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Atmospheric Measurement Techniques
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Discussions

Six years of high-precision quasi-continuous atmospheric greenhouse gas measurements at Trainou Tower (Orléans Forest, France)

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Abstract

Results from the Trainou tall tower measurement station installed in 2006, are presented for atmospheric measurements of CO_2, CH_4, N_2O, SF_6, CO, H_2 mole fractions and Radon-222 activity. Air is sampled from four sampling heights (180 m, 100 m, 50 m and 5 m) of the Trainou 200 m television tower in the Orléans forest in France (47°57′53″ N, 2°06′45″ E, 131 m a.s.l.). The station is equipped with a custom-build CO_2 analyzer (CARIBOU), which is based on a commercial NDIR analyser (Licor 6252), and a coupled gas chromatographic GC system equipped with ECD and FID (HP6890N, Agilent) and a reduction gas detector (PP1, Peak Performer). Air intakes, pumping and air drying system are shared between the CARIBOU and the GC systems. After some initial problems, we achieved short-term repeatability (1 sigma, over several days) for the GC system of of 0.05 ppm for CO_2, 1.4 ppb for CH_4, 0.25 ppb for N_2O, 0.08 ppb for SF_6, 0.88 ppb for CO and 3.8 for H_2. The repeatability of the CARIBOU CO_2 analyser is 0.06 ppm. In addition to the in-situ measurements, weekly flask sampling is performed, and flask air samples are analysed at the LSCE central laboratory for the same species as well for stable isotopes of CO_2. The comparison between in-situ measurements and the flask sampling showed averaged differences of 0.08 ± 1.4 ppm CO_2, 0.69 ± 7.3 ppb CH_4, 0.64 ± 0.62 ppb N_2O, 0.01 ± 0.1 ppt SF_6 and 1.5 ± 5.3 ppb CO for the years 2008–2012.

At Trainou station, the mean annual increase rates from 2007 to 2011 at the 180 m sampling height were 2.2 ppm yr^{-1} for CO_2, 4 ppb yr^{-1} for CH_4, 0.78 ppb yr^{-1} for N_2O and 0.29 ppt yr^{-1} for SF6 respectively. For all species the 180 m sampling level showed the smallest diurnal variation. Mean diurnal gradients between the 50 m and the 180 m sampling level reached up to 30 ppm CO_2, 15 ppm CH_4 or 0.5 ppb N_2O during night whereas the mean gradients are smaller than 0.5 ppm for CO_2 and 1.5 ppb for CH_4 during afternoon.

1 Introduction

The atmospheric greenhouse gas (GHG) measurement group (RAMCES) at LSCE/Gif-sur-Yvette is running today a global network of 8 in-situ stations and 13 flask sampling sites at 12 fixed surface sites, and one on-board a small aircraft. At LSCE the air samples are analysed for CO_2 isotopes (δ^{13}C and δ^{18}O) and for CO_2, CH_4, N_2O, SF_6, CO and H_2 mole fractions. The RAMCES CO_2 and Radon-222 monitoring program was initiated in 1980 at Amsterdam Island observatory (Gaudry et al., 1992; Ramonet and Monfray, 1996) and was extended at Mace Head, Ireland, in 1992 (Biraud et al., 2000, 2002) and at two further sites in France (Gif-sur-Yvette and Puy de Dome) in 2011. The three western European sites reflect different environments from a marine site occasionally influenced by long range transport over Europe (Mace Head), to sites which are more influenced by rural (Puy de Dôme) and urban activities (Gif-sur-Yvette).

Europe has a long history of atmospheric CO_2 monitoring at continental stations, in which the LSCE network participates. To avoid the influence of local trace gas sources, mountain stations such as Schauinsland (Germany), Mt. Cimone (Italy) or Puy de Dôme (France) were traditionally chosen, and a data selection is performed at these sites to obtain a greenhouse gas record reflecting regional scale continental sources and sinks (Schmidt et al., 2003; Cundari et al., 1990). However such measurements are difficult to reproduce by atmospheric transport models due to the influence of topography on air mass transport and mixing (Geels et al., 2007). Consequently, other approaches needed to be developed to complement regional scale emission inventories, through airborne measurements or high towers that avoid being strongly influenced by topography. The frequency of the airborne measurements is still a limiting factor, as well as the bias towards good weather conditions (Stephens et al., 2007). A very promising approach is therefore to establish new stations on tall towers (> 100 m) which are used as television transmission tower (Bakwin et al., 1998; Haszpra et al., 2001). Gloor et al. (2001) showed that the concentration footprint of the Wisconsin 500 m tall tower is in the order of 10^6 km^2.

In the frame of the European projects CHIOTTO (Continuous HIgh-precisiOn Tall Tower Observations of greenhouse gases, http://www.chiotto.org) and CarboEurope IP (http://www.carboeurope.org), eight European tall towers have been equipped or upgraded with high precision measurements systems for continuous greenhouse gas monitoring (Vermeulen et al., 2007). Results and instrumental set-ups are published by Thompson et al. (2009), Popa et al. (2010), Vermeulen et al. (2011). Our group has equipped a new station within Orléans Forest called Trainou Tower, with instrumentation for atmospheric CO_2, CH_4, CO, N_2O, SF_6, H_2 and Radon-222 measurements. The measurements at 4 levels of Trainou Tower (5 m, 50 m, 100 m, 180 m) are completed by regular airborne measurements between 100 m and 3000 m altitude close to the tower. IUP Bremen installed in the frame of the TCCON (Total Carbon Column Observing) network a ground based FTS to analyse the column abundances of CO_2, CH_4, N_2O (Messerschmidt et al., 2011).

In the following chapters of the paper, we present the station location, the instrumental setup, data transmission, quality control and the time series of atmospheric CO_2, N_2O, CH_4, SF_6, CO and H_2 measurements.

2 Sites description

The station (Trainou Tower, TRN) for atmospheric greenhouse gas observation is located in the "Centre" region in France (47°57′53″ N, 2°06′45″ E, 131 m above sea level (a.s.l.) at a 200 m transmitter mast. We equipped four sampling levels on this tower at 5 m (TR0), 50 m (TR1), 100 m (TR2) and 180 m (TR3). Trainou station is about 15 km northeast of the city of Orléans (116 000 habitants) and about 100 km south of Paris. Five small villages (< 2000 habitants) are located nearby the station. In the surrounding of the station, the area is covered by forest (30 %) and agriculture fields (50 %) (source: INSEE 2008, National Institute of Statistic and Economic Study, 2008, http://www.insee.fr).

Using the anthropogenic emissions estimated from bottom up studies for the region “Centre” for 2000 (CITEPA, 2005, http://www.citepa.org) we can identify the main local and regional sources by sector. For CO_2, the three main emission sectors are transport, agriculture and households. More than 50 % of the CH_4 emissions in this region are released by livestock production (dairy cows) and about 25 % from waste treatment (landfills). For N_2O, the agriculture sector (fertilizer applications to croplands) contributes in this region for more than 90 % of the anthropogenic emissions.

For the year 2005, we studied the wind direction and velocity distribution using the Trajectory Viewer 1.1 developed at ECN (Energy research Centre of the Netherlands, http://www.ecn.nl/) and the model output from FLEXPART (Stohl et al., 2005). Figure 1 shows that the dominating wind direction at the 180 m level is southwest followed by northeasterly winds. The distribution of the wind velocity shows maximum value at $6\,m\,s^{-1}$.

3 Measurement systems

The atmospheric measurement station at Trainou Tower consists of a combined air inlet system piloted by the custom-made CO_2 instrument (CARIBOU), a coupled GC analyser system for CO_2, CH_4, N_2O, SF_6, CO and H_2, a Radon-222 analyser and a flask sampler unit. In the following chapters, these five parts are described in detail. Meteorological sensors (see Sect. 3.4) and seven independent inlet lines (DEKABON 1300, 1/2″ o.d.) are installed on the tower. Three inlet lines are disposed at the 180 m level, one at the 100 m, two at 50 m level and one at the 5 m level. For Radon-222 gas measurements a 65 mm inner diameter rigid tubing is installed at the 180 m level. The inlet lines are transferred to the container, which houses the measurement systems.

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3.1 Air inlet and drying system

The pumping and air drying system is controlled by the CARIBOU CO_2 analyser software (see below). It consists of three identical branches of pumps and cooling traps for the 50 m, 100 m and 180 m levels, which allows delivering to the analysing instruments at any time dried air from each level (Fig. 2). Therefore we are able to analyse all three levels at least once each 30 min, without risk of incomplete flushing of air from the level which was passed before. The three air sampling lines are flushed constantly with 15 L air $\min^{-1}$ by the primary pumps (Neuberger N815KNE). To protect the pumps, two filters (40 µm and 7 µm, TF series from Swagelok) are installed. Depending on the meteorological conditions, the filters need to be changed at least every 6 months. From each inlet line, a secondary pump (Neuberger N86KTE) collects an air flow of 5 L $\min^{-1}$, which is then dried in two steps. First, the air passes through a glass trap (decanting bowl 120 mL), which is hosted in a commercial refrigerator regulated at 5 °C in order to remove the main water content from air. To remove condensed water, the traps are evacuated automatically once a day. In a second step, air is further dried by passing through 335 mL glass traps cooled in an ethanol bath to −60 °C using an cryogenic cooler (Thermo Neslab CC-65). The cooling traps are filled with glass beads to increase the surface area for water vapour condensation. These cooling traps are changed once per week, by a technician who maintains the station regularly. This setup allows us to provide dried air, with a dew point of less than −50 °C to the analysing instruments.

3.2 In-situ CO_2 analyser (CARIBOU)

LSCE and CEA/IRFU (Institute of Research into the Fundamental Laws of the Universe) developed new robust CO_2 continuous monitoring stations, named CARIBOU. Within the RAMCES network, four of these stations have been installed. The first one is located at Biscarrosse, France (inlet at 116 m a.s.l.) since May 2005, the second one

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at Hanle, India (4517 m a.s.l.) since August 2006, and the third one at Trainou Tower, France. Finally, in summer 2007, a fourth one was installed at Ivittuut, Greenland.

The CARIBOU systems are designed to make high precision measurements (short-term repeatability in the order of ±0.01 ppm), with high hardware reliability, and require low maintenance. The design also allows full remote control, automated data retrieval and on-line display capability.

The CARIBOU system consists of two main subsystems: (a) an analysis unit which includes a commercial non-dispersive, infrared (NDIR) gas analyzer (LI-6252, LI-COR, Lincoln, Nebraska, USA), pressure, flow and temperature regulators controlled by a Programmable Logic Controller (PLC), and an industrial PC used to configure and control the equipment; (b) a pumping unit, which includes the pumps for three air inlets, and a refrigerator for preliminary drying of air to be analysed (see Sect. 3.1).

The CARIBOU design is inspired from the CSIRO Loflo analyser (Da Costa and Steele, 1997). A schematic view of the system is shown in Fig. 3. The CARIBOU regulates the flow in the sample and reference cells ($20 \pm 0.03\,\mathrm{mL\,min^{-1}}$) and the pressure inside the cells at 1080 ± 0.03 mbar with a combination of 4 flow-controllers (Redwood Fluistor NC-1500 and Bronkhorst F201CHBD11V) piloted by fuzzy logic algorithms. The box containing the NDIR analyser and the hardware necessary to regulate the gas flow and the pressure is thermally regulated. Moreover, there is an additional temperature control of the NDIR cells themselves ($40 \pm 0.05\,^{\circ}\mathrm{C}$). The thermal and pressure control of the instrument minimize the drift of the instrument, allowing calibrations to occur once per week. A low flow of $20\,\mathrm{mL\,min^{-1}}$ and the weekly calibration frequency allows the calibration gas tank to last more than 10 yr. The system is implemented by a 16 position micro-electric valve (Valco Vici) to select the gas to be measured (ambient air, calibration gases, etc. . .). The parameters for temperature and pressure regulation are summarized in Table 1.

3.2.1 On-line data transmission and remote control

The CARIBOU unit has its own control system with an internet link to the LSCE laboratory (Gif-sur-Yvette) which allows remote supervision, configuration and maintenance. The raw data are downloaded automatically every day (or more frequently if needed) by a central computer at LSCE, which allows for database operations. This computer is also in charge of daily tasks such as making connections or checking station health. It will trigger alarms or warnings in case any abnormal condition is detected, such as poor pressure or temperature regulation. The remote control further allows the user to have full access to most of the process variables like pumps, valves, temperature regulation set points, duration of gas analysis. Measurement sequences are created via an inbuilt sequencer and most of the data (CO_2, pressures, temperatures, valves states, etc...) can be plotted on screen for a rapid diagnostic.

3.2.2 Calibration and quality control

At Trainou station, the CARIBOU calibration of the full span of the instrument is carried out every 8 days using 6 station standard gases with a concentration range of 340–450 ppm. These station standard gases have been calibrated against the WMO X2007 scale (Zhao and Tans, 2006) at the LSCE using the Loflo 2D analyser in 2006 and 2011. The difference between the calibration in 2006 and 2011 was for all 6 cylinders smaller than 0.05 ppm. Therefore we used the arithmetic mean of both calibrations. For each calibration sequence, we repeat a pyramid-like pattern 8 times, injecting the calibration gases and the reference gas in ascending and descending order of concentrations; each standard gas analysis lasts 10 min. For the following calculations, a mean of the last 4 min of analysis is taken. To determine and correct the instrument drift, the reference gas is injected for 10 min in the sample cell once per hour. After drift correction using the hourly reference gas analysis, the calibration results showed that the residual drift is lower than 1 ppb per day, which allows the calibrations of the instrument to be done no more frequently than once every 8 days to maintain precision at 0.01 ppm.

Between two full span calibrations, the ambient air measurement cycle, which lasts 7 h, is repeated 24 times. The ambient air measurement cycle is a sequence composed of five 10 min passages of the air from 180 m, 100 m, 50 m, 180 m and 50 m levels bracketed by 10 min reference gas analysis (one every hour). Every 23 h, the 5 times of ambient air measurements are replaced by a so called target gas for quality control during 50 min. All data processing applied to the air measurements is also applied to the target gas measurements, in order to monitor the instrument performance and long-term stability. The upper panel of Fig. 5 shows the time series of target gas for the CARIBOU. We found a mean CO_2 standard deviation of 0.06 ppm. Part of this variation is caused by flushing problems of the pressure regulator. At the beginning of the measurements, the flushing period was only 10–20 min, which was not adapted for the target flow (20 mL min^{-1}) and the quality of the pressure regulators. The increase of the flushing period end of 2008 to 50 min leads to smaller variations of the target gas.

3.3 GC measurement system for analysis of atmospheric CO_2, CH_4, N_2O, SF_6, CO and H_2

The GC measurement system is based on a commercial gas chromatograph (GC), 6890N from Agilent Technologies, which was modified in our laboratory (Messager, 2007). The modifications were done in accordance to the workshop of harmonisation of measurement techniques in the frame of the CHIOTTO project and of the existing GC system in our central laboratory in Gif-sur-Yvette. After optimisation, the GC-system was installed at Trainou station in July 2006. Our GC system is equipped with a Flame Ionisation Detector (FID) in order to detect CH_4 and CO_2 (via Nickel catalyst) and an Electron Capture Detector (µECD) for N_2O and SF6 (Lopez et al., 2012). In October 2008, we coupled a second GC containing a Reduction Gas Detector (PP1 analyser, Peak Laboratories) to the existing GC system to analyse simultaneously CO and H_2 (Yver et al., 2011).

Figure 4 shows a schematic of the gas flow though the GC system. The principal parameters are summarised in Table 2. A 16 position valve (Valco Vici, UWE, micro-electronic actuator) #7 is used to switch between the four air inlets (180 m, 100 m, 50 m and 5 m height), standard and target gases. The sample loops are flushed with dry ambient air or standard gas with a flow rate of 200 mL min^{-1}, controlled by the EPC (Electronic Pressure Control, AUX 5). After 45 s, EPC AUX 5 is closed, allowing a pressure and temperature equilibration during 30 s. The three sample valves (#1a, #1b and #5) are then switched simultaneously in order to transfer the content of the sample loops to the separation columns. All valves are installed in a closed electrical rack system, to protect for short term temperature variations.

For the CO_2/CH_4 branch Nitrogen (5.0, 99.999 %) is used as carrier gas for the separation on a packed Haysep Q column. At a flow rate of 50 mL min^{-1} (EPC AUX 3), CH_4 elutes about 70 s after injection and CO_2 120 s after injection. After the CH_4 peak is analysed on the FID, valve #4 is switched from the bypass to the Nickel catalyst at 390 °C, which converts CO_2 to CH_4 permitting the CO_2 analysis on the FID. The efficiency of the Ni catalyst for reduction of CO_2 to CH_4 is better than 96 %. To supply hydrogen to the FID and the Ni catalyst, we used hydrogen generators from Parker/Balston (model A9150 until summer 2008 and after model 9200). In 2010 we replaced the hydrogen generator again with a NM-H2 250 (FDBS). Synthetic air is supplied by a combination of compressor (Jun Air) and a purifier Parker (Chromgas 1000).

For the N_2O/SF_6 branch, a 5 % CH_4 in Argon (ECD quality) is used as carrier gas. The separation of the peaks is performed on two packed Haysep columns. 70 s after injection, when N_2O and SF_6 are on the analytical column, the pre-column is back flushed by turning valve #3. This avoids that compounds with longer retention times are polluting the analytical column. N_2O and SF_6 are analysed on the ECD 150 s and 180 s respectively after injections.

Electron capture detectors are known for their non-linear responses when measuring N_2O and the possible problem of co-elution of N_2O and CO_2, depending on the column setup. As described in more detail by (Lopez et al., 2012; Schmidt et al., 2001), we determine the non-linear response of the ECD detector using a reference sample diluted with N_2O and CH_4-free air. Methane is used to determine the dilution factor, as the response of the FID for CH_4 is linear within the chosen range. We found that the µECD at Trainou underestimates the N_2O concentration with increasing values, but a linear correction can be added to describe the response of the ECD in the range of 300 to 350 ppb (Messager, 2007; Lopez et al., 2012). The slope of the correction function would be 0.07 for the N_2O measurements at Trainou station. A two-point calibration strategy with one working standard of 315 ppb and a second one of 340 ppb N_2O was therefore chosen in order to correct for the non-linear behavior of the µECD (see Sect. 3.3.2).

We have tested the co-elution of N_2O and CO_2 using a small amount of Ascarite (Fluka, #11133, 5–20 mesh), followed by a magnesium perchlorate [$Mg(ClO_4)_2$] drying which removes CO_2 from a reference sample. As described by Lopez et al. (2012) the influence of the CO_2 co-elution is negligible for the N_2O measurements at Trainou. They reported also about a cross sensitivity of N_2O and SF_6, at Gif-sur-Yvette station, when SF_6 peaks exceeded 15 ppt. At Trainou station we never observed SF_6 mole fractions larger than 14 ppt, but we were careful not using calibration gases with elevated SF_6.

In order to add CO and H_2 measurements, we coupled a reduction gas detector (RGD) from Peak Performer, to the Agilent GC in 2008 (Yver et al., 2011). The sample loop of the RGD is connected in series with the sample loop of the FID and ECD. The analysis is performed by reduction of mercuric oxide and detection of mercury vapor by UV absorption. Synthetic air (Air Liquide, high purity) purified by an additional filter in the chromatograph is used as carrier gas. Aliquots of air are flushed through a 1 mL sampling loop. After equilibration, the sample is injected onto the columns. The pre-column (Unibeads) is used to separate H_2 and CO from other components and the analytical one (Molecular Sieve) effectively separates H2 and CO before being analyzed by the mercury detector. The oven temperature is controlled at 105 °C and the catalytic chamber is heated to 265 °C.

The non-linearity of the RGD detector is regularly determined using a set of cylinders spanning a H_2 mole fraction between 213 and 996 ppb and CO mole fractions between 157 and 523 ppb. The standard cylinders for H_2 were calibrated at MPI Jena and for CO by NOAA/CMSL. During the test of the analyzer in our laboratory, we performed a non-linearity test with 11 standard cylinder for H_2 and 5 for CO. During operation at Trainou station the number of standard cylinders had to be reduced to only 4 for both species due to logistic problems. In general the standard cylinders are evaluated every 6–12 months. Over the described measurement period the non-linearity of the RGD at Trainou did not change significantly for CO and H_2 in the range of observed mixing ratios. However, for H_2, a shift in the non-linearity was observed for mixing ratios above 800 ppb. As the observed mole fractions are below 650 ppb, all data are corrected with the same third degree polynomial fit. Only the quality control gas (Target) with a H_2 mole fraction above 800 ppb is affected by this choice with an observed shift over time (see Sect. 3.3.2) .

With this set up, we are able to realize the injection and the detection of one sample within five minutes, allowing 12 ambient air or standard gas injections during one hour.

3.3.1 Data acquisition and remote control

For the full control of the GC system, data acquisition and remote control, we are using one PC, which is equipped with the chromatography software CHEMSTATION (A.09.03) from Agilent. To treat the signal of the PP1 GC in the same way and to synchronise the two GCs, we added an AD converter (Agilent Technologies Inc 35900E). The CHEMSTATION software offers the possibility to schedule the switching of all valves, to control the temperature of the oven and the detectors and to regulate the flow of the carrier gases and the flushing of the sample loops. The detector signals of both GCs are recorded by the CHEMSTATION and at the end of each injection method, the integration of the peaks is performed.

Once a day, we transfer automatically the raw data (chromatograms and integrated peak areas and heights) via ftp to a central computer at LSCE. From there, peak areas and heights, sample information, etc., are read by the database and computed to concentration values. Chromatograms and other additional information are stored separately in case of necessary re-evaluation of the data. We have at any time the possibility to access remotely from our institute the CHEMSTATION at Trainou Tower in case modifications to the methods, sequences or integrations are needed.

3.3.2 Calibration and quality control

To correct for possible drift of the measurement system, we decided to perform the working standard analysis every 30 min. As the ECD and also the RGD show a non-linear behaviour, we inject a working standard low (WL) and a working standard high (WH) in order to apply a two point calibration. These standards are produced by Deuste Steininger (Mühlhausen, Germany), and filled in 40 L aluminium cylinders. The concentration range is chosen to bracket the atmospheric concentration range for all analysed gases at Trainou station. As the first working standards did not contain H_2, a working standard "special" (WS) is used to calculate the H_2 concentration. The non-linearity of the RGD is corrected using a third-degree polynomial fit. This fit is determined by measuring a range of four standard gases (Yver et al., 2011).

Like for CO_2 CARIBOU measurements, a target gas, with a known concentration value in-between the WL and WH concentration is analysed every 1–2 h. A typical one hour sequence consist of WH, WL, WS, Target, 180 m, 100 m, 50 m, WH, WL, WS, 180 m, 100 m, 50 m, 180 m. With this frequency of calibration, the theoretical lifetime of working standards is between 1.5 and 2 yr and for the target gas 3–4 yr.

The target gas is used to calculate the short-term repeatability (on a daily basis) and the long-term reproducibility. Figure 5 shows the time series of the hourly target gas injection for CO_2, CH_4, N_2O, SF_6 and since July 2009, also for CO and H_2. The large gaps in winter 2006/2007 are due to electrical power supply problems. We had then to stop all measurement systems between October 2006 and February 2007. In

November 2007, the ECD was broken, and could only be replaced in August 2008. For the whole period of analysis, we found a mean standard deviation of the hourly target gas injection of 0.14 ppm for CO_2, 3.1 ppb for CH_4, 0.70 ppb for N_2O, 0.8 for SF_6, 1.8 ppb for CO and 17 ppb for H_2. We can identify several periods where the GC was not working very well for different trace gas analysis increasing the standard deviation of our target measurements. In 2009 we had repeated problem with hydrogen generators, producing not sufficient dry hydrogen. After the replacement of the hydrogen generator in 2010, we can achieve a CH_4 repeatability of 1.4 ppb. Similar problems, as said above, but caused by the ECD can be reported for the N_2O reproducibility. In 2009 the ECD was working perfectly and the target gas showed a standard deviation of only 0.21 ppb.

To link the station to the international calibration scales, the working standards have been initially calibrated against gas tanks calibrated by the WMO calibration centres at NOAA (Zhao and Tans, 2006; Dlugokencky et al., 2005; Hall et al., 2007) or MPI Jena (Jordan and Steinberg, 2011). Before the end of the lifetime and in case of drift or jump in the quality control gas, the working standards at the station are reanalysed in our laboratory in Gif-sur-Yvette. The details about the instrumentation used to calibrate our station standards in our laboratory and the WMO scales for different gases are summarised in Table 3.

3.4 Other instrumentation

3.4.1 Meteorological sensors

Meteorological sensors are installed at the 180 m (TR3) and at the surface level on the top of the container about 5 m above ground (TR0). To measure the wind speed and direction, we are using a sensor from Young (Model 05103L) and for the temperature and humidity a sensor from Vaisala (HUMICAP HMP45A). The data acquisition and transfer to the database is taken over by the CARIBOU software (see Sect. 3.2)

3.4.2 Flasks sampling

Weekly flasks sampling is performed from an independent sampling line at the 180 m level with a standard flask sampler used in the French GHG network. The sampling unit consist of a diaphragm pump (Model N86 KNDC, KNF Neuberger) which draws air through a chemical drying cartridge filled with anhydrous magnesium perchlorate [$Mg(ClO_4)_2$]. Air is collected in 1 L glass flasks sealed with PTFE (polytetrafluoroethene) O-rings (Normag Labor- und Prozesstechnik, Ilmenau, Germany). Flasks are collected in pairs and pressurized to 2 bar absolute pressure. The sampling started with a low frequency in 2006. Since June 2007, a regular sampling is performed, during the weekly maintenance of the station. The flasks are transported to our central lab at Gif-sur-Yvette and analysed for mixing ratios of CO_2, CH_4, N_2O, SF_6, H_2, and CO by gas chromatography (GC). The isotopic composition of CO_2 is determined using a Finigan MAT252 isotope ratio mass spectrometer (IRMS), equipped with a trapping box for cryogenic separation of CO_2 from air.

3.4.3 $^{14}CO_2$ sampling

In cooperation with Institut für Umweltphysik at University of Heidelberg, we installed a sampler for $^{14}CO_2$ sampling. Integrated atmospheric $^{14}CO_2$ samples are collected from the 180 m inlet line over two weeks in CO_2-free sodium hydroxide solution since January 2008. The flushing rate is adjusted in order to sample CO_2 from a total volume of 20–25 m^3 of air. The sampling and analysis technique is described in detail by Levin et al. (1980).

3.4.4 Radon-222 measurements

In June 2009, we installed a Radon measurement instrument at Trainou, which was tested between January 2007 and May 2009 in Gif-sur-Yvette (Yver et al., 2009). The detection method based on a double filter was installed in cooperation with ANSTO, Australia. In the double filter method (Whittlestone and Zahorowski, 1998;Zahorowski et al., 2004), ambient air is continuously pumped through two 200 L cylinders and through a first filter to the analysis chamber. During this first step, Radon-222 (^{222}Rn) disintegrates as the time residence is ten times higher than its half-life and the filter retains all solid particles letting just ^{222}Rn coming in the analysis chamber. In this chamber, ^{222}Rn daughters are produced and collected on a second filter. The *alpha*-decay of these daughter elements is then counted. The instrument is regularly calibrated with known quantity of ^{222}Rn emitted by a ^{220}Ra source. The inlet line is installed at the 180 m level.

3.4.5 Atmospheric boundary layer (ABL) depths measurements

Since December 2010, a vertically pointed aerosol lidar system (ALS300, Leosphere, Orsay, France) to monitor ABL depths is operated routinely at Trainou Tower. All details of the instrumental description and the first time series of ABL depths can be found in Pal et al. (2014).

3.5 Comparison of the different instruments and flasks analysis

In 2007 and from 2009 to 2012, the GC system and the CARIBOU analysed CO_2 mole fraction at the 50 m, 100 m and 180 m sampling level. The sampling of the different levels for both analysers is not synchronised, but both analysers are sampling between 1 and 2 times per hour each level. In case of the GC, it is a single injection and in case of the CARIBOU a 10 min interval with a frequency of 1 Hz. In order to compare both values, we used the 1 h mean values, which risks a maximum time shift of 50 min, in case of only one injection per analyser at the beginning and the end of the one hour interval, respectively. The mean differences and the 1-sigma standard deviations are summarised in Table 4 for the different years and the different sampling level. The values correspond to the GC measurement minus CARIBOU measurement. Most of the time the CO_2 difference between both analysers was in the order of 0.1 ppm or better, with the exception of the year 2007 and 2011, where the GC measures around 0.15 ppm higher values at all three sampling level. This indicates a possible leakages or a calibration problem of the GC, but afterwards we were not able to dedicate it to one specific analyser.

In parallel to the GC measurements weekly flask sampling at the 180 m level was carried out and analysed on the GC system in the LSCE central lab in Gif-sur-Yvette (see Sect. 3.4.2). During the period 2007–2012 we monitored a mean difference between GC Trainou and flasks of -0.08 ± 1.4 ppm CO_2, -0.69 ± 7.3 ppb CH_4, -0.64 ± 6.2 ppb N_2O, 0.01 ± 0.1 ppb SF_6 and 1.5 ± 5.34 ppb CO respectively.

4 Measurement of ambient air

Figure 6 shows the hourly averaged time series of CO_2, CH_4, N_2O and SF_6, CO, H_2 mole fraction and ^{222}Rn activity for the four sampling heights (180 m in blue, 100 m in green, 50 m in red and 5 m in black). The lowest sampling level (5 m) was only added in October 2010. As already described in Sect. 3.3.2 all measurement systems were stopped between October 2006 and February 2007. In November 2007, the ECD was broken, and could only be replaced in August 2008 leading to gaps in the time series of N_2O and SF_6.

4.1 Growth rates and seasonal variations

The CO_2 time series shows a seasonal cycle with minimum value in summertime (August) and a wintertime maximum (January) as expected. Superimposed on this signal are synoptic and diurnal peaks generally associated with regional pollution events and changes in the boundary layer height. Diurnal variations with CO_2 mole fractions of up to 550 ppm during summer have been monitored at the lowest sampling level, 5 m above ground whereas at the 180 m level elevated mole fractions of up to 450 ppm occurs from time to time in winter. The amplitude of the diurnal variations decreases with the increasing sampling height. We computed a CO_2 annual growths rate of 2.2 ppm per year for the 180 m sampling level between 2007 and 2012, considering all-day round measurements.

The CH_4 time series shows a mean seasonal cycle of approximately 70 ppb peak to peak amplitude with higher values during January and lowest values end of July. High short term (diurnal variations) occurs during winter correlated with pollution events of other trace gases, when the nocturnal PBL height is low. During these events the CH_4 mole fraction can increase to up to 2400 ppb at the lowest and 2050 at the 180 level. Averaged over the plotted measurement period, CH_4 increased 4.1 ppb per year at Trainou station (180 m sampling).

N_2O mole fractions at 180 m sampling height increase with an average annual growth rate of 0.78 ppb per year. Again the lower sampling levels show larger variability likely reflecting local emissions from soil and other sources. In the study of Lopez et al. (2012), N_2O emissions in the catchment area of Trainou station are discussed in detail.

The SF_6 increase rate at Trainou 180 m sampling level corresponds to 0.29 ppt per year. Superposed to this trend, are few events with elevated SF_6 mole fractions of nearly 15 ppt at lower sampling levels and approximately 10 ppt at the highest sampling level.

CO and H_2 time show seasonal cycles with minimum value in July (CO) or September (H_2) as described by Yver et al. (2011). Superimposed on this signal are diurnal peaks and synoptic peaks. In winter the diurnal variations with CO or H_2 mole fractions of up to 700 ppb have been monitored at the lowest sampling level, 5 m above ground whereas at the 180 m level elevated mole fractions of up to 450 ppb occurs from time to time in winter. In summer H_2 mole fraction can be smaller at the lower levels, than at the 180 m level due to soil sink.

^{222}Rn activity is only measured at the 180 m level.

4.2 Mean diurnal variation and vertical gradient

Figure 7 summarises the mean diurnal variation of CO_2, CH_4, N_2O, SF_6, CO and H_2 mole fraction and ^{222}Rn activity for the four sampling level averaged by month and hour of day. The *x* axis of each month covers an interval between 00:00 and 24:00 (GMT), where midnight GMT corresponds to 23:00 local time at Trainou station. CO_2, CH_4 and N_2O mole fractions show larger increases during night time, with strong accumulations at ground levels. During afternoon, when vertical mixing is strong, the gradients between the different levels are small.

Amplitudes of the diurnal variation and also night time gradients between sampling levels are largest between May and October for CO_2 mole fractions. Largest diurnal variations are observed on the sampling level close to the ground and therefore close to local sources, but we still observe small diurnal cycles of CO_2 mole fraction at the 180 m sampling height as the nocturnal boundary layer is sometimes above 180 m. But also CO_2 accumulated during night below the 180 m sampling height can be seen as small peak, in the late morning, when vertical mixing starts and increases. A maximum gradient between the 5 m level and the 180 m level (see Fig. 8) of 30 to 50 ppm CO_2 is reached at 05:00 GMT when the nocturnal boundary layer is below 180 m. The CO_2 gradients between 180 m and 100 m or 50 m sampling lines are approximately 5 ppm or 10 ppm, respectively. In the afternoon 12:00 to 16:00 GMT the monthly mean CO_2 mole fraction of the sampling levels between 50 and 180 m agree within 0.5 ppm during March to November and within 1 ppm during the winter months, respectively. Even though the Trainou tower is surrounded by forest we do not observe in the mean gradients for spring or summer lower day time CO_2 mole fractions at the lower levels of the tower due to local net uptake as described by Vermeulen et al. (2011) and Popa et al. (2010) at Cabauw or Bialystok tall tower, respectively.

The mean diurnal variation of the CH_4 mole fraction show similar patterns as for CO_2, with a stratification of the different sampling levels during night time. However the amplitude of the 5 m level is less distinctive, indicating weaker local emissions compared to CO_2. The night time CH_4 gradients between 180 m and 100 m or 180 m and 5 m sampling level are approximately 30 ppb or 15 ppb respectively. The afternoon values of all sampling levels agree within 1–2 ppb.

At Trainou tower the mean diurnal cycle amplitudes for N_2O are approximately 0.5 ppb for the 50 m, 100 m and 180 m sampling level. During February, March, April, August and September, the 5 m sampling level clearly shows accumulation of N_2O during night time, which corresponds to large N_2O emissions from arable land shown by Lopez et al. (2012) for the catchment area of Trainou.

SF_6 shows only a weak diurnal cycle without accumulation during night. No significant gradient build up between the 50, 100 and 180 m sampling level. Peaks shown in Fig. 7 can be attributed to single SF_6 "events".

CO shows a noticeable seasonal behavior, with large diurnal cycles and vertical gradients between October and March and very small diurnal cycles between April to September with small vertical gradients, also during night time.

For H_2, in winter, there is almost no difference between the three heights (50 m, 100 m, 180 m) whereas in summer, due to the influence of the soil sink the gradient can reach up to 20 ppb between the 50 m and the 180 m inlet and even up to 60 ppb between the 5 m and the 180 m line. With the soil sink predominating during nighttime, when the boundary layer is low and the emissions reduced, the lowest mixing ratio are encountered at 5 m. A more detailed analysis of H_2 and CO is presented by Yver et al. (2011).

5 Conclusions

A new fully automated measurement system to analyse simultaneously atmospheric CO_2, CH_4, N_2O, SF_6 CO and H_2 was installed on a 200 m transmission tower at Trainou in the forest of Orléans. The station was installed in summer 2006 starting with a CO_2 analyser and a GC system for CH_4, N_2O and SF_6 and consecutively upgraded with new instrumentation for CO and H_2, ^{222}Rn analysis and $^{14}CO_2$ sampling. After some logistical problems in the starting phase of the installation, the station delivers high quality measurements fulfilling the requirements of the WMO recommendations. In June 2012 the Electron Capture Detector developed a leak and therefore we had to close the station for some months and to take out of service the GC system. In 2013 the station will be upgraded by CRDS analysers to measure CO_2, CH_4, CO and N_2O following the ICOS recommendations. The new instrumentation will have the advantage requiring less maintenance, than the GC system. During the last years the maintenance of the GC, operated remotely was, with 10 service visits per year, quite time consuming taking into account the 180 km distance between Trainou and our laboratory in Gif-sur-Yvette.

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References

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, doi:10.1034/j.1600-0889.1998.t01-4-00001.x, 1998.

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, T. G., and Jennings, S. G.: European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland, J. Geophys. Res.-Atmos., 105, 1351–1366, doi:10.1029/1999jd900821, 2000.

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, G., and Jennings, S. G.: Quantification of carbon dioxide, methane, nitrous oxide and chloroform emissions over Ireland from atmospheric observations at Mace Head, Tellus B, 54, 41–60, doi:10.1034/j.1600-0889.2002.00228.x, 2002.

Cundari, V., Colombo, T., Papini, G., Benedicti, G., and Ciattaglia, L.: Recent Improvements on Atmospheric CO_2 Measurements at Mt-Cimone Observatory, Italy, Nuovo Cimento C, 13, 871–882, doi:10.1007/Bf02512003, 1990.

Da Costa, G. and Steele, L. P.: A low-flow analyser system for making measurements of atmospheric CO_2, in: Report of the Ninth WMO Meeting of Experts on Carbon Dioxide concentration and Related Tracer Measurement Techniques, World Meteorological Organization, Geneva, 16–20, 1997.

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, J. Geophys. Res.-Atmos., 110, D18306, doi:10.1029/2005jd006035, 2005.

Gaudry, A., Kanakidou, M., Mihalopoulos, N., Bonsang, B., Bonsang, G., Monfray, P., Tymen, G., and Nguyen, B. C.: Atmospheric Trace Compounds at a European Coastal Site – Application to CO_2, CH_4 and Cos Flux Determinations, Atmos. Environ. a-Gen., 26, 145–157, doi:10.1016/0960-1686(92)90267-O, 1992.

Geels, C., Gloor, M., Ciais, P., Bousquet, P., Peylin, P., Vermeulen, A. T., Dargaville, R., Aalto, T., Brandt, J., Christensen, J. H., Frohn, L. M., Haszpra, L., Karstens, U., Rödenbeck, C., Ramonet, M., Carboni, G., and Santaguida, R.: Comparing atmospheric transport models for future regional inversions over Europe – Part 1: mapping the atmospheric CO_2 signals, Atmos. Chem. Phys., 7, 3461–3479, doi:10.5194/acp-7-3461-2007, 2007.

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, doi:10.1029/2001jd900021, 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, doi:10.1029/2000jd900600, 2001.

Jordan, A. and Steinberg, B.: Calibration of atmospheric hydrogen measurements, Atmos. Meas. Tech., 4, 509–521, doi:10.5194/amt-4-509-2011, 2011.

Lopez, M., Schmidt, M., Yver, C., Messager, C., Worthy, D., Kazan, V., Ramonet, M., Bousquet, P., and Ciais, P.: Seasonal variation of N2O emissions in France inferred from atmospheric N_2O and Rn-222 measurements, J. Geophys. Res.-Atmos., 117, D14103, doi:10.1029/2012jd017703, 2012.

Messager, C.: Balancing of regional greenhouse gases fluxes from atmospheric measurements, Univ. Paris 7, Paris, 176 pp., 2007.

Messerschmidt, J., Geibel, M. C., Blumenstock, T., Chen, H., Deutscher, N. M., Engel, A., Feist, D. G., Gerbig, C., Gisi, M., Hase, F., Katrynski, K., Kolle, O., Lavrič, J. V., Notholt, J., Palm, M., Ramonet, M., Rettinger, M., Schmidt, M., Sussmann, R., Toon, G. C., Truong, F., Warneke, T., Wennberg, P. O., Wunch, D., and Xueref-Remy, I.: Calibration of TCCON column-averaged CO_2: the first aircraft campaign over European TCCON sites, Atmos. Chem. Phys., 11, 10765–10777, doi:10.5194/acp-11-10765-2011, 2011.

Pal, S., Lopez, M., Schmidt, M., Ramonet, M., Gibert, F., Xueref-Remy, I., and Ciais, P.: Investigation of the atmospheric boundary layer depth variability and its impact on the 222Rn concentration at a rural site in France: Evaluation of a year-long measurement, J. Agr. Forest Meteorol., submitted, 2014.

Popa, M. E., Gloor, M., Manning, A. C., Jordan, A., Schultz, U., Haensel, F., Seifert, T., and Heimann, M.: Measurements of greenhouse gases and related tracers at Bialystok tall tower station in Poland, Atmos. Meas. Tech., 3, 407–427, doi:10.5194/amt-3-407-2010, 2010.

Ramonet, M. and Monfray, P.: CO_2 baseline concept in 3-D atmospheric transport models, Tellus B, 48, 502–520, doi:10.1034/j.1600-0889.1996.t01-2-00008.x, 1996.

Schmidt, M., Glatzel-Mattheier, H., Sartorius, H., Worthy, D. E., and Levin, I.: Western European N_2O emissions: A top-down approach based on atmospheric observations, J. Geophys. Res.-Atmos., 106, 5507–5516, doi:10.1029/2000jd900701, 2001.

Schmidt, M., Graul, R., Sartorius, H., and Levin, I.: The Schauinsland CO2 record: 30 years of continental observations and their implications for the variability of the European CO_2 budget, J. Geophys. Res.-Atmos., 108, 4619, doi:10.1029/2002jd003085, 2003.

Stephens, B. B., Gurney, K. R., Tans, P. P., Sweeney, C., Peters, W., Bruhwiler, L., Ciais, P., Ramonet, M., Bousquet, P., Nakazawa, T., Aoki, S., Machida, T., Inoue, G., Vinnichenko, N., Lloyd, J., Jordan, A., Heimann, M., Shibistova, O., Langenfelds, R. L., Steele, L. P., Francey, R. J., and Denning, A. S.: Weak northern and strong tropical land carbon uptake from vertical profiles of atmospheric CO_2, Science, 316, 1732–1735, doi:10.1126/science.1137004, 2007.

Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, Atmos. Chem. Phys., 5, 2461–2474, doi:10.5194/acp-5-2461-2005, 2005.

Thompson, R. L., Manning, A. C., Gloor, E., Schultz, U., Seifert, T., Hänsel, F., Jordan, A., and Heimann, M.: In-situ measurements of oxygen, carbon monoxide and greenhouse gases from Ochsenkopf tall tower in Germany, Atmos. Meas. Tech., 2, 573–591, doi:10.5194/amt-2-573-2009, 2009.

Vermeulen, A. T., Schmidt, M., Manning, A., Moors, E., Moncrieff, J., Haszpra, L., Stefani, P., and Lindroth, A.: CHIOTTO, Final Report ECN, PettenECN-E–07-052, 118, 2007.

Vermeulen, A. T., Hensen, A., Popa, M. E., van den Bulk, W. C. M., and Jongejan, P. A. C.: Greenhouse gas observations from Cabauw Tall Tower (1992–2010), Atmos. Meas. Tech., 4, 617–644, doi:10.5194/amt-4-617-2011, 2011.

Whittlestone, S. and Zahorowski, W.: Baseline radon detectors for shipboard use: Development and deployment in the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res.-Atmos., 103, 16743–16751, doi:10.1029/98jd00687, 1998.

Yver, C., Schmidt, M., Bousquet, P., Zahorowski, W., and Ramonet, M.: Estimation of the molecular hydrogen soil uptake and traffic emissions at a suburban site near Paris through hydrogen, carbon monoxide, and radon-222 semicontinuous measurements, J. Geophys. Res.-Atmos., 114, D18304, doi:10.1029/2009jd012122, 2009.

Yver, C., Schmidt, M., Bousquet, P., and Ramonet, M.: Measurements of molecular hydrogen and carbon monoxide on the Trainou tall tower, Tellus B, 63, 52–63, doi:10.1111/j.1600-0889.2010.00520.x, 2011.

Zahorowski, W., Chambers, S. D., and Henderson-Sellers, A.: Ground based radon-222 observations and their application to atmospheric studies, J. Environ. Radioactiv., 76, 3–33, doi:10.1016/j.jenvrad.2004.03.033, 2004.

Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, J. Geophys. Res.-Atmos., 111, D08s09, doi:10.1029/2005jd006003, 2006.

Table 1. Parameters of temperature and pressure regulation for the CARIBOU CO_2 analyser. The reproducibility of the standard gas is 0.02 ppb.

Licor Cell pressure regulation	< 0.1 mbar rms
Thermal regulation	0.1 °C rms
Gas flow regulation	0.1 mL/min rms
Reproducibility of standard gas	0.02 ppm rms
Typical residual drift after drift correction	1 ppb/day

Table 2. Settings and regulation of the GC parameters.

	CO_2 and CH_4	N_2O and SF_6	CO and H_2
Oven temperature (column)	80 °C	80 °C	106 °C
Sample loops	15 mL	10 mL	1 mL
Flow through sample loops	200 mL min^{-1}	200 mL min^{-1}	200 mL min^{-1}
Carrier gas	Nitrogen 5.0	Ar/CH4 (5 %) ECD quality	Synthetic air
Carrier gas (flow)	50 mL min^{-1}	40 mL min^{-1} (backflush: 55 mL min^{-1})	15 mL min^{-1}
Analytical Columns	Haysep-Q, 80–100 mesh (12′ × 3/16″ SS)	Haysep-Q, 80–100 mesh (6′ × 3/16″ SS)	Molecular Sieve 5° 30 1/4″
Pre-Column		Haysep-Q, 80–100 mesh (4′ × 3/16″ SS)	Unibeads 1s column 30 1/4″, 60/80
Detector	FID	µECD	RGD
Detector temperature	300 °C	395 °C	265 °C
	H2 Flow: 50 mL min^{-1} Air Flow: 400 mL min^{-1} FID Methanizer: 390 °C		

Table 3. Primary calibration scales at the LSCE central lab, which are used to calibrate the station standards. CO_2 calibration of the working standards is performed generally with the Loflo (NDIR) analyser. The other gases are calibrated by GC system.

Component	Instrument	Range	# of tanks	Scale
CO_2	Loflo	318–468 ppm	7	WMO X 2007
CO_2	GC (LSCE)	365–462 ppm	6	WMO X 2007
CH_4	GC (LSCE)	1634–2081 ppb	6	NOAA04 scale
N_2O	GC (LSCE)	302–340 ppb	6	NOAA 2006A
SF_6	GC (LSCE)	6–15 ppb	6	NOAA 2006
CO	GC (LSCE)	41–595 ppb	6	NOAA-GMD/WMO 2004
H_2	GC (LSCE)	430–810 ppb	3	MPI/EUROHYDROS 2007

Table 4. Mean annual CO_2 difference and 1-sigma standard deviation for the three ambient air lines at Trainou Station (GC – CARIBOU).

Year Δ CO_2 (ppm)	50 m sampling level Δ CO_2 (ppm)	100 m sampling level Δ CO_2 (ppm)	180 m sampling level
2007	0.12 ± 1.75	0.12 ± 1.0	0.15 ± 0.75
2009	0.11 ± 1.3	0.05 ± 1.01	−0.06 ± 1.0
2010	0.07 ± 1.05	0.03 ± 1.09	−0.02 ± 0.88
2011	0.13 ± 0.82	0.18 ± 1.1	0.21 ± 1.1
2012	−0.01 ± 1.26	0.07 ± 0.97	−0.07 ± 0.81
2007–2012	0.08 ± 1.00	0.09 ± 1.05	0.01 ± 0.93

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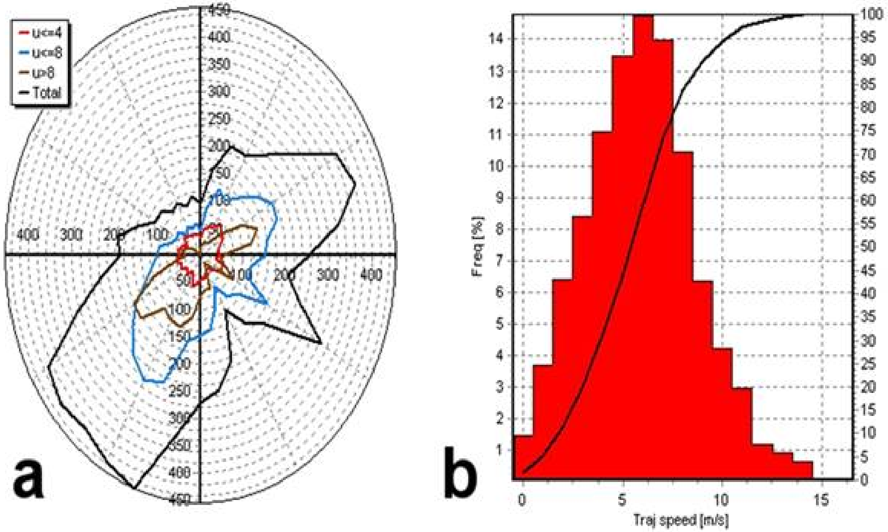

Fig. 1. Wind rose at Trainou station (180 m) for four different wind classes **(a)** and frequency distribution of wind velocity **(b)** calculated with Trajectory Viewer 1.1 developed at ECN (Energy research Centre of the Netherlands, http://www.ecn.nl/) and from model FLEXTRA (Stohl et al., 2005) for the year 2005.

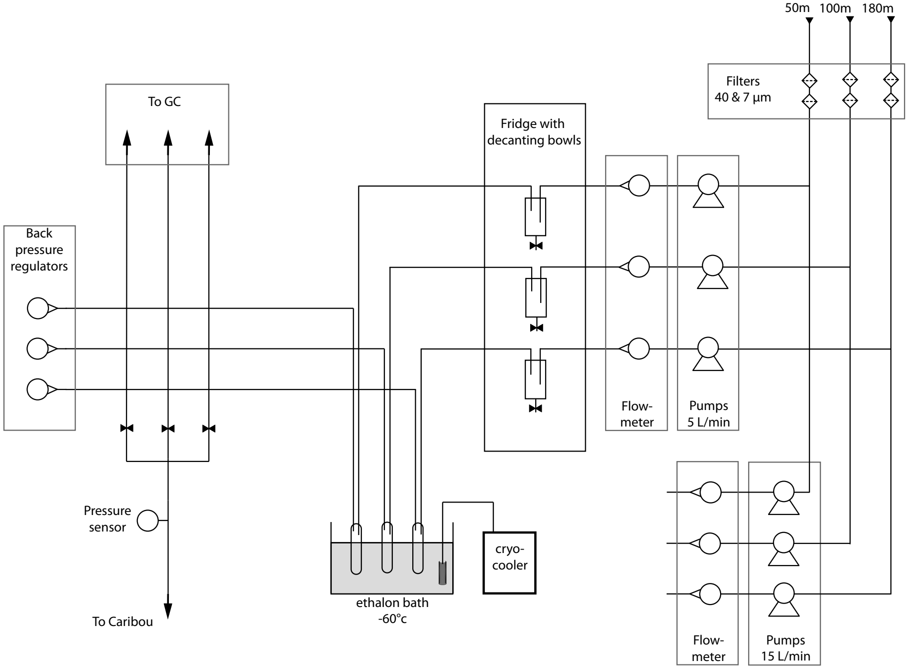

Fig. 2. Schematic view of the air inlet and drying system controlled by the CARIBOU software. The dried air is used for GC and CARIBOU analysis.

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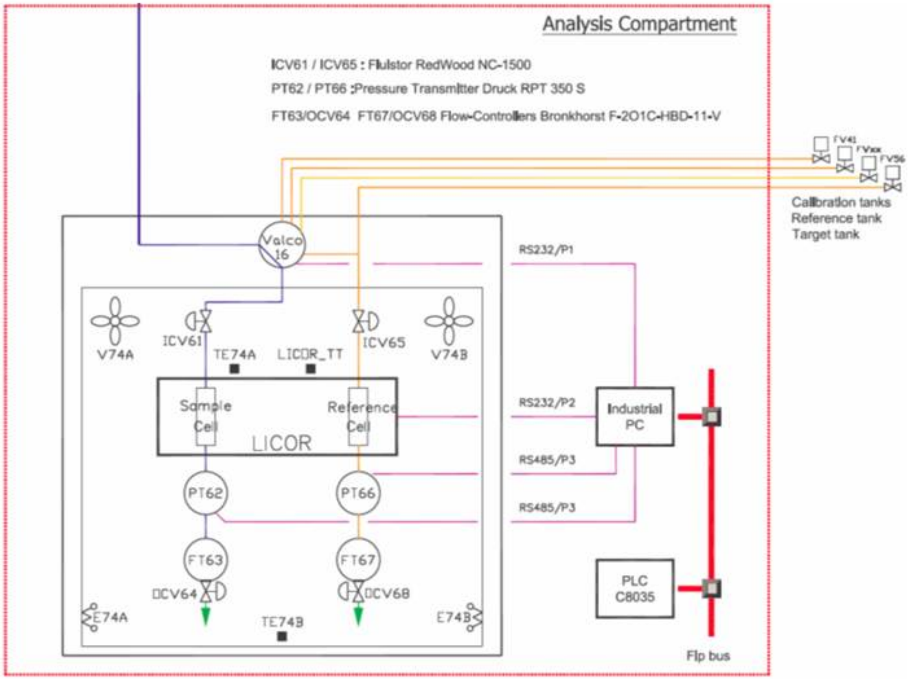

Fig. 3. Schematic of CARIBOU CO_2 analyser component.

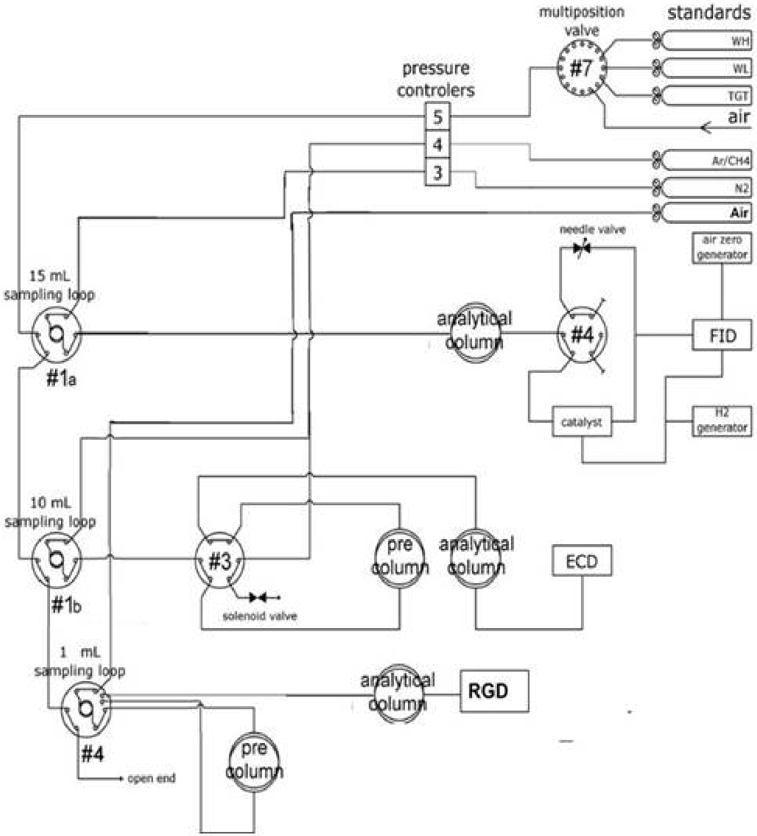

Fig. 4. Schematic of the two coupled gaschromatographic (GC) systems. The FID and the ECD detector are housed in a GC 6890N from Agilent Technologies, the RGD in a PP1 from Peak Laboratories. The three sample loops are flushed with the same sample and injected at the same time.

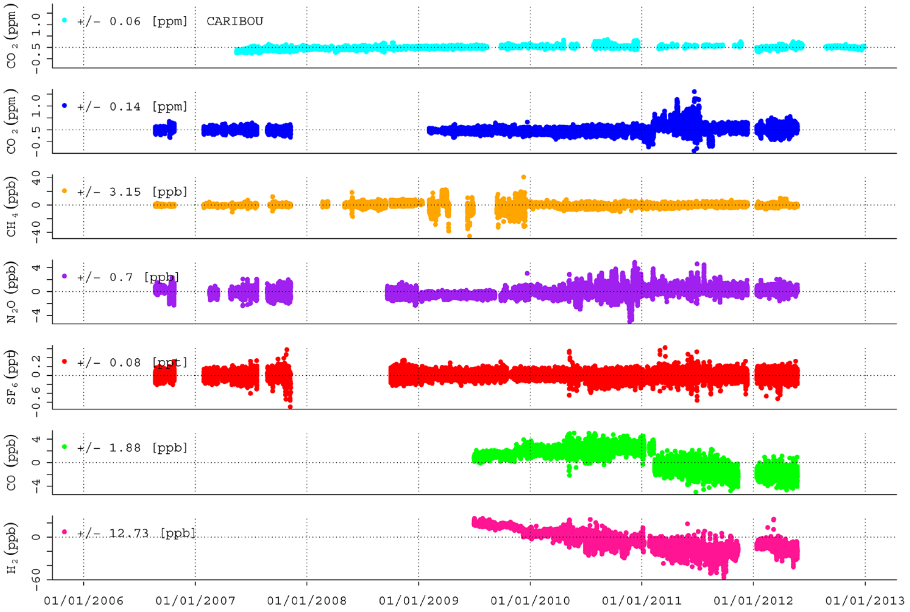

Fig. 5. Long-term reproducibility of the target gases for CO_2 measured with the CARIBOU and for CO_2, CH_4, N_2O, SF_6, CO and H_2 measured with the coupled GC system. For all species the differences between measured data and their mean values are plotted against time.

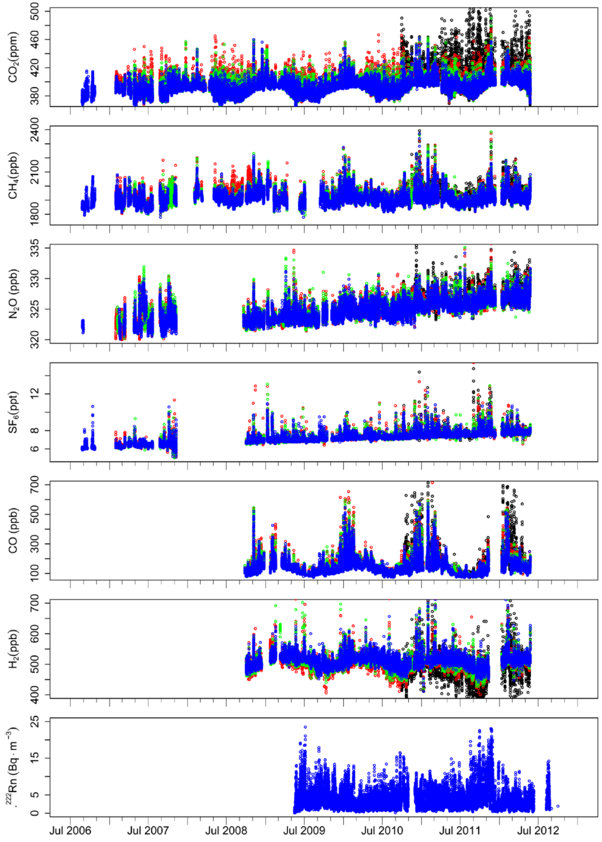

Fig. 6. Time series of atmospheric CO_2, CH_4, N_2O and SF_6, CO, H_2 and ^{222}Rn measurements from the 180 m (blue), 100 m (green) 50 m (red) and 5 m (black) inlet line. From November 2007 to September 2008 the N_2O and SF_6 measurements were interrupted due to broken ECD. (Electron capture detector). CO, H_2 and ^{222}Rn analysers were installed in 2008 and 2009 at the station.

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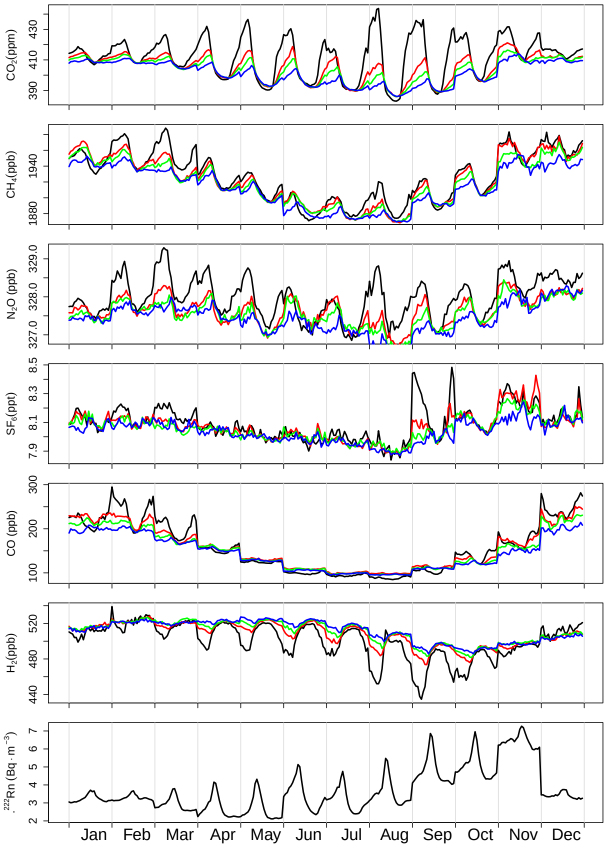

Fig. 7. Mean diurnal cycles of CO_2, CH_4, N_2O, SF_6, CO, H_2 and ^{222}Rn for the sampling levels 5 m (black), 50 m (red) 100 m (green) and 180 m (blue).

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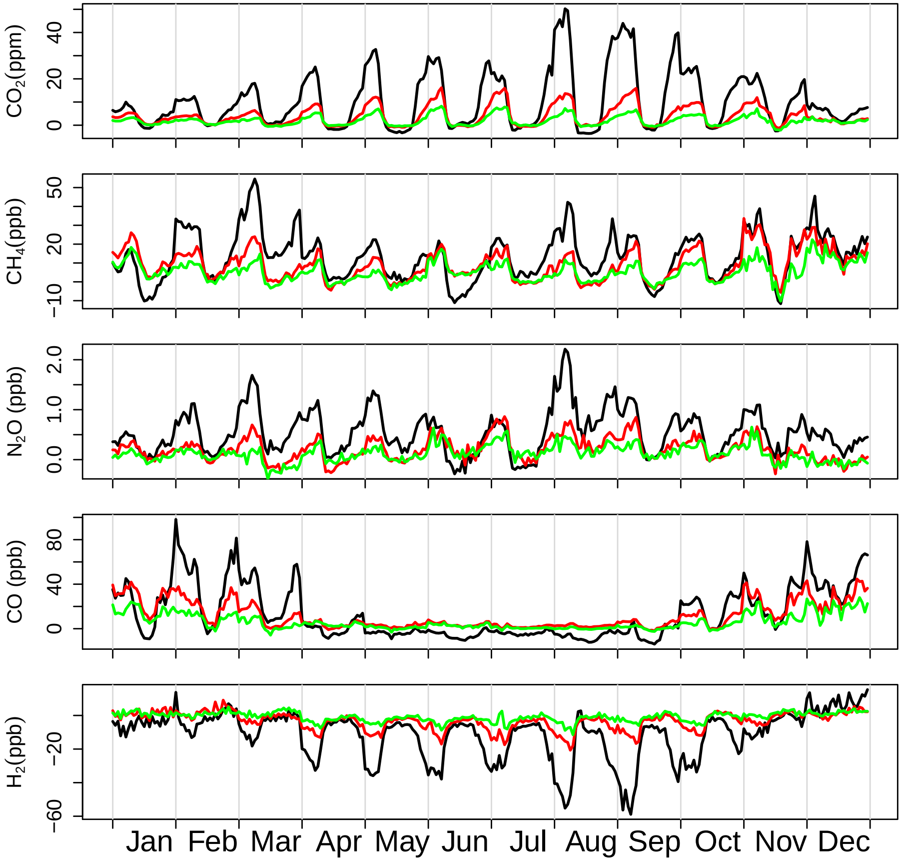

Fig. 8. Vertical gradient of the mean diurnal cycles between the 5 m and 180 m sampling level (black), the 50 m and 180 m sampling level (red) and the 100 and 180 m sampling level (green) for CO_2, CH_4, N_2O, CO and H_2 .