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Continuous measurements of atmospheric oxygen and carbon dioxide on a North Sea gas platform

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Abstract

A new atmospheric measurement station has been established on the North Sea oil and gas production platform F3, 200 km north off the Dutch coast (54°51′ N, 4°44′ E). Atmospheric mixing ratios of O_2 and CO_2 are continuously measured using fuel cell technology and compact infrared absorption instruments, respectively. Furthermore, the station includes an automated air flask sampler for laboratory analysis of the atmospheric mixing ratios of CO_2, CH_4, CO and O_2 and isotope measurements of $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{14}C$ from CO_2. This station is – to our knowledge – the first fixed sea based station with on-site continuous O_2 and CO_2 measurements and therefore yields valuable additional information about the CO_2 uptake in coastal marine regions, specifically the North Sea. This paper presents the measurement station and the used methodologies in detail. Additionally, the first data is presented showing the seasonal cycle as expected during August 2008 through June 2009. In comparison to land-based stations, the data show low day-to-day variability, as they are practically free of nightly inversions. Therefore, the data set collected at this measurement station serves directly as background data for the coastal northwest European region. Additionally, some short-term O_2 and CO_2 signals are presented, including very large (over 200 per meg) and fast negative atmospheric O_2 excursions.

1 Introduction

Highly precise and accurate atmospheric O_2 measurements offer a significant contribution to our understanding of the global carbon cycle (Bender et al., 1996; Keeling et al., 1993; Keeling and Shertz, 1992). Specifically, combined measurements of atmospheric O_2 and CO_2 can be used to partition land and ocean CO_2 uptake (Keeling et al., 1996; Langenfelds et al., 1999). The difference in behaviour of O_2 and CO_2 in ocean-atmosphere exchange yields valuable information about the global carbon cycle in general and the ocean CO_2 uptake in particular, which cannot be acquired

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from measurements of CO_2 mixing ratios alone. The significance of the understanding of CO_2 uptake processes has been recognised by the Intergovernmental Panel on Climate Change (IPCC) (Denman et al., 2007).

Measuring atmospheric O_2 mixing ratios is not a straightforward exercise. The variations of O_2 are in the same order of magnitude as for CO_2, but they are to be detected against a much higher background. The atmospheric O_2 mixing ratio is about 209 460 ppm (Machta and Hughes, 1970), compared to around 380 ppm for CO_2 (Forster et al., 2007). The first technique to measure atmospheric O_2 with the required precision was based on interferometry and was developed by Keeling (1988a, b). Several other methods to measure atmospheric O_2 have been designed during the past decennia, including e.g. mass spectrometry (Bender et al., 1994), a paramagnetic analyzer (Manning et al., 1999), vacuum ultraviolet absorption (Stephens, 1999) and a technique using fuel cells (Patecki and Manning, 2007; Stephens et al., 2007; Thompson et al., 2007).

Systematic measurements of atmospheric O_2 have begun in 1989 by means of flask sampling at three sites (Keeling and Shertz, 1992). Since then, the flask-sampling network for atmospheric O_2 measurements has been extended over the globe (Bender et al., 2005; Manning and Keeling, 2006; Tohjima et al., 2008) and later on also included continuous on-site measurements (Kozlova et al., 2008; Popa, 2008; Thompson et al., 2009; Valentino et al., 2008).

In order to extend the existing data sets of atmospheric O_2 and CO_2, we have established a new atmospheric measurement station on the North Sea oil and gas production platform F3, 200 km north off the Dutch coast (54°51′ N, 4°44′ E). The measurement station includes instruments that continuously measure atmospheric O_2 and CO_2 mixing ratios on-site using the aforementioned fuel cell technique and infrared absorption respectively. The location of the station is favourable since local effects – except for sea-atmosphere exchange – are easily avoided. Furthermore, atmospheric inversions (causing large variability at land based stations) practically do not occur at sea, resulting in stable and calm O_2 and CO_2 signals. This station is – to our knowledge

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– the first fixed sea based station with on-site continuous O_2 and CO_2 measurements and will yield valuable information about the CO_2 uptake in coastal marine regions, specifically about the North Sea.

A fuel-cell based atmospheric O_2 analyzer is commercially available (Oxzilla II, Sable Systems). However, in order to measure atmospheric O_2 at the required precision in the range of 1:10^6 (WMO, 2008) with this instrument, substantial re-design is necessary. The setup design comprises extensive gas handling techniques, including sample drying and pressure and temperature stabilization. Besides that, measurements are performed differentially, which implies continuous comparison to a known reference gas standard. Moreover, the setup is calibrated on a daily basis with a suite of two known calibration gases. This paper firstly describes the instrumental setup and analysis methods, subsequently the measurement site and finally the obtained initial results, including the first three quarters of a year of atmospheric O_2 and CO_2 data.

2 Method and site description

2.1 O_2 and CO_2 analyzers

Both the O_2 and the CO_2 analyzers are commercially available instruments. For O_2 measurements we use the Oxzilla II instrument, available from Sable Systems, which was also used in a similar way by e.g. Stephens et al. (2007), Thompson et al. (2007) and Patecki and Manning (2007). The CO_2 measurements are performed using two CarboCaps GMP343 from Vaisala. These compact and inexpensive CO_2 analyzers have not been used before for atmospheric measurements concurrently with O_2.

The operational principle of the Oxzilla O_2 analyzer is based on fuel cell technology. These fuel cells (MAX-250) consist of a lead anode, a gold cathode and weak acid serving as an electrolyte. The O_2 from the incoming air stream initiates a net reaction in the fuel cells as given in Eq. (1).

$$O_2 + 2Pb + 4H^+ \rightarrow 2H_2O + 2Pb^{2+} \quad (1)$$

This reaction generates a current, which is linearly proportional to the partial pressure of the O_2 in the sampled air. The partial pressure of O_2 also depends on the total pressure of the measured air. This requires a linear correction of the measured output signal to standard barometric pressure of 1013 mbar using the measured pressure P, measured by an accurate pressure sensor, as shown in Eq. (2).

$$O_2 \text{ corrected} = O_2 \text{ measured} \cdot \frac{1013}{P} \quad (2)$$

The fuel cells are temperature sensitive, therefore the Oxzilla is provided with an integral temperature compensation circuit. The Oxzilla is a differential analyzer, which continuously measures a reference gas on one fuel cell, while measuring sample air on the other fuel cell. In order to increase the measurement precision and to eliminate fuel cell differences, reference and sample are switched between both fuel cells at regular time intervals of 5 min.

The Vaisala CarboCap GMP343, a non-dispersive infrared analyzer, is used for measuring the CO_2 mixing ratio in the sample air by measuring a specific range of infrared absorption lines of CO_2 in the sample air and comparing this to absorption in a close-by frequency range without CO_2 absorption. Our setup includes two CO_2 analyzers, each placed in series with one of the fuel cells to benefit from the same switching principle as for the O_2 measurements. The CO_2 analyzers are built into the housing of the O_2 analyzer to ensure similar temperature stability for both O_2 and CO_2 measurements.

2.2 Gas handling

Due to the required precisions in atmospheric O_2 and CO_2 mixing ratios, the air streams that are to be analyzed by the aforementioned analyzers, require extensive preconditioning. This includes several aspects, such as air-drying and pressure stabilization. The details of the gas handling are described in this section and are shown schematically in Fig. 1.

The sample air enters the system at the air inlet, consisting of a funnel and a fil-

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ter (5 μm). Subsequently, the sample air is pre-dried by a Nafion membrane column (Perma Pure, MD 110 72 S). The Nafion pre-drier uses a counter-flow of dry air to remove about 60% of the water content from the sample air. The outer side of the column is supplied with dry air from the "AutoSampler" outlet air stream (see Sect. 2.5). The risk of influencing the sample air is therefore negligible, since the dry air on the outer side is the dried air stream that has been sampled just a few minutes earlier and has therefore an almost identical composition. For more details see Neubert et al. (2004).

The sample air is pumped through the system using a diaphragm pump (KNF, PM21972-86). A combo pressure regulator (VICI, PR50A30Z2) was used to smooth out pressure fluctuations introduced by the pump. A Valco 4-port, 2-way valve (ET44UWE) is used to select between the sample air and a set of calibration gases, which are selected by a 16-port multivalve (Valco, EMT2SD16MWE). The reference gases, which are continuously measured concurrently with the sample (or calibration) gas, are selected by two 2-way solenoid valves (Parker Skinner, 71215SN1MF00N0C111C2), using the second reference cylinder during the times that the first needs replacing. The flow in the air stream from the selected reference gas is stabilized by a mass flow controller (Bronckhorst, F-201C-FAC-22-V) to around 40 ml/min. All reference and calibration cylinders are filled at our laboratory using a RIX SA-3 compressor modified for atmospheric measurements (without adding CO and oil) (Mak and Brenninkmeijer, 1994). The cylinders are kept horizontally in order to increase the long-term stability of the gas standards (Keeling et al., 2007).

Thereafter the system consists of two parallel lines. Water vapour is removed from both air streams by the drying system, shown in Fig. 2. The system consists of two identical sides (A and B), which alternately dry the air streams. These consist of a cryo-cooler (Neslab CC-100) and glass traps in a Dewar filled with a thermo fluid (SilOil) and include a heating coil. The glass traps are partly filled with glass beads in order to increase the contact surface of the air streams, so that more water vapour is frozen in the traps. By using two identical sides, the water from one of the cryo-traps (side B in Fig. 2) can be removed while the other (side A in Fig. 2) is drying the air streams at

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a temperature of around −90°C. The water is removed from the traps by back-flushing with air while the temperature of the thermo fluid is around +40°C. This drying system does therefore not need servicing in the form of replacing cryo-traps and can run unattended during long periods of time. More details are given by Neubert et al. (2004).

Since both O_2 and CO_2 are measured differentially, the pressure in both lines has to be identical. For that reason the pressure in both lines is equalized – after drying the air streams – using a 1 mbar full-scale pressure transducer (MKS, 223B), a regulating valve (MKS, 248A) and a pressure control unit (MKS, 250E). The regulating valve equalizes the pressure in the sample (or calibration) line to the reference line with a precision of 0.3% of the full-scale. A second Valco 4-port, 2-way valve is used to switch both air streams between both fuel cells and CO_2 analyzers each 5 minutes as described in the Sect. 2.1.

Remaining parts of the setup, which do not require extensive explanation, include filters, tubing (1/8″ and some 1/16″ stainless steel (Swagelok) and 1/4″ Dekabon tubing) and fittings (Swagelok), 2-way valves (Swagelok, SS-41S2), Solenoid 2-way valves (Parker Skinner, 71215SN1MF00N0C111C2), pressure and flow sensors for remote monitoring of the system (resp. SunX, DPH/A07 and AE sensors 50S-5). We avoided the use of T-junctions in the setup in order to not introduce fractionation of the measured air (Manning, 2001).

Valve actuation, pump operation and signal recording of O_2, CO_2 and additional parameters like pressure and flow were done by software programmed in Pascal (Delphi). This software furthermore automated the sequencing of the calibration procedure (see Sect. 2.3) and the data transfer by email.

2.3 O_2 and CO_2 calculations and calibration

To increase the measurement precision of the O_2 and CO_2 measurements, reference and sample are switched between the fuel cells and CarboCaps at regular time intervals of 5 min. For O_2, this yields a double differential O_2 signal, which is defined by

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Eq. (3) (Thompson et al., 2007).

$$\Delta(\Delta) = (S_1 - R_2) - (R_1 - S_2) \quad (3)$$

S and R are the O_2 mixing ratios of the Sample and the Reference gases in % O_2 and the subscripts indicate the respective fuel cells on which they were measured. The $\Delta(\Delta)$ symbol indicates that this is a double differential signal. Each measurement period of 5 minutes consists of approximately 500 data points (the output interval of the Oxzilla is set to 0.6 s). The values for S and R are determined using the average of the final 200 data points before the next switch of the gases between the fuel cells. The optimal amount of data points was obtained using the Allen variance of the data. The $O_2\Delta(\Delta)$ (%) is the change in the differentially measured O_2 signal and is proportional to the difference between the mixing ratios of the sample and the reference gas.

The raw $O_2\Delta(\Delta)$ values are expressed in % O_2. Internationally, the common way to report O_2 mixing ratios is by using the $\delta(O_2/N_2)$ value (per meg) which is reported relatively to a standard ratio as given in Eq. (4) (Keeling and Shertz, 1992).

$$\delta(O_2/N_2) = \left(\frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1 \right) \quad (4)$$

For natural air, $\delta(O_2/N_2)$ is a very small number, and is therefore usually expressed in per meg, which is obtained by multiplying Eq. (4) by 10^6.

The relationship between the mixing ratio in ppm (μmol/mol) and per meg for atmospheric oxygen is calculated by multiplying the amount in ppm by the standard mole fraction of oxygen in air, which is defined as: XO_2=0.20946 (Machta and Hughes, 1970). The relationship between ppm and per meg is given in Eq. (5).

$$1\,\text{ppm} = \frac{1}{0.20946} \approx 4.7742\,\text{per meg} \quad (5)$$

The $O_2\Delta(\Delta)$ value is first converted to the apparent mole fraction (δXO_2) and secondly to $\delta(O_2/N_2)$ by correcting for the dilution by the amount of CO_2 in the sampled air using

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Eq. (6) as described in Keeling et al. (1998). Corrections for other atmospheric species, such as Argon, are not included since their variations in natural air are negligible.

$$\delta(O_2/N_2)_{sample} = \frac{\delta XO_2 + (\Delta CO_2 \cdot XO_2)}{(1 - XO_2) \cdot XO_2} (\text{in per meg}) \quad (6)$$

Where XO_2=0.20946 and ΔCO_2=$[CO_2]_{sample}$−363.29 (ppm), which is the CO_2 mixing ratio of the sample gas minus that of an arbitrarily defined standard atmospheric composition. δXO_2 is the difference between the relative O_2 apparent mole fraction of the sampled and the reference air, which is obtained by calibration of the Δ(Δ) signal. For this calibration we use 2 gases, which are measured on a 23-hour basis, with respect to the same reference gas as the sample measurements. The sample δXO_2 values are defined using a linear interpolation between the measurements of both calibration gases. This yields a linear calibration line which converts the measured Δ(Δ) signal to δXO_2 values. For this, the $\delta O_2/N_2$ values of the calibration gases are converted to apparent mole fractions, using their measured CO_2 mixing ratio and the same Eq. (6). An average linear calibration line is obtained for each reference gas period (consisting of several weeks). Each calibration cylinder is measured for 1 h and 15 min. The average of the last 3 switching cycles, i.e. 15 min, is used for determining the linear calibration lines. The amount of data that is used is relatively small, due to the long flushing time of the drying system. Further explanation is given in the Sect. 3.4.

The obtained $\delta(O_2/N_2)$ values are relative values on a predefined scale. In this paper all $\delta(O_2/N_2)$ values are expressed relatively to our Groningen CIO scale, which is defined by air cylinder "2534" and maintained by a suite of reference cylinders. More information about this scale is presented in Sirignano et al. (2008). Thanks to a newly-purchased suite of primary reference cylinders, filled and calibrated by R. F. Keeling, SIO-UCSD, La Jolla and an intercomparison programme within CarboEurope IP, our internal scale will be tied to that of other locally maintained scales soon.

A similar differential approach is used for the calculations of the mixing ratio of CO_2, since the air streams are also switched between the CarboCaps with intervals of 5 minutes. For CO_2 the Δ(Δ) value is the change in the differentially measured CO_2 signal

and is directly proportional to the difference between the sample and the reference gas mixing ratios. Each measurement period of 5 minutes consists of approximately 150 data points (the output interval of the CarboCaps is set to 2 s). The values for S and R (see Eq. 3) are the mixing ratios of CO_2 of the Sample and the Reference gases (in ppm) and are determined using the average of the final 80 data points before the next switch of the gases between the CarboCaps. The optimal amount of data points was again obtained using the Allen variation. Due to the larger internal volume – compared to the fuel cells – the flushing time for the CarboCaps is longer. Another way to determine the values for S and R is by fitting the data of each switching cycle with an exponential function. This method, however, proved to be more vulnerable to errors, especially in cases where the difference between the values for S and R is small. Therefore the average of the last part of the measurements was used. There is no need for any conversion, since the CarboCaps measure in ppm directly. As for O_2, linear calibration provides a conversion from the $\Delta(\Delta)$ value to the CO_2 mixing ratio of the sample gases.

The $\delta O_2/N_2$ values and the CO_2 mixing ratios for the calibration gases are determined in the CIO laboratory using respectively Dual Inlet Isotope Ratio Mass Spectrometry (IRMS, MicroMass Optima) and Gas Chromatography (Hewlett-Packard model 6890). Additional information is provided in Sirignano et al. (2008).

2.4 Measurement site description

The atmospheric measurement site F3 is situated in the central North Sea. The closest land (the Netherlands) is located 200 km away from the measurement station. It is therefore an ideal location for measuring atmospheric background mixing ratios and studying air-sea interaction of CO_2 and partitioning of CO_2 emissions between the land biosphere and oceans. The data from this measurement station will be a valuable contribution to the existing European data sets of atmospheric O_2 and CO_2, since only few atmospheric measurements stations exist that are equipped to measure atmospheric O_2 continuously. Moreover, this station is the first fixed sea based atmospheric mea-

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surement station with on-site continuous O_2 and CO_2 measurements.

The F3-FB-1 (short: F3) platform produces both oil and gas. Until 2008 it was owned by the Dutch oil company (Nederlandse Aardolie Maatschappij, NAM) and after that it was transferred to Gaz de France (GdF) Suez. It is situated 200 km north of the Dutch coast (54°51′ N, 4°44′ E), see Fig. 3. The main local source of CO_2 is the gas power plant on the platform itself. Besides that there are occasional helicopters, supply ships and tankers, a diesel engine for the operation of cranes and a small permanent gas flare for safety purposes. The total average CO_2 production at the platform is about 100 Tonnes of CO_2 per day, which is 5 times smaller than the daily CO_2 production of a typical LNG carrier (BP, 2007). The platform consists of two parts connected by a bridge of 60 meters. One part is the production platform, the other is the accommodation platform. The positioning of the production platform – where the main CO_2 sources are – was intentionally north of the accommodation platform, for safety purposes. As the prevailing wind direction is south-west, potential leakages or fires are blown away from the accommodation platform, as is the exhaust from the power plant and the gas flare. The ideal situation for atmospheric measurements on this oil and gas platform is therefore on the south-west corner of the accommodation platform. This is where the air-inlet of our measurement system as described in the previous sections is situated. In case of northern wind an influence might be expected from local CO_2 production, however the air inlet is partly shielded by the accommodation platform itself. Other possible local influences on the measurements include the air-conditioning system at the accommodation platform and the constant seawater circulation for cooling purposes in the production process, resulting in artificial upwelling. The air-inlet is on the topmost deck, which is 46 m above sea level. The North Sea depth at the platform is 44 meters. The distance from the power plant exhaust and the gas flare to the air-inlet of our measurement system is around 90 and 130 m respectively.

As the location of the platform is remote, the measurement setup requires extensive automation. This is achieved largely by using internally developed software and internet access to the measurement computer. Remaining servicing like replacing ref-

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erence cylinders is managed by the platform staff.

2.5 Additional equipment

Our measurement station is also equipped with an automatic air flask sampler (Neubert et al., 2004). This 'AutoSampler' fills air flasks, which are to be shipped back to the lab for analysis. The analyses include measurements of the mixing ratios of CO_2 and $\delta O_2/N_2$ for crosschecking of the continuous instrument. Furthermore other greenhouse and trace gas measurements, such as CH_4 and CO mixing ratios, are performed, as well as measurements of the isotopic composition of CO_2 ($\delta^{13}C$, $\delta^{18}O$ and $\Delta^{14}C$). CO mixing ratios and $\Delta^{14}C$ are important indicators for contamination of the sample air with CO_2 from local sources. Low $\Delta^{14}C$ values indicate the influence of fossil fuel combustion. CO is a side product in fossil fuel combustion, and high CO values therefore also reveal local influences, see e.g. Gamnitzer et al. (2006).

Laboratory measurements of the flask samples are done using aforementioned Dual Inlet Isotope Ratio Mass Spectrometry (IRMS) (for $\delta O_2/N_2$, $\delta^{13}C$ and $\delta^{18}O$), gas chromatography (for CO_2, CH_4 and CO) and Accelerator Mass Spectrometry (for $\Delta^{14}C$). More information on the measurement techniques can be found in Sirignano et al. (2008) and van der Plicht et al. (2000).

The platform includes meteorological facilities as well, governed by the Royal Netherlands Meteorological Institute (KNMI). All required meteorological data (temperature, pressure, relative humidity, cloud cover, wind speed and wind direction) are measured continuously as well as parameters related to the sea surface, like mean tidal level and wave height.

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3 Results and discussion

3.1 Laboratory tests

Before the installation on the platform the measurement system has been tested in the CIO laboratory. The tests under laboratory-controlled "ideal" circumstances yielded satisfactory results. The test setup did not include the air-drying system (Fig. 2), as the tests were performed using dry air cylinders. Figure 4 shows the results of a longer-term test. In this test two cylinders were constantly measured differentially during a period of 9 days. Both the $\delta O_2/N_2$ and the CO_2 signal showed sufficient stability in this period. The long term (9 days) measurement precision (1σ standard deviation) were 5 per meg and 0.3 ppm for $\delta O_2/N_2$ and CO_2 respectively. On the short term (0.5 hours) the 1σ standard deviations were 4 per meg and 0.28 ppm respectively. Although the CO_2 precision is lower than state-of-the-art, these results are satisfying, since we are mainly interested in the Atmospheric Potential Oxygen (APO) which is a combination of O_2 and CO_2 (see Sect. 3.3) and in the calculation of APO the O_2 precision contributes the largest error. Furthermore, the CarboCap CO_2 analyzers are cheap and require practically no maintenance.

3.2 Target measurements

Besides the calibration cylinders, which are measured every 23 h, the measurement sequence also includes the measurement of a target cylinder. This cylinder is also measured every 23 h for 1 h and 15 min. The measurements of the target cylinder are treated as if they were air samples, in order to obtain a reliable indicator for precision and (long-term) measurement accuracy for the system. Each target measurement period yields a result, which is the average of the three last 5 min measurement periods. Figure 5 shows the results of the measurements of the target cylinder during spring 2009 for both $\delta O_2/N_2$ and CO_2. The averages of the target measurements are indicated. The indicated error is based on the total number of averages of three single

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measurements, measured during this period. Each of these sets of three measurements gave an average and a standard deviation, the indicated errors are the averages of these standard deviations. These are the best estimate of the 1σ standard deviation of our measurements. We find 16 per meg for $\delta O_2/N_2$ and 0.2 ppm for CO_2, the result for $\delta O_2/N_2$ is rather disappointing. For the entire period shown in Fig. 5, the measurement precision of the target measurements, based on the spread of the 3-point averages around the long-term mean, was 8 per meg for $\delta O_2/N_2$ and 0.3 ppm for CO_2. For $\delta O_2/N_2$ this improvement is according to expectations, as the 3-point averages should be $\sqrt{3}$ times as precise as the 1σ standard deviation of the single measurements. For CO_2, the long-term instability and drifts apparently are becoming more significant. As the CO_2 measurements are more accurate on a molar basis than for $\delta O_2/N_2$, the simultaneous improvement for $\delta O_2/N_2$ and worsening for CO_2 are consistent nevertheless. Measurements of the target cylinder in other periods show similar results. The behaviour of the target cylinder shows more spread for $\delta O_2/N_2$ than expected based on the laboratory test results. We are currently working on improvements of the system, which are discussed in Sect. 3.4.

3.3 Atmospheric observations

The continuous measurements for $\delta O_2/N_2$ and CO_2 have been started at the end of August 2008. Flask samples have been collected on a weekly basis, generally during well-mixed atmospheric conditions and preferred wind direction (between south and west). Figure 6 shows the combined first data from the F3 platform for continuous and flask measurements between August 2008 and June 2009. Although the measurements do not yet cover an entire year, the amplitude of the seasonal cycle of $\delta O_2/N_2$ can be estimated. The seasonal amplitudes are about 110 per meg for $\delta O_2/N_2$ and 16 ppm for CO_2. This compares well to data from the same latitude from GLOBALVIEW-CO2 (2008) as well as to the observations at other stations at comparable latitudes, e.g. Lutjewad, the Netherlands (van der Laan et al., 2009), Mace Head, Ireland (Sirignano et al., 2008) and Ochsenkopf, Germany (Thompson et al., 2009).

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Although measurement precision for the continuous $\delta O_2/N_2$ measurements still should (and can) be improved substantially, the results in Fig. 6 clearly indicate the partial seasonal cycle as expected during autumn through spring. Moreover, the comparison between the continuous measurements and the flask samples shows a good agreement for both CO_2 and $\delta O_2/N_2$. The $\delta O_2/N_2$ scale for the continuous measurement system is coupled to the scale of the IRMS in the CIO laboratory. Here we measure the flask samples as well as the calibration and reference gas cylinders for the continuous measurements, enabling a direct comparison of $\delta O_2/N_2$ measurements on an identical scale.

Most noticeably when studying the results in Fig. 6, is that in contrast to land-based stations, the data from the platform do not show any diurnal cycles caused by a nightly inversion layer. In marine environments these inversions are practically absent, as is evident from the figure. Therefore, the data set collected at this measurement station serves directly as background data for the coastal northwest European region.

The continuous measurements show also local effects on smaller time scales. An example is shown in Fig. 7a, during a day in November 2008. These data show an inverse relationship between $\delta O_2/N_2$ and CO_2. In Fig. 7b the relationship between $\delta O_2/N_2$ and CO_2 is plotted, where the slope of the correlation represents the oxidative ratio (OR) between $\delta O_2/N_2$ and CO_2. The $\delta O_2/N_2$ values have been converted to ppm using Eq. (5). This yields an OR of -1.31 ± 0.09, most likely representing local fossil fuel combustion (from e.g. a supply ship, tanker), changing air masses or a combination of both.

Another small-scale event series measured by the continuous measurement system is shown in Fig. 8. These results show very large $\delta O_2/N_2$ decreases during the afternoons on three consecutive days. No concurrent CO_2 signal is observed during these periods. These were days with mainly little cloud cover, indicating high solar irradiance. The size of the $\delta O_2/N_2$ signal is huge compared to other naturally occurring phenomena and the rate of change is relatively fast. Although smaller in size, similar observations have been published by Lueker et al. (2003). In their observations at

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the coastal station Trinidad Head, these $\delta O_2/N_2$ decreases were caused by upwelling events. As our observations are significantly larger, we have studied the possibilities of artefacts or sources of contamination. Most of the effects can be ruled out immediately because of the lack of change in the mixing ratio of CO_2. The only remaining possibilities were the use of liquid nitrogen on the platform or fractionation due to temperature variations at the air inlet (Blaine et al., 2006). The first possibility can be ruled out, as there are no cryogenics on the platform. The second effect might have some influence, but the size of the signal is larger than what could be expected for thermal fractionation at the air inlet or even leaks (R. F. Keeling, personal communication, 2009). Also, the cloud cover record in this period does not fit the $\delta O_2/N_2$ signal, which makes thermal fractionation very unlikely. To be sure, the air-inlet has recently been shielded off from direct sunlight (but this has not lead to any noticeable difference so far). Excluding other possibilities, we therefore suggest that the observed O_2 effects are very likely to be real and indicate marine O_2 uptake. This suggestion is supported as the $\delta O_2/N_2$ signal fits the wave period measurements at the platform, which suggests a correlation with marine phenomena.

The O_2 content in average North Sea water is about 9 g/m^3 (corresponding to 6.5 ml/l) (Garcia et al., 2006). A rough estimate, based on a water column with a depth of 45 m, and the assumption that the water column is taking up O_2 from an air column of well-mixed air with a height of about 2 kilometres, gives the following result. In the hypothetical situation that all marine O_2 is removed, this would then lead to a possible marine uptake corresponding to a decrease of around 3500 per meg from the atmosphere. The observed signal is about 10 times as small, thereby indicating a marine undersaturation of 10%, so our observations correspond to a delivery of oxygen to the seawater of about 10% of the saturation value. Hence, the seawater must have been undersaturated by at least this amount.

Using the obtained CO_2 and $\delta O_2/N_2$ values, the atmospheric potential oxygen (APO)

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can be obtained (Battle et al., 2006; Stephens et al., 1998). APO is defined by Eq. (7):

$$\mathrm{APO} = \delta \mathrm{O_2/N_2} + \frac{1.1 \cdot \Delta \mathrm{CO_2}}{\mathrm{XO_2}} (\mathrm{in\,per\,meg}) \quad (7)$$

Where XO_2 and ΔCO_2 are defined as explained with Eq. (6). The ΔCO_2 value is multiplied by 1.1, which is the global average stoichiometric ratio between O_2 and CO_2 in photosynthesis and respiration processes of the land biosphere. This implies that APO is unaffected by activity of land biota and is therefore principally sensitive to ocean-atmosphere exchange of O_2 and CO_2 and only partly to fossil fuel combustion.

Figure 9 shows the atmospheric potential oxygen (APO) for both the continuous measurements as well as for the flask measurements. APO values for both independent measurement systems generally agree nicely. The data show a part of the seasonal cycle as expected during the period August through June. The amplitude of the APO signal – about 75 per meg – is smaller than the $\delta O_2/N_2$ signal (about 110 per meg), since the seasonality for land biota is removed from the signal (as explained with Eq. 7). The remaining part of the seasonality is the oceanic seasonality (in which we are interested), although it is still influenced by the seasonal difference in fossil fuel combustion (Sirignano et al., 2008). A longer time series is required in order to make a more comprehensive analysis, including the trend and the correction for fossil fuel influences.

3.4 Discussion

The continuous $\delta O_2/N_2$ and CO_2 measurement system will be improved during the coming period. Several aspects leading to improvements in measurement precision and accuracy will be considered. The calibration periods can be optimized, e.g. by a shorter period of calibration and target cylinder measurements, higher flow rates in the system, increasing the calibration frequency, increasing the amount of calibration cylinders from 2 to 3 or more and increasing the cross-checking frequency of calibration cylinders in the CIO laboratory. Other measures to improve the measurement

system include minimizing the flushing volume with respect to the switching between fuel cells and CarboCaps, minimizing the flushing volume of the drying system, replacing the (long-used) fuel cells with new ones and improving the temperature stability of reference, calibration and target cylinders.

4 Conclusions and outlook

We have presented a new atmospheric measurement station in the North Sea, together with the initial results. Both continuous CO_2 and $\delta O_2/N_2$ measurements and flask sampling will be continued during the coming years. By means of simultaneous CO_2 and $\delta O_2/N_2$ measurements over longer time series (several years), information about the CO_2 uptake by the North Sea region can be estimated. Future research will focus on data collection at the platform and comparison of the data to other European datasets. Our atmospheric measurements will be a valuable contribution to the marine studies that have been performed in the North Sea region. Recent studies show that the total North Sea CO_2 sink is declining over the past years (Thomas et al., 2007). During the summer period, there is a difference between the northern and the southern North Sea. The shallower part south of 54°N is a CO_2 source, whereas the deeper part north of that boundary is a sink for CO_2 (Bozec et al., 2005). The location of the platform at 54°51′ N, 4°44′ E is therefore ideal in order to compare atmospheric data with the data from marine measurements from North Sea cruises. The atmospheric measurements at the F3 platform can possibly be extended with on-site marine measurements. Additional data can be obtained by measurements of the partial pressure of CO_2 (pCO_2) and O_2 in the seawater surrounding the platform. The results will be used in model studies, which will reveal more details about regional and global CO_2 uptake by coastal seas and the world's oceans.

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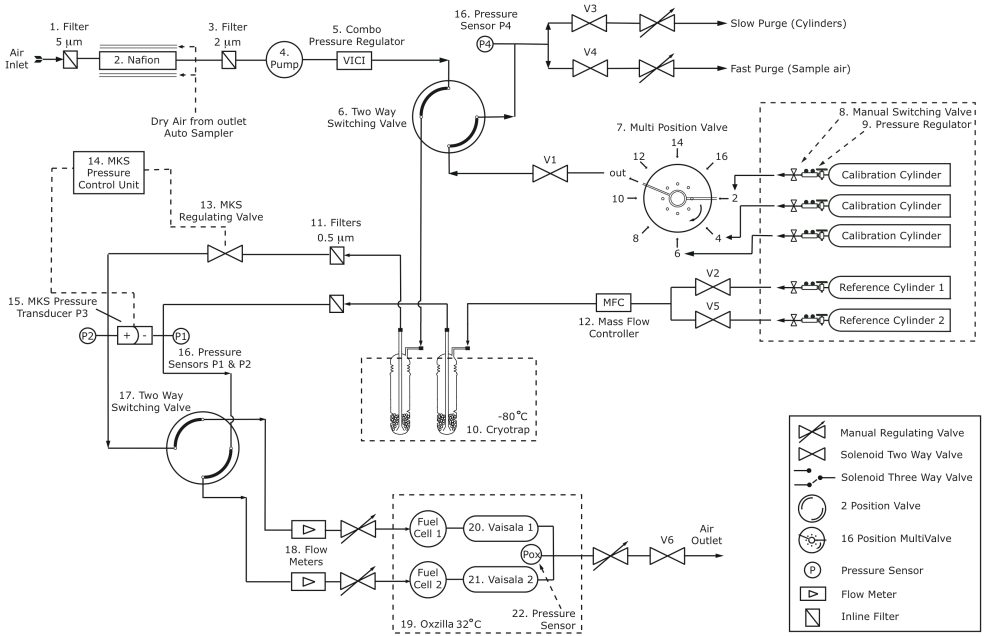

Fig. 1. Schematic of the measurement setup for continuous on-site O_2 and CO_2 measurements. The included gas handling techniques are shown: sample drying (see also Fig. 2) and pressure and temperature stabilization.

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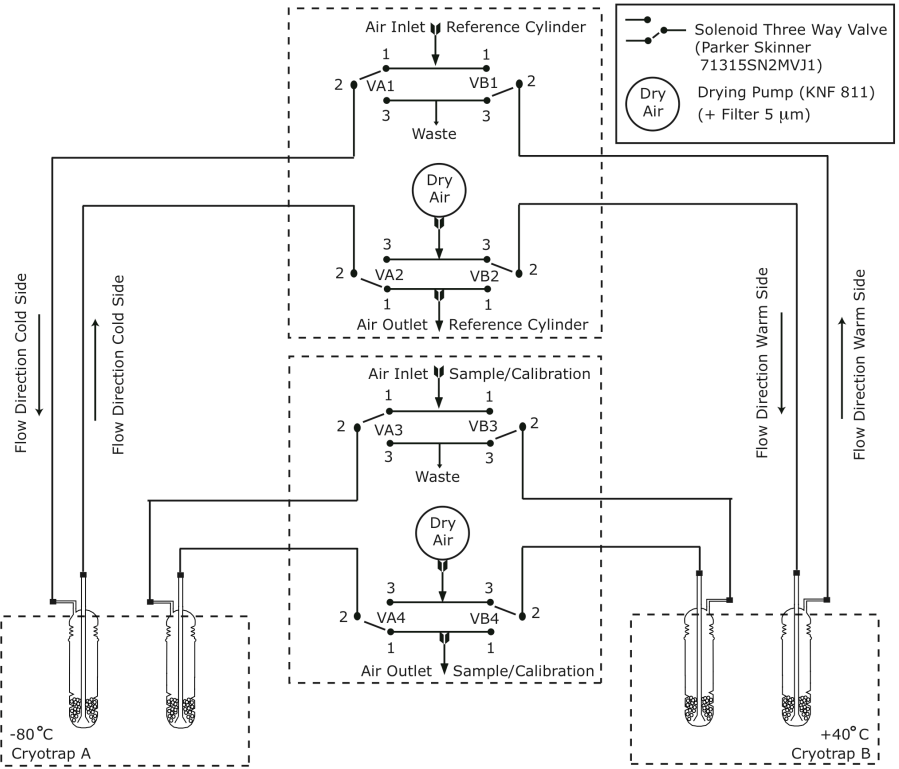

Fig. 2. Schematic of the automated air-drying setup. Cryo-trap A and B are alternately cold (−80°C) or warm (+40°C) in order to respectively freeze out water from the sample or to clear the traps of ice.

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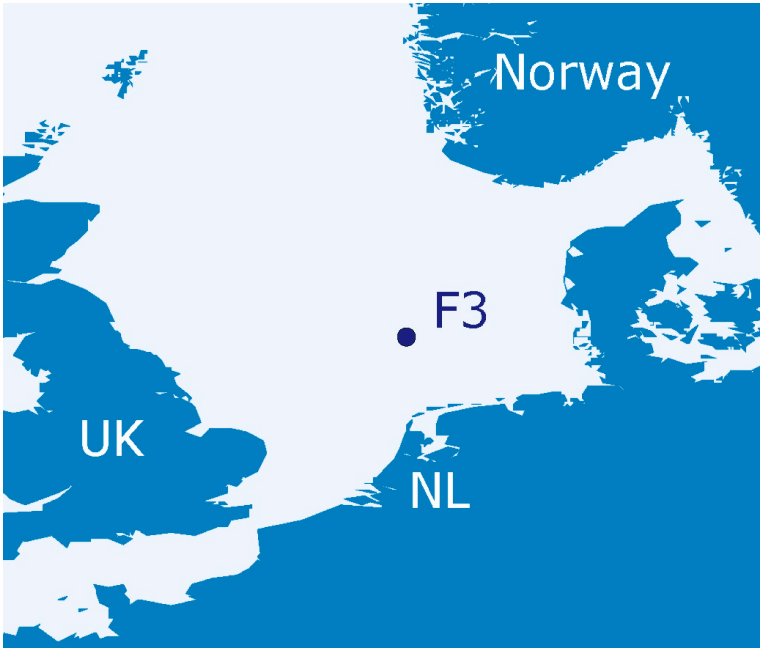

Fig. 3. Location of the atmospheric measurement station on oil and gas production platform F3.

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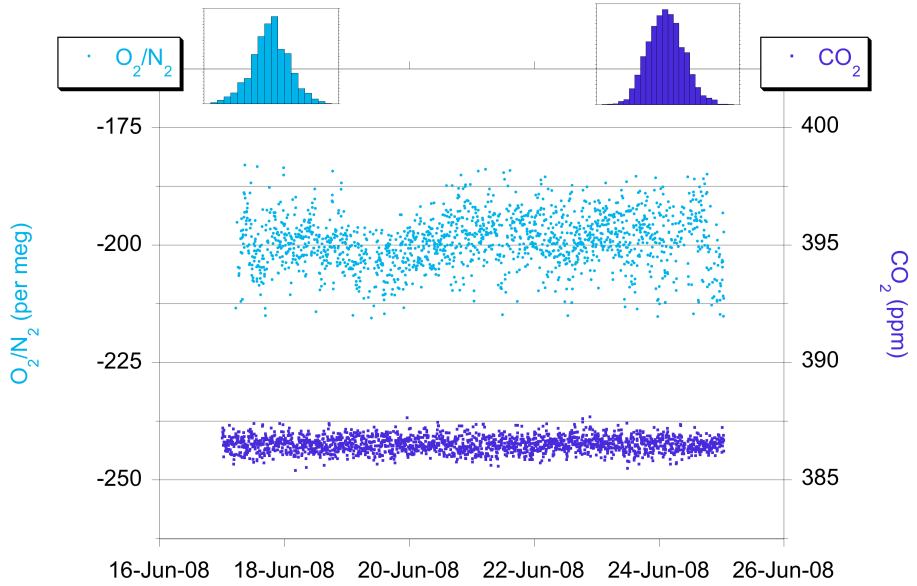

Fig. 4. Measurements of $\delta O_2/N_2$ (lighter circles) and for CO_2 (darker squares) during a laboratory test run of the measurement system. The insets show the distributions of the $\delta O_2/N_2$ and CO_2 data points. Both y-axes have been adjusted so that their ranges are nearly the same on a molar basis.

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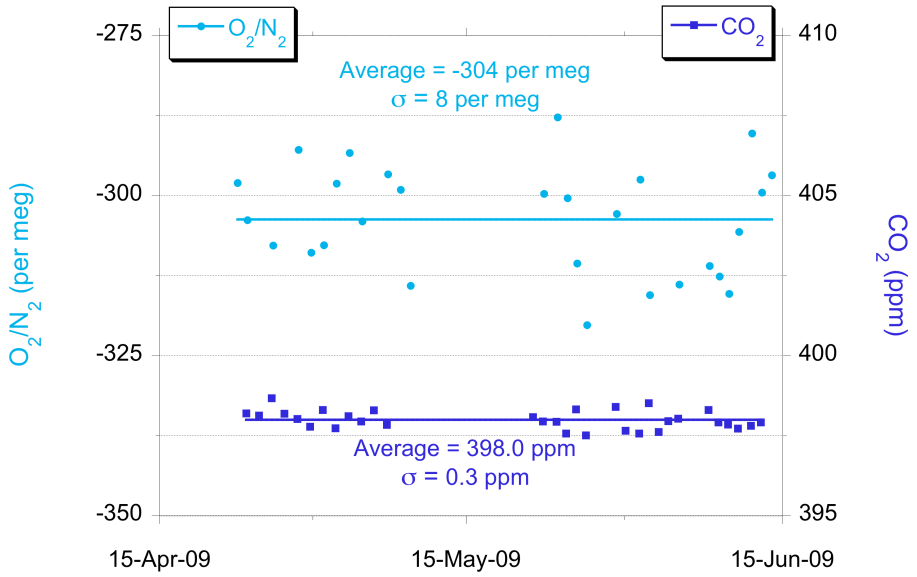

Fig. 5. Measurements of the target cylinder for $\delta O_2/N_2$ (lighter circles) and for CO_2 (darker squares), measured during April through June 2009. Both y-axes have been adjusted so that their ranges are nearly the same on a molar basis.

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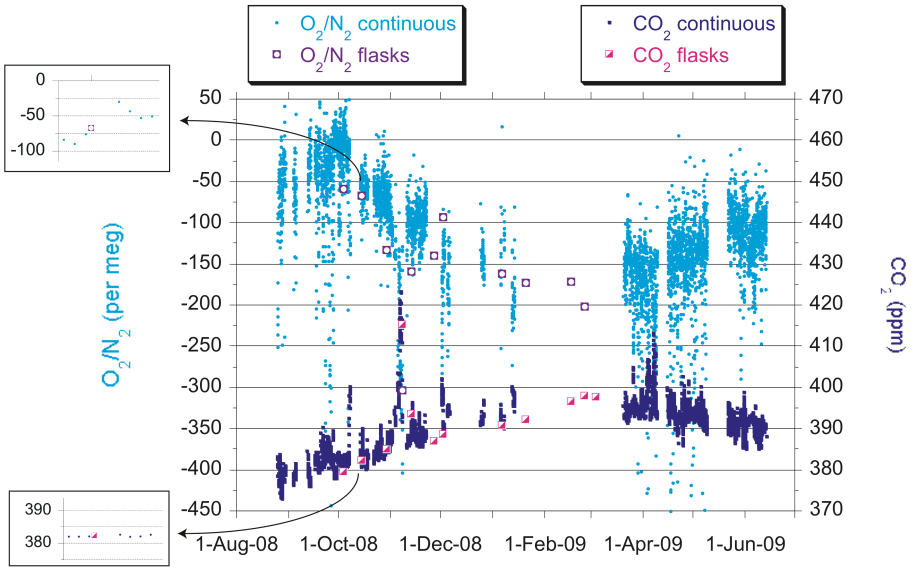

Fig. 6. Observations at the F3 platform for the period August 2008 through June 2009. The continuous measurements of $\delta O_2/N_2$ (small light circles) and CO_2 (small dark squares) were performed with the Oxzilla/CarboCap setup as described in Sect. 2. Also shown are measurements of flask samples (open symbols). The close-ups (insets on the left) demonstrate the good agreement between the flask samples and the continuous measurements. Both y-axes have been adjusted so that their ranges are nearly the same on a molar basis. Although the measurements do not yet cover an entire year, the amplitude of the seasonal cycle of $\delta O_2/N_2$ can be estimated. The seasonal amplitudes are about 110 per meg for $\delta O_2/N_2$ and 16 ppm for CO_2. This compares well to other observations.

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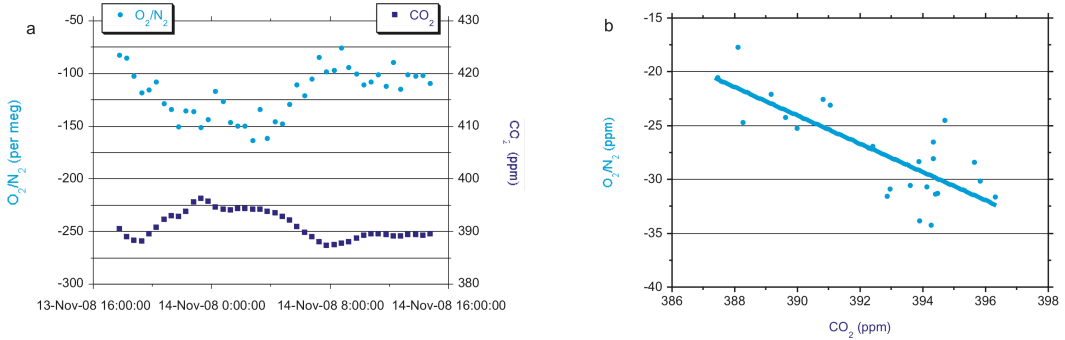

Fig. 7. Observations at the F3 platform for $\delta O_2/N_2$ (lighter circles) and CO_2 (darker squares) on 13 and 14 November 2008 **(a)** and correlation between $\delta O_2/N_2$ and CO_2 during the peak **(b)**.

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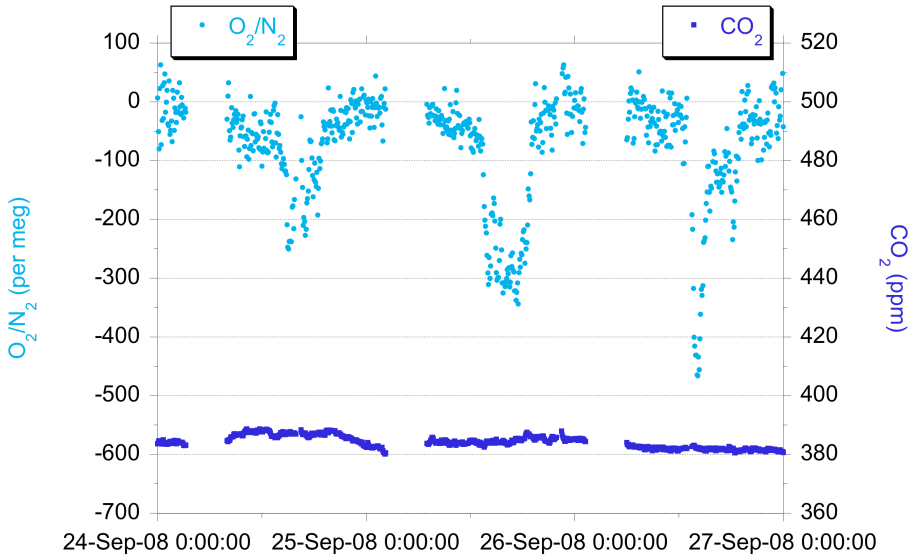

Fig. 8. Observations at the F3 platform for $\delta O_2/N_2$ (lighter circles) and CO_2 (darker squares) during 24 through 26 September 2008.

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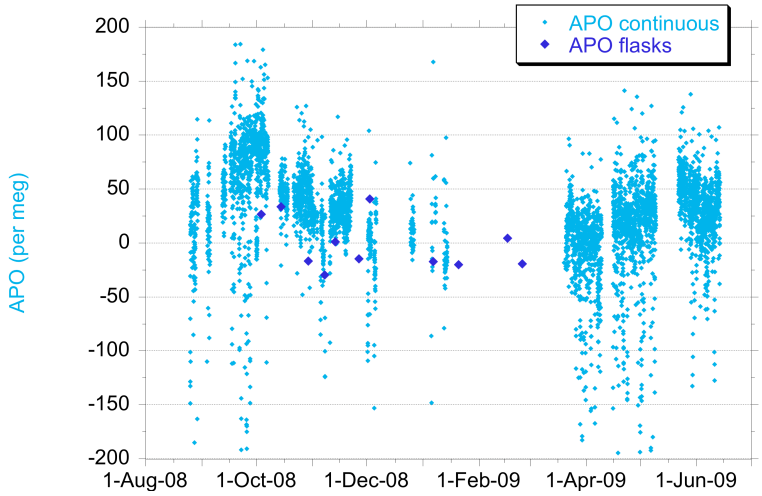

Fig. 9. Results of APO at the F3 platform for the period August 2008 through June 2009 showing the seasonal cycle as expected during this period. The results for the continuous measurement system (smaller diamonds) are shown together with the results of the flask samples (larger diamonds). The amplitude of the seasonal cycle of APO is around 75 per meg, and is composed of the oceanic APO seasonality and is also influenced by the fossil fuel combustion seasonality.

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