

Continuous low-maintenance CO₂/CH₄/H₂O measurements at the Zotino Tall Tower Observatory (ZOTTO) in Central Siberia

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Abstract. To monitor the continental carbon cycle, a fully automated low maintenance measurement system is installed at the Zotino Tall Tower Observatory in Central Siberia (ZOTTO, 60°48' N, 89°21' E) since April 2009. A cavity ring-down spectroscopy (CRDS) analyzer continuously measures carbon dioxide (CO₂) and methane (CH₄) from six heights up to 301 m a.g.l. Buffer volumes in each air line remove short term CO₂ and CH₄ mixing ratio fluctuations associated with turbulence, and allow continuous, near-concurrent measurements from all tower levels. Instead of drying the air sample, the simultaneously measured water vapor is used to correct the dilution and pressure-broadening effects for the accurate determination of dry air CO₂ and CH₄ mixing ratios. The stability of the water vapor correction was demonstrated by repeated laboratory and field tests. The effect of molecular adsorption in the wet air lines was shown to be negligible. The low consumption of four calibration tanks that need recalibration only on decadal timescale further reduces maintenance. The measurement precision (accuracy) of 0.04 ppm (0.09 ppm) for CO₂ and 0.3 ppb (1.5 ppb) for CH₄ is compliant with the WMO recommendations. The data collected so far (until April 2010) reveals a seasonal cycle amplitude for CO₂ of 30.4 ppm at the 301 m level.

1 Introduction

For the global climate, the most important greenhouse gases are water vapor (H₂O), carbon dioxide (CO₂) and methane (CH₄) (Kiehl et al., 1997). According to the IPCC Fourth Assessment Report (IPCC, 2007), CO₂ and CH₄ are the most important anthropogenic drivers of climate change: in 2005 the global mean mixing ratio was 379 μmol/mol (molar parts

per million, ppm) CO₂ and 1774 nmol/mol (molar parts per billion, ppb) CH₄. For the understanding of the global carbon cycle the long term monitoring of sources and sinks of these two gases are indispensable. In particular with regard to the spread in future climate projections, more investigation is needed to reduce the uncertainty in global coupled carbon cycle climate model simulations (Huntingford et al., 2009).

Atmospheric gas concentrations integrate the signal of exchange processes between land and ocean. Atmospheric measurements from observational networks have thus been used to infer surface-atmosphere exchange fluxes using inverse models (Gurney et al., 2002; Rödenbeck et al., 2003; Peylin et al., 2005). This so-called top-down approach has a high potential for providing meaningful carbon budgets on regional to continental scales. The atmospheric signal has particular advantages compared to measurements on plot level (e.g. from eddy covariance measurements), because it integrates the heterogeneous carbon release due to natural (fire, pests, windstorms) and anthropogenic disturbances (forest harvesting) (Körner, 2003). These disturbances primarily influence the human footprint in the carbon cycle of temperate and boreal forests (Magnani et al., 2007).

The localization of a supposed carbon sink on the Northern Hemisphere (Tans et al., 1990) needs further investigation. Different analytical methods such as remote sensing and inventory data (Schulze et al., 1999; Myneni et al., 2001), as well as the inversion models (Schimel et al., 2001; Gurney et al., 2002; Rödenbeck et al., 2003) suggest that a significant fraction of the Northern Hemisphere carbon sink is located in boreal forests. A carbon sink of 1.5 ± 0.6 PgC/yr is identified in this region by analyzing the vertical distribution of CO₂ in the atmosphere (Stephens et al., 2007), in line with an estimate of 1.3 ± 0.5 PgC/yr according to net ecosystem productivity estimates (Luysaert et al., 2008). On the other hand, the region's wetlands are an important source of methane (Friborg et al., 2003). In future, a warmer climate with thawing permafrost makes microbial decomposition and



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fire disturbances more likely, which increases the carbon transfer to the atmosphere on decadal time scales (Schoor et al., 2008). Given the huge total estimate of 1672 G carbon stored in permafrost soils (Tarnocai et al., 2009), even small changes in the carbon fluxes could have a large potential impact on the global carbon cycle.

Sites for measuring atmospheric background signals are mainly situated on remote coastal or mountain stations to suppress local disturbances for inverse model estimates of carbon sources and sinks. Terrestrial sites are difficult to incorporate into global models (Rödenbeck et al., 2003), in particular because of the heterogeneous sources and sinks and the complex meteorological conditions close to the surface (Gerbig et al., 2003a, 2009). However, recent developments in forward and inverse high resolution models show promising results to better integrate those sites in inversions (Peylin et al., 2005; Sarraz et al., 2007; Lauvaux et al., 2008; Trusilova et al., 2010).

Measurements from tall towers (> 200 m) offer an opportunity to alleviate this difficulties: they provide access, at least during daytime, to the relatively well mixed planetary boundary layer (Stull, 1988) that is better represented in current global models and represents regions on larger scale than measurements closer to the ground (Gloor et al., 2001). During night time, in addition to sampling the stable boundary layer profile, tall towers often allow sampling of the residual layer air, whose gas concentrations correspond to those of the previous day.

Greenhouse gas measurements on tall towers have been pioneered in the 1990s in the United States (Bakwin et al., 1998) and in Hungary (Haszpra et al., 2001), and the network has been extended during the last decade in Europe (CHIOTTO project (Vermeulen, 2007)). The Max Planck Institute for Biogeochemistry (MPI-BGC) equipped tall towers with CO₂, CH₄, CO, N₂O, and O₂/N₂ (and partly SF₆) measurements in Bialystok in Poland (Popa et al., 2010), near Zotino in Russia (Kozlova et al., 2008), and on top of the Ochsenkopf mountain in Germany (Thompson et al., 2009).

1.1 The ZOTTO Site

The Zotino Tall Tower Observatory (ZOTTO) is located in Central Siberia at 60°48' N, 89°21' E, approximately 20 km west of Zotino village at the Yenisei River (114 m a.s.l.). The ecosystem in the light taiga around the station comprises *Pinus sylvestris* forest stands (about 20 m height) on lichen covered sandy soils (Schulze et al., 2002). The closest large city Krasnoyarsk (950 000 inhabitants) is situated about 600 km south of the station. Two day lasting transport of equipment to this remote location is only possible in winter, implying an inherent need to reduce maintenance efforts and the consumption of consumables.

Siberian ecosystems are of major importance for future climate developments: they are especially projected to face increases in winter temperature and precipitation that feed back

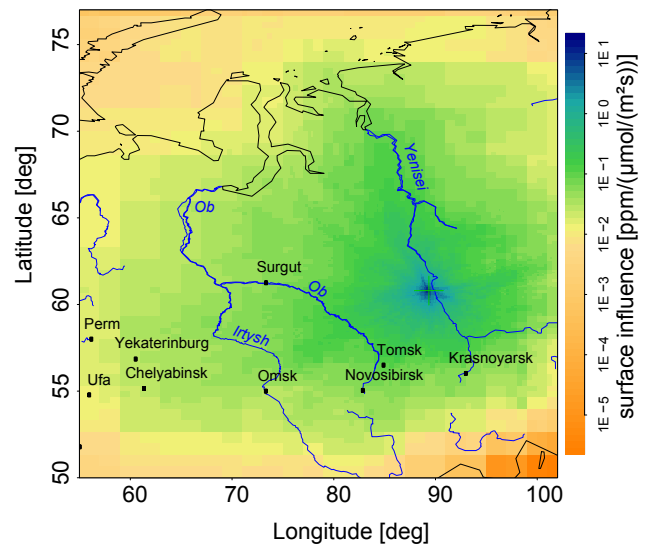


Fig. 1. STILT footprint for ZOTTO 301 m level, made from 5 days back trajectories from 1.5.–30.11.2009

to the ecosystem (Bedritsky et al., 2008). Nevertheless, they are poorly covered with atmospheric measurement stations (e.g. GAW network). This lack will be reduced by long-term observations at the ZOTTO station. Additional stations are built up that focus mainly on South West Siberia such as the so-called 9-tower network (Arshinov et al., 2009a), and aircraft measurements have been performed (Lloyd et al., 2002; Styles et al., 2002; Paris et al., 2008; Arshinov et al., 2009b).

A further argument for long-term measurements at ZOTTO is given by Lagrangian transport model STILT calculations (Lin et al., 2003; Gerbig et al., 2003b). The integrated surface influence of 5 days back trajectories based on ECMWF forecast data for the 2009 vegetation period is plotted in Fig. 1. It shows the near field of the tower having the main influence on the measured mixing ratios (up to 10 ppm/(μmol/(m²s))). The area with a surface influence above 0.1 ppm/(μmol/(m²s)) covers about 1 000 000 km² of Central Siberia, slightly deformed towards the west in direction of the Ob swamplands and northwards along the Yenisei River. Thus, the ZOTTO footprint covers permafrost regions as well. Moreover, model simulations indicate a good signal to noise ratio especially in Central Siberia to detect changes in carbon fluxes in Eurasia with inverse methods (Karstens et al., 2006). Altogether, it proves ZOTTO as a good location to further investigate ecosystem functioning of the continental boreal region.

In the past, the ecosystems around ZOTTO were monitored for several years by aircraft (Lloyd et al., 2001, 2002; Styles et al., 2002) and Eddy covariance systems (Valentini et al., 2000; Röser et al., 2002; Shibistova et al., 2002). The construction of a new 304 m tall tower finished in September 2006 (Schulze et al., 2010). Aerosol and carbon monoxide measurements are done on 301 m and 52 m tower heights

(Heintzenberg et al., 2008; Mayer et al., 2009); ozone and NO_x are analyzed from 30 m level (Vivchar et al., 2009). Until June 2007, a complex gas measurement system for CO₂, O₂, CH₄, CO, and N₂O based on gas chromatography, paramagnetic sensors, and near-infrared spectroscopy was operated providing trace gas information for five tower levels (Kozlova et al., 2009). Replacing this complex system, we present in this paper the equipment of the site with a new low maintenance high precision CO₂/CH₄ measurement system that started operating in April 2009. In the subsequent sections we describe the detailed overall setup, validate the data, and present the first data series.

2 Experimental setup

2.1 Air flow diagram

The setup that allows selecting the air stream from one of the six tower levels (301 m, 227 m, 158 m, 92 m, 52 m, and 4 m a.g.l.) and transferring it to the gas analyzer is described in Fig. 2. A detailed part list is given in Table 1. The main part of the setup is situated in an air conditioned laboratory container within a measurement bunker at the base of the tower.

On the tower, the mushroom-shaped inlets (I1–I6) are equipped with 5 μm polyester filters. The relatively large surface of the ring shaped vent minimizes the possibilities of blocking the line, e.g. due to freezing in winter. All inlets are connected to 12 mm tubing (EATON Synflex 1300, Sertoflex), through which air is drawn to the measurement bunker at a flow rate of 15 l/min by piston pumps (CF1–CF6) to limit the time of air exchange in the lines, and to minimize wall effects.

In the measurement bunker a tee junction splits up the gas flow; a small amount of 150 standard cubic centimeters per minute (sccm) of air is extracted by the gas analyzer's internal pump from one tower level at a time. The air from all the lines not being analyzed is continuously purged at a flow rate of 150 sccm through a common line by a single purge pump (CP1) and controlled by a combination of needle valves (NV12–NV17) and flow meters (FM8–FM13) in order to assure similar conditioning of all lines.

The type of the needle valves (NV7–NV11) differs for each line, according to its flow characteristics. On the 301 m level line, no needle valve is used to minimize the pressure drop; however, to avoid pressure fluctuations in the analyzer due to the motion of the pump piston, an additional air buffer volume is located upstream the flushing pump (CF1) for the 301 m line. The needle valves in all the other lines are chosen to match the pressure conditions in the 301 m line (~ 680 to 700 mbar).

Downstream, custom made 8 l stainless steel spheres act as buffer volumes on each sample line. They allow a continuous, near-concurrent measurement of six heights with only

one single analyzer. While one line is analyzed, the others are continuously flushed with the same flow. Laboratory experiments have demonstrated the ideal mixing characteristic of the buffers. Consequently they integrate the air signal from every inlet with an e-folding time of approximately 37 min (8 l/150 sccm at 700 mbar, see also Sect. 2.5), bridging the time span between two consecutive measurements for each line.

To allow selective measurements of individual tower levels, 3-way solenoid valves V1–V6 are installed further downstream that switch the airflow between purge pump and analyzer. Those valves are characterized by easy to seal NPT threads, a big body orifice for minimal pressure drop, and small leak rates (< 1 μl/s guaranteed). If the power supply of the valves and sensors fails, the measurement from 301 m is the default.

To select between measuring ambient air and calibration gases, the ambient air from the tall tower passes another two simultaneously switched 3-way solenoid valves V7–V8. For monitoring the analyzer's incoming air flow, a high quality, metal sealed, and well calibrated flow meter FM7 is installed. All flow meters in the setup are free of moving parts, thus requiring almost no maintenance and are, with the exception of flow meter FM7, not in contact with the analyzed air. The only active flow control of the whole system is performed by the analyzer itself.

In contrast to all tall tower instrumentation known to the authors, the pump of the analyzer is located downstream the measurement cell. This avoids an additional pump with its risk for leaks in the sampling line. The temperature corrected pressure record after an extensive, 25 h leak test showed leak rates less than 0.4 μl/s in all lines. Taking a maximal observed CO₂ gradient of 1000 ppm in the laboratory container at 1 bar versus 300 ppm sample air at 0.7 bar, at the above leak rate the influence on the CO₂ concentration would be less than 0.02 ppm per line.

As there is no drying system, adsorption on additional large surfaces and potential leaks are excluded. We expect the remaining maintenance efforts to concentrate on regular annual pump maintenance, adjustments of needle valves to keep the pressure in all lines constant within a 650–700 mbar range, and annual filter cleanings.

2.2 The CO₂/CH₄/H₂O analyzer

The CO₂, CH₄, and H₂O measurement is performed by an EnviroSense 3000i analyzer (Picarro Inc., USA, CFADS-17) based on the cavity ring-down spectroscopy technique (CRDS) (Crosson, 2008). The decay time of laser light inside a cavity equipped with highly reflective mirrors is measured for several wavelengths around 1.651 μm for CO₂ and H₂O (data output after ~4 s) and 1.603 μm for CH₄ (data output after ~1 s). The volume mixing ratios of the main isotopes ¹²C¹⁶O₂, ¹²C¹H₄, and ¹H₂¹⁶O are obtained by mathematical analysis of the spectral line shape. An

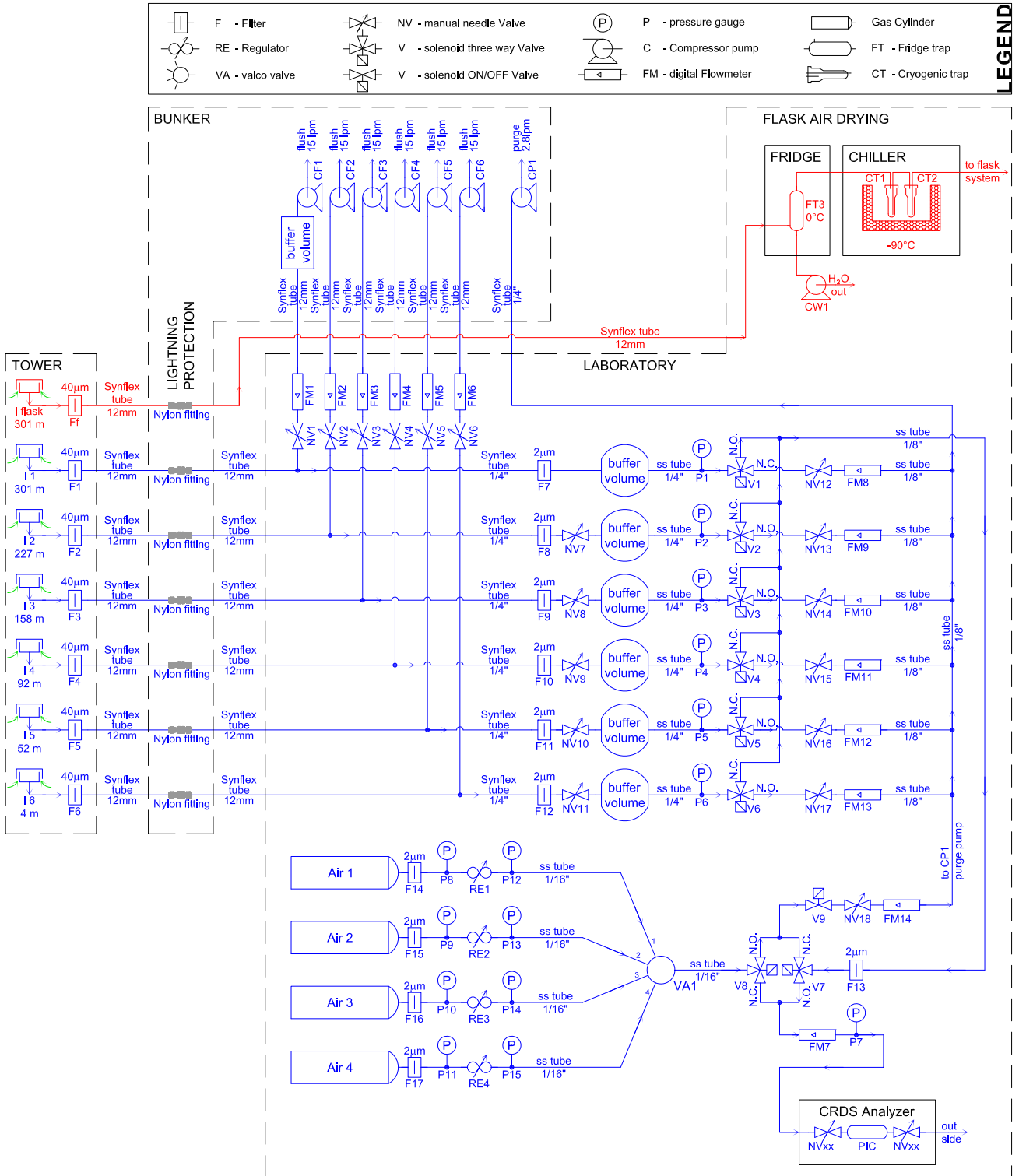


Fig. 2. Flow diagram of the CO₂/CH₄ measurement system at ZOTTO.

Table 1. Part list of ZOTTO setup.

Element	Company	Type	Symbol in Fig. 2
inlets	Solberg Filter, Continental Industrie GmbH, Germany	F-15-100	I1-6
filters 40 µm	Swagelok, BEST Fluidsysteme GmbH, Germany	SS-12TF-MM-LE and SS-8F-K4-40	F1-6
filters 2 µm	Swagelok, BEST Fluidsysteme GmbH, Germany	SS-4FW-2	F7-13
flushing pumps	Gardner Denver Thomas GmbH, Germany	617CD32	CF1-6
purge pump	KNF Neuberger GmbH, Germany	N86KNE	CP1
3-way solenoid valves	Gems Sensors GmbH, Germany	G3415-LC-24VDC-VAC	V1-8
12 position multiport valve	Valco Instruments Company Inc. from Machery-Nagel GmbH & Co. KG, Germany	EMTMA-CE	VA1
needle valves	Hy-Lok D Vertriebs GmbH, Germany	NV3H-12M-R	NV1-6
needle valves	Swagelok, BEST Fluidsysteme GmbH, Germany	SS-4MG SS-SS4	NV7-8 NV9-11
needle valves	Swagelok, BEST Fluidsysteme GmbH, Germany	SS-2MG	NV12-18
flow meters 0–20 l/min	Sensortech GmbH, Germany	FTAL020NU	FM1-6
flow meter 0–500 ml/min	MKS Instruments Deutschland GmbH, Germany	179B52CS3BM	FM7
flow meter 0–1000 sccm	Sensortech GmbH, Germany	FBAL001DU	FM8-14
pressure sensor 0–1 bara	Sensortech GmbH, Germany	CTE8001AK0	P1-7
pressure sensor 0–210 bar	Synotech Sensor und Meßtechnik GmbH, Germany	GCT-2251210BGC42C06	P8-11
pressure regulator	Tescom Europe GmbH & CO. KG, Germany	64-344XKA412-S	RE1-4
laboratory temperature and converter	Electrotherm GmbH, Germany LKM electronic GmbH, Germany	K6S-E-4LS-200C-G1/4A-120 and LKM-214	not shown

outlet proportional valve controls the pressure and the temperature of the cavity to constant conditions of 187 mbar (140.0 ± 0.04 Torr) and 40.000 ± 0.004 °C. The mass flow of sample air through the cavity is linearly correlated with the inlet pressure (~ 150 sccm at 700 mbar).

Laboratory analyzer tests with humidified tank air (at 1.2% H₂O level) show a typical standard deviation of the raw data (0.2 Hz) below 0.06 ppm for CO₂, 0.5 ppb for CH₄, and 0.001% (10 ppm) for H₂O. To assess the long term stability of the analyzer, 200 h continuous measurement of air from a high-pressure tank was analyzed by the Allan variance technique (Allan, 1987), using “Alamath AlaVar 5.2” software. The continuous decrease of the Allan variance suggests that the chosen calibration interval of 100 h is sufficient.

Raw data from repeated measurements of calibration gas tanks reveal a long term drift of the analyzer of less than 0.25 ppm and 3.2 ppb per year for CO₂ and CH₄, respectively (similar to (Crosson, 2008)).

The CRDS analyzer response is linear. The standard deviation of the residuals from the measurement data to the lin-

ear fit are 0.05 ppm and 0.05 ppb for a concentration range of 354–453 ppm CO₂, and 1804–2296 ppb CH₄.

The characteristic of the CRDS technology does not easily allow calibrations with air of non-natural composition. Experiments with synthetic air revealed residuals in the CO₂ calibration up to 1 ppm related to pressure broadening effects due to varying N₂, O₂ and Ar content in the calibration gases and the isotopic composition of CO₂ (Tohjima et al., 2009; Chen et al., 2010). To avoid problems, all our calibration tanks were filled with air of ambient isotopic composition. Even though the CRDS analyzer still detects only the main isotopes, there is no further isotope correction needed: the error that appears during the calibration emerges with the opposite sign during the measurement and thus cancels out. Measurement inaccuracies due to variations in the isotopic composition of ambient air ($\delta^{13}\text{C}_{\text{VPDB}} = 7.5\text{--}9.0\text{‰}$, $\delta^{18}\text{O}_{\text{VPDB}} = 0.5\text{--}2.5\text{‰}$) are too low to influence the measurement (<0.01 ppm at 400 ppm level) (Allison et al., 2007; Chen et al., 2010).

The H₂O measurement was calibrated using a dew point mirror (Dewmet, Michell instruments Ltd., UK) in the 0.7 to 3.0% H₂O range for another CRDS analyzer of the same type (model G1301-m, CFADS-30). Thus the actual values H₂O are calculated from the reported values H₂O_{CRDS} by the following formula (units in %):

$$\text{H}_2\text{O} = 0.0292 + 0.7719 \cdot \text{H}_2\text{O}_{\text{CRDS}} + 0.0197 \cdot \text{H}_2\text{O}_{\text{CRDS}}^2 \quad (1)$$

The nonlinear component is due to the self pressure broadening effect of water vapor.

Note that H₂O measurements from all CRDS analyzers have been calibrated to the same scale after production, so this formula also applies to the ZOTTO instrument.

2.3 Calibration system

To guarantee the required stability of the measurement, an automated calibration sequence is initialized every 100 h. The notional life time of the 200 bar high pressure tanks exceeds 60 years, but every 10 years a successive recalibration of the tanks is suggested to exclude drifts in the mixing ratios and to adapt to the concentration range of the changing ambient air conditions. ‘‘Cucumber’’ intercomparison experiments between different stations and laboratories are intended to ensure the link to WMO scale during this time (<http://cucumbers.uea.ac.uk/>). WMO recommends an inter-laboratory comparability of 0.1 ppm for CO₂, 2 ppb for CH₄ (GAW Report No.186, 2007)).

The long usage time challenges the long term stability of the calibration gases. Therefore high pressure aluminum tanks are preferred to steel ones (Kitzis et al., 1999). However, the calibration gas composition can be changed through diffusive and surface processes (Langenfelds et al., 2005). High pressure tank regulators corrupt the gas concentration due to the long lasting storage, too (Da Costa et al., 1999). Life times of at least 12 years can be assured by careful gas handling like in tank calibrations, usage exclusively above 30 bar and pre-use regulator flushing procedures (Kitzis et al., 1999; Daube Jr. et al., 2002; Keeling et al., 2007).

To further reduce effects from the pressure regulators, polychlorotrifluoroethylene (PCTFE) is preferentially used as sealant to reduce gas permeation (Sturm et al., 2004). Our own laboratory experiments confirm the advantages of a PCTFE-equipped pressure regulator to suppress CO₂ corruption in the withdrawn air after storage (Winderlich, 2007). Additionally, the stability of the CO₂ concentration in tanks was observed to be better when they are stored in horizontal position (Keeling et al., 2007).

Hence, our calibration system consists of four horizontally stored aluminum tanks (50 l, Luxfer, C/O Matar, Italy) equipped with Ceodeux PCTFE cylinder valves (D 200 series, D20030163, Rotarex Deutschland GmbH, Germany), PCTFE sealed pressure regulators (RE1-RE4 in Fig. 2), and metal sealed high pressure transmitters (P8–P11).

Table 2. Comparison of flask data with deconvolved CRDS data.

Tank name	ID number	CO ₂ [ppm]	CH ₄ [ppb]
Calibration Tank 1	D478665	354.71 ± 0.08	1804.73 ± 1.60
Calibration Tank 2	D436606	394.60 ± 0.06	1899.26 ± 1.49
Calibration Tank 3	D436607	453.12 ± 0.08	2296.69 ± 2.05
Target Tank	D478666	404.40 ± 0.08	1947.43 ± 1.37

As the analyzer has a linear response (Sect. 2.2), the three tanks of our setup are sufficient for the calibration. The fourth tank is used as target gas for quality control and further experiments. The CO₂ and CH₄ concentrations in the gas tanks that are currently used at ZOTTO (Table 2) were determined in the GASLAB of the MPI-BGC Jena and are traceable to scales of the World Meteorological Organization (WMO) maintained in NOAA/ESRL (WMO-X2007 for CO₂ (Zhao et al., 2006), NOAA-2004 for CH₄; Dlugokencky et al., 2005).

2.4 Water correction

Water influences the measurement of CO₂ and CH₄ by dilution and pressure broadening. At constant pressure in the optical cavity, dilution decreases the trace gas concentration linearly with increasing water vapor pressure, whereas pressure broadening is a nonlinear effect (Chen et al., 2010). For comparisons between different stations and for the use in atmospheric models, the dry mixing ratio is important, since wet mixing ratios show alterations just by changing water concentrations.

The analyzer already includes a first order water correction function:

$$\frac{\text{CO}_{2\text{wet}}}{\text{CO}_{2\text{dry}}} = 1 - 0.01244 \cdot \text{H}_2\text{O}_{\text{CRDS}} \quad (2)$$

Experiments with a Licor LI-610 humidifier revealed the necessity for a second order water correction function (Chen et al., 2010). The associated tests were performed for the CFADS-17 instrument in January 2009. A simpler setup had to be developed for ZOTTO, because the time-consuming laboratory experiments required a large amount of space, extensive flow regulations, and drift corrections due to temperature-dependent CO₂ dissolution in the water reservoir of the humidifier.

To humidify air, it suffices to pass it over a water droplet in a vessel (F. Meinhardt and R. Schmitt, personal communication, 2008). The modified setup for the experiments in September 2009 and June 2010 is based on a stainless steel water trap with a volume of 19 cm³ and an inner surface area of less than 140 cm² to reduce surface effects (Fig. 3a, adapted from (Popa, 2007)). The air from a high pressure

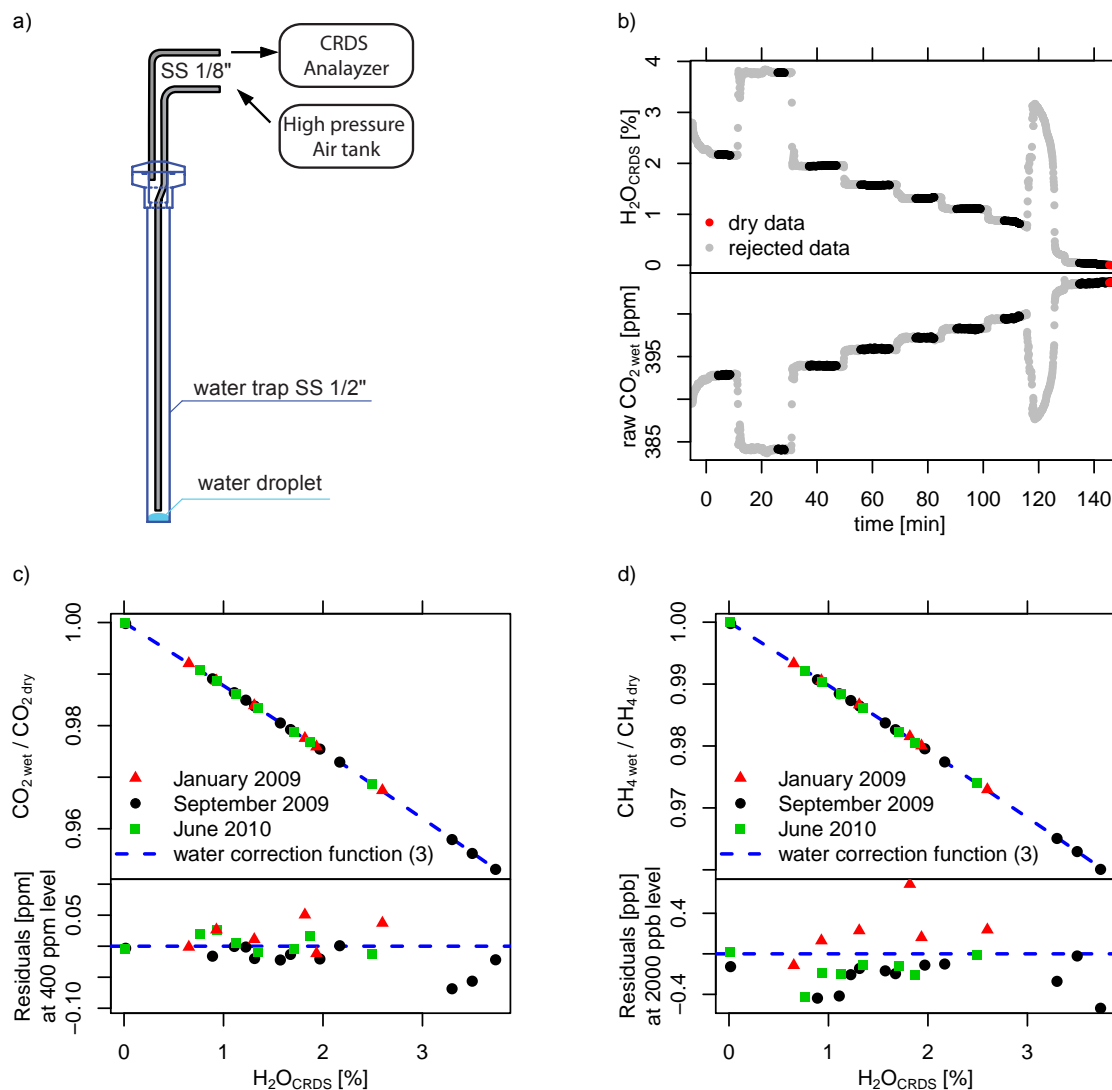


Fig. 3. Experiments at various water vapor levels: (a) setup; (b) H₂O and CO₂ time series of an experiment in September 2009; correction function derived from all experiments for (c) CO₂ and (d) CH₄.

tank flows through a dip-tube that almost touches a water droplet (<1 ml) at the bottom of the trap. The humidified air leaves the trap through an outlet on its top towards the analyzer with the same pressure as it left the pressure regulator at the high pressure tank. Because temperature changes of the trap to achieve different dew points resulted in unstable conditions, the trap was held at constant temperature within an ice bath, whereas the pressure of the flushing gas was changed: with decreasing absolute pressure, the relative amount of water vapor increases, even though the partial water vapor pressure stays the same at constant temperature. For this freely controllable water vapor time series, the analyzer's readings give CO₂ and CH₄ wet mixing ratios X_{wet} for a H₂O_{CRDS} range from 0% to almost 4% (Fig. 3b).

The pressure variations trigger changes in the air adsorption processes at the metal surfaces of the trap. To ensure

equilibration, data points 1.5 min before and 3 min after pressure changes are rejected (grey dots in Fig. 3b). Additionally, the required pressure stability of the CO₂/CH₄ measurement was confirmed experimentally since changing inlet pressure did not influence the instrumental reading of the mixing ratios above the internal sample cell pressure (187 mbar).

When the water droplet is completely evaporated, the analyzer detects the dry mixing ratio X_{dry} for CO₂ and CH₄ (red dots in Fig. 3b), and the water correction function can be directly inferred (Fig. 3c, d). The relation between H₂O content and the $X_{\text{wet}}/X_{\text{dry}}$ ratio for CO₂ and CH₄ are fitted with a second order H₂O correction function:

$$\frac{X_{\text{wet}}}{X_{\text{dry}}} = 1 - a \cdot \text{H}_2\text{O}_{\text{CRDS}} - b \cdot \text{H}_2\text{O}_{\text{CRDS}}^2 \quad (3)$$

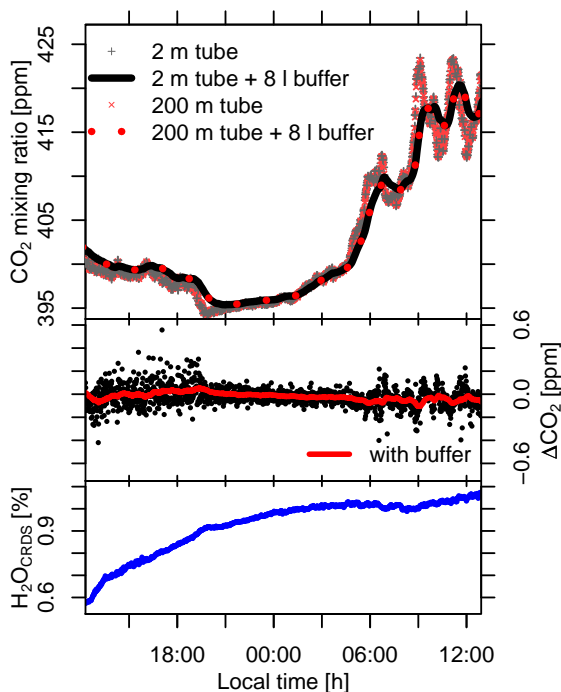


Fig. 4. Comparison of CO₂ measurement through 200 m and 2 m wet tubes (only a subset of data shown).

The experiments conducted in January and September 2009 are in good agreement, indicating temporal stability of the water correction function. The average fit parameters for both experiments are $a=(1.205 \pm 0.002) \cdot 10^{-2}/\%$ and $b=(2.03 \pm 0.08) \cdot 10^{-4}/\%^2$ for CO₂ and $a=(1.007 \pm 0.005) \cdot 10^{-2}/\%$ and $b=(1.45 \pm 0.18) \cdot 10^{-4}/\%^2$ for CH₄, while H₂O is given in percent. A repeated experiment in June 2010 confirms these parameter values. All raw data points (Fig. 3b) were grouped according to the set H₂O levels; thus only the binned and averaged CO₂ and CH₄ ratios are shown in Fig. 3c and d for better visibility.

Hence, the CO₂ accuracy better than 0.1 ppm relies on the water vapor measurement having the precision better than 200 ppm H₂O at a 400 ppm CO₂ level, which is easily achieved with the CRDS technique.

The standard deviation of the residuals of the individual fits indicates a repeatability of the water-corrected measurement within 0.03 ppm and 0.3 ppb for CO₂ and CH₄, respectively.

2.5 Influence of long inlet tubes

Although the analyzing system guarantees high quality data for moist ambient air samples, it has to be ensured, that the air sample remains unaltered on the way from the different tower inlets to the analyzer. The most important source of disturbances is assumed to be caused by water vapor. Ac-

cording concerns resulted in deploying air drying systems directly at the inlet of some towers (Vermeulen, 2007).

Here we try to evaluate the disturbances caused by water vapor in the inlet system. Due to the 300 mbar pressure drop in the 300 m inlet tube, the dew point is suppressed by 1 to 2 K per 100 m (dew point calculation based on H₂O saturation pressure from Goff equation (Murphy et al., 2005)). Thus, condensation of water is highly unlikely which permits neglecting liquid water in our first order estimates.

We set up two CRDS analyzers (CFCD3-3 and CFADS-14) to measure ambient air simultaneously through a 2 m and a 200 m tube (1/2" Dekabon) at LSCE in Gif-sur-Yvette. The 200 m tube was stored outside (winter days, temperature -1 to 5 °C, relative humidity 79 to 98%). The inlets of both lines were closely attached to each other. The data was recorded in 60 s averages, corrected for dilution and pressure broadening by water (see Sect. 2.4), and calibrated.

In our experiment, both instruments ran in parallel for three days. Accounting for the time delay, the linear interpolated 200 m data was time shifted by 1683 s. Thereafter it differed from the 2 m line by $-(0.03 \pm 0.24)$ ppm CO₂, $-(0.27 \pm 0.59)$ ppb CH₄ (compare Fig. 4) during the entire test period.

To simulate the deployment of the 8 l buffer volumes, the time series were convolved with an exponential function. Any condensation at the walls of the stainless steel buffers can be excluded due to the reduced dew point associated with the low pressure (≤ 700 mbar). Because a well mixed volume V with the concentration c_0 will respond to an incoming flow f and the concentration c_1 with a time-dependent function

$$c(t) = c_1 + (c_0 - c_1)e^{-t/\tau} \text{ with time constant } \tau = \frac{V}{f}, \quad (4)$$

this function can be applied also to the buffer volumes ($\tau=37$ min, see Sect. 2.1). The differences become less noisy: $-(0.03 \pm 0.04)$ ppm CO₂, $-(0.28 \pm 0.21)$ ppb CH₄.

This test accounts only for small flow rates of the analyzers (240 and 270 sccm). In ZOTTO the flushing of the tubes at a 60 times larger rate (15 l/min) will outweigh additional influences of the longer tube (300 m) and higher H₂O concentrations in summer. Hence, the influence of long tubing on the gas concentration measurement can be neglected.

2.6 Data acquisition

A custom-made LabVIEW™ program (National Instruments Germany GmbH) installed on a central measurement PC controls all switching processes, calibration cycles, and signal processing. A data acquisition card (PCI-6225) acts as central hardware interface, to read sensor voltages (together with SCB-68 I/O card), and to control the solenoid valves with a relay board (ER-16 SPDT; all made by National Instruments Germany GmbH). The central measurement PC is connected to the CRDS analyzer via serial RS232 cable.

For time synchronization of the different data sets collected on the site (meteorology, aerosols, CO), the measurement PC was equipped with a high quality time card (Clock-Card PCI Pro, Beagle Software, USA) and was set as central time server for other instruments via internal Ethernet network.

Data points are recorded every 30 s, including the average from the raw data of the analyzer and the current reading of all sensors. Additionally, all one second raw data from the CO₂/CH₄ analyzer is archived. Each tower level is sampled for 3 min. For data analysis, first three data points (1.5 min) are rejected. All 6 tower levels, starting at the top, are consecutively measured within 18 min.

The post-processing code is written with the R software (<http://www.r-project.org/>) and removes a few outliers that originate from sporadic malfunction of valve V5 (replaced in September 2009), maintenance interruptions, etc. Afterwards, all CO₂ and CH₄ data points are corrected for dilution and pressure broadening from water by applying a second order function based on the 30 s averaged H₂O raw data (see Sect. 2.4).

For CO₂ and CH₄ calibration, every 100 h each of the three calibration tanks is measured for 8 min. This time span generously allows the calibration gases to flush the pressure regulators and remove the wet ambient air from the part of the tubing used conjointly. The mean of the last four minutes gives the analysis values for the linear calibration curve (see Sects. 2.2 and 2.3). Between two calibrations, the fit parameters are linearly interpolated to account for the drift of the analyzer.

2.7 Flask sampling system

To provide information on a larger number of species (CO₂, CH₄, CO, N₂O, isotopes, etc.), to validate continuous measurements and to bridge potential breakdowns of the continuous analyzer, air samples are collected from the 301 m level in 11 glass flasks twice a week; however the series has several interruptions lasting for several weeks to months due to transport shortages.

To remove the water vapor, the sampled air passes through a glass trap within a fridge at 2 to 5 °C and through two stainless steel traps cooled to −90 °C (Fig. 2). Prior to filling the flasks, the tower tubing is flushed at a flow rate of 2 l/min for 40 min to prevent adsorption from affecting gas concentrations. During filling, air is pumped at a flow of 2 l/min through three flasks for 15 min by an upstream compressor pump (KNF Neuberger GmbH, Germany, Type: PM22619-814). When a pressure of 13 psig (~900 mbar above ambient) is reached in the flasks, flushing of the flasks continues and the excess flow is released via an excess flow valve.

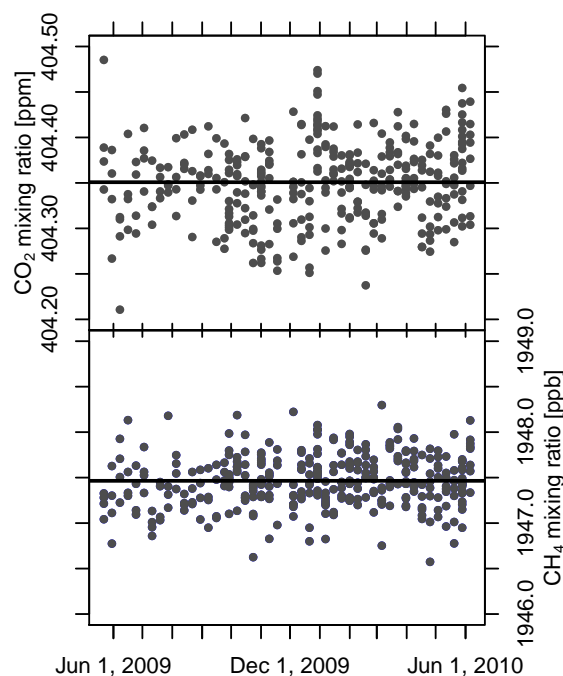


Fig. 5. Target tank time series (black line represents the mean).

2.8 Meteorological measurements

Various meteorological instruments have been installed at ZOTTO in the year 2007. They record meteorological variables (3 dimensional wind, temperature, humidity, radiation) in a vertical profile on the tower as well as a number of soil parameters in vertical and horizontal profiles at two ground locations. A detailed description is given in the supplement of this paper (see <http://www.atmos-meas-tech.net/3/1113/2010/amt-3-1113-2010-supplement.pdf>).

3 Results and discussion

3.1 Data quality assessment

The station was equipped with the new analyzing system in April 2009. The measurement is authorized by Russian FSTEC agency and the system is operational since 20 May 2009. Up to the most recent data (30 April 2010), the total time of missing data due to humidification experiments (Sect. 2.4), maintenance or malfunctions is limited to 91 h (1.1%).

To monitor the accuracy of the instrument, one target tank is measured every 200 h for 8 min randomly distributed

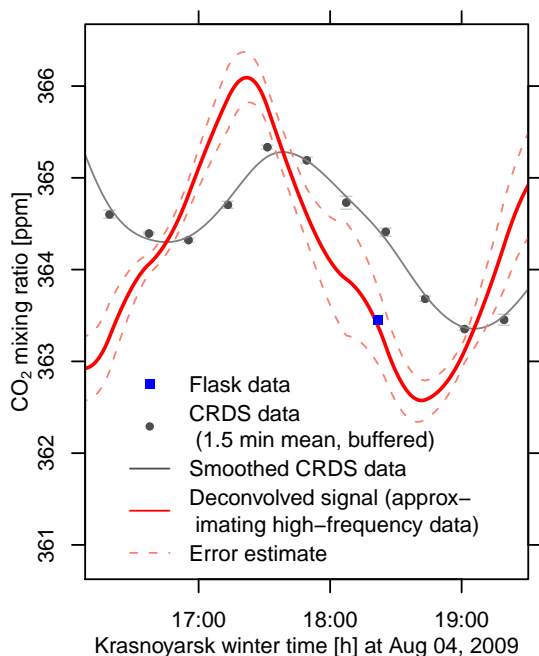


Fig. 6. Comparison of flask data with deconvolved CRDS data.

between two calibration cycles, and is treated like ambient air measurement data. After applying the calibration procedure (Sect. 2.6), the measured CO₂ and CH₄ concentrations of the target tank are 404.35 ± 0.04 ppm and 1947.5 ± 0.3 ppb for the whole time period so far (Fig. 5). A comparison with values from the Jena GASLAB in Table 2 (404.40 ± 0.08 ppm/ 1947.4 ± 1.4 ppb) indicates an adequate accuracy of the system for dry air measurements. The CO₂ measurement is slightly biased, but the deviation is still within the error limit of the Jena GASLAB calibration laboratory, thus statistically insignificant. Earlier calibrations of the CRDS system are highly repeatable, which indicates that the accuracy is limited by the noise of the laboratory calibration.

In conclusion the accuracy of the instrument is 0.09 ppm for CO₂ and 1.5 ppb for CH₄, if statistical independence between target tank measurement of the CRDS analyzer, calibration laboratory (Table 2), and H₂O correction (Sect. 2.4) is assumed.

We used laboratory analysis of the flask samples for comparison with the CRDS data. Flask analysis has a measurement precision of 0.08 ppm CO₂ and 1.3 ppb CH₄. Influences on CO₂ and CH₄ concentrations through the long storage at ZOTTO (max. 363 days) can be excluded, as the storage in glass flasks using PCTFE seals was intensively investigated for periods up to 420 days (GAW Report No.161, 2003). For the flask comparison, the integrating effect of the different air volumes has to be taken into account: $\tau=37$ min for the 8 l buffer and $\tau_0=0.5$ min for 1 l flasks (at 2 slm flow, Eq. (4)). Generally, the measured concentration $c(t)$ through a well

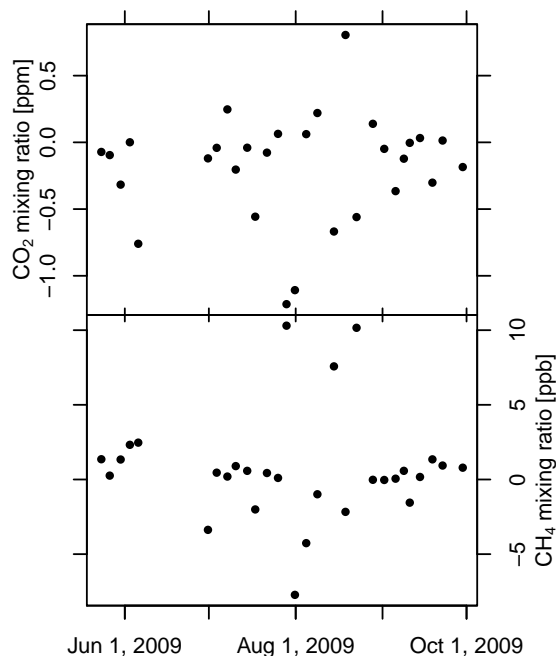


Fig. 7. Time series of differences between flask and deconvolved in situ data.

mixed volume can be calculated by convolving the in-situ concentration $s(t)$ with the response function $g(t)$ of the volume:

$$c(t) = g(t) * s(t) = \int_0^t g(t-t')s(t')dt' \text{ with } g(t) = \frac{1}{\tau}e^{-t/\tau}. \quad (5)$$

The CRDS analyzer measures the integrated concentration $c(t)$. By taking the derivative of Eq. (5) we get a solution as an approximation for the highly variable in-situ data:

$$s(t) = c(t) + \tau \frac{dc(t)}{dt} \quad (6)$$

Figure 6 illustrates this deconvolution exemplarily for one flask measured in 4 August 2009. Three consecutive data points of the CRDS analyzer are combined to one (representing 1.5 min, grey dots) and give the basis for a smoothed spline (grey line, degrees of freedom is 2/3 of the length of the data series), representing $c(t)$. Equation (6) gives the approximate in-situ data (red line). For our attempt to estimate the errors (red dashed line) we used the standard deviation of the three combined CRDS data points (light grey bars) scaled with the factor $\sqrt{\tau}/\sqrt{\tau_0}$ that accounts for the deconvolution uncertainty.

For overall comparison we used 77 flasks from 29 different points in time. The mean difference \pm standard deviation between currently all available flask data and the in-situ approximation is -0.2 ± 0.4 ppm for CO₂ and 0.7 ± 3.7 ppb for

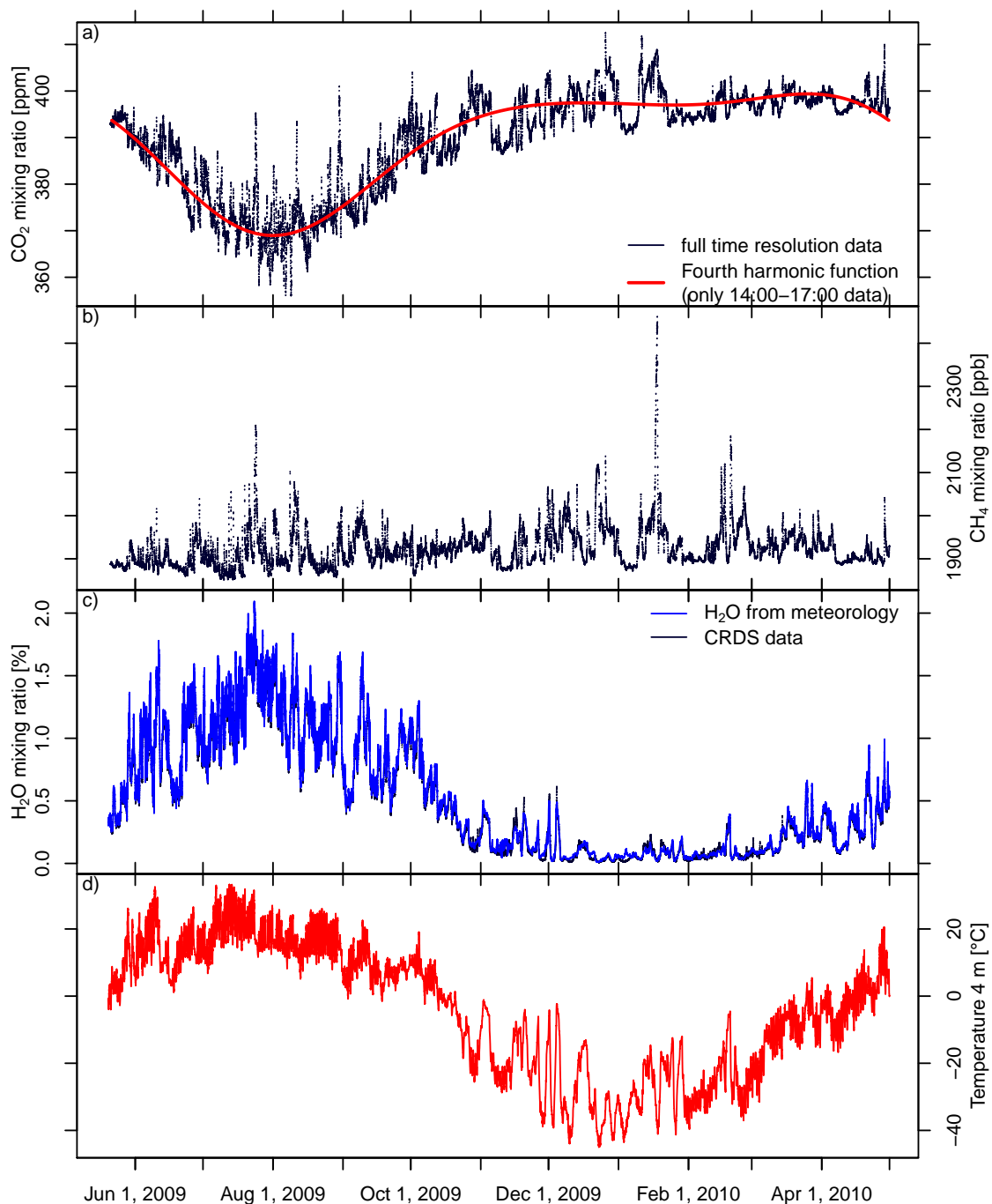


Fig. 8. ZOTTO time series from 20 May 2009 to 30 April 2010 for (a) CO₂, (b) CH₄, and (c) H₂O for 301 m height; (d) temperature at 4 m height

CH₄ (Fig. 7). The results are in line with other comparisons (e.g. Popa et al., 2010) despite having only the buffered signal $c(t)$ available and no high-frequency in-situ signal $s(t)$. Hence, larger deviations in Fig. 7 are a sign of atmospheric variability ($s(t)$) that was smoothed out by the 81 buffer volumes in the CRDS data ($c(t)$).

3.2 CO₂, CH₄ and H₂O measurement series

The CO₂/CH₄/H₂O measurement series from six tower levels covers the whole vegetation period in 2009. All CO₂ data points of the 301 m level are plotted in Fig. 8a. The day time values during well-mixed conditions in the

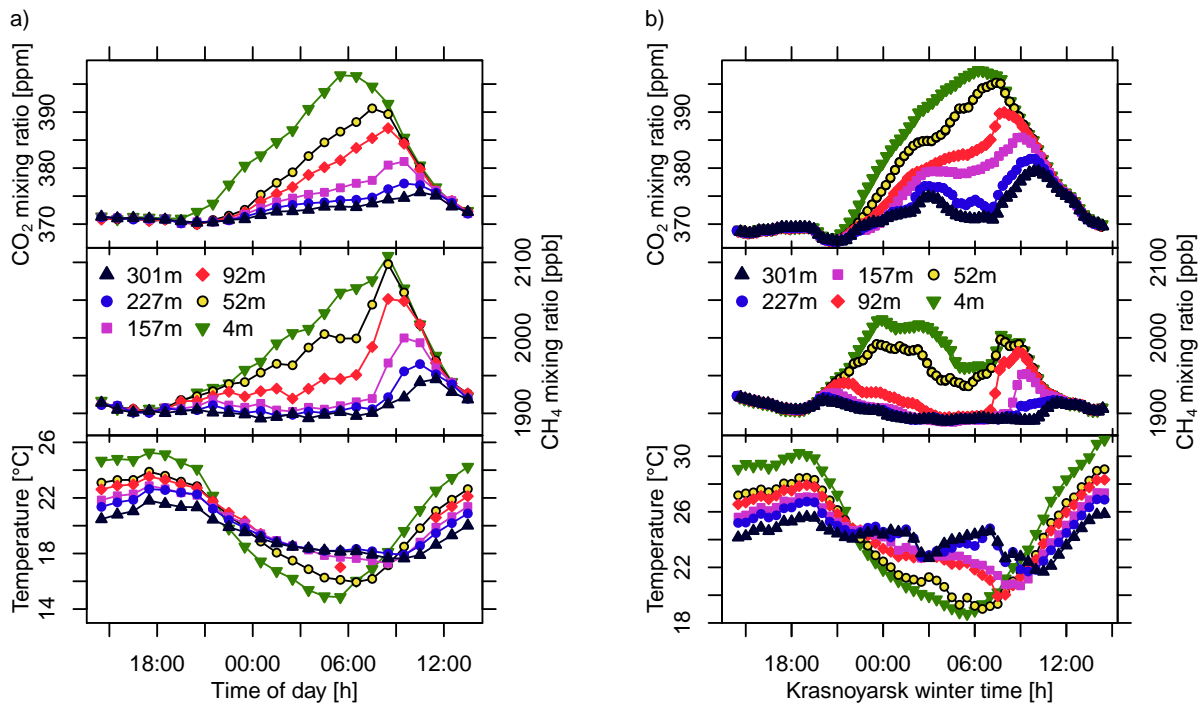


Fig. 9. ZOTTO time series from 6 tower heights for CO₂, CH₄, and temperature: (a) average July 2009; (b) from 22 to 23 July 2009.

planetary boundary layer (14:00 to 17:00 local time zone) can be fitted by a 4th harmonic function, and reveal a seasonal cycle amplitude of 30.4 ppm. This number is comparable with previous values of 26.6 ppm at ZOTTO in the year 2007 (Kozlova et al., 2008). The amplitude is more pronounced than at continental tall tower sites with stronger marine influence, e.g. Bialystok, Poland with 23 ppm (Popa, 2007), or even Ochsenkopf, Germany with 15.5 ppm (Thompson et al., 2009) at the uppermost tower levels (300 and 163 m a.g.l., respectively).

In contrast to CO₂, the CH₄ concentration has an almost flat baseline, which does not vary throughout the year (Fig. 8b) with concentration spikes during the vegetation period. They are most pronounced during July, when most biotic activity in the surrounding bogs takes place and forest fires occur.

The water vapor measurement was compared to the meteorological data series of air temperature and relative humidity. WMO recommends the Goff equation from 1957 to calculate the saturation water vapor according to air temperature (Murphy et al., 2005). The saturation water vapor is multiplied with relative humidity and pressure from the tower top level to receive absolute H₂O concentration from meteorology (Fig. 8c), which correlates well with the calibrated H₂O from the CRDS analyzer (Eq. 1): the slope is 1.038 (still consistent with 1.3% relative error in H₂O calibration and 2% uncertainty in relative humidity measurement) and the correlation coefficient $R^2=0.998$. This procedure represents an

independent check on the calibration, and validates the transfer of our laboratory tests with CFADS-30 (Sect. 2.2) to the CFADS-17 instrument deployed in ZOTTO.

The profiles of CO₂ and CH₄, given by the measurements at different height levels, as well as vertical tracer gradients provide information on trace gas fluxes at local to regional scales. The implemented air buffer volumes allow a quasi continuous measurement from all tower heights with only one instrument. Furthermore, they remove short term fluctuations from atmospheric turbulences; such fluctuations have for example been observed in the Bialystok time series of CO₂ at the 300 m top level (Popa et al., 2010), with a standard deviation of 3 min integrated samples over 40 min (our buffer integration time) amounting to 1.1 ppm during July 2009. This facilitates interpretation when using atmospheric transport models, which do not represent turbulence. As a side effect, the buffered, less variable data takes full advantage of the low-noise analyzer signal.

The combination of integrating buffer volumes and fast line to line switching enhances the representativeness of our data compared to other up-to-date tall tower data series. Usually a distinct diurnal cycle in CO₂ and CH₄ mixing ratios becomes visible on monthly averages only (e.g. July 2009, Fig. 9a), whereas it is revealed already on hourly timescales in our data, e.g. during the summer night from 22 to 23 of July 2009 shown in Fig. 9b. Immediately after sunset, the ground cools faster than the overlaying air as it has a broader long wave radiation spectrum. Thus, the air in the lower

300 to 500 m stratifies to a stable nocturnal boundary layer (Stull, 1988). This inversion layer traps the emitted CO₂ and CH₄ during night. The closer to the ground the air parcel is located, the higher the concentration rises. As soon as the morning sun light warms the surface again (starting shortly before 06:00, Fig. 9), the air starts vertical mixing from the ground and the carbon that was trapped in the surface layer gets diluted with increasing air layer thickness. Thus, the concentration differences between adjacent tower heights fade away until they all reach the concentration of the well-mixed boundary layer during the day. The concentration profiles generally behave similar throughout the summer season, but the point in time varies, when the concentrations of different heights split up. Occasionally, local convective transport merges the concentration time series of different levels and large-scale transport may alter the concentration on all levels. In winter, inversions occur for several days and decouple the time series at the six levels.

Combining these tracer gradients, the meteorological data, and prospective eddy covariance flux measurements with the information from footprint models render investigation of high resolution spatio-temporal flux patterns possible at the regional scale.

4 Summary and conclusions

In April 2009, the Zotino Tall Tower station was equipped with a CRDS analyzer to measure CO₂, CH₄, and H₂O in non-dried sample air. The H₂O measurement and the associated correction is temporally stable enough to guarantee a high quality of the CO₂ and CH₄ measurement and compares well to meteorological data. The water corrections on the CO₂ and CH₄ measurement were validated over a 17 months period with a simple experimental setup. The effect of molecular adsorption in the long air lines was investigated and shown to be negligible.

Regular target tank measurements reveal a precision of the instrument of 0.04 ppm for CO₂ and 0.3 ppb for CH₄. Adding measurement uncertainties of the calibration tanks and the water correction, the accuracy is 0.09 ppm CO₂ and 1.5 ppb CH₄. The difference between the continuous data and flask data is -0.2 ± 0.4 ppm for CO₂ and 0.7 ± 3.7 ppb for CH₄. This corroborates, in an independent way, the good quality of wet air measurements.

Without any drying system the maintenance is considerably reduced. Furthermore, the system sensors for diagnostic values (e.g. flow, pressure, etc.) are free of moving parts, which minimizes the possibility of failures. Calibration tanks will have to be recalibrated on a decadal timescale.

The data is temporally integrated by the use of buffer volumes in each air line, allowing a continuous, near-concurrent measurement from six heights. The 37 min integration time of each line suffices to bridge the 18 min period during which the analyzer is measuring other lines. The results are

six smooth data series, which are not influenced by high-frequency fluctuations associated with turbulent eddies. This allows a temporally highly resolved observation of the nocturnal boundary layer developments, thus enabling to better estimate local night time respiration. Additionally, footprint calculations confirm that the data from the tower's uppermost level will provide a valuable basis for future inverse modeling approaches for the central Siberian region.

Supplementary material related to this article is available online at:

<http://www.atmos-meas-tech.net/3/1113/2010/amt-3-1113-2010-supplement.pdf>

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