Validation of the Greenhouse Gas Balance of the Netherlands. Observational constraints on CO2, CH4 and N2O from atmospheric monitoring station Lutjewad.

Laan, Sander van der

Chapter 2

Station Lutjewad

2.1 Site description

The research presented in this thesis was based on data from the atmospheric measurement station Lutjewad, see fig. 2.1. This station was setup in the year 2000 by the Centre for Isotope Research (CIO) of Groningen University. It is close to the city of Groningen on the northern coast of the Netherlands, at 6º 21' E, 53º 24' N, 1 m a.s.l. The station is situated directly next to a dike (see fig. 2.2) with the Waddensea to the north, and an almost perfectly flat rural landscape to the south. Within this agricultural area the closest -small- village (about 200 inhabitants[3]) is at a distance of about two kilometres. On the seaside, sporadically flooded overgrown mud plains pass into the Waddensea with its tidal flats. About six kilometres to the north the island of Schiermonnikoog, one of the five inhabited islands in the Waddensea, is situated separating the Waddensea from the North Sea.

The location for the station was chosen such that the sampled air can be characterized as "Middle-European background" with northern air masses, and air masses which are influenced by anthropogenic and biogenic sources (and sinks) with southerly winds. The primary objective of Lutjewad is to monitor the currently most important anthropogenic long lived greenhouse gases CO_2, CH_4 and N_2O and to study their

Fig. 2.1. Station Lutjewad and its location in Europe.

[3] 190 in 2006. Source: http://www.demarne.nl.

main sources and sinks by use of the related tracers CO, SF_6, O_2 and ^{222}Radon, and the isotopes $^{14}O_2$ and $^{13}CO_2$ as well as meteorological data.

The measurement site is equipped with a 60m tall metal frame tower with air intakes at 7 m, 40 m and 60 m above ground. The ambient air is sucked through polyethylene/aluminium tubing (1/2" O.D., Synflex 1300, Eaton, Gembloux, Belgium and transported to a small laboratory in the building nearby. In order to prevent condensation of water vapor in the sample air, which is needed to prevent oxygen isotope exchange between CO_2 and water, thereby adulterating the CO_2's stable isotopic signature (Gemery et al., 1996), each sampling line is equipped with a Nafion dryer (MD 110-72-S, Perma Pure, Toms River, New Jersey). A Nafion dryer consists of a stainless steel tube with a polymer membrane tube inside. The membrane material is only permeable for water vapor, which is actively absorbed by sulfonic acid groups and moved along the water vapor gradient. The incoming air from the air intake in the tower passes through the inner tube, while the volume between the inner and outer tubes is flushed with dry gas from the output of the cryogenic cooler (see below) in the opposite direction. The flushing time from the Nafion and the cryogenic cooler and back is short enough to not have a gradient in the sample air except for the gradient in the amount of water vapor. The Nafion predryer removes between a half and two-thirds of the water vapor content from the sample air stream, depending on temperature and humidity (Neubert et al., 2004). The remaining moisture is frozen from the sample air in a glass cold trap which is placed in a dewar vessel containing an oil based heat-/cool fluid. This fluid can be cooled down to below -50°C by means of an immersion cryogenic cooler, or heated to +40°C using a resistor at the bottom of the dewar. The majority of the air which is not used is pumped back to the nafion to dry the new incoming air. For a detailed description of our drying system see Neubert et al. (2004). To achieve continuous operation, two of these drying systems are installed and used alternately: if one is cooling, the other is heated and flushed with air to the outside to remove the collected water. Following the drying stage, the sampled ambient air is used for analysis.

Fig. 2.2. Station Lutjewad.

Online measurements are performed with a HP Agilent HP6890N gas chromatograph (GC), see fig. 2.3, which semi-continuously analyses the mixing ratios of CO_2, CH_4, N_2O, CO, and SF_6 (Chapter 3). To fulfil our high requirements regarding measurement precision and accuracy and to measure all five species (practically) simultaneously at least 6 times per hour, the GC had to be strongly modified (Van der Laan et al., 2009a, chapter 3). CO_2, CH_4 and CO are detected by Flame Ionization (CO_2 and CO are first converted to CH_4 with a nickel catalyst methanizer) and N_2O and SF_6 using an Electron Capture Detector. The measured mixing ratios are reported with reference to an internationally recognized scale of the World Meteorological Organization (WMO), we achieve and maintain this by using two reference cylinders which are regularly calibrated with 5 primary cylinders supplied by the NOAA (Tans et al., 2003).

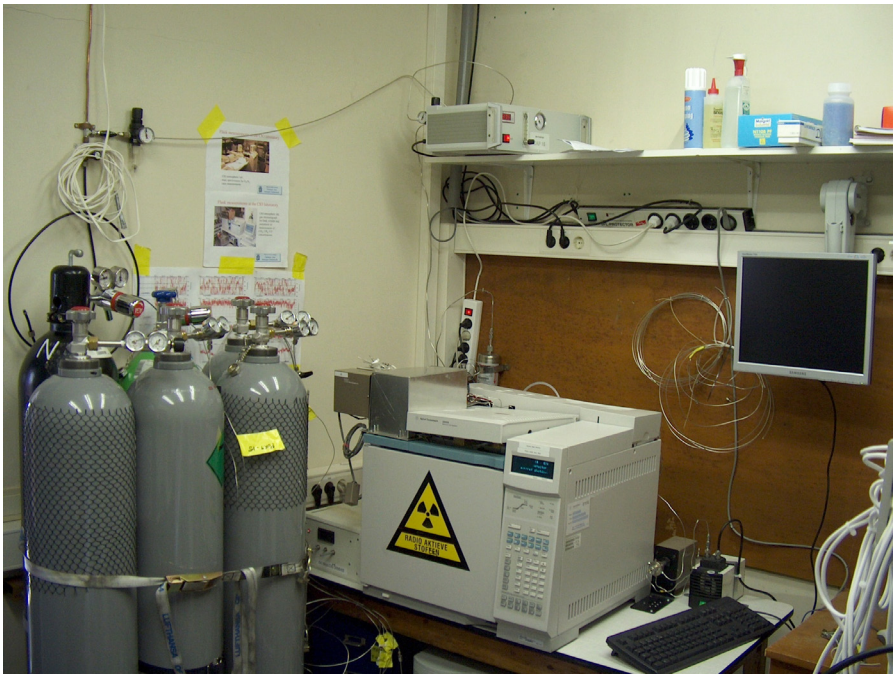

Fig. 2.3. An Agilent HP 6890N gas chromatograph was modified in order to measure semi continuously and with high precision the ambient mixing ratios of CO_2, CH_4, N_2O, SF_6 and CO.

Daily performance and long term stability is checked by replacing a sample measurement with a well-known target cylinder every 12 hours. Besides the online GC measurements, also 2.5 litre glass flasks are filled with air from 60 m to analyze the air in more detail at the CIO laboratory. The sampled air can be analyzed for the mixing ratios of: O_2 (i.e. O_2/N_2 ratios), CO_2, CH_4 and CO, stable isotopes (^{13}C, ^{14}C, ^{18}O in CO_2) and, using Accelerator Mass Spectrometry (AMS), $^{14}CO_2$ (Van der Plicht et al., 2000). In his study, $^{14}CO_2$ measurements were highly important since this isotope of CO_2 can be used to distinguish CO_2 from fossil fuel combustion. The filling of the flasks is done by a flask autosampler (Neubert et al., 2004), see fig. 2.4, which can be either remotely controlled or operated automatically through algorithms via the sequence table in the control software. Opening and closing of the flasks is done by actuating two highvacuum valves (Louwers, Hapert, NL) sealed with Viton o-rings, operated by home-made electric motor actuators. They are filled to atmospheric pressure to prevent the air sample from adulteration by pressure gradient driven differential permeation through the o-rings, most prominently visible in O_2/N_2 ratios (Sturm et al., 2004).

Because of the "grab sample" character of single flasks, one would need many samples to get an accurate representation of the signal. However, high costs involved in the AMS $^{14}CO_2$ analysis prevent this. Therefore, also monthly and biweekly integrated samples are taken for conventional $^{14}CO_2$ analysis (using counter tubes) since October 2000. Using this technique, the CIO has created already a long record of $^{14}CO_2$ from the nearby television tower of Smilde (52°54'N, 6°24'E, 12 m asl), about 30 km south of Groningen where similar measurements taken from about 90m above ground level already started in the 1960's (Meijer et al., 1995). The sampling technique is based on flushing the sample air through a 1.5N NaOH (hydroxide) solution which takes up the CO_2 molecules, see fig. 2.5.

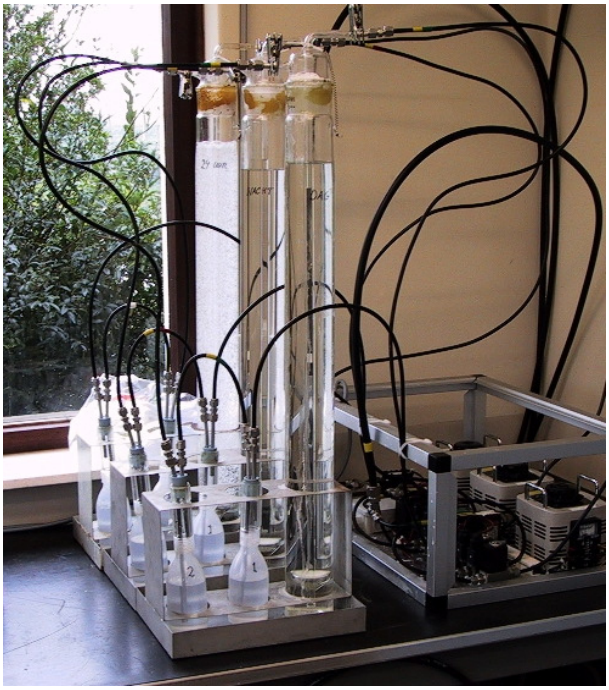

Fig. 2.5. Sampling tubes for CO_2. These are analyzed at the lab in Groningen for $^{14}CO_2$.

The absorbed CO_2 can be driven out in the lab in Groningen by applying an acid, and after cleaning it is measured in a proportional counter tube. Currently, three of these systems are applied at Lutjewad. One sampler is flushed continuously, one only with "background" northern winds (between 310° and 15°) and the third only with mainly anthropogenically influenced southern winds (between 100° and 250°).

Station Lutjewad has been equipped with a ^{222}Radon (^{222}Rn) detector since September 2005. In this thesis, the concentrations of ^{222}Rn are used to translate the ambient mixing ratios of CO_2 and CH_4 to their surface emissions. The ^{222}Rn detector installed at Lutjewad is a so-called two-filter dual-flow loop system, fig. 2.6 A. With a flow of 80 l min^{-1} air is flushed from the tower to the detector. Meanwhile, any ^{220}Rn will be decayed during travel and any other (radioactive) decay products and aerosols are filtered out before the sample air enters the detector. The sample air is circulated at high speed in a 1500 l delay chamber where ^{222}Rn decay products are sampled on a filter. The decay of the ^{222}Rn daughters is then detected by a photo-multiplier and counted per half hour interval.

To investigate the effects of, for example, moisture content and temperature on its surface emissions, an automated ^{222}Rn soil flux chamber was

installed in 2006 next to the building, see fig. 2.6 B. ^{222}Rn and also CO_2 are measured from this chamber as well as from soil probes. Temperature, humidity and groundwater level measurements are performed as well.

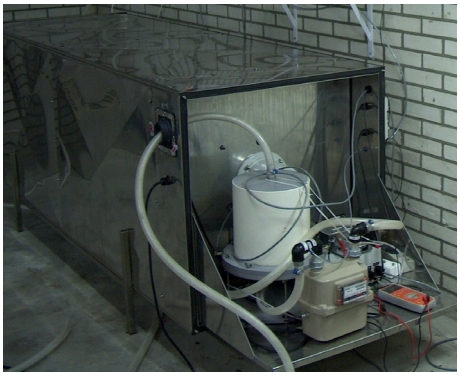

Fig. 2.6 A. ^{222}Rn detector (inlet at 60m).

Fig. 2.6 B. ^{222}Rn soil chamber.

An eddy covariance flux system, see fig. 2.7, was installed in the summer of 2006 in the mast at 50 m height. With this system, fluxes of CO_2 and H_2O as well as sensible and latent heat of the area below the mast (about 1-15 km in distance) can be determined. Depending on the wind direction and wind speed, an average flux is determined for the agricultural area or, with northerly winds, for the reclamation area, tidal flats and sea.

At 25 m height, a scintillometer was installed by the Meteorology and Air Quality (MAQ) group of Wageningen University in April 2006, see fig. 2.8. An infrared transmitter is installed in the church tower of the nearby village Hornhuizen and the signal is received in the mast. Small intensity fluctuations (or scintillations) of the light-beam can be used to estimate sensible heat fluxes from the path (about 2 km) between the village and the measurement tower.

Fig. 2.7. Eddy covariance system at a height of 50 m.

Fig. 2.8. Scintillometer (receiver) in the Lutjewad tower at 25 m.

For the purpose of interpretation of the data the mast is equipped with an arsenal of meteorological instruments (Gerritsma and Neubert, 2002) which are given in table 1.

Table 1. Basic meteorological measurement instruments at Lutjewad.

	ground	7 m	40 m	60 m	-0.5 m
Temperature		X	X	X	X
Relative Humidity		X	X	X	X
Wind speed		X	X	X	
Wind direction				X	
Atmospheric Pressure		X			
Precipitation	X				
Solar Radiation (IR,Vis)	X				
Groundwater table					X

References

Gemery, P. A., Trolier, M., and White, J. W. C.: Oxygen isotope exchange between carbon dioxide and water following atmospheric sampling using glass flasks, J. Geophys. Res., 14415 - 14420, 1996.

Gerritsma, R., and Neubert, R. E. M.: Meteorological Measurements at the atmospheric monitoring and sampling station Lutjewad (Province of Groningen), Centre of Isotope Research, Groningen University, Internal report CIO-IR/39/02, available upon request., 2002.

Neubert, R. E. M., Spijkervet, L. L., Schut, J. K., Been, H. A., and Meijer, H. A. J.: A Computer-Controlled Continuous Air Drying and Flask Sampling System, J Atmos Ocean Tech, 21, 651–659, 2004.

Sturm, P., Leuenberger, M., Sirignano, C., Neubert, R. E. M., Meijer, H. A. J., Langenfelds, R., Brand, W. A., and Tohjima, Y.: Permeation of atmospheric gases through polymer O-rings used in flasks for air sampling, J. Geophys. Res., 109, 2004.

Tans, P., Zhao, C., and Masarie, K.: "Maintenance and propagation of the WMO Mole Fraction Scale for carbon dioxide in air" in Report of the Eleventh WMO Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques, Tokyo, Japan, 25-28 September 2001, edited by S. Toru, World Meteorological Organization, Geneva, 2003.

Van der Laan, S., Neubert, R. E. M., and Meijer, H. A. J.: A single gas chromatograph for atmospheric mixing ratio measurements of CO_2, CH_4, N_2O, SF_6 and CO, Atmos. Meas. Tech., 2, 549-559, 2009.

Van der Plicht, J., Wijma, S., Aerts, A. T., Pertuisot, M. H., and Meijer, H. A. J.: Status report: the Groningen AMS facility. Nuclear Instruments and Methods in Physics Research B172, 58-65, 2000.