction processes.

Regarding (3), we note that the cylinder which showed the lowest depletion rate, D420482, was filled at ZOTTO and contained 0.5 ppm H_2O, compared with 3.5–5 ppm H_2O in MPI-BGC filled WTs. We examined other WTs used in 2006, and found consistent results, in terms of higher water content leading to greater O_2 depletion. However, hypothesis (2) could also explain the improved results with D420482, since this cylinder had already been filled and used previously in 2006. We also considered the fact that, despite

exclusively using Luxfer aluminium cylinders, some were manufactured in the UK and others in the US. The UK plant is known to use a different cleaning process, and may have different tolerances on the surface roughness of the interior walls. Our results, however, found no correlation in depletion rates based on source of manufacture. We also examined data from a TT cylinder over a 7-month period, which, in contrast to WT, is not used continuously and thus has a much longer lifetime. The O_2 depletion, however, was of similar magnitude as that for WTs, which tentatively suggests that the above-mentioned preferential desorption from the cylinder walls (which is pressure but not time dependent) could be the prevailing factor leading to the observed O_2 depletion rates, rather than surface reaction processes.

For cylinder ND21972 the observed O_2 depletion is much more pronounced, decreasing by over 20 ppmEquiv over the cylinder lifetime. In addition, and of greater impact on the precision of our tower air measurements, the average of the absolute difference between two consecutive WT values is 1.8 ppmEquiv for ND21972, compared to 0.5 ppmEquiv for all other WTs. Thermal fractionation effects could cause O_2 depletion in a cylinder similar to a Rayleigh-type distillation (Keeling et al., 2007), and could occur, for example, had the Blue Box doors been inadvertently left open and the front of the box was colder than the back. However, our Blue Box temperature data do not support such a possibility. The most likely cause for the poor performance of ND21972 would seem to be from a leak at the cylinder head valve fitting. Keeling et al. (1998) state that a leak would result in O_2 enrichment in the cylinder, rather than the depletion we observed. However, such an enrichment occurs only under conditions where the leak is through an orifice with characteristic diameter smaller than the mean free path between molecular collisions (Knudsen diffusion). Thus, particularly because no other solution appears plausible, we hypothesise that perhaps a larger leak might have resulted in the observed O_2 depletion and increased scatter for cylinder ND21972. There was no noticeable increase in the rate of depletion of the cylinder, however a leak could be through an orifice larger than that giving rise to Knudsen diffusion but still small enough not to be noticeable from the depletion rate.

As shown in Fig. 4, CO_2 data show remarkable precision and stability over each WT's lifetime, with slight evidence for a small CO_2 decrease as the cylinder is depleted, but not for all cylinders. This is in contrast to other workers, who frequently find CO_2 concentration increases as the cylinder is depleted, typically of 50 ppb, and sometimes much greater (Keeling et al., 2007). Our results support the conclusion of Keeling et al. (2007), that the measures we have taken to eliminate thermal and gravitational fractionation for O_2, placing cylinders horizontally in a thermally insulated enclosure, also give improved CO_2 stability.

Interestingly, cylinder ND21972 also shows comparatively worse stability for CO_2, with the average of the absolute difference between two consecutive WT values being 9.1 ppb,
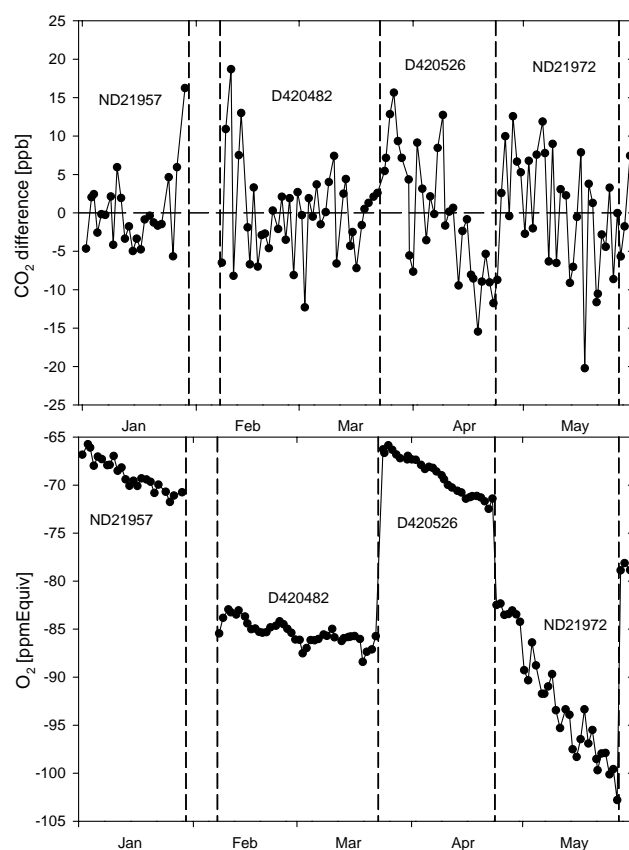

Fig. 4. WT concentrations for CO_2 (upper panel) and O_2 (lower panel), shown from January to June 2007. Each point shows the revised WT concentration which is recalculated at the end of each WSS calibration cycle. In order to highlight small changes, CO_2 results are shown as differences from the mean concentration over the lifetime of each WT cylinder (each WT is taken offline when its pressure has decreased to 15 bar), and displayed in ppb units. O_2 measurements are shown in "ppmEquiv" units, that is the (calibrated) O_2 mole fraction as measured by the Servomex O_2 sensor (a change of 1 ppmEquiv in O_2 is equal to a change of 6.04 per meg in O_2/N_2 ratio, if all other species are held constant). The vertical dashed lines indicate when a new WT cylinder was brought online, with cylinder IDs indicated in the Figure.

compared to 5.8 ppb for all other WTs. If one assumes that the increase in scatter in O_2 concentrations for ND21972 is all due to mass-dependent fractionation (clearly an oversimplification, but nevertheless illustrative), one would expect an increase in the average CO_2 scatter of ~8.8 ppb, which, although higher, is of the same approximate magnitude as the observed average increase of 3.3 ppb. Our CO_2 data also provide further evidence that thermal fractionation effects could not have caused the 20 ppmEquiv O_2 depletion in this cylinder. Keeling et al. (2007) have measured the relative thermal sensitivities in air for $(CO_2/N_2)/(O_2/N_2)$, and found values between 7 and 11 ppb CO_2/ppmEquiv O_2 (depending on cylinder pressure). Thus, a 20 ppmEquiv O_2 depletion, if due

to thermal fractionation, should be accompanied by a CO_2 depletion of at least 140 ppb, in contrast to the observed depletion of less than 10 ppb. By the same argument, we can also state that thermal fractionation processes can not be responsible for the observed O_2 depletion in any of our WTs.

4 Data evaluation results

The primary tool used for evaluating our concentration data during routine operation is another cylinder called the "Target Tank" (TT), whose concentrations have been defined at MPI-BGC before being shipped to ZOTTO. The first level of evaluation is done in real-time by analysing the TT approximately once every 10 h on the O_2 and CO_2 system, and once every 13 h on the GC system, where the analysis and data processing protocols are identical to that for a WSS cylinder. Using the most recent "good" WSS calibration results, the TT data are converted into concentration units by our LabVIEW™ program, and if these results are outside given tolerances from the "declared" MPI-BGC values, a flag is raised on all subsequent tower air measurements, indicating that these data may be suspect.

The next level of evaluation is to answer the questions, how precise, and how accurate are our concentration measurements of tower air, when defined with the calibration scales computed with our WT, WSS, and LSS cylinders? These questions are also answered with results from our TT analyses, as detailed in the following subsection.

4.1 Data repeatability and comparability

In Table 2 we present results on the repeatability and comparability achievements for measurements made at the ZOTTO site and compare them with the goals we have set, which are the same as those set in the European Commission-funded "*CarboEurope-IP*" and "Integrated Carbon Observing System (ICOS)" programmes (the full definitions of these terms are given in detail in Miller; Expert Group Recommendations, 2007). The goals are based on a consideration of requirements for the data to be scientifically useful, as well as what is considered realistically achievable from an analytical and sampling standpoint.

We consider repeatability, defined as the closeness of agreement between results of successive measurements of the same measure, to be a proxy for the precision of our measurement system. However, the nature of continuous ambient air measurements is such that it is not possible to make successive measurements of the same measure, in contrast to flask or high pressure cylinder analyses, where clearly the repeatability can be both easily determined and improved by analysing multiple sample aliquots. Thus, the best estimate we can give for repeatability at ZOTTO is to calculate the standard deviation of the average of two consecutive analyses from a given high pressure cylinder. We then report

the mean value of these standard deviation calculations over a stated time interval. To report the standard deviation of the average of a larger number of analyses would likely bias the results more favourably but is inappropriate, since this is not an option with ambient air measurements from the tower. We do, however, examine how these standard deviations vary over time, since it is an inherent characteristic of any analytical system that the repeatability performance will not be constant. We use the TT cylinder because it is independent from the procedures used to establish our calibration scales.

As shown in Table 2, we were within the repeatability goals for CO_2, O_2, and CH_4, but not for CO and N_2O. In the case of CO_2, our repeatability was more than an order of magnitude better than the goal. In the case of CO, we previously obtained repeatability values of about ± 0.7 ppb (November/December 2006), but this performance degraded somewhat after February 2007, when changes were made to the GC setup which improved CH_4 repeatability, but conversely resulted in worse CO repeatability. In the case of N_2O, clearly work must be done to improve our results.

Additional sources of uncertainty may be introduced by our air intake system (e.g. pumps, refrigerator traps, air intakes on the tower, and potentially very long lengths of Synflex tubing) which are not apparent from cylinder analyses. Thus, as a check on the TT-derived values, we calculated typical standard deviations of two consecutive sample air measurements (from all 5 heights on the tower), during selected periods when ambient concentrations were relatively stable, shown in the "from airlines" column of Table 2. The successive air measurements were 16 min apart for O_2 and CO_2, and 12 min apart for the GC species, and thus incorporate ambient variability as well as analytical imprecision. With the exception of CO_2, the results were very similar to the TT-derived results, suggesting that our methodology of quoting system repeatability from TT analyses is valid, and that effectively no additional analytical imprecision was introduced from the air intakes, pumps, etc. The value for CO_2 was much worse (but still within the goal), which shows that the analytical precision which can be obtained for CO_2 is much greater than ambient variability, even under stable conditions.

In the case of O_2, although our results were very good, two observations were puzzling. First, data from the 300 m height gave slightly worse repeatability than the other heights. In terms of ambient variability, this height should be the most stable. In terms of analytical artefacts, a major difference in November/December 2006, was that we sampled from 300 m with a 1/4 inch OD Synflex line, at a flowrate of 150 mL/min (compared to 12 mm OD tubing from 227 and 92 m, at a flowrate at that time of 15 Lpm), leading to a relatively long residence time of about 30 min for sample air in the Synflex tubing. In February 2007, suspecting that this was the cause of the worse repeatability, we changed to using 12 mm OD tubing from the 300 m height, at a flowrate of 5 Lpm, reducing the residence time to ~3 min. The

repeatability performance, however, did not improve. With this new arrangement, if there were still a tubing length or residence time-induced artefact, for example owing to absorption/desorption characteristics of O$_2$ from the inner walls of the tubing, we would expect it to scale proportionally with the other tower heights. But, for example, we found no differences in O$_2$ data repeatability between the 52 m and 227 m heights.

The second observation, also from the 300 m height only, was that during several extremely cold periods (less than $-30°C$) in November/December 2006, O$_2$ data showed unusual scatter. We were not able find correlations in our data or diagnostic parameters to explain these observations. One possible cause, however, is that the fan on the aspirated inlet may have stopped working, for example owing to ice blockage. This hypothesis is further supported by the fact that the O$_2$ scatter decreased again only after the temperature warmed back up to approximately 0°C (see Fig. 3a and b in Kozlova et al., 2008). In addition, we did not observe such scatter during subsequent cold periods in 2007, when we had changed to using a 12 mm OD sampling line, with no aspirated inlet. In future, we will add the status of the aspirated inlet fans to our diagnostic parameters.

The average calculated concentrations of all TT measurements over a given time interval, compared to the MPI-BGC "declared" concentrations provides a measure of the comparability of the ZOTTO calibration scales over that time interval (Table 2). MPI-BGC has very well established links to the international carbon cycle community (including CarboEurope) through its participation in several intercomparison programmes, and acquisition of primary calibration standards from the WMO-certified CCL. This provides indirect linkage of the ZOTTO measurements to these communities. Thus we consider our comparability to MPI-BGC to be the closest proxy to estimate the accuracy of the ZOTTO data, insofar as one can consider the CCL calibration scales to be "accurate".

Our comparability results (Table 2) were similar to those for repeatability, that is, we were within the goals for CO$_2$, O$_2$, and CH$_4$, but not for CO and N$_2$O. The values shown in Table 2 are average offsets from MPI-BGC, with associated 1σ standard deviations, computed over the same time periods as for the repeatability results, that is 6 and 4 months, respectively for O$_2$ and CO$_2$, and GC species.

An interesting observation with our CO results is that during the 4 month period used to compute the values in Table 2, the repeatability was about a factor of two better for the first half of the period than the average for the whole period, whereas the comparability was about a factor of two better for the second half. In the first half of the period, we also found atypical CO calibration curve coefficients. In hindsight, it appears that the FID methaniser required up to two months to stabilise after the system had been shutdown for modifications in February 2007. Thus the CO peak integration parameters, established in February 2007,

were optimised for a non-steady state system. When the methaniser stabilised, our repeatability became worse, because the integration parameters were not optimised for those conditions, whereas the comparability became better since the methaniser was performing more consistently. With this knowledge, we are confident of improving both repeatability and comparability for CO to the stated goals in future.

Improvements for N$_2$O are less straightforward, however it is well known that the ECD requires a very long time to stabilise after any "down-time" or other interruptions to routine operation (A. Jordan, personal communication, 2004). This fact has clearly made it difficult to optimise ECD settings at a site where scientists only visit two times per year. One obvious step which would lead to improvements in N$_2$O comparability (but not repeatability) is to increase the frequency of WSS calibrations, as mentioned above.

On the one hand we consider our comparability (accuracy) results to be conservative, since, for example, if the concentration of any species were drifting in the TT cylinder, our results would be negatively influenced. In fact, as stated above, we found that O$_2$ became depleted over time in the TT, in a similar fashion as in our WTs. On the other hand, it is a clear weakness that we were tied to only one international laboratory (MPI-BGC). Unfortunately, we were unable to join the European intercomparison programmes because of the remoteness of the ZOTTO site, and the difficulty of importing/exporting equipment in/out of Russia. There is, however, one other source of comparability, which could provide additional information, albeit also only to MPI-BGC. According to our calibration methodology (Sect. 3), two new WSS calibration standards from MPI-BGC will be incorporated into the system each year, with their concentrations to be determined on the internal S1 calibration scale. These standards, however, will have been previously analysed at MPI-BGC, thus the measurements from these standards during the transition period, before they are incorporated as new WSSes, can be used as an additional comparability tool. This procedure has the advantage of examining for drifts in comparability between the field station and MPI-BGC over the long-term based on the continually revised calibration scales at both locations.

4.2 O$_2$ fractionation issues

Atmospheric O$_2$ sampling problems caused by the introduction of artefacts from various O$_2$ fractionation mechanisms have been discussed previously (e.g. Keeling et al., 2007; Blaine et al., 2006; Stephens et al., 2007; Manning, 2001). Here we present only a short overview of additional findings we have observed at ZOTTO. To minimise fractionation at the air intakes on the tower which can occur at low flowrates ($\sim<0.5$ Lpm; Manning, 2001), we fitted aspirated inlets on all low-flow (150 mL/min) intakes, following Blaine et al. (2006). The higher flow intakes do not require aspirated inlets, however, a "tee" junction is required to divide

the flow, siphoning off only 150 mL/min to the analysers. The phenomenon of O_2 fractionation (relative to N_2) at tee junctions has been well established in experimental testing (e.g. Manning, 2001). Effective elimination of such fractionation and an understanding of the underlying mechanisms, however, has remained elusive. What is known, is that the degree of fractionation is most sensitive to temperature variations at the tee, is also sensitive to pressure pulsations, and is dependent on the flow ratio at the tee (ratios closer to 1:1 result in less fractionation), thus we have tried to minimise these influences as described in Sect. 2.1.

Comparison tests of sampling lines with and without a tee from the 52 m height, however, showed that the buffer volumes used were not effective at removing all fractionation, with residual fractionation between the two lines of 10–15 per meg (the line with the tee gave lower O_2 concentrations; flowrate of the line with the tee was 15 Lpm, giving a flow ratio at the tee junction of 99:1). Reducing the line flowrate to 3 Lpm (flow ratio = 19:1) appeared to result in a reduction in fractionation (to 5–10 per meg), but did not eliminate it. Next we installed a "dip-tube" into the tee, following Stephens et al. (2007) and as suggested by M. Bender at Princeton University (personal communication, 2000). We found that a 1/8 inch OD dip-tube, extending 12 cm upstream of the tee inside the 12 mm OD Synflex tubing gave no noticeable improvement. However, dip-tubes extending 32 cm, of either 1/8 or 1/16 inch OD tubing, appeared to eliminate fractionation to within 1–2 per meg. In the case of 1/8 inch OD, 32 cm-length tubing, our results were different from those observed by Stephens et al. (2007), who found that a dip-tube of this length and OD still gave large fractionation. The fact that Stephens et al. (2007) had a much greater tee flow ratio of 200:1 may possibly explain these differences. Our 1/16 inch OD results (32 cm length) agree with their study. According to Stephens et al. (2007), the positioning of the 1/8 inch OD dip-tube inside the housing tubing is also important, however, the 1/16 inch OD dip-tube proved to be insensitive to its radial positioning. Our dip-tubes were all installed in the centre of their housing tubing, and we did not test the influence of the dip-tubes' positioning. Although also not tested, we suspect that the temperature stability of this arrangement is important, to ensure that no radial gradients in O_2 concentration can develop inside the 12 mm tubing. We also caution other workers that in our successful tests with the 32 cm long dip-tubes, the buffer volumes were still present, and we did not test at the original higher flowrates (12–15 Lpm).

5   Concluding discussion

At the new atmospheric monitoring station in central Siberia, ZOTTO, our automated measuring system for continuous, multi-species atmospheric measurements became partially operational (with measurements to 52 m height) in November 2005, and fully operational in October 2006 (to 300 m height, after the tower construction was completed). We measured CO_2, O_2, CH_4, CO, and N_2O from five heights on the tower (4, 52, 92, 227, and 300 m) using three gas analysers (NDIR CO_2 analyser, paramagnetic O_2 analyser and a gas chromatograph). Our approach is unique in the sense that it combined the three analysers into a single integrated measurement system, sharing peripheral equipment such as a cryogenic cooler, refrigerator, and thermally insulated enclosure for calibration standards, having common designs for air intakes, pumps and air-drying methodology, and sharing calibration standards. In addition, a single, custom-written LabVIEW™ program controlled the entire system, and created standardised data output and diagnostic files for all species.

Precision and accuracy were improved for all species by drying the sample air prior to analysis and, in the case of O_2, drying to a dew point of $\sim-90°C$ is required. Drying to $\sim-60°C$ (at 1.5 bar pressure), as often performed by workers not measuring O_2, would introduce a 9 per meg offset in measured O_2 concentrations (owing to dilution). Because of high sensitivity of the paramagnetic O_2 sensor, very stable temperature and pressure regimes were necessary. Thus we built an active temperature controlled box (hourly temperature variability $\pm0.006°C$), and incorporated active pressure control (short-term control to ±0.0005 mbar). Despite the large seasonal variations in ambient temperature (approximately 70°C range) our air conditioning system typically maintained the laboratory container temperature at $23\pm1°C$ (with somewhat worse performance during spring and autumn). Such temperature stability was found to be necessary for all three analysers to achieve the required precisions.

With the GC, to eliminate the difficulty of frequent transport of high pressure cylinders to the very remote site, we used gas generators for all fuel and carrier gases, with the exception of Ar/CH_4 for the ECD. In future, it would be ideal to eliminate the need for Ar/CH_4 cylinders by employing a new ECD methodology for N_2O measurements using CO_2-doped N_2 as carrier gas (Hall et al., 2007), with the N_2 supplied by our existing generator.

We took a calibration methodology previously used for flask-based measurements of atmospheric O_2 (Keeling et al., 1998) and applied it to our continuous measurements and the full suite of five gas species measured at ZOTTO, where all five species shared the same calibration standards. The methodology uses four standards to calibrate the analysers on a frequent basis, defining initial "S1" calibration scales for each species. The procedure for replacing these standards as they are depleted is such that the S1 scales are internally consistent, and can be propagated indefinitely into the future. With the help of automated data "flagging" routines implemented by our LabVIEW™ program, we reported all tower air measurements on the S1 calibration scales in realtime, significantly reducing the need for post-processing of data. A further suite of long-term standards is analysed on a much less frequent basis, to check for possible drifts in the

S1 scales, resulting in corrected "S2" scales. The S1 to S2 scale translations will typically be determined only in hindsight, and will result in retrospective correction of all tower air measurements.

Analyses of "Working Tank" (WT) standards bracketed all tower air or calibration standard analyses for all three analysers, resulting in much higher precision. In the case of O_2 and CO_2, these WTs (50 L cylinders) were depleted on an approximate monthly basis, thus we built a facility for filling and preparing high pressure working standards on-site. For O_2, we observed depletion rates during the lifetime of the WT cylinders of about 5 ppmEquiv, about 5 times greater than observed by other workers (Manning, 2001). Possible reasons include a higher system flowrate, or interior wall "conditioning" or surface reaction processes, which may have been enhanced at ZOTTO because of using new cylinders or because of MPI-BGC filled cylinders having relatively high water content, but definitive reasons were not clear.

Using a dedicated "Target Tank" (TT) cylinder, we have reported the data repeatability and comparability from our measurement system (proxies for precision and accuracy, respectively). We found repeatability of ±0.003 ppm (CO_2), ±1.5 per meg (O_2), ±0.6 ppb (CH_4), ±1.7 ppb (CO), and ±0.3 ppb (N_2O). This led to comparability better than the goals specified in the European Union "CarboEurope" and "ICOS" programmes for CO_2, O_2, and CH_4, but not for CO and N_2O. Difficulties were encountered with CO and N_2O because the methaniser and ECD were found to require up to 2 months to stabilise after any interruption to routine operation. Several possible improvements were identified which we are confident will give better CO and N_2O results in future.

We found that previous methods (for example, employed at some CHIOTTO towers) to eliminate fractionation of O_2 at "tee" junctions were not sufficient, but an improved method employing a 32 cm-long "dip-tube" upstream of the tee eliminated fractionation, at least to the level of 1–2 per meg. These improved results were obtained at a relatively low flowrate from the tower of 3 Lpm. Without the dip-tube, we found the level of fractionation to increase in proportion to the flowrate from the tower, in other words, with higher flow ratios at the tee junction. Thus we encourage low flowrates of 3–5 Lpm for all O_2 measurement systems employing tees (even for 300 m of 12 mm OD tubing, the residence time at 3 Lpm is only $\sim$3 min).

Because all data and diagnostic information were available only at a frequency of once every 2–3 months (owing to necessary official approvals for release), three essential elements were required to ensure a successful measurement system: (1) a very high degree of computer automation of all parts of the system; (2) all system components and functioning must be very reliable and robust; (3) a skilled, competent technician must be on-site at all times. We found that no degree of automation or reliability was sufficient to remove the re-

quirement of a skilled technician on-site, owing mostly to the long delay in access to data and diagnostics, and also due to the complexity of our measurement system and the very high levels of precision and accuracy required.

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References

Bakwin, P. S., Tans, P. P., Zhao, C. L., Ussler, W., and Quesnell, E.: Measurements of Carbon-Dioxide on a Very Tall Tower, Tellus B, 47, 535–549, 1995.

Bakwin, P. S., Hurst, D. F., Tans, P. P., and Elkins, J. W.: Anthropogenic sources of halocarbons, sulfur hexafluoride, carbon monoxide, and methane in the southeastern United States, J. Geophys. Res.-Atmos., 102, 15915–15925, 1997.

Bakwin, P. S., Tans, P. P., Hurst, D. F., and Zhao, C. L.: Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program, Tellus B, 50, 401–415, 1998.

Blaine, T. W., Keeling, R. F., and Paplawsky, W. J.: An improved inlet for precisely measuring the atmospheric Ar/N_2 ratio, Atmos. Chem. Phys., 6, 1181–1184, 2006, http://www.atmos-chem-phys.net/6/1181/2006/.

Chapin, F. S., Sturm, M., Serreze, M. C., McFadden, J. P., Key, J. R., Lloyd, A. H., McGuire, A. D., Rupp, T. S., Lynch, A. H., Schimel, J. P., Beringer, J., Chapman, W. L., Epstein, H. E., Euskirchen, E. S., Hinzman, L. D., Jia, G., Ping, C. L., Tape, K. D., Thompson, C. D. C., Walker, D. A., and Welker, J. M.: Role of land-surface changes in Arctic summer warming, Science, 310, 657–660, 2005.

Gloor, M., Bakwin, P., Hurst, D., Lock, L., Draxler, R., and Tans, P.: What is the concentration footprint of a tall tower?, J. Geophys. Res.-Atmos., 106, 17831–17840, 2001.

Hall, B. D., Dutton, G. S., and Elkins, J. W.: The NOAA nitrous oxide standard scale for atmospheric observations, J. Geophys. Res.-Atmos., 112, D09305, doi:10.1029/2006JD007954, 2007.

Haszpra, L., Barcza, Z., Bakwin, P. S., Berger, B. W., Davis, K. J., and Weidinger, T.: Measuring system for the long-term monitoring of biosphere/atmosphere exchange of carbon dioxide, J. Geophys. Res.-Atmos., 106, 3057–3069, 2001.

Hurst, D. F., Bakwin, P. S., Myers, R. C., and Elkins, J. W.: Behavior of trace gas mixing ratios on a very tall tower in North Carolina, J. Geophys. Res.-Atmos., 102, 8825–8835, 1997.

Jordan, A., Manning, A. C., Schultz, U., Seifert, T., Gloor, M., Heimann, M., and Schulze, E.-D.: Continuous GC measurements of trace gases at the Ochsenkopf monitoring station, Toronto, in: Report of the Twelfth WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, WMO TD No. 1275, 191–194, 2005.

Keeling, R. F. and Shertz, S. R.: Seasonal and Interannual Variations in Atmospheric Oxygen and Implications for the Global Carbon-Cycle, Nature, 358, 723–727, 1992.

Keeling, R. F., Manning, A. C., McEvoy, E. M., and Shertz, S. R.: Methods for measuring changes in atmospheric O$_2$ concentration and their application in southern hemisphere air, J. Geophys. Res.-Atmos., 103, 3381–3397, 1998.

Keeling, R. F., Manning, A. C., Paplawsky, W. J., and Cox, A. C.: On the long-term stability of reference gases for atmospheric O$_2$/N$_2$ measurements, Tellus B, 59, 3–14, 2007.

Kocache, R.: The Measurement of Oxygen in Gas-Mixtures, J. Phys. E Sci. Instrum., 19, 401–412, 1986.

Kozlova, E. A., Manning, A. C., Kisilyakhov, Y., Seifert, T., and Heimann, M.: Seasonal, synoptic, and diurnal scale variability of biogeochemical trace gases and O$_2$ from a 300 m tall tower in central Siberia, Global Biogeochem. Cy., 22, GB4020, doi:10.1029/2008GB003209, 2008.

Manning, A. C., Keeling, R. F., and Severinghaus, J. P.: Precise atmospheric oxygen measurements with a paramagnetic oxygen analyzer, Global Biogeochem. Cy., 13, 1107–1115, doi:1110.1029/1999GB900054, 1999.

Manning, A. C.: Temporal variability of atmospheric oxygen from both continuous measurements and a flask sampling network: Tools for studying the global carbon cycle, Ph.D. thesis, University of California, San Diego, La Jolla, California, USA, 202 pp., 2001.

Manning, A. C.: A calibration and intercomparison scheme for continuous, multi-species measurements from a network of tall towers in Europe, Toronto, in: Report of the Twelfth WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, WMO TD No. 1275, 109–115, 2005.

Miller, J. B.: Report of the Thirteenth WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, Boulder, CO, WMO TD No. 1359, 2007.

Myneni, R. B., Keeling, C. D., Tucker, C. J., Asrar, G., and Nemani, R. R.: Increased plant growth in the northern high latitudes from 1981 to 1991, Nature, 386, 698–702, 1997.

Stephens, B. B., Bakwin, P. S., Tans, P. P., Teclaw, R. M., and Baumann, D. D.: Application of a differential fuel-cell analyzer for measuring atmospheric oxygen variations, J. Atmos. Ocean. Tech., 24, 82–94, 2007.

Styles, J. M., Lloyd, J., Zolotoukhine, D., Lawton, K. A., Tchebakova, N., Francey, R. J., Arneth, A., Salamakho, D., Kolle, O., and Schulze, E. D.: Estimates of regional surface carbon dioxide exchange and carbon and oxygen isotope discrimination during photosynthesis from concentration profiles in the atmospheric boundary layer, Tellus B, 54, 768–783, 2002.

Tans, P.: Observational Strategy for Assessing the Role of Terrestrial Ecosystems in the Global Carbon Cycle: Scaling Down to Regional Levels, in: Scaling Physiological Processes: Leaf to Globe, edited by: Ehleringer, J. R., and Field, C. B., Academic Press, Inc., San Diego, 179–190, 1993.

Trivett, N. and Koehler, A.: Guide on Sampling and Analysis Techniques for Chemical Constituents and Physical Properties in Air and Precipitation as Applied at Stations of the Global Atmosphere Watch, Part 1: Carbon Dioxide, Geneva, WMO TD No. 980, 39 pp., 2000.

Vermeulen, A. T., Hensen, A., Gloor, M., Manning, A. C., Ciais, P., Eisma, R., van den Bulk, W. C. M., Mols, J. J., and Erisman, J. W.: CHIOTTO – Continuous HIgh precisiOn Tall Tower Observations of greenhouse gases, in: Inverse modelling of national and EU greenhouse gas emission inventories, edited by: Bergamaschi, P., Behrend, H., and Jol, A., JRC, Ispra, 49–62, 2004.

Vermeulen, A. T., Pieterse, G., Hensen, A., van den Bulk, W. C. M., and Erisman, J. W.: COMET: a Lagrangian transport model for greenhouse gas emission estimation – forward model technique and performance for methane, Atmos. Chem. Phys. Discuss., 6, 8727–8779, 2006,
http://www.atmos-chem-phys-discuss.net/6/8727/2006/.

Worthy, D. E. J., Platt, A., Kessler, R., Ernst, M. K., and Racki, S.: The greenhouse gases measurement program: Measurement procedures and data quality, in: Canadian Baseline Program, Summary of Progress to 2002, edited by: Worthy, D. E. J., Meteorological Service of Canada, Downsview, Ontario, 97–120, 2003.