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СНІОТТО

Final report

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Colofon

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Summary

The CHIOTTO project objective is to build an improved infrastructure for the continuous monitoring of the concentrations of greenhouse gases on the European continent above the surface layer using tall towers. The project is based on and extends previous research projects (AEROCARB, T-COS and TACOS).

The project is an important step towards a fully operational continuous observing system in the framework of the Kyoto Protocol for the sources and sinks of the most important greenhouse gases (CO_2 , CH_4 , N_2O , CO, SF_6) over Europe.

An important aspect of the objectives is the establishment of high quality calibrations for the existing and new atmospheric measurement stations, and the implementation of a near-online data-transmission system for tall tower measurements. We monitor the intercomparability of the concentration measurements between the institutes operating the air sampling networks.

Quality controlled atmospheric concentration, CO_2 flux and additional meteorological data are archived in a data centre accessible to the scientific community through the World Wide Web. We integrated existing flux towers in the vicinity of the tall towers with the atmospheric stations networks in a synergetic approach enabling the tall towers to become atmospheric monitoring sites for use in transport models.

The CHIOTTO project played a big role in bringing together experts and novices on the field of high precision concentration measurement techniques. Through the development of a list of common instrumentation, equipment, calibration, database and quality control we made a big step towards an operational European network of high quality measurements of all relevant greenhouse gases.

The network covers a very large part of the most densely populated part of Europe with the highest greenhouse gas emission totals. We also implemented eight operational continuous observing sites, now delivering their data to the scientific community. The network will continue (CO_2 observations) as an important part of the Atmosphere component of CarboEurope, in GEOMON-IP and in IMECC in FP6. This achievement is also being recognized as a unique network on the international level.

The coordinator and the other partners took part in the setup of the scientific strategy of the CarboEurope-IP in the year 2003. The precision targets set in CHIOTTO, the calibration protocol and the data communication are taken over as building blocks of the Atmosphere Component of CarboEurope IP.

The high precision calibration gas facility in Jena that was developed in the CHIOTTO project is now being used and extended in the CarboEurope-IP and GEOMON-IP projects and will be part of the envisaged ICOS infrastructure initiative. The adapted intercomparison rotation scheme and use of high pressure cylinders for ring tests is now being employed in the CarboEurope-IP, also using the experience gained in the cluster co-project TACOS.

The project's actual outcome

- A recommended equipment list for all stations.
- A central calibration protocol.
- A central intercomparison protocol.

- Three new Tall Tower measurement stations performing continuous high precision measurements of the most important greenhouse gases and related tracers, the last stage of the fourth station was implemented just after the end of the project.
- An upgrade of four existing Tall Tower measurement stations in order to perform continuous high precision measurements of the most important greenhouse gases and related tracers.
- A time series of high precision concentration observations at most stations of half (new) and one-three (existing) years.
- A virtual interface for remote control of most systems.
- A central database for storing and retrieving the observation data.
- An operational system for preparing working standards.
- All stations equipped with Calibration gases, Archive Standards and a set of Travelling standards, produced using the working standard production system.
- An operational calibration system for all tall tower measurements systems.
- An operational system for measurements of CO₂ fluxes at two representative sites within the flux footprint of the tall towers.
- Observational data of CO₂ fluxes at two representative sites within the flux footprint of the tall towers.
- On line reports of atmospheric concentration data.
- A website for dissemination of the CHIOTTO project and its results.
- A final report.

Dissemination

The work performed in CHIOTTO was disseminated among the relevant scientific communities through presentations and contributions to symposia, workshops and meetings like those of the 'WMO expert group on CO_2 and related tracers measurements'. The basic setup of the measurements, calibration systems and working standard preparations and the results will be communicated through several peer-reviewed scientific articles.

The CHIOTTO website http://www.chiotto.org serves as a communication forum for the broad public and for internal communication for the project partners by the use of an electronic message and data exchange forum based on the Viadesk Web software.

The concentration measurement results are stored in the CHIOTTO central database for use by the project partners. Part of the concentration data (CO_2 , CH_4 and CO) is also stored on the central database for the Atmosphere Component of CarboEurope IP, where it can be used by the CarboEurope IP project partners, following the CE-IP data use policy. Most partners will also submit their observational greenhouse gas concentration data in the long run to the GAW Greenhouse Gas Data Centre, from that moment on that data will be available to anyone.

1. Overview of CHIOTTO

1.1 Introduction

According to the Kyoto protocol, 174 countries shall have in place, no later than 2008, a national system for the estimation of anthropogenic emissions from all sources and removals by all sinks of the greenhouse gases not controlled by the 1992 Montreal Protocol. Countries are however committed to show substantial progress by the year 2002, thus invoking an urgent need for a monitoring system of sinks and sources.

In recent years it has become clear that the traditional atmospheric greenhouse gas observing system has severe gaps. Until recently, continental monitoring stations have not been considered relevant because of the large variability of the signals, caused by the proximity to the land-biosphere atmosphere exchange fluxes and the strong, spatially concentrated sources.

The horizontal gradients of greenhouse gas concentrations, which carry information on the magnitude and spatial distribution of sources and sinks, are quite small. If we are to infer fluxes at the regional level, it is thus necessary to sample close to the earth surface and on a continuous basis to capture the signal of greenhouse gas exchange fluxes. This calls for measurements in the boundary layer. Here the variability in concentrations (diurnal cycles) is huge, because the air is to a large extent influenced by local sources and sinks. In order to separate the effect of local (few tens of km) variability from the regional signal, one needs to continuously monitor concentrations above the surface layer (100 meters), complemented for CO_2 by eddy flux towers to characterize the contribution of 'local' biospheric exchange.

If the gases are measured at sufficient height above ground (ideally a few hundred meters), then a fairly homogeneous signal that integrates fluxes over a footprint on the order of a circle of 500 to 1000 km is obtained. Continuous measurements also permit to optimise the signal to noise ratio of the measurements.

Because of the natural variability of the signals in the atmosphere, the time series needed for successful inverse calculation of fluxes by atmospheric transport models (ATM's) should extend over a long time frame of at least several years. Time series of 5-10 years or longer will be required in order to be able to distinguish trends in time, because of a response to e.g. climate change on ecosystem CO_2 fluxes or emission reduction measures. At this time no infrastructure yet exists that can provide us with such data.

The new approach followed in this project is to continuously sample CO_2 and other greenhouse gases (some also related to the carbon cycle) like CH_4 , CO, N_2O , and SF_6 on tall towers, together with tracers that help validate the realism of transport simulation with atmospheric models like C_2Cl_4 and ²²²Rn. We think that it is possible to monitor the European carbon balance as well as the emissions of greenhouse gases on the regional scale (areas of approximately 1 million km²) in support of the Kyoto Protocol using a pan-European observing system of a carefully designed and well calibrated network of atmospheric concentration measurement sites. With the implementation of the CHIOTTO project Europe made a head start in applying such an approach using existing and new tall tower observation sites.

In Europe, a few tall towers in the Netherlands, Hungary, Germany and Sweden existed that were already equipped with devices that permit online measurements of the CO_2 concentration and in some cases related tracers. In the CHIOTTO project the measurements at

the existing towers were improved and extended and the network of towers was further extended by new towers in Great-Britain, France, Poland and Italy. This has largely increased the spatial coverage of the studied area. The footprints of these towers together cover Europe fairly well (Figure 1.1). One further objective of the project was to help sustain existing measurements and partly implement new ones, while ensuring high data quality and a high standard of calibration and inter-comparison.

The tower-based observations will also be useful and important as ground-truthing data for calibration and verification of future remote-sensing (satellite) data.

1.2 Specific objectives

- 1. Implement new tall tower stations and complement existing tall tower stations enabling the continuous monitoring of the sources and sinks of the most important greenhouse gases in Europe.
- 2. Design and implement a standardized protocol for calibrating measurements of CO_2 , CH_4 , N_2O , CO and SF_6 at selected tall towers, to a level of precision enabling the use of tall tower concentration records in atmospheric transport models for estimation of annual average regional fluxes.
- 3. Set up a near real-time transmission system of tall tower data, including archiving, quality control, and accessibility.
- 4. Implementation of a technical support and servicing unit for tall tower measurements.
- 5. Establish a link between tall tower concentration measurements and CO_2 surface flux data for evaluation of the representatively of tall tower data for regional scales.

1.3 Objectives of CHIOTTO

The CHIOTTO project objective is to build an improved infrastructure for the continuous monitoring of the concentrations of greenhouse gases on the European continent above the surface layer using tall towers. The project is based on and extends existing research projects (AEROCARB, TCOS Siberia and TACOS). This project forms an important step towards a fully operational continuous observing system in the framework of the Kyoto Protocol for the sources and sinks of the most important greenhouse gases (CO_2 , CH_4 , N_2O , CO, SF_6) over Europe.

An important aspect of the objective is the establishment of high quality calibrations for the existing and new atmospheric measurement stations, and the implementation of a near-online data-transmission system for tall tower measurements.

We have monitored the inter-comparability of the concentration measurements between the institutes operating the air sampling networks. Quality controlled atmospheric concentrations, CO_2 flux and additional meteorological data are archived in a data centre accessible to the scientific community through the World Wide Web.

The precision and accuracy of our measurements will be extremely important as the data will be used also in global (inverse) transport models and data assimilation systems and for extended averaging times, where systematic offsets in the measurement become very problematic and can lead to large errors in the fluxes derived from concentration differences between stations and/or times. So not only the repeatability of the system needs to be high to measure accurately small concentration differences between levels and as a function of time, also the comparability of measurement sover longer time and between stations needs to be very good. We decided to follow the precision recommendations of the WMO Expert panel on CO_2 and related tracers measurement techniques. As laid down in the report of the 22^{nd}

meeting of this Group in Sendai, Japan in 2002 gives an overview of the target for the required precision and accuracies for the relevant tracers.

Gas species	Precision ¹	Accuracy ²						
O ₂ /N ₂	±5 per meg	±10 per meg						
CO ₂	±0.05 ppm	±0.10 ppm						
CH ₄	±2.0 ppb	±3.0 ppb						
CO	±1.0 ppb	±3.0 ppb						
N ₂ O	±0.1 ppb	±0.2 ppb						
SF ₆	±0.1 ppt	±0.2 ppt						
Rn ⁽³⁾	0.2 Bq m ⁻³ or 10%	10%						

Table 1.1Recommended Targets for the precision (in the lab) and accuracy (between
stations) for the most relevant greenhouse gas concentration measurements.

We integrated existing flux towers in the vicinity of the tall towers with the atmospheric stations networks in a synergetic approach enabling the tall towers to become atmospheric monitoring sites for use in transport models.

In the project we have implemented all new and existing measurements systems. We have worked on establishing the precision targets for the measurements and implemented a calibration and inter-comparison protocol to achieve those targets for the individual towers and between towers.

In Table 1.1 an overview is given of the tall towers in the CHIOTTO project, their positions, the parameters measured and the operators. In Figure 1.1 the positions of the towers can be viewed on the map of Europe. Figure 1.1 also gives the influence function of the group of towers for 2002.

In the 1^{st} year of the CHIOTTO project we have defined the exact requirements for the equipment to be used and we have defined the measurement, calibration and data submission protocols. These are the foundation of the project. On the basis of this information the new equipment was purchased, customized, installed and tested. This continued into the 2^{nd} year.

In the third and last year and the following 6 month extension, most of the towers have been equipped and started either the initial or operational mode.

Major problems encountered in the project were related to trivial practical issues, though these caused rather large delays. The ordering and delivery process for the needed equipment took in most cases a very large time. The selected GC system had delivery times of minimally six months, in some cases up to a year.

Large problems were encountered in selecting, ordering and getting delivered the right type of high pressure tanks and pressure regulators. The demands posed by the high precision measurements on the materials and instruments forced us to use very non-standard and specific products that were difficult to find and to get them actually delivered and turned out to be much more expensive than had been anticipated in the original budget. This caused that all partners have invested much more effort and (own institute) money into this project than the official budget shows.

The CHIOTTO concentration data will be used in for example the FP6 CarboEurope-IP to derive estimates for the strengths of CO_2 sources and sinks of Europe, in combination with other measurements types and other (global and local) networks. CHIOTTO will continue as

an integral part of the atmospheric component of the CarboEurope-IP that has officially started in January 2004.

The coordinator and the other partners took part in the setup of the scientific strategy of the CarboEurope-IP in the year 2003. The precision targets set in CHIOTTO, the calibration protocol and the data communications are taken over as building blocks of the Atmosphere Component of CarboEurope IP.

The high precision calibration gas facility in Jena that was developed in the CHIOTTO project is now being used and extended in the CarboEurope-IP and GEOMON-IP projects and will be part of the envisaged ICOS infrastructure initiative. The adapted intercomparison rotation scheme and use of high pressure cylinders for ring tests is now being employed in the CarboEurope-IP, also using the experience gained in the cluster co-project TACOS.



CHIOTTO influence function

Figure 1.1 The influence function for the year 2002 of the 8 CHIOTTO tall towers derived by the COMET trajectory model (See Chapter 4)

		Hght	Pos	sition	Co	oncent	ratior	n mea	surer	nent (l	evels)	Flux	meas	
Name		(m)	Lon	Lat	CO_2	CH_4	N_2O	SF_6	CO	222 Rn	Flasks	CO_2	CH_4	Operator
Cabauw	NL	200	04°56	' 51°58	' 4	4	4	4	4	1	\checkmark	2		ECN
Griffin	UK	232	-2°59)' 56°33	' 1	1	1	1		1				UEDIN
Hegyhatsal	Н	117	16°39	' 46°57	" 4	1	1	1	1		\checkmark	2		ELTE
Orleans/Trainou	F	131	2°07	' 46°58	3	3	3	3	3	1	\checkmark			LSCE
Norunda	S	102	17°28	' 60°05	4	2						2	2	LUPG
Florence	Ι	245	11°16	' 43°49	' 1	1	1	1	1					UNITUS
Ochsenkopf	D	163	11°49	' 50°03	3	3	3	3			\checkmark			MPIBGC
Bialystok	PL	300	22°45	' 52°15	' 5	5	5	5	5		\checkmark			MPIBGC

Table 1.2Tall tower data summary

1.4 Description of the Tall Tower sites

In the following paragraphs all tower sites are described concerning their coordinates, layout, surroundings, characteristics of the tower and the equipment. For all towers a concentration footprint is shown, calculated with the COMET transport model (see chapter 4 for model details). The red area shows the region from which the emissions contribute to a concentration signal equal to that of 1% of the maximum concentration per unit emission in mass per unit of time and unit of area, that maximum is reached for the model pixel in which the tower is located. Grid size in this calculation was 10 arc seconds longitude and latitude.

1.4.1 Orleans (Trainou) tower - LSCE (TRA)

Station summary				
Code:	TRA			
Location:	Trainou (Orléans), France			
Coordinates:	Lat 47° 57' 54' N			
	Long 02° 06' 45' E			
	Alt 131 m ASL			
Measured species:	continuous CO ₂ , CH ₄ , CO, N ₂ O, SF ₆ concentrations (vertical			
gradient)				
	continuous meteorological parameters (180m)			
	flask samples from 180 m			
Sampling heights (AGL)): 50m, 100m, 180m			



Figure 1.2 Concentration footprint of Orleans tower for 2005

The main scientific objective for LSCE is to add to the European network a new tall tower infrastructure for continuous monitoring of greenhouse gas concentration in France. The equipment for the station includes a NDIR CO₂ analyser, a gas chromatograph for CH₄, CO, N₂O and SF₆ measurements, and a ²²²Rn monitor. Weekly flask samples will be analyzed at LSCE for CO₂, CH₄, N₂O, SF₆ and CO (quality control) and for ¹³C and ¹⁸O isotopes in CO₂. One of the challenges of the project is to design a well calibrated network of atmospheric concentration measurement sites with on-line data transmission.

Tower negotiation

The major obstacle for the implementation of the instruments is that the TDF Company (http://www.tdf.fr/), owner of the pylon in Orleans, had decided to strongly increase the rental rate of the offered space in the Orleans tower since the initial negotiations. As reported last year TDF asked for 80kEuro/year rent, to equip 3 heights of their tower with meteorological sensors and tubing and that we can use $12m^2$ room for the equipment. A second quotation was proposed by TDF: 100 000 Euro single payment and 15 000 Euro per year, if the contracting is longer than 5 years. Neither is possible for our consortium from a financial point of view. The difficulty is that TDF owns most of the towers above 100m in France. A letter sent by the ministry of communication and the ministry of environment helped to reduce the price to 10kEuro/year if we contract for ten years. LSCE agreed to this price and the formalities of the rental have now been arranged. The tubing for the air sampling from all 3 levels as well as the measurement container and the instrumentation has been installed. Continuous measurements started from September 2006 on.

Gaschromatographic system

A fully automated GC system for semi-continuous atmospheric measurements of CO, CH₄, N₂O and SF₆ has been developed and optimized at LSCE, respecting the guidelines of the CHIOTTO harmonization workshop (Figure 1.3). To obtain the reproducibility of the GC-system LSCE used three tanks calibrated by NOAA-CMDL (Boulder, CO). Using 2 cylinders as standards (working high and working low), the third cylinder was treated as so called target gas. The reproducibility of the target gas is ± 1.6 ppb for CO, ± 1.2 ppb for CH₄, ± 0.3 ppb for N₂O and ± 0.06 ppt for SF₆. The values assigned by NOAA were reproduced within the measurement error.

The system was built in 2003 and optimized in 2004. Since summer 2004 ambient air collected from the roof of our laboratory has been analyzed at Gif-sur-Yvette.



Figure 1.3 Schematic of the plumbing of the gas chromatographic system for Trainou Tower



Figure 1.4 *Photograph of the gas chromatograph set up including calibration tanks, cryogenic cooler, hydrogen and air generator*

NDIR System (CARIBOU)

 CO_2 is measured continuously with a NDIR analyser called CARIBOU, based on a LICOR 6252 which is temperature and pressure regulated. The development of this instrument was carried out in cooperation with DAPNIA a department of the CEA, Saclay, France. The CARIBOU was delivered to LSCE in December 2004.

The pressure of the reference and sample cells are regulated individually and absolutely to about 1080 mbar. The relative pressure difference between both cells is less than 0.1 mbar. The flow rates through the reference and sample cells are regulated to 20 ml/min, ensuring a long lifetime of the cylinder (half a year for the reference gas to several years for the working standards).

The CARIBOU system has been tested in the Saclay laboratory. Table 1.3 shows the measurements performed on standard gases during 11 days. The data were only processed using a single initial calibration, and drift correction obtained by measuring the signal on the reference gas once per hour. The reproducibility obtained is about 0.02 ppm, except for tank

W413, which had a leaking regulator, and therefore has a larger variability in the measurements.

Table 1.3Reproducibility of the measurements after drift correction, and using a single
calibration curve

Tank name	CO2 concentration by LOFLO (ppm)	Mean CARIBOU after drift correction (ppm)	Standard deviation (ppm)
W353	352,988	352,999	0,0225
W395	395,454	395,497	0,0190
W413 *	412,909	412,871	0,0833

Table 1.4Overview of current status of measurements at Orleans, measurement device,
starting date of actual operational use at the tower and the estimated obtained
precision

Gas	Method	Operational	Precision
CO ₂	Caribou	Sep-06	0.02 ppm
222 _{Rn}	ANSTO	Sep-06	50 mBq.m ⁻³
CH4	GC-FID	Sep-06	0.8 ppb
СО	GC-FID		2 ppb
N ₂ O	GC-ECD		0.3 ppb
SF ₆	GC-ECD		0.1 ppt

1.4.2	Bialystok Tall Tower measurement station – MPI-BGC (BIK)	
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Station summary			
Code:	BIK		
Location:	Bialystok, Poland		
Coordinates:	Lat 53°13'N		
	Long 23°01'E		
	Alt 180m ASL		
Measured species: continuous CO_2 , CH_4 , CO , N_2O , SF_6 concentration gradient)			
continuous O_2/N_2 ratio (vertical gradient)			
	continuous meteorological parameters		
	flask samples from 30m and 300m AGL		
Sampling heights (AGL): 5m, 30m, 90m, 180m, 300m			



Figure 1.5 Concentration footprint of Bialystok tower for 2005

MPI-BGC is responsible for the setup and operation of a new tall tower measurement station, located near Bialystok, Poland, shown in Figure 1.6. Figure 1.7 shows the plumbing diagram of Bialystok Tall Tower.



Figure 1.6 BIK tall tower

Measurement description

Continuous measurements: CO₂, O₂/N₂, CH₄, CO, N₂O, SF₆

The measurement system was designed, built and extensively tested in Jena, Germany. In June 2005 it was partly uninstalled and transported to Bialystok, Poland. The system was then re-installed and tested at the final location. Continuous measurements are running since the end of July 2005.

Continuous measurements characteristics:

- sampling heights: 5m, 30m, 90m, 200m, 300m above ground level; supplementary control sampling lines from 30m and 300m;
- data frequency:
 - CO_2 , O_2/N_2 : one data point every 3min

- CH₄, CO, N₂O, SF₆: one data point every 14min
- equipment:
 - CO_2 LiCor 7000 IR analyzer
 - O_2/N_2 Oxzilla fuel cell analyzer
 - CH₄, CO Agilent gas chromatograph FID
 - N₂O, SF₆ Agilent gas chromatograph ECD
- Software:
 - Labview: general system control; CO₂, O₂/N₂
 - Chemstation: gas chromatograph (CH₄, CO, N₂O, SF₆)

Flask sampling

The automatic flask sampling system was built by NIWA, New Zealand, and it is fully operational since Sep 2005, after some changes made by MPI engineers. Flask sampling system characteristics:

Flask sampling system characteristics:

- sampling heights: 30m and 300m above ground level
- flask samples type: 1L European standard; possibility for SIO and NOAA type flasks
- sampling pressure: 1.6 1.8 bar abs
- samples taken in pairs

Two intensive flask sampling campaigns took place so far in order to check the system and to compare with the continuous measurements. Such campaigns will be repeated every few months.

Currently one flask pair per week is sampled from the 300m height. A comparison routine between tower flask and aircraft data was started in 2006; for this, supplementary flasks are taken in the same time with the flight.

Meteorological measurements

The meteo measurement system was installed on the tower in February 2005 and is running since June 2005. The data transmission is done by CAN-BUS and the data are coupled with the rest of the measurement data by a Labview program.

Meteorological parameters measured:

- wind speed and direction (at 300 m)
- pressure (at 30 m and 300 m)
- temperature (at 5 m, 30 m, 90 m, 180 m, 300 m)
- humidity (at 30 m, 300 m)



Figure 1.7 Plumbing diagram of Bialystok Tall Tower (BIK)

Table 1.5	Overview of current status of measurements at Bialystok, measurement device,
	starting date of actual operational use at the tower and the estimated obtained
	precision

Gas	Method	Operational	Precision
CO ₂	LICOR 6252	Sep-05	0.04 ppm
02	Oxzilla FC2	Sep-05	8 per meg
CH ₄	GC-FID	Sep-05	0.7 ppb
CO	GC-FID	1	0.6 ppb
N ₂ O	GC-ECD	G., 05	0.3 ppb
SF ₆	GC-ECD	Sep-05	0.03 ppt

1.4.3 Angus Tall Tower - UEDIN (TTA)

Station Summary	
Code:	TTA
Location:	Balclak Farm, Tealing, near Dundee, UK
Coordinates:	Lat 56° 33.3' N
	Long 2° 59.2′ W
Height asl:	313 m
Tower Height:	229.5 m agl
Measured Species:	CO_2 , CH_4 , N_2O , SF_6 , CO and H_2 at 222 m agl; ²²² Rn at 50 m agl



Figure 1.8 Concentration footprint of Angus tower for 2005

A picture of the Angus tall tower is shown in Figure 1.9.



Figure 1.9 Tall Tower Angus. Image taken during an AEROCARB flight on 16

Measurement description

The system for the main CHIOTTO gases was designed and built at the University of Edinburgh. The system was extensively bench-tested before being installed at TTA during the summer of 2005. Since August 2005, the system has been fully operational and the precision has equaled that found in the laboratory.

The measurements are all continuous in time and are made from a sampling location at 222 m above groundlevel, i.e. just below the top of the tower.

 CO_2 in air is measured by an infra-red gas analyser (LI-7000) at a sample rate of 0.1 Hz. Measurements are stored as a mean and standard deviation over a 10-minute averaging interval.

The atmospheric concentrations of CH_4 , N_2O , SF_6 , CO and H_2 are measured every 12 minutes; peak areas and peak heights of the chromatograms are recorded. An Agilent 6890 gas chromatograph with an FID measures CH_4 ; the same analyser with an ECD measures N_2O and SF6. An RGA3 analyser measures H_2 and CO. The Agilent was installed in early June 2005, the RGA3 was added in July 2005. The laboratory tests and initial field tests confirmed the relative precision for the system as: SF_6 : 1-1.4%, N_2O : 0.5-0.06%, CH_4 : 0.6-0.7%, CO_2 : 0.25%. Subsequent tests with the Traveling Standards have shown these targets to be easily achieved.

A Radon detector was purchased from the Australian Nuclear Science and Technology Organization (ANSTO) in 2003 and was commissioned by ANSTO staff in early October 2004 (Figure 1.10). Since then it has run continuously and almost without interruption. The Radon detector is calibrated automatically once per month by the ANSTO Portable Calibration Unit and background radon checks are performed every 6 months. The Operational Specifications of the ANSTO TTA Radon Detector are shown in

Table 1.6.



Figure 1.10 ANSTO Radon detector outside main building, TTA

Tuble 1.6 Operational specifications of the Highs Internetion	Table 1.6	Operational	specifications	of the An	gus ²²² Rn	monitor
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Parameter	Value	
Sampling Height	50 m AGL	
Flow Rate	$65 \mathrm{l} \mathrm{min}^{-1}$	
Detector Volume	15001	
Lower Limit of detection	30 mBq m^{-3}	
Typical Sensitivity	$0.30 \text{ cps} / \text{Bq m}^{-3}$	
Sampling rate	30 minutes	
Response time	45 minutes	
Thoron reduction factor	Approx 98%	

Meteorological Parameters

Air temperature and relative humidity are measured automatically at heights of 222, 150, 50 and 5 m above ground level; wind speed and direction are also logged at a height of 5 m. MATLAB scripts are used to process the data from the Radon, GCs and weather stations and the intention is to make this a routine operation.

Sampling Protocol

The sampling protocol for the GC-based system is shown in Figure 1.11. The system is based on measuring the inevitable drift in the gas chromatograph FID and ECD detectors; we alternately measure a known concentration (e.g. from a working standard) in a six minute period, then switch to the unknown sample (i.e. the tower inlet air) in the next six minute period and switch back again to the known source for the next six minute period. By doing this, we can allow for the drift in the analyser over time. At the beginning of each day, our standard tank is alternately compared to the 4 Working Standards; there are three replicates from each of the Working Standards with the first of each of the Working Standards also being fed to the IRGA for a CO_2 check. After this calibration, we start the first of three calibrations of the LI-7000 by feeding in gas alternately from a Target Tank and the Standard gas bottles. Once the first set of three checks on the Li-7000 is complete, the system switches over to monitoring tower air (i.e. from the 222 m level) with alternate 6 minute periods coming from the Standard Tank to check for GC drift as before.



Figure 1.11 Sampling protocol for the GC system at Angus Tall Tower

The system is controlled by a series of precision valves and flow controllers under the overall software control of the PeakSimple System. Figure 1.12 shows a schematic of one of the control files that runs under PeakSimple.

Intake Sampling



Table 1.7	Overview of current status of measurements at Angus, measurement device,
	starting date of actual operational use at the tower and the estimated obtained
	precision

	precision		
Gas	Method	Operational	Precision
CO ₂	LICOR 6252	Aug-05	0.04 ppm
222 _{Rn}	ANSTO	Sep-03	50 mBq.m ⁻³
CH4	GC-FID	Aug-05	0.7 ppb
CO	GC-FID		0.6 ppb
N ₂ O	GC-ECD		0.3 ppb
SF ₆	GC-ECD	Aug-05	0.03 ppt
CO ₂	LICOR 6252		0.04 ppm

1.4.4	Florence	Tall Tower	measurement	station ·	- UNITUS ((FIR)
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Station summary		
Code:	FLO	
Location:	Florence	ce, Italy
Coordinates:	Lat	43°49' N
	Long	11°16' E
	Alt	245 m ASL
Measured species:	continu	ious CO ₂ ,
	CH ₄ , N	I_2O , SF ₆ concentrations (one level)
	continu	ous meteorological parameters
Sampling heights (AGL)	:	200m



Figure 1.13 Concentration footprint of Florence tower for 2005

The tower and its location are shown in Figure 1.14.





Figure 1.14 Florence tall tower and satellite image of the region

Measurement description

Continuous measurements: CO₂, CH₄, N₂O, SF₆

The measurement system was built after a visit to the Max Planck Institute of Jena in February 2004, and tested at the University of Tuscia, Italy. It was transferred to the tower in August 2005. The data set is not complete and the accuracy for N_20 and SF_6 is below the CHIOTTO precision requested due to problems with the ECD detector; these were partially resolved in winter 2005.

For safety reasons UniTus was not able to stay in the Florence location. The tower will be disassembled. Together with the owner of the Florence site (RAI WAY) a new place has been located near the city of Orvieto, Italy. The new tower is located on the top of Monte Peglia (850 m. above sea level) and its height is 150 meters. Before the transfer the equipment was

tested again in the laboratory at the University of Tuscia to resolve the problems with the ECD. The equipment was installed in the new tower in summer 2006.

Continuous measurement characteristics:

- sampling heights: 200 m above ground level
- data frequency: CO₂, continuously CH₄, N₂O, SF₆: one data point every 10 min
- equipment: CO₂ – LiCor 6252 IR analyzer CH₄, CO – Trace gas chromatograph - FID
 - $N_2O,\,SF_6 \quad \ \ Trace \;gas\; chromatograph ECD$
- software: Labview: general system control; CO₂, Chrom-Card: gas chromatograph (CH₄, CO, N₂O, SF₆)

Meteorological measurements

The meteorological measurement system was installed on three levels of the tower in September 2005 and is running since May 2006. An electric spike caused the failure of one of the tree stations during winter 2005/2006.

Meteorological parameters measured:

- global radiation (200 m)
- wind speed and direction, temperature (at 5 m, 50 m, 100 m, 200 m)
- pressure (5 m)

Table 1.8	Overview of current status of measurements at Florence, measurement device,
	starting date of actual operational use at the tower and the estimated obtained
	precision

Gas	Method	Operational	Precision
CO ₂	LICOR 6252	Aug-05	0.7 ppm
CH ₄	GC-FID	Aug-05	7 ppb
N ₂ O	GC-ECD		2 ppb
SF ₆	GC-ECD	Aug-05	0.4 ppt

1.4.5 Cabauw station - ECN (CBW)

Station Description

······	
Station Code:	CBW
Location:	Lopik, The Netherlands
Coordinates:	Latitude: 51°58'N
	Longitude: 4°55'E
	Altitude: -2 ASL
Tower height:	213 m
Meas. heights:	200, 120, 60, 20 metres
Measurements:	Continuous CO ₂ , CH ₄ , CO, N ₂ O, SF ₆ , ²²² Rn
	Continuous meteorological parameters (KNMI)



Figure 1.15 Concentration footprint of Cabauw tower for 2005

ECN is responsible for the measurements at Cabauw tower, in the center of the Netherlands. The tower itself is operated as a meteorological observation site for planetary boundary layer studies by the KNMI Meteorological Office. The tower and its location are shown in Figure 1.16.



Figure 1.16 Cabauw tower (NL), with a height of 213 m above ground level. (left). Cabauw tower is situated at a very flat predominantly grassland area in the mid-West of the Netherlands (right, CORINE2000 land-use map).

Measurement description

The measurements in the old setup, using a Siemens Ultramat 3 NDIR for CO_2 and a Carlo Erba GC system for CH_4 , were continued until May 2004. Because of the required replacement of tubing, pumps and the electric system, all measurements of the old setup were stopped at the end of May 2004. In the five months period after the removal of the equipment all tubings from the cellar of the Cabauw building up to the 200m level were replaced by the required Synflex tubing. All the permapure dryers from the four inlet levels have been cleaned, regenerated and tested. Also the complete pressurized gas supply installation has been renovated. After the tower owner installed a completely new electrical power facility in October 2004, the Cabauw cellar room was ready for the installation of the new instrumentation.

The new setup was built up during October and November 2004 (see Figure 1.18). In September 2004 the CIO Groningen flask sampler arrived together with the attached cryocooler system, completing the CHIOTTO instrument setup. From then on all parts of the system were working satisfactorily and in the months thereafter a stability test of the complete system was performed at ECN, operating all parts in parallel. Afterwards the system was transferred from the ECN laboratory to Cabauw tower. The routine measurements started in December 2004, together with the arrival of the Working Standards from the Jena Lab. In Figure 1.17 the plumbing diagram of the new GC setup is shown.



Figure 1.17 Cabauw GC system setup



Figure 1.18 Simplified plumbing diagram of the Cabauw tower sampling system

As also found by the other groups, the problem with the employed high H_2 and air flow through the FID detector often causes problems with the flame being blown out when switching flow from the methaniser during the GC run. Automatic flame ignition does not work in the setup employed because of the high N_2 flow. Ignition is only successful if this N_2 flow is first reduced manually. As soon as the flame is on, this flow can be elevated again. By reducing the N_2 flow just before the switching of the methaniser we succeeded in reducing the probability of the flame being blown out. This worked fine in the Petten lab from April to November 2004 and at Cabauw tower from November 2004 until February 2005. From then on different problems have prevented the CO measurements on the GC from functioning.

The Licor CO_2 monitor of type 7000 continued to work perfectly in the specially built temperature and pressure controlled box during the whole reporting period. Minor periods with data loss occurred due to problems with the Windows XP USB communication stack. The multi-threaded, multi protocol communication and real-time CabauwTER control software worked well and only underwent some small modifications to increase its functionality.

In Figure 1.19 the installed equipment in the cellar room of the Cabauw central building is shown. From the moment of installation all the equipment performed well.



Figure 1.19 The analysis equipment in the cellar of Cabauw tall tower



Figure 1.20

Inlet pumps, filters, selection and flow control section (left) and ANSTO ²²²Rn gradient monitors (right) at the Cabauw central building


Figure 1.21 Detail of the modified CIO design silicon oil filled cryo-cooled vapor trap at Cabauw showing the five glass cooling fingers

Due to the remote control through the direct internet link from the lab in Petten to the controlling PC at Cabauw most problems can be traced quickly and can be solved very fast in most cases using the remote connection. Figure 1.22 shows the total data coverage for the greenhouse gas concentration measurements for all 4 vertical inlet levels. Except for CO the data coverage over the whole period is better than 95%. The interruptions in 2005 were mainly due to power interruptions at the Cabauw infrastructure.



Figure 1.22Data coverage overview for the greenhouse gas concentration measurements at Cabauw for the CHIOTTO measurement setup in the period November 2004 to December 2005 (color of line corresponds to the inlet level: black=200m, red=120m, yellow=60m, blue=20m).

The ANSTO ²²²Rn monitor arrived at Petten in October 2005 and was installed at Cabauw at the beginning of November 2005, taking air from the 200 meter above ground level. After the commissioning of the ²²²Rn monitor by ANSTO the monitor functions very well. A second monitor to start measuring vertical gradients by also measuring at the 20 m level was commissioned in March 2006 and also has functioned very well since then. The vertical gradient measurements of ²²²Rn as performed at Cabauw are quite unique, as there are only two other places in the world where this kind of measurements is made.

starting date of actual operational use at the tower and the estimated obtained precision				
Gas	Method	Operational	Precision	
CO ₂	LICOR 7000	Nov-04	0.05 ppm	
Flask sampler	CIO	Nov-04		
²²² Rn	ANSTO	Nov-05	50 mBq.m^{-3}	
CH_4	GC-FID	Nov-04	2 ppb	
CO	GC-FID		1 ppb	
N_2O	GC-ECD		0.4 ppb	
SF ₆	GC-ECD		0.2 ppt	

Table 1.9	Overview of current status of measurements at Cabauw, measurement device,
	starting date of actual operational use at the tower and the estimated obtained

1.4.6	Ochsenkopf	Tall Tower	Measurement Station	n - MPI BGC (OXK)
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Station Description		
Station Code:	OXK	
Location:	Ochsenkopf,	Germany
Coordinates:	Latitude	50°01'49'
	Longitude	11°48'30'
	Altitude:	1022 m
Tower height:	163 m	
Measurement heights:	163, 90 and 2	23 metres
Measurements:	Continuous C	D ₂ , CO ₂ , CH ₄ , CO, N ₂ O and SF ₆
	Continuous n	neteorological parameters



Figure 1.23 Concentration footprint of Ochsenkopf tower for 2005

MPI-BGC was responsible for the extension of the Ochsenkopf station to include continuous measurements of CH_4 , CO, N_2O and SF_6 , for improvements to the existing O_2 and CO_2 measurement system, and for the station's ongoing operation. A photo of the OXK tower is shown in Figure 1.24.



Figure 1.24 OXK tall tower

Measurement description

Continuous measurements: CO₂, O₂, CH₄, CO, N₂O, and SF₆

Continuous O_2 and CO_2 measurements started in May 2002, however, after several considerable instrumental failures, the station was shut down in September 2004. In March 2005, work began on improving and extending measurements at OXK. The first stage of this work was the testing of a new O_2 analyser and a GC in Jena, and the subsequent installation of the O_2 and CO_2 analysers at OXK in August 2005. In the second stage, ongoing tests of the O_2 and CO_2 instruments were made at OXK and quality data collection began at the end of November 2005. The final stage of the OXK upgrade was the installation of the GC and the supporting gas handling system. For this work to be done, O_2 and CO_2 measurements were temporarily stopped in mid February, but were resumed again once the main part of this installation was completed in late April. Continuous measurements of all species have been made from June 2006 onwards.

Continuous measurements characteristics

All continuously measured species are sampled in a rotating cycle from the three sampling heights: 23, 90 and 163 m above ground level. An overview of the instrumentation and sampling frequency is given in Table 1.10. Figure 1.25 shows a picture of the instrumentation, while a schematic of the measurements is provided in Figure 1.26.

Type of Measurement	Sampling Frequency	Instrumentation
O ₂	1 per 60 sec	Oxzilla FC-2
CO_2	1 per 60 sec	LICOR 6252
CH ₄	1 per 18 min	GC Agilent 6890 – FID
CO	1 per 18 min	GC Agilent 6890 – FID
N_2O	1 per 18 min	GC Agilent 6890 – ECD
SF ₆	1 per 18 min	GC Agilent 6890 – ECD

Table 1.10Overview of current status of measurements



Figure 1.25 OXK instrumentation including GC in foreground

Flask sampling

A flask sampler was installed at OXK in June 2006 so that isotopic ratios of C (in CO₂) can be measured, but also to provide an ongoing cross-check for the continuous measurements. Flasks are filled in triplets to a pressure of 1.6 - 1.8 bar (absolute). Currently the 1L European standard flasks are being used, however, it is also possible for SIO and NOAA type flasks to be used. At present, all flasks are sampling at a height of 163 m.

Meteorological measurements

Meteorological measurements began in May 2002. Data transmission is made via CAN-BUS and the data are subsequently incorporated with the other measurement data using LabVIEW software. The following meteorological parameters are measured:

- wind speed and direction (163 m)
- pressure (90 m)
- temperature (23, 90 and 163 m)
- humidity (90 m)

obtained precision			
Gas	Method	Operational	Precision
CO ₂	LICOR 6252	Jan-06	0.05 ppm
O2	Oxzilla FC2	Jan-06	6 per meg
CH4	GC-FID	Apr-06	0.4 ppb
СО	GC-FID	_	2 ppb
N ₂ O	GC-ECD		0.3 ppb
SF ₆	GC-ECD	Jan-06	0.2 ppt

Table 1.11	Overview of current status of measurements at Ochsenkopf, measurement
	device, starting date of actual operational use at the tower and the estimated
	obtained precision



Figure 1.26 Schematic of the O2, CO2 and GC continuous measurement systems

1.4.7 LUPG – Norunda tower (NOR)

Station Description

Station Code:	NOR	
Location:	Norunda, Sw	eden
Coordinates:	Latitude	60°05'N
	Longitude	17°28'E
	Altitude	45 ASL
Tower height:	102 m	
Meas. heights:	100, 35 metre	28
Measurements:	Continuous CO_2 , CH_4 ,	
	Continuous n	neteorological parameters



Figure 1.27 Concentration footprint of Norunda tower for 2005

A photo of the Norunda tower is shown in Figure 1.28.



Figure 1.28 Norunda Tall tower

CH₄ concentration and fluxes

The methane measurement system was installed at the end of August 2003 in the Norunda tower. The system comprises a tunable diode laser TGA-100 (Figure 1.29) manufactured by Campbell Inc., USA. The delivery included installation by a team from Campbell and it was performed during 5 days including final testing and functional verification. The laser is cooled by means of a cryo-cooler which means that liquid nitrogen is not needed.



Figure 1.29 The TGA-100 tunable diode laser installment at the Norunda field station

The system was set up initially for sampling of air at three different locations:

- 1. Mean absolute measurement of CH₄ concentration at the 102 m level.
- 2. Fluctuation measurements at the 97 m level with air intake as close as possible at the sonic measurement volume.
- 3. Same as 2) but at the 33 m eddy covariance level.

The latter two measurements will also provide mean values at 97 and 33 m, thus allowing the gradient and the flux to be estimated.

Before the eddy covariance measurement system was installed, the precision and stability of the system was tested. Each measurement cycle comprises 5 minutes with ten 30-second steps each (called measurement 'sites'); these steps are the following:

- 1. Air sampling from intake EC1 dummy to allow pressure to stabilize
- 2. Measurement of concentration from intake EC1
- 3. Measurement of concentration from intake EC2
- 4. 5. Air sampling from absolute measurement site, ACM, dummy during 60 seconds
- 6. Measurement of zero gas concentration
- 7. Measurement of span gas concentration
- 8. Measurement of zero gas concentration
- 9. Measurement of mean absolute concentration ACM
- 10. Measurement of zero gas concentration

The flow rate is high when EC measurements are performed, typically 10 litres per second, while it is much lower during ACM measurements. For fluctuation measurements the absolute value is not critical, error will be independent of offset and dependent on sensitivity. Eddy covariance systems at 33 and 97 m level were installed in June 2005 and data has been collected since then (with interruptions because of technical problems with the TGA-100 cooling system). Sonic anemometers, type USA-1 made by Metek, Germany were installed on new booms at 33

and 97 m. Air flow was adjusted so that the same time delay was obtained from both levels. Because of the technical difficulties of performing time sharing with one tunable diode laser serving two flux levels and at the same time performing absolute concentration measurements we have not been able to use any standard eddy covariance software. The new software has been developed and is working well. The software receives two signals from the methane analyzer; the methane concentration and the solenoid status (Figure 1.30). The solenoid switching and the timing of events is controlled by the TGA-100's own computer and is thus completely independent from the flux computer.



Figure 1.30 An example of a 1-hour sampling scheme for the TGA-100 system. Blue color indicates concentration and red color indicates solenoid status. Based on the solenoid status, the software performs the different tasks: calibration, absolute concentration measurements and flux measurements for the two different levels

The TGA-100 is a delicate instrument and requires continuous maintenance and hands-on attention almost daily. Unfortunately the selection of the laser diode cannot be made on the basis of objective criteria. Methane diodes appear to be particularly sensitive. With an appropriate diode the system can function without any problems for a long period of time. The main problems encountered were a pump failure (manufacturer's error) in December 2003 and contuous problems with the cryo-cooler from mid-summer 2005 until now. The manufacturer's specifications concerning the TGA-100 noise level, ca. 7 ppb, turned out to be correct. A typical illustration of the magnitude of the variations in the ambient methane concentration at 10 Hz above the forest is shown in Figure 1.32. The peak-to-peak variation is typically 50 ppb, i.e, almost an order of magnitude larger than the noise. Although the signal-to-noise ratio should ideally be higher than that obtained here, it is possible to measure fluxes with relatively large variations from time to time.



Figure 1.31 The insulated box for the LI-6262 Analyzer (left) and control unit with solenoids and data logger(right) in the Norunda system



Figure 1.32 The raw signal from the TGA-100 measured at 97 m with a frequency of 10 Hz

The CO_2 concentration in Norunda tower is only measured at the top level, 102 m. The gradients are obtained from the ordinary system comprising 12 levels, of which 8 are above the canopy. The absolute accuracy of the old system is not as high as required in CHIOTTO, but the relative accuracy is good enough for gradient measurements. In the CHIOTTO system, the CO_2 concentration is measured by an infrared gas analyzer, LI-6262 (Li-Cor Inc., Lincoln, Nebraska, USA) contained in a temperature controlled and insulated box (Figure 1.31). Initially we found that the temperature variations were too large, in the order of $\pm 1^{\circ}$ C, and modifications were necessary. By moving the pump outside of the box and by installing a fan inside the box for

better mixing and reduction of temperature gradients, the temperature variations are now down to ca. ± 0.4 °C. With a calibration interval of 4 hours, the precision of half-hourly mean values is estimated to be ca. 0.04 ppm. This value is obtained when pure N₂ and technical air is used as a reference. This precision can be at least doubled when several calibration gases are available and when a reference gas with a concentration close to ambient is used. Temperature variations in the Li-cor and reference gas concentrations are shown in Figure 1.33 and Figure 1.34.

Technical problems were related mainly to two things: bad membranes in the pump and valves not conforming to the specifications regarding pressure sensitivity. The first problem can be solved by having a more frequent schedule for maintenance (membrane replacement) and the latter by installing new valves, which can withstand a higher pressure. LUPG also plans to install a flow regulator in the CO_2 system which would improve both performance and the early discovery of potential problems. Broadband has been installed in Norundato allow remote surveillance of measurements.



Figure 1.33 Temperature variations in the LI-6262 Analyzer during 1 September to 15 October 2004



Figure 1.34 The variation in CO₂ concentration of the reference gas (technical air) during the period 1 September to 15 October with measurements every 4th hour. The last minute during a 5minute measurement period is used for both zero and span gas during the calibration period. The data shown are after correction for pressure and temperature variations. There is also a long term drift that has to be considered for the high precision estimates

si p	recision	operational use al	t the tower and ti
Gas	Method	Operational	Precision
CO ₂	LICOR 6252	2005	0.04 ppm
CH4	TDL TGA-100	Aug-03	7-50 ppb
CH ₄	GC-FID	2006	
СО	GC-FID		
N ₂ O	GC-ECD	2005	
SF ₆	GC-ECD	2005	
CO ₂	LICOR 6252		0.04 ppm

Table 1.12Overview of current status of measurements at Norunda, measurement device,
starting date of actual operational use at the tower and the estimated obtained
precision

1.4.8 Hegyhatsal Tall Tower (HUN)

Station Description			
Station Code:	HUN		
Location:	Hegyhatsal, H	Hungary	
Coordinates:	Latitude	46°57' N	
	Longitude	16°39' E	
	Altitude	248 ASL	
Tower height:	117 m		
Meas. heights:	10, 48, 82, 11	5 metres	
Measurements:	Continuous CO ₂ , CH ₄ , N ₂ O, CO, SF ₆		
	Continuous n	neteorological parameters	



Figure 1.35 Concentration footprint of Hegyhatsal tower for 2005

A photo of the Hegyhatsal tower is shown in Figure 1.36.



Figure 1.36 Hegyhatsal tall tower

Measurement description

Since the beginning of the project CO_2 and meteorological parameters have been continuously measured at the Hegyhátsál tower at four elevation levels from 10 m to 115 m (10 m, 48 m, 82 m, 115 m). During the project only short data gaps occurred due to technical problems, which is surprisingly good, taking into account that there is no local staff at the station, the tower is remotely located and access is restricted. The data availability for the period of 2003-2005 varies between 83.6% and 93.7% depending on the monitoring level. Air samples have also been taken for NOAA's global flask sampling network every week at 96 m above ground level. A gas chromatographic system capable of long term continuous unattended operation was constructed for the quasi-continuous in-situ measurements of the atmospheric concentrations of CH_4 , N_2O , SF_6 and CO. The system was installed at Hegyhátsál tower in January, 2006. Air intake for the GC is mounted on the tower at 96 m elevation above ground level.

Table 1.13	Overview of current status of measurements at Hegyhátsál, measurement device,
	starting date of actual operational use at the tower and the estimated obtained

	precision		
Gas	Method	Operational	Precision
CO ₂	LICOR 6252	Sep-05	0.04 ppm
O2	Oxzilla FC2	Sep-05	8 per meg
CH4	GC-FID	Jan-05	0.7 ppb
CO	GC-FID		0.6 ppb
N ₂ O	GC-ECD		0.3 ppb
SF ₆	GC-ECD	Sep-05	0.03 ppt
CO ₂	LICOR 6252	_	0.04 ppm

1.5 The CHIOTTO measurement database

1.5.1 Introduction

CHIOTTO data series are stored in the central Research Database of MPI-BGC. It supports archiving and retrieving of data. CHIOTTO data are at first accessible to CHIOTTO members and will be published later according to the CARBOEUROPE data policy.

The Research Database allows retrieving and downloading data from one data series or from multiple series resulting in a common time column. Columns that are of no interest can be suppressed and a time range can be chosen across borders of uploaded files. Download is possible in different formats.

The Research Database can archive different data versions and data products. Corrected data sets can be stored while old versions will remain in the database flagged as *replaced* (or *rejected* in case of deletions). This allows referring to database content in publications and avoids broken links between data products and their source data.

Additionally we have begun to document air sampling activities together with analysis results from the CHIOTTO tower in Białystok and will soon start with Ochsenkopf tower.

1.5.2 Finished Activities

- Basic functionality of database system
- Agreement on data file layout
- File Watchdog as client's part of the automated file transfer to the database
- User rights are supported
- Time series can be uploaded, displayed and downloaded
- Time series can be retrieved per towers and projects
- Display and download can be constrained by time range
- Display and Download can merge time series and allows choosing timestamp format
- Server is behind the firewall
- Undoing file upload is possible

1.5.3 Current activities

Because of higher priorities for other than CHIOTTO issues concerning the database system and much longer implementation time than estimated for versioning of time series data, no substantial changes of the database system have been achieved concerning CHIOTTO data within the last 12 months. However, upload of new versions replacing old ones in the database have become possible recently. The metadata topic still has to be addressed. Data series structures and data will be completed as soon as new ones are provided.

Database Overview

The database design is very general in order to allow storing diverse item classes like projects, sites, samples, methods and measured and derived values in the same set of tables. The schematics of the database are shown in Figure 1.37, Figure 1.38, Figure 1.39 and Figure 1.40.



Figure 1.37 Basic Database Design

An item like a site is linked to other items like its name, coordinates, drawn samples and measured values. Items can be objects (e.g. sites and samples), values (e.g. coordinates and names) and actions (e.g. projects and measurements).



Figure 1.38 Sample Data Structure

Distinct item classes and predefined vocabulary (e.g. names of methods and variables) instead of free text are a precondition for convenient data retrieval, flexible presentation of data and compatibility to metadata standards. Flexibility without reprogramming can nevertheless be achieved through a definition level that describes all classes of items and their links which can be used in the data level.

New types of descriptions and variables are simply entered in the definition level and can be used instantly as all form windows adapt themselves to item definitions. Form windows for the definition level will allow scientists rather than computer specialists to introduce such changes.

Communication between clients and application server is done per HTTPS to enforce encryption of passwords and of transferred data.



Figure 1.39 System Architecture



Figure 1.40 Automated File Transfer to the Database

The client can be any computer on which an Internet browser can be used. While special features are usable only if Java Script is enabled, all basic functions like data retrieval and input works with pure HTML.

The client's browser communicates with our application server that runs IBM WebSphere. We use Java Servlets and Java Server Pages to produce HTML pages dynamically from database content according to your requests and to process your data input.

The database system IBM DB2 runs on the same server. A firewall protects it against hacker attacks and lets through only HTTPS requests that come in via a proxy server.

The automated file transfer bridges the gap between the database that resides on a server behind the firewall in MPI-BGC Jena and the file system in another institute.

On a computer of the institute the File Watchdog is installed and looks into an upload directory and if it finds a file, it sends its content per HTTPS to the application server. There it is uploaded to the database. The file is moved from the upload directory to an archive directory within the institute.

The upload procedure can handle different file layouts that conform to rules on file names, version numbers, uniformity of data rows below file headers, usage of measurement timestamps and basic quality flags. Within these rules the upload procedure is flexible regarding the number of header rows, position and format of version numbers, order and number of data columns and date and time formats.

2. Measurement results

2.1 ANGUS Tall Tower (TTA) results

Figure 2.1 below show typical concentrations of the main CHIOTTO gases and ²²²Radon from the Tall Tower Angus for the first six months of the full operational status of the tower.



Figure 2.1Typical concentration patterns of greenhouse gases and 222 Rn measured at Tall
Tower Angus

Breaks in the data set are usually associated with a failure in the cryo-cooler; this was rectified in early March 2006. Precision and accuracy levels for this data are at the level described in WP3. We have performed a trajectory analysis for the past 3 years for air arriving at Angus and this shows just how infrequently air passes over mainland Europe before reaching Angus. By far the majority of trajectories show air coming from the south-west, west and north-west to Angus. We are about to use the Angus data in conjunction with the UK Met. Office model NAME to explore the source-concentration relationships. Currently, the CO and H₂ measurements are reported as 'peak area' from the gas chromatograph since we have only recently been able to obtain scale gases with calibrated concentrations of H₂ and CO from our suppliers. We have kept previously used target tanks at the site so we will be able to back-calculate the actual concentrations of H₂ and CO since our records began. The radon monitor continues to operate almost without user intervention and we are nearing two complete years worth of data for this instrument.

2.2 BIALYSTOK (BIK) Results

2.2.1 Repeatability

For estimating the repeatability, we use the standard deviation of the target measurement results; the 'target' is a constant gas from a high pressure cylinder measured every few hours. The following table shows the typical repeatability we achieved so far, having the data only partly quality checked; after the final check a slight improvement is probable.

Species	Long term	Short term	
	1 stdev	1 stdev	
CO_2	0.1 ppm	0.025 ppm	
O_2/N_2	14 permeg	3 permeg	
CH_4	0.83 ppb	0.63 ppb	
CO	0.42 ppb	0.33 ppb	
N_2O	0.26 ppb	0.14 ppb	
SF_6	0.07 ppt	0.04 ppt	

 Table 2.1
 Typical repeatability

The 'long term' column shows the standard deviation of the target measurement, calculated for the whole period August 2005 to May 2006 (for CH_4 , CO, N_2O and SF_6 the target measurement was used starting from November 2005, see Figure 2.2 for CO).

For 'short term' the typical standard deviation of the target measurement for the time between two calibrations of the instruments was considered, which was about 40 hours for CO_2 and O_2/N_2 and 120 hours for the other species.

For a 15 min time interval, the average standard deviation for O_2/N_2 is about 3 permeg, and for CO_2 smaller than 0.01 ppm.



Figure 2.2 Example of target measurement result

2.2.2 Data overview

The data series we have so far covers the time between the end of July 2005 and May 2006. There are some gaps, caused mainly by power instability and computer problems.

The CO_2 concentration series from the start of the measurement until the end of 2005 is shown in Figure 2.3; the data from 2006 are not included as they have not yet been quality controlled.

Part of the seasonal cycle can already be observed, but a longer data series is necessary for a complete picture.



Figure 2.3 CO₂ concentration from the end of July 2005 to January 2006. Different colors represent the different sampling heights above ground, between 5m and 300m

As expected, for the summer data, a strong day-night cycle dominates the variability, while in the winter time the synoptic signal is stronger. The diurnal variation is much stronger at the levels closer to the ground, due to the proximity of the land biosphere exchange.

The mean diurnal cycle for the CO_2 data between July and October is shown in Figure 2.4. Hourly averages were calculated from the data. The variation is influenced by the land biosphere – atmosphere gas exchange and by vertical transport. Vertical mixing becomes efficient after midday; between 6 p.m. and 6 a.m. vertical mixing is poor and the CO_2 released from land biosphere respiration accumulates at the lower levels. In the morning the CO_2 accumulated near ground starts to be transported vertical, and at the same time the land biosphere photosynthesis starts taking up CO_2 . The result is a fast CO_2 concentration decrease near ground and a delayed concentration peak at higher levels.



Figure 2.4 CO₂ mean diurnal variation for different heights above ground, in the time interval July to October 2005. The x-axis represents the hour; the first 16 hours are repeated (as hours 24-40) for visual reasons



Figure 2.5 *CH*₄ mean vertical gradient for summertime (1 August to 8 September 2005), calculated as the difference between the concentration at 5m and at 300m above ground level

The additional measurement of the O_2/N_2 ratio helps to distinguish between different CO_2 sources. For each mol of CO_2 produced (or removed), a certain quantity of oxygen is used (or released). The variation of oxygen for one mol CO_2 is source specific. For example, for the

exchange between land biosphere and atmosphere the average oxygen to CO_2 molar ratio is considered to be 1.1, while for fossil fuel combustion it is 1.4.

Our measurements show the expected anti-correlation between CO₂ and the O₂/N₂ ratio for the day – night signal as well as for synoptic and seasonal variations (Figure 2.6). This relation can be expressed by the APO, defined as: APO(permeg) = O_2/N_2 (permeg)+4.8 * 1.1 * (CO₂(ppm)-350).



Figure 2.6 CO_2 , O_2/N_2 and APO at 300m above ground level. APO is by definition insensitive to land biosphere – atmosphere exchange

The data series for CO_2 , CH_4 , CO, N_2O and SF_6 for Aug-Dec 2005 is shown in the following Figure 2.7. Some similar features can be observed for different species, more obvious in winter. The correlation between different species contains information about the air mass origin and emission sources. For example, the main CO sources are anthropogenic; on this basis, the good correlation between CO_2 and CO synoptic signal is evidence for anthropogenic CO_2 sources.



Figure 2.7 CO_2 , CH_4 , CO, N_2O and SF_6 at 300m above ground level, from the start of measurements until the end of 2005. The y-axis represents the concentration

2.2.3 Comparison with other measurements

The comparison with other measurements is an important means for validation, especially for a new measurement station. Figure 2.8 shows a comparison for CO_2 and O_2/N_2 , between the continuous measurement results and flask samples taken at the same location. The flask samples were taken from 300 m height using separated inlets and gas paths, and measured in Jena at the MPI-BGC laboratories.

2.3 OCHSENKOPF (OXK) Results

2.3.1 Seasonality

During the winter months (November 2005 to February 2006) very little variability is seen in O_2 and CO_2 and no diurnal cycle (Figure 2.9). The observed variability can be attributed to anthropogenic sinks and sources of O_2 and CO_2 . In summer, the daily variation is much greater due to the diurnal dependence on photosynthesis and respiration (see below).

2.3.2 Diurnal variation

In the summer-time data (May to June 2006), a diurnal variation is seen in O_2 and CO_2 for all 3 heights, but is shown here only for the 23 m sampling height (Figure 2.10). O_2 and CO_2 are negatively correlated with an average correlation coefficient of -1.1 owing to O_2 production and CO_2 uptake by photosynthesis and vice-versa for respiration. The O_2 maximum occurs at

approximately 16:45 coinciding with the CO_2 minimum, but the O_2 minimum occurs later (at 7:10) than the CO_2 maximum (at 06:00). The amplitude varies from day to day in May and June, most likely due to variations in wind speed and light intensity, which affect the atmospheric mixing and photosynthetic activity, respectively.



Figure 2.8 Comparison between BIK continuous measurements and flasks results for O_2/N_2 (upper panel) and CO2 (lower panel), showing good agreement between the two measurement types

2.4 HEGYHATSAL (HUN) results

The long term trend measured at the Hungarian tall tower site (Hegyhátsál) correlates well with the global one (Figure 2.11). The 3-4 ppm surplus compared to the marine boundary layer reference mixing ratio is probably caused by the net contribution of the European anthropogenic sources. The fluctuation in the growth rate correlates well with the Southern Oscillation Index with a lag-time of 9 months.



Figure 2.9 Seasonal variability at 23 m (cyan), 90 m (blue) and 163 m (magenta) for O_2/N_2 (upper panel) and for CO_2 (lower panel)



Figure 2.10 Monthly average diurnal cycles for December 2005 to June 2006 for the 23 m level, Left is O_2/N_2 , right is CO_2 diurnal pattern for the five months.



Figure 2.11 Temporal variation of the early afternoon (12-16 h LST) atmospheric CO₂ mixing ratio compiled from the data series measured at two Hungarian sites, K-puszta (KPU, 46°58'N, 19°33'E, 125 m, 1981-1999) and Hegyhátsál (HHS, 46°57'N, 16°39'E, 248 m, 1994-2005). The black line indicates the marine boundary layer reference mixing ratio (GLOBALVIEW-CO2, 2005)

The linear trend at Hegyhátsál from 1994 to 2004 was 1.85 ppm/year. However, it masks the significant seasonal differences. While the spring (March-May) trend was only 1.53 ppm/yr, the summer (June-August) trend was much higher, 2.17 ppm/yr. During the same period the amplitude of the annual cycle decreased from 36.5 ppm to 28.7 ppm. The shape of the annual cycle also changed: the length of the summer CO_2 deficit period (relative to the annual average) slightly increased. It started earlier while its ending time remained unchanged (Figure 2.12). These changes are explained by the increasing length of the growing season and its earlier onset. This explanation is also supported by the 'regional scale' direct surface-atmosphere CO₂ flux measurements. These measurements also indicate a significant decrease in the summer net biospheric CO_2 uptake which explains the decreasing annual amplitude and the higher than average mixing ratio increase in the summer months. The cause of the decreasing summer net biospheric uptake must be the climate anomaly experienced between the late 90s and 2003. The climate of the region of the measurements, especially in the summer season, became gradually warmer and drier. The region became a significant net CO₂ source during the extremely hot and dry 2003. After 2003 cooler and wetter years came and the net ecosystem exchange (NEE) of the region returned to negative (Figure 2.13).



Figure 2.12 Changes in the length and start date of the CO_2 deficit season at Hegyhátsál. CO_2 deficit and surplus seasons are defined relative to the annual average



Figure 2.13 The net CO₂ exchange of the region of the Hegyhátsál tall tower site, as well as the average temperature and precipitation amount in the growing season measured at a nearby meteorological observatory (Szentgotthárd-Farkasfa, 46°55'N, 16°19'E, 312 m asl)

It has already been discussed for years that global warming may turn the biosphere from a net CO_2 sink to a net source, constituting a significant positive feedback to the warming. Having one of the longest regional scale NEE measurements and a prolonged climate anomaly the Hungarian measurements provide the experimental evidence under natural conditions that the expected drier and warmer future climate may turn the biosphere into a significant net CO_2 source indeed.

Based on the HYSPLIT model a concentration footprint calculation and visualization software has been developed to determine the region of influence of the measured signal and to scrutinize the influence of the different atmospheric circulation patterns. For this purpose we adopted the method of Gloor et al. (2001). It has been found that changes in the location and size of the concentration footprint is generally associated with synoptic events. In case of frontal overpasses free tropospheric air can be transported downwards to the surface, or air masses with different history may replace the air mass over the site. Under such conditions the mixing ratio of CO_2 changes abruptly which can be clearly detected by the measurements (Figure 2.14).



Figure 2.14 On 14 December, 2003, a pseudo-cold front passed over the tower. After the front the footprint ascended by more than 1400 m, and its distance from the tower increased by 250 km

2.5 NORUNDA (NOR) results

2.5.1 Methane

Observations of methane exchange in forest soil shows that, depending on conditions, soil can both emit and consume methane (e.g., Fiedler et al., 2005). Well aerated soils are normally considered to be sinks of methane (Kähkönen et al., 2002; Crill 1991) and soil moisture and nitrogen fertilization seem to be the factors that affect the methane consumption the most (Steudler et al., 1989). Keppler et al. (2006) reported emission of methane from leaves and litter, a hitherto not so well known phenomenon, and the estimated magnitude, 62-236 Tg yr⁻¹ for plants and 1-7 Tg yr⁻¹ for litter could have a highly significant impact on the global budget.

Keppler et al. concluded that the methane was produced by abiotic processes and that possibly lignin and pectin were involved. Recently Crutzen et al. (2006) reanalyzed old boundary layer data from mixed tropical savanna and forest vegetation in Venezuela that indicated nocturnal boundary layer accumulations at rates similar to those found by Keppler et al. (2006).

The first results from the EC measurements showed that there was emission from the forest not only in the summer but also in autumn and winter. Typical mean daily emission rates were in the order of 0.05 mg CH_4 m⁻² h⁻¹ with a range from zero to ca 0.4 mg CH_4 m⁻² h⁻¹ (Figure 2.15) with similar magnitude at both levels (Figure 2.16). For comparison with Keppler et al. we scaled these values against the foliage mass and received typical values of 50 ng CH_4 g⁻¹ D.M. h⁻¹ with a range 0-400 ng CH_4 g⁻¹ D.M. h⁻¹ which is in the same order as the values reported by Keppler et al. for intact leaves. The high emission rates in autumn are in contradiction with the results obtained by Keppler et al. who showed that the emissions increase with temperature. However, we must keep in mind that the EC fluxes represent the whole ecosystem, i.e., foliage, litter and soil. It is possible that the soil emissions might increase when the ground water table is high, which it normally is in the autumns and winter. It is thus necessary to study the exchange of the different compartments in order to understand the results obtained here.



Figure 2.15 Daily mean net methane fluxes from the Norunda forest from 33 m (top) and 97 m (bottom)



Figure 2.16 The methane flux at 33 m plotted against the flux at 97 m

We also found a diurnal variation in the fluxes during summer with highest values around noon indicating that solar radiation was affecting the emissions (Figure 2.16). Turbulent fluxes are inherently variable and therefore the variations in the mean diurnal cycle for the 14-day period in June is also quite large.



Figure 2.17 The mean diurnal course of the methane fluxes from the Norunda forest during a 14-day period in June 2005. Units are mg $CH_4 m^{-2} s^{-1}$

The gradient measurements (concentration difference between 35 and 97 m) in 2004 gave some puzzling results showing both negative and positive gradients. We expected to find only negative gradients, i.e., fluxes from the atmosphere to the stand (because forests with well aerated soils are 'known' to be sinks for methane) and we therefore made a few measurements with chambers on both litter and foliage in order to try to understand the behavior of the system. Surprisingly, all chamber measurements clearly showed emission of methane supporting the results shown above (spruce and pine emitted ca 20 ng CH₄ g⁻¹ D.M. h⁻¹).

Apparently there are occasions with methane being emitted from the surface into the atmosphere (Figure 2.18, lower panel). There are several periods with emission, the gradient reaching up to 20 ppb. Plotting the gradient against wind direction reveals that these emissions occur at several different wind directions (Figure 2.19). As can be seen on the map (Figure 2.20), there are several wetland areas in almost all directions around the Norunda tower. They are within a couple of kilometers and it is most likely these who contribute to the emissions. There is no CH_4 uptake detected at this time of year (September 2003, Figure 2.18 lower panel).



Figure 2.18 The variation of methane concentration during 4-12 September 2003 at the 102 m level in the Norunda tower (top) and the concentration difference between the 97 m and 33 m levels (bottom). Negative values indicate a flux into the atmosphere. Units are in ppm

RESUL_C 20030904-20030912 Independent variable : dir11 (dir5)



Figure 2.19 *The mean methane concentration gradient (difference) plotted against wind direction*



Figure 2.20 Map of the surroundings of the Norunda tower (marked with green dot). The green areas are forests while the pink are wetlands

The ambient CH_4 concentration at the 102 m level shows a weak seasonal variation with minimum in spring and maximum in autumn (Figure 2.17). The decreasing trend in CH_4 concentration shown is not confirmed since we do not yet know the accurate concentration of the span gas.



Figure 2.21 The CH4 concentration variation over time at the102 m level in the Norunda tower. The bars at the bottom of the figure indicate occasions when the span gas was replaced

2.5.2 CO₂

The long-term measurements of the CO_2 concentration and gradient at the 102 m level of the Norunda tower started in 1995. These measurements were not aimed at obtaining the very high precision and accuracy as laid out in CHIOTTO, and therefore the accuracy is not high enough for the data to be used in inverse modeling. It gives however a good picture of the trends and seasonal variation in this region of Europe. The amplitude winter-summer is in the range of 20 ppm showing the strong impact of the vegetation in this forested region (Figure 2.22). We also notice an increasing trend in concentration until 2001, that is more clearly seen in a plot of only the mean concentration in December each year (Figure 2.23). December is probably the month which is the least influenced by the activity of the vegetation, but on the other hand, it is more affected by anthropogenic emissions since it is a cold moth which requires heating of houses.





Figure 2.23 The mean monthy CO₂ concentration in December each year during the period 1995-2005 in the Norunda tower at 102 m level

2.6 CABAUW (CBW) results

The measurements by ECN at Cabauw for CO_2 and CH_4 have been performed since 1992. In Figure 2.25 the CO_2 concentrations are shown for the period of 2000-2006. In the period from 1992-2004 the observation have been performed using a Siemens Ultramat 5 NDIR with a resolution of 0.5 ppm. Calibration was daily using a single working standard calibrated against NOAA CMDL secondary standards and Nitrogen gas (5.0) as zero. Regular monthly calibrations were performed directly against NOAA CMDL secondary standards. In the year 2003 and 2004 the Siemens NDIR system was having large problems including a total collapse in the summer of 2003.

Starting November 2004 the system was replaced by the CHIOTTO setup and the CO_2 measurements are since then performed using the Licor 7000 NDIR with considerably increased accuracy, half-hourly target gas measurements and daily 4 point calibrations against the CHIOTTO working standards.

As an illustration a small data set covering 6 days in June 2006 is shown in Figure 2.24. For each of the displayed components large vertical gradients occur during night time, when the atmospheric stability is high and the mixing layer height at Cabauw is very low. During most of these nights with stable conditions the boundary layer height is lower than 200 meter, so that the 200m inlet or even some of the lower inlets sample air from residual layers above the boundary layer during the night. There are also nights however, like the night of June 10 in Figure 2.24, where also the highest sampling levels are affected by the night time accumulation.

An interesting feature of these vertical gradient measurements is that in the early morning, when the stable layer is broken down by the increased turbulence due to incoming solar radiation and associated latent and sensible heat fluxes, the polluted air is being mixed in with the overlying residual layers. This process can be seen witnessed at the 200 and or 120 meter level when the measurements at these inlets display a sudden rise at the moment that the polluted air from the boundary layer reaches the respective level.

Furthermore Figure 2.24 illustrates the large correlation of the diurnal concentration pattern for CH_4 and CO_2 . Allthough both components have very different sources and sinks with different temporal and spatial distribution their concentration change in time is very similar. This is because the main determinant factor is the dilution factor which depends on the meteorology (wind speed, mixing layer height and atmospheric stability).



Figure 2.24 *Cabauw tall tower measurements of CO*₂, *CH*₄ and ²²²*Rn during 6 days in June* 2006

The night time concentrations in stable conditions always show a rise of concentration for both CO_2 and CH_4 , because at night the assimilation by plants is not active and instead CO_2 is respired by plants and soil. This emission signal (which is even more enhanced by antropogic emissions) is strongly amplified by the atmospheric conditions during night time. The strong uptake of CO_2 by the biosphere during daytime is strongly weakened in the atmospheric concentration signal due to the higher boundary layer levels and generally higher windspeeds and turbulence.

Underlying the hourly pattern is a synoptic concentration pattern that is related to the origin of the air mass sampled in the station. In the period displayed in Figure 2.24 the day time concentration levels of CH_4 and CO_2 go down by about 50 ppb and 10 ppm respectively in the period from June 9 to June 12. In winter time these synoptical changes determine for a large part the pattern of concentration with time, in summer time the influence of the more local fluxes is more dominant.

From the ²²²Rn time series in Figure 2.24 we can determine that the air mass arriving at June 12-14 is more continental than that arriving at June 9, as the ²²²Rn levels during daytime are much higher at June 12-14. Maximum ²²²Rn levels are reached at Jun 14, when also day time CH₄ concentrations peak due to the continental emissions and CO₂ concentrations are low due to the continental uptake by the biosphere.

As can be seen from Figure 2.25 the atmospheric annual growth rate of the CO2 concentration detected is very close to the NOAA ESRL estimate derived from the global network. The observed seasonal amplitude of the concentration signal of around 30 ppm is quite representative for 50 degrees N latitude. Also clear is that the measured data forms an nice continuous series throughout the period with no noticeable offset between the two used systems before and after mid 2004.



Figure 2.25 Continuous measurements of the CO₂ hourly concentration at Cabauw 200m AGL from 2000 to 2006 using the Siemens Ultramat NDIR (till 2004) and the CHIOTTO setup with the LICOR NDIR.

As can be seen from Figure 2.25 the local 'noise' in the concentrations due to the effect of more local emissions is larger than for other sites. This local signal is even larger at the lower measurements levels, where nighttime accumulation can lead to concentration levels around 500 ppm at the 20m AGL inlet. The 200m AGL inlet is often above the nighttime inversion (>50% of the time) and in these circumstances the groundlevel emissions are not 'seen' there.



Figure 2.26 *CO*₂ diurnal profile (ppm) for Cabauw for Winter (Upper left), Spring (Upper right), Summer (Lower left) and Autumn (Lower right).



Figure 2.27 *CH*₄ diurnal profile (ppm) for Cabauw for Winter (Upper left), Spring (Upper right), Summer (Lower left) and Autumn (Lower right).

In Figure 2.26 the diurnal concentration pattern for Cabauw is shown for all four measurements heights (years 2000-2005). Obvious are the higher concentrations in winter when emissions are high and biospheric uptake is low. Also mixed layer heights are lower leading to lower dilution in the boundary layer. The lowest concentrations are observed in summer, when biospheric uptake is largest and fossil emissions relatively low. Biospheric uptake is also visible in the lower concentrations at 20m level than at the higher levels during the middle of the day. This minimum concentration is reached at 15 UTC, which is 17 hour local summer time. The average vertical profile in summer conditions at 15 UTC is still 3 ppm. This points to a serious possible negative artefact of day time near-surface observations of CO_2 in places/conditions where the surface has an active biosphere, in the sense that the observed concentration is not representative of the large scale concentration in the mixed layer but determined very locally. Tall tower vertical gradient data will allow to produce a good estimate of the mixed layer mean concentrations.

A striking feature is the lower concentrations at 200 meter compared to the other levels during day time in winter. This is due to conditions in winter with very stable conditions, in which the mixed layer height also during day time is lower than 200 meter. This usually is connected with very cold (blocking) high pressure conditions, with easterly winds.

In Figure 2.27 the diurnal patterns are shown for CH_4 . The pattern is largely the same for CH_4 as for CO_2 for all seasons. As there is hardly any uptake compared to the emission fluxes the inverse vertical gradient during day time in the growing season does not appear for CH_4 like for CO_2 . Another difference is the relatively low concentration in winter compared to the summer, for CO_2 these winter concentrations are much larger then in the other seasons. This is because the emissions of CO_2 are relatively large in winter time, while those of CH_4 are even lower when they are originating from microbial activity that is lower at lower temperatures.
3. High precision measurement system results

3.1 Operational system for preparing the working standards

In order for any analyzer at a tower to achieve high precision measurements, analysis of several different calibration standard gases is necessary. These standard gases should cover the full range of atmospheric mixing ratios that can be expected at the respective tower site, taking into consideration all expected diurnal, seasonal, and inter-annual variability. They should have accurately determined concentration assignments using primary standard gases that provide the link to internationally accepted calibration scales. These demands outline the requirements for an operational system for preparation of such calibration gases that has been set up at MPI-BGC. The whole process of preparing standard gases requires the preparation of high-pressure cylinders, a pumping unit to fill the cylinders with dried air, a 'spiking' system to ratios artificially adjust the mixing, and trace gas analytical measurement facilities. Such a complete system for preparing reference standards was completed at MPI-BGC institute in 2004, and is described below.

3.1.1 Compressor

In 2003 MPI-BGC installed a high pressure air pumping facility at the institute that can fill empty high pressure cylinders with 150 bar of dry air (Figure 3.1).



Figure 3.1 Rix compressor facility and multitrap system

The facility consists of an oil-free compressor (Rix Sweet Air 6A 5-L), a drying system to reach a dewpoint of at least -60 °C and a multi-trap system to selectively reduce most of the relevant gas species to below ambient concentration.

The incoming air is dried using a triple cartridge of magnesium perchlorate. This replaced the initially used molecular sieve 13X as drying agent, since this caused significant modifications of the CO_2 and N_2O mixing ratios of the air (initially depletion, later addition), creating additional work for spiking. The multi-trap system comprises a set of cartridges filled with different sorbents or catalysts. Each single cartridge can optionally be put in line in order to deplete one or several species from atmospheric air, thus producing air mixtures with sub-ambient mixing ratios of these compounds. Reduction of compounds is being done for CO_2 and N_2O (molecular sieve 13X), CH_4 (Hopcalite), CO (Sofnocat 514). Reducing SF_6 to sub-ambient conditions

turned out to be particularly difficult, due to the physical properties of this gas. Experiments to take out SF₆ were made with a cooling fluid system around one cartridge containing activated charcoal (-20°C). The efficiency of this approach was limited by the heat transfer and turned out to be insufficient at the required flow rates for filling the cylinders. This made the admixture of small portions of synthetic air necessary for the preparation of standard gases with sub-ambient concentrations of SF₆. An additional difficulty arose from the existence of a ¹⁴C accelerator mass spectrometer (AMS) in our institute which uses SF₆ as an electrical insulator. The air intake line of the pumping system was initially placed on the institute's top roof in the Northern corner of the institute. This location turned out to be influenced by the exhaust gases from the AMS laboratory that are highly contaminated with SF₆. As a consequence the whole pumping facility had to be moved to the South Western corner of the institute building. To exclude interference from the AMS vent gases cylinder filling was carried out using wind direction information from the institute's meteorological station.

3.1.2 Spiking system

The 'spiking apparatus' set up at MPI is shown in Figure 3.2. It allows us to spike additional amounts of any gas species we wish to measure into previously filled cylinders. This way the mixing ratio ranges for each individual species can be created independently.



Figure 3.2 Spiking system

A reference gas with predefined mixing ratios is produced as follows: After filling the cylinder with outside air a first analysis is made. The remaining amount of any compound that is needed to meet the target concentration is calculated. To add these amounts of gas a precisely calibrated volume is filled to the pressure needed with the respective pure gases or a defined pre-mixture. These amounts of gas are then transferred with small amounts of compressed air. After allowance is made for good mixing within the cylinder, it is then re-analyzed in the laboratory for its trace gas composition, O_2/N_2 -ratios and dew point.

3.1.3 Primary calibration scales

According to WMO recommendations each atmospheric measurement station should maintain a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases to working standards, and from working standards to atmospheric measurements. To achieve this traceability the WSS standard gases of all CHIOTTO stations have assigned concentration values by MPI-BGC. At MPI we have primary secondary standards (PSS) in our lab that were purchased directly from the WMO-Central Calibration Laboratory (CCL) (NOAA/CMDL, in

the case of CO_2 and CH_4) and that have been recalibrated by the WMO-CCL recently. This direct link has enabled us to propagate retroactive changes in the assigned values of higher level reference gases by the WMO-CCL that had been announced in 2005 for CO_2 and CH_4 all the way to measured values for atmospheric air.

3.2 Operational system for calibration of all the tall tower measurements

A written document detailing the calibration protocol to be followed at each tower has been written and provided to the participants. The philosophy of this protocol involves different steps using different levels of standard gases:

- defining the analyser response by daily calibration of the signal using four working secondary standards (WSS)
- checking the WSS calibration for drifts in these standards using three long term secondary standards (LSS) and adjusting their assignments accordingly in order to safeguard the long term consistency over many years
- monitoring the performance of the above calibration protocols at each tower ('Target' standards)
- checking the tower measurement results by intercomparison with other CHIOTTO towers and the MPI-BGC using two sets of each three traveling secondary standards (TSS).

The realization of this philosophy was retarded by long delays in the times of delivery for several components needed for the operational system. Major problems encountered along the way to produce standard gases included the compressor manufacturer (Rix), the cylinder company (Luxfer) and the valves supplier (Rotarex). E.g., delivery of the high pressure cylinders for storing long term calibration gases for the CHIOTTO project took 6 months longer than expected. In addition, visual inspection of the purchased Luxfer aluminum cylinders revealed some spots on the internal surface on some of the cylinders. It was refused by the company that this implied a production mistake. However, evidence has been published that inappropriate surface cleaning may cause instabilities of the CO₂ mixing ratio of standard gases in high pressure cylinders. Attempts to clean the cylinder were made with Air Liquide (Krefeld). This procedure did not produce satisfactory results. Therefore, some suspicion still remained that drifts in the CO_2 mixing ratio of standards in these specific cylinders might occur with time. This would make them unsuitable for long term storage of calibration standards. As the operation of the analytical systems of the CHIOTTO tower stations depends on the availability of WSS, the production of these reference gases was given first priority and their preparation started in 2004. Only cylinders that proved to have a proper internal surface were used for this purpose. They have been provided for all tower sites. The fact that all towers took longer than expected to install their analytical infrastructure meant that no tower was prevented from beginning their measurements because of waiting for their WSS's from MPI-BGC.

The LSS's are projected to last for up to 20 years before being depleted. Each time that LSS's are analyzed, the WSS calibration scale should be reassessed and potentially adjusted. For this reason any potential CO_2 storage drift in the LSS is even more crucial. Before beginning the preparation of these standard gases a thorough investigation of the properties of cylinders with the questionable surface was made. In order to exclude CO_2 drifts of 0.2 ppm over 10 years a drift rate of 0.02 ppm/year needs to be detectable. Such an extremely small trend can only be detected with an extremely precise instrument, such as a 'LOFLO' CO_2 analyzer which we have at MPI-BGC. The CO_2 stability of a gas in one of the suspect cylinders was monitored over a few months with this instrument. As can be seen in Figure 3.3 there is no apparent drift in CO_2 within the test period with a standard deviation of the daily mean results of < 0.003 ppm. This provides good evidence that the cylinders are appropriate for usage for long term reference standards. However, the additional time of testing did not leave enough time for the production

of all CHIOTTO LSS standards within the time of the project. This will be completed by MPI-BGC within the next few months.



Figure 3.3 *CO*₂ mixing ratios of dried standard air in Cylinder D420469 monitored with a LOFLO CO₂ analyzer

3.3 Report on the data quality and data inter-comparability

In order to merge the observational data of different towers good intercomparison is a crucial pre-requisite. Although all towers are linked to common calibration scales differences in the instrumental setups at the individual towers may cause offsets for real air analysis which must not be interpreted as bio-geochemical signals.

To check the inter-comparability of all towers an additional set of six Luxfer high pressure cylinders called Traveling Secondary Standards (TSS's) were prepared in 2005 with a range of concentrations for each component. These six cylinders rotate in two sets of three between the towers. Their purpose is to identify, quantify and monitor over time any deviations in the analysis results of the different tower systems. This should provide diagnostic information on calibration scale differences or other causes for measurement discrepancies. As a result an estimate of the accuracy of the measurement results is obtained. In addition, they shall ensure that the working standards at each tower do not drift in concentration over time.

The TSS cylinders have made a first rotation. The intercomparison results of TSS analysis data that have been submitted are summarized in Table 3.1 and Figure 3.4 to Figure 3.7. They are presented as the difference of the results from the individual laboratories compared to the results determined at MPI. This allows us to directly compare all differences between the other laboratories. In Table 3.1 this inter-laboratory agreement is also compared to the CHIOTTO target accuracy as specified previously.

The results for the individual compounds are:

• CO₂: The mean CO₂ mixing ratio differences between the towers range from 0.00 to 0.36 ppm. Most towers that supplied data are within the limits of the targeted scale accuracy.

However, for two towers a significant calibration offset is apparent. The cause for this offset needs to be identified in order to reach the targeted accuracy goal.

- CH₄: In the case of CH₄ the situation looks much better, with mean CH₄ mixing ratio differences between the towers of between 0.1 and 2.4 ppb. All participants are meeting the target accuracy of 3.0 ppb and most of them even comply to within 2 ppb.
- CO: Only two towers were equipped to analyze CO and gave mean CO mixing ratio differences of 1.1 ppb and 12 ppb. Comparing with a target accuracy of 3 ppb this documents good performance at one tower and a severe problem at the other.
- N₂O: The mean N₂O mixing ratio differences between the towers range from 0.06 to 0.59 ppb. Except for the excellent agreement between one tower station and MPI-BGC the CHIOTTO target has not yet been met in the group. Moreover, two additional towers appeared to have a noticeable but very consistent offset (std. dev. 0.04 and 0.14 ppb).
- SF₆: Mean SF₆ mixing ratio differences between the towers range between 0.01 and 0.09 ppt. This means that all tower participants agree to better than half of the initially set accuracy target for SF₆.

In summary, these preliminary results document that the CHIOTTO intra-tower accuracy goals are already met for many species within the first rotation, although we do not have all results from all towers. At the same time, they underline the necessity of the intercomparison project. Whereas in some cases a bad reproducibility already gives indication for a bad functioning of an instrument, there are other cases where the instrumental precision suggests a very good performance although the accuracy limits are not met.

At the time of TSS analysis some GC's were struggling with poor ECD performance due to instrument problems, which was limiting their N_2O precision noticeably. Given the experience in other intercomparison activities (TACOS) these first results are likely to converge with ongoing rotations.

It will need further rotations to draw conclusions on the stability of the intercomparability of the tower stations that will be performed within the CarboEurope IP WP 2.5.

	MPI-BGC						
Gas species	Interlab. scale accuracy	BIK	CBW	HEG	FIR	ORL	TTA
$\overline{\text{CO}_2}$	0.1 ppm	-0.12 ± 0.06	$\textbf{-0.36} \pm 0.12$	0.03 ± 0.08	-0.35 ± 0.70	0.00 ± 0.03	
CH_4	3.0 ppb	$\textbf{-0.9}\pm0.8$	-2.4 ± 1.0	0.8 ± 2.3		-1.1 ± 0.6	0.1 ± 0.3
CO	3.0 ppb	-1.1 ± 2.1		-11.7 ± 6.6			
N_2O	0.2 ppb	0.28 ± 0.04	0.59 ± 0.41	0.30 ± 0.76		-0.50 ± 0.14	-0.06 ± 0.08
SF_6	0.2 ppt	0.01 ± 0.02	-0.09 ± 0.03	0.02 ± 0.15		0.02 ± 0.00	0.02 ± 0.02
O_2/N_2	10 per meg						

Table 3.1Summary of mean TSS analysis deviations between CHIOTTO tower stations and
MPI-BGC



Figure 3.4 TSS Intercomparison results for CO2



Figure 3.5 TSS Intercomparison results for CH4



Figure 3.6 TSS Intercomparison results for N2O



Figure 3.7 TSS Intercomparison results for SF6

4. Using the potential of Tall Tower observations: Lagrangian Modeling

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4.1 Introduction

While there have been extensive intercomparisons of global coarse-resolution transport models on monthly and annual time-scales [Law et al., 1996; Bousquet et al., 1996; Gurney et al., 2002], little attention has so far been paid to model differences on synoptic to diurnal scales above the continent. Partly because coarse-resolution transport models are not able to resolve the short-term variability, but also because matching observation data are usually not available.

Usually the misrepresentation of sub-grid scale variability by the relatively coarse models is assumed to cause a random representation error in the inversion routines. This error is then added to the (usually also assumed random) measurement error. However, the representation error will usually cause biases (Riccio et al, 2006). The treatment of measured data as predictors of cell-averaged values therefore requires a more sophisticated approach or much higher model resolutions. Receptor oriented models like the COMET model described in this work, try to avoid this pitfall.

Observations of concentrations in the atmosphere will always contain a mixture of signals from different sources at different locations and times. When measurements are available at time intervals of less than one per hour, the time scales of the signals that are superimposed on one and another can be divided in:

- the global background mean (time scale: one year)
- the latitudinal mean gradient (time scale: month)
- the synoptic average elevation (time scale: week)
- the contribution of regional sources within 200-2000 km distance (time scale: few days)
- the contribution of local sources within 100 km (time scale: few hours).

In practice, there are no clearly defined cut-off limits that allow for a sharp separation of these temporal and spatial scales and the definition used here is based more on practical insights and experience.

The global observation system in place for monitoring the greenhouse gas concentrations has been devised in such a way that the signal of local, regional and synoptic time scales is minimal. As a result of this strategy the measurement locations are all rather remote sites with air travel times to the areas with large emissions of at least one to several days. The main characteristic of the data sets obtained by these stations is that it contains a mixed signal representative for continental or even larger areas and that this signal is very diluted, leading to high requirements for measurement precision.

In order to derive emissions from concentration signals with relatively high spatial resolution it is necessary to measure more closely to the source regions. The problem is that the atmospheric concentration signal then contains information on all mentioned temporal and spatial scales. Use of a high resolution atmospheric transport model to estimate the influence of atmospheric dilution processes is then required.

The mathematical reversibility of the atmospheric mixing processes is however limited due to their chaotic nature (Lighthill, 1986; Pine et al., 2005). The resulting unpredictability and

irreversibility at larger temporal and spatial scales requires that the source signal is captured close to the sources in order to allow for model inversions of that signal, before the signal is irreversibly lost in random noise. High-resolution Lagrangian model experiments show that the atmosphere can carry high concentration signals for periods up to about 10 days and for distances up to several thousands of kilometers (Vermeulen et al, 2005; Stohl, 2003), often along frontal systems in extended filamental structures.

4.2 The COMET model

In this chapter we will use the COMET model, a Lagrangian model that follows single air mass trajectories (Vermeulen et al, 2001) to capture the main variability of methane and carbon dioxide concentrations observed within major source areas like NW Europe. We will concentrate here on the performance of the COMET model in forward concentration simulations using a predefined emission map.

The COMET (CO₂ MEthane Transport) model is a Lagrangian model that can be used for both predictive and inverse modelling purposes. COMET uses backward trajectories to establish the source-receptor relationship, the so-called source-receptor matrix (SRM). The calculations described in this paper were performed using trajectory and mixing layer height data derived from three nested grids with 3-hourly resolution ECMWF analysed meteorological data. The vertical resolution used is T61. Using these meteorological data, the 3D 144 hour backward trajectories were calculated from the ECMWF wind fields using the Flextra model (Stohl et al., 1999).

In forward mode the COMET model retrieves the emissions for the grid cells under the current circular source area and calculates the concentration changes and eventually isotopic composition for the modelled components in the column of air with the current mixing layer height.

The height of the well-mixed layer $H^m[t]$ is determined using the bulk Critical Richardson number approach. The bulk Richardson number, Ri, is the dimensionless ratio of buoyant suppression of turbulence to shear generation of turbulence and it is usually defined as follows:

$$Ri = \frac{g}{\theta} \frac{\partial \theta}{\partial z} \left[\frac{\partial U}{\partial z} \right]^{-2}$$
 {3}

where g is the gravitational acceleration $[m \text{ s}^{-2}]$, θ the potential temperature [K], z [m] the height variable and U [m s⁻¹] the horizontal wind speed. The critical bulk Richardson number is chosen as Ri_c=0.25, although suggestions in the literature range from 0.2 to 1.0. There is also some suggestion of hysteresis, where the Richardson number of a flow must drop below Ri_c before the flow becomes turbulent, where on the other hand a turbulent flow can exist up to Ri=1.0 before the flow becomes laminar. Such hysteresis effects are not included in the COMET model, where it is assumed that when Ri≤Ri_c, the flow is turbulent, whereas for Ri>Ri_c, the flow is assumed to be laminar. ECMWF data are used for calculation of the potential temperature and horizontal wind speed gradients. It is important to note that the established height of the mixed layer $H^m[t]$ has a significant effect on the calculated concentrations in the well-mixed layer.

Emission data are retrieved from emission inventories per source category on a regular grid; in this case for methane the high resolution (a spatial resolution of 10'x10' and a 3-hourly time scale) METDAT database (Berdowski et al., 1998) is used; the base year for the emissions in METDAT is 1995.

4.2.1 Results

The COMET model was applied to simulate the hourly concentrations at Cabauw tower for the year 2002. Simulations were performed using 3D 96-hour backward trajectories and meteorological data using meteorological fieds at a resolution of $1.0^{\circ}x1.0^{\circ}$ (grid index 1 of Table 1.2). In the next chapter, the results of a sensitivity analysis for the COMET parameters to determine the best performance of the model will be shown.

The results of the forward simulated concentrations are shown in Figure 4.1. Figure 4.1 shows the measured and modelled time series at Cabauw for a four-month period. For Cabauw, the mean mixed layer concentration was calculated using the Cabauw vertical concentration profile observations along the tower, taking into account only those observations that fall within the (modelled) mixed layer.

The model captures the diurnal variation in concentration very well. Both timing and height of the daily maxima and minima are realistic. Also, the synoptic variation and build-up of the concentration in high pressure anticyclonic conditions are represented well by the model. Figure 4.2 further illustrates the correlation between model and measurements. The COMET model explains about 72% of the variability in the measured concentrations at Cabauw for the whole series of hourly observations in 2002. The Root Mean Square Error (RMSE) is estimated at 141 ppb, which is about two orders of magnitude higher than the measurement error. Overall, the concentrations predicted by the model above the global background of 1760 ppb are 4% higher than the observations. This can be due to systematic errors in the model or in the underlying data, like emission rates and mixed layer height.



Figure 4.1 Hourly mixed layer average CH_4 concentration (ppm) at Cabauw, Feb-May 2002 as measured (light blue) and modelled (dark blue) with the COMET model in forward mode

Figure 4.2 shows a scatter plot of the measured versus modelled hourly concentrations of CH_4 at Cabauw for the year 2002.



Figure 4.2 Scatter plot of hourly predicted versus measured mixed layer concentrations of CH₄ [ppm] for Cabauw, using the COMET model in forward mode and 3D trajectory data for arrival at 20 m height



COMET CBW 2002 Performance for CH_4 as function of time of day, 1 hr sample freq.

Figure 4.3 Correlation (R^2) and RMSE of COMET 2002 forward predicted CH₄ hourly concentrations compared to the observed mixed layer concentration as a function of the hour of the day

Figure 4.3 shows the correlation and RMSE of the forward simulated concentrations with the observed mixed layer concentrations as a function of the hour of the day. Results are best for the afternoon hours and for the early morning. The model shows less performance for the remaining transition hours, where the mixed layer height changes considerably with time. Then the exact height as well as the timing of the changes becomes critical for the determination of the least squares fit.

4.3 COMET simulations of CO₂

For the CO_2 simulations we coupled the FACEM deposition model (Pieterse et al, 2006) to the Lagrangian CO_2 and Methane Transport (Comet) model (Vermeulen, 1999). By initializing the Lagrangian box concentrations to background concentration data provided by Globalview- CO_2 (GlobalView, 2005), and by employing estimates for the spatial and temporal distribution of sources and sinks for carbon dioxide, the Comet model provides the means to calculate the hourly averaged CO_2 concentrations for any given receptor in the well-mixed planetary

boundary layer. For this case study, the Facem model was used to provide the strength estimates for the GPP, NPP and NEP for the European domain, with a 1-hourly time resolution and a spatial resolution of 0.5°. Furthermore, the global Takahashi dataset (Takahashi, 2002) was used to provide estimates for the exchange of carbon dioxide from the atmosphere to the ocean. Finally, the Edgar-FT dataset (Olivier, 2005) was used to provide the anthropogenic emission estimates.

Comet model calculations were then performed for the Cabauw Tall tower site in the Netherlands and compared with the 1-hourly averaged concentration measurements for the year 2002. The following cases were considered for the calculations:

- First, the calculations were performed by including the Takahashi and Edgar-FT datasets only;
- For the second case, the GPP dataset was added to the Takahashi and Edgar-FT datasets;
- The third case was the same as the second case, but with the GPP dataset replaced by the NPP datasets;
- The last case was again equivalent to the second case, but with the NEP dataset included instead of the GPP dataset.

This set of cases allow for subsequent validation of the photosynthesis scheme (Case 2), the autotrophic respiration scheme (Case 3) and the heterotrophic respiration scheme (Case 4). Case 1 was added for reference and gives insight in the magnitude of the contribution by anthropogenic sources. The results for the different cases, as compared to all measurements in 2002, are shown in Table 4.1.

Table 4.1	Combined Facem and Comet model performance for prediction of CO_2				
	concentrations at the Cabauw Tall tower, using different datasets for source and				
	sink strength estimates: (Case 1) anthropogenic and oceanic estimates, (Case 2)				
	anthropogenic, oceanic and GPP estimates, (Case 3) anthropogenic, oceanic				
	and NPP estimates (Case 4) anthropogenic oceanic and NFP estimates				

		10 /	
Measurements	R^2	St. dev. [ppm]	Bias [ppm]
Case 1	0.64	9.0	-9.0
Case 2	0.44	10.6	-13.3
Case 3	0.65	12.1	-8.5
Case 4	0.65	21.2	-0.3

From these results, it can be clearly seen that incorporating the NEP as an estimate for the biosphere-atmosphere exchange yields the best model to measurement correspondence, both in terms of correlation as well as in variability and bias. This indicates excellent performance of all processes included in the Facem model, especially considering the completely different behavior of the modeled concentration for Case 2, as measured by a poor correlation (R^2 =0.44). This concentration signal represents the measured signal without accounting for the respiration processes. However, by adding the respiration processes, the correlation is again maximized and the bias between model and measurements is almost completely removed. In Figure 4.4, a zoom of the modeled and measured concentrations is shown.



Figure 4.4 Selected period for evaluation of the combined Facem en Comet model performance for the prediction of CO₂ concentrations at Cabauw tower. Different sets of source and sink strength estimates were taken into account: (Case 1) anthropogenic and oceanic estimates, (Case 2) anthropogenic, oceanic and GPP estimates, (Case 3) anthropogenic, oceanic and NPP estimates, (Case 4) anthropogenic, oceanic and NPP estimates

From this figure, several features can be discerned. First of all, the variability of the modeled signal, as compared with the measured signal, seems to be small in terms of anthropogenic and oceanic contributions (Case 1). The GPP (Case 2) is clearly responsible for a large uptake of CO_2 . However, this uptake is greatly reduced by autotrophic and heterotrophic respiration, as illustrated by the signals corresponding to Case 3 and 4. Case 4 in some occasions over-predicts the measured variability, as can also be seen in Table 4.1, but most resembles the measured signal.

These signals also allow for an assessment of the feasibility of extraction of the biospheric signal from measured concentrations. As the signal for Case 4 most closely resembles the measured signal and the signal for Case 2 is least resembling, it can be expected that it will be difficult, if not impossible, to extract the GPP signal directly from concentration measurements, at least not with adequate accuracy. This is mainly due to the well-mixed state of the planetary boundary layer during daytime, resulting in significant dilution of information in the measured signal. During nighttime, the signal is clearly dominated by respiration processes and the measurements seem to provide a lot of information about these processes. Estimates for nighttime respiration could be derived from the nighttime concentration measurements, provided that accurate estimates for the anthropogenic sources and an adequate description of atmospheric transport are available. However, nighttime conditions are currently still hard to reproduce by atmospheric transport models and uncertainties introduced by these models will limit accurate footprint analysis for nighttime concentrations.

4.4 Conclusions/Discussion

The COMET model is able to reproduce most of the variability of the diurnal and synoptic concentration signal of methane and carbon dioxide in the atmospheric boundary layer. Due to the availability of information about the vertical profile of the methane concentrations, the model performs better in comparison with observations for the Cabauw tall tower site, than for a surface level site like Mace Head.

The overall agreement between modelled and measured concentrations of methane is good at all timescales. Model performance is less for midnight hours and for the early morning transition hours in which the well-mixed layer grows. Best model performance is obtained for the midday and afternoon results, which yield an explained variability of 84% for the whole year of hourly methane observations in 2002.

Tall tower observations provide the unique possibility to extend the surface concentrations to the total mixed layer for most of the climatological conditions of Europe. The mean mixed column concentration can be modeled more robustly by the COMET model than the more locally influenced surface concentration. The mixed layer column concentration presents us with the results of fluxes of much larger regions. This larger footprint extends up to 500-1000 km and this may allow successful application of inverse methods to the Tall Tower observations, especially when more or less overlapping information from a network of towers like the CHIOTTO tall tower network is used.

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5. Accompanying flux tower operation results

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One of the objectives of WP6 in the CHIOTTO 'description of work'-document is to quantify the contribution of specific land use types to the large scale flux. This large scale flux is measured at the Cabauw tower, located in the centre of the Netherlands (51.971 °N, 4.927 °E) in a 'polder' 0.7 m below average sea level. To assess the contribution of surrounding land use types to the flux measured at Cabauw, measurements at different land use types in the surroundings of the Cabauw tower were made and various modelling tools were applied. The first part decribes the measurements made during the project and the second part describes the usage of a mesoscale model in combination with a transport model to assess the 'footprint' of the Cabauw tower.

5.1 Measurements

For the CHIOTTO project three sites were instrumented: the permanent measuring structure at Cabauw and mobile systems based at Haastrecht and Langerak.

The Cabauw tower is a main measuring site of the Meteorological Service of the Netherlands (KNMI). Cabauw is situated in the centre of the Netherlands (51°58'N, 4°56'E, elevation - 1.7m) in the centre of a mainly agricultural area. In this area the grassland is used for grazing cows and sheep. A large part of the area is peat land or peat land covered by river sediments. To enable agricultural use the land is drained, causing oxidation of the peat. The work executed at Cabauw takes place in close collaboration with KNMI. Meteorological data (such as precipitation, radiation, temperature and wind speed) are measured by KNMI and may be used for the project. The greenhouse-gas concentration measurements are made by ECN. In May 24 2003 an eddy-correlation system was installed at 100 m height. The measuring system is based on a 3D ultrasonic anemometer (Gill R3-50) in combination with a fast open-path infrared gas analyser (Li-Cor LI-7500). A full description of the system is given by Aubinet et al., 2000 and Moncrieff et al., 1997.

At the foot of the Cabauw tower an eddy correlation system is installed at a height of 5 meters, measuring fluxes of grassland on clay covering peat.

Additional land use specific data were collected by a mobile station. From July 2003 to June 2004 the mobile station was placed in at Haastrecht (52°00'N, 04°48'E, elevation -0.7m). The Haastrecht site is a grassland site situated on a peat soil with a relatively high water table. The main land use is pasture grazed by cows and sheep. In January 2005 the station was moved to Langerak (50°00'N, 04°48'E, elevation -0.7m) and data has been collected at this site from 26 January 2005 until 14 April 2006. Langerak is situated about 2 km west from the Cabauw tower and the soil consists of peatland covered by river sediments (clay). In May 2005 maize was sown and in October it was harvested. Before and after the maize it was bare soil.

The mobile station measured the turbulent fluxes using the eddy-correlation technique. The measuring system was also based on a 3D ultrasonic anemometer (Gill R3-50) in combination with a fast open-path infrared gas analyser (Li-Cor LI-7500) placed on the top of a 4 m mast. With a separate datalogger (Campbell CR10X) the following parameters were measured: net radiation (REBS Q7), incoming and reflected short wave radiation (Kipp&Zonen CM5), soil

moisture (Campbell CS615) and rainfall (EM Arg-100). Every 2 weeks soil respiration (Ciras EGM-1), LAI (Li-Cor LAI-2000) and crop height was measured.

5.2 NEE and respiration: variability between years and ecosystems

Measurements of the Net Ecosystem Exchange (NEE) have been done from 2002 until 2005 for various ecosystems. Table 5.1 gives an overview of the sites where measurements have been made in these years. This table also shows the vegetation at the sites and the abbreviations of the datasets used in the figures. Langerak is close to Cabauw and is therefore called Cabauw 2. At Haastrecht measurements where made from the end of July 2003 until the end May 2004. These datasets are merged to get a full year of data. Using these measurements response curves will be determined for all land use types and years.

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Site	Vegetation	2002	2003	2004	2005
Loobos	Coniferous forest	L2	L3	L4	L5
Haastrecht	Grass		Н		
Langerak	Maize				Cabauw2 05
Cabauw	Grass		Cabauw 1 03		

Table 5.1Overview of measurement-sites and years

Respiration

For each dataset a respiration curve is derived, based on temperature [Lloyd and Taylor, 1994]. For the analysis, observations of NEE are used that meet the following criteria: shortwave radiation smaller than 1 W m⁻² (nighttime values), no precipitation and the friction velocity higher than 0.1 m s⁻¹. The data is binned in 48 temperature classes. The following model was fitted to the bin-averages:

$$R_{int} = R_0 \exp\left(\frac{B_d}{R^*} \left(\frac{1}{T_{ref}} - \frac{1}{T_{bin}}\right)\right)$$
(1)

Figure 5.1 shows the results from the fit for every site and year. It can be seen that the respiration curves for the Loobos site are comparable except 2003. This might be caused by the summer-drought of 2003. The binned respiration for maize (Langerak) is bigger than for the coniferous forest (Loobos). The two respiration curves for grass (Haastrecht and Cabauw) show a big difference.

NEE

For each dataset a light-response curve is derived, based on short-wave radiation. For the analysis, observations of NEE are used that meet the same criteria as mentioned above for the respiration part. The data is binned in 48 radiation classes. The following model Falge et al., 2001 was fitted to the bin-averages:

Alle ecosystemen Binned ecosystem respiration



Figure 5.1 Response curves of respiration for various sites and years

$$MEE = \frac{aQOPP_n}{OPP_n + aQ} - R_{evo}$$
(2)

Figure 5.2 shows the results from the fit for every site and year. Since we used all data, we assume no differences in footprint (wind direction and growing season of vegetation). For example maize in Figure 5.3 shows a big spreading around the fitted model, which may be caused by part of the data being in, and another part being outside of the growing season, when the land lies bare. This hypothesis is supported by Figure 5.4, where the analysis on NEE is repeated for temperatures between 20 and 25 °C. In this case the data is binned in 10 radiation classes. In this graph the observations of NEE for maize don't show a big spread around the fitted model.

Another problem is the big spread of the respiration-observations at Haastrecht around the fitted model. This might be caused by the merging of the datasets of 2003 and 2004, which had very different precipitation patterns and amounts.

Figure 5.2 and Figure 5.3 show a big difference between Haastrecht and Cabauw, which are both grassland sites. In the warm season (Figure 5.3) the NEE for both sites is comparable. This indicates that the big differences in Figure 5.2 and Figure 5.3 have their causes outside the growing season. The high respiration of Haastrecht is explained by the presence of organic soils while at Cabauw these are covered by a clay layer.



Figure 5.2 Response curves of NEE for various sites and years



Figure 5.3 Response curves of NEE for various sites and years, but only for values with 20 $^{\circ}C < T_{air} < 25 \ ^{\circ}C$





Figure 5.4 *Mean diurnal CO*₂ *fluxes at Cabauw and Haastrecht (copied from 2nd year CHIOTTO report)*

Figure 5.4 compares the mean diurnal variation of NEE during the summer of 2004 measured at the two heights along the Cabauw tower and at the Haastrecht site. There is a difference between the patterns at night and during daytime. At night, the CO_2 fluxes at 100 m are suppressed relative to the other height and site. This is likely to be the result of emissions from the soil accumulating within the stable nighttime boundary-layer, which often does not exceed 100 m height. We can also see the CO_2 stored in these boundary-layers during the night being released during the course of the morning, causing a positive flux and apparently delayed uptake during the mornings. After this, however, for CO_2 there is a strong similarity between the fluxes at Haastrecht and Cabauw 100m, and an underestimation relative to the measurements at Cabauw 5 m. Higher uptake at the latter site/height can be the result of better drained soils, less soil respiration (see previous section) or the presence of maize in the flux footprint. Also the daytime flux divergence between these heights may be related to boundary layer growth and entrainment, see e.g. Vila-Gerau et al 2005. This combination of factors makes interpretation of 100 m fluxes rather ambiguous.

5.4 Modelling

With the combination of a regional atmospheric model and a Lagrangian transport model we next analyze the footprint of the tall tower and the contributions of the main land-use types around Cabauw to the observed concentration.

5.4.1 Description of the models

We use a regional atmospheric model (RAMS, **R**egional Atmospheric Modelling System,Cotton et al., 2003; Pielke et al., 1992) forced by ECMWF analysis data for the period 5 May 2005 to 15 May 2005 to resolve the effect of complex surface conditions in high resolution (up to 2km). The standard land surface model in RAMS, LEAF-2 (Walko et al., 2000), has been replaced by the SWAPS-C land surface model (Ashby, 1999; Hanan et al., 1998) to include carbon exchange processes within the mesoscale modelling environment. This is complemented by a submodel simulating anthropogenic emissions (Olivier and Berdowski, 2001), disaggregated to high spatial and temporal resolutions, as well as a marine surface scheme simulating fluxes of heat and CO_2 from prescribed SSTs and δpCO_2 fields (Takahashi et al., 1997). CO_2 is transported as a passive, non-reactive, scalar in the atmosphere (Eulerian transport).

The dynamics from the mesoscale model (wind, potential temperature and turbulent coefficients) are subsequently used to drive a transport model, HYPACT. HYPACT (HYbrid Particle And Concentration Transport Model, Walko et al., 2001) is a combined Lagrangian and Eulerian transport model and it represents a state-of-the-art methodology for predicting the dispersion of air pollutants in 3-D, mesoscale, time dependent wind and turbulence fields. The model is developed by ATMET (http://www.atmet.com), formerly called the *ASTER Division of Mission Research Corporation. A big advantage of HYPACT is that it uses a similar structure (physics and run-time) as RAMS. With this model it is possible to emit particles from various sources related to land use types. These particles can be marked according to the land use emitted from and the time when the particles were emitted. As a result, the contribution of land use types to the flux measured at the Cabauw tower can be quantified. The period 5 to 15 May 2005 is selected as a period with an interesting build-up of CO₂ concentrations.

A first step is to simulate the aforementioned period with RAMS to obtain high resolution meteorological dynamics, which will be used to drive HYPACT. A couple of steps had to be taken to prepare the model for the simulations, such as:

• Determination of CO2-parameters and Jarvis/Stewart-parameters for grass to get better CO2- and latent heat-fluxes above grass, which is the major land use type in the vicinity of Cabauw. Flux measurements, taken at Haastrecht and Cabauw, are used to optimize the parameters. The parameters are optimised against the measurements by minimising the sum of squares, R^2 , of model predictions, $X_{predicted}$, and measurements, $X_{observed}$:

$$R^{2} = \sum \left(X_{predicted} - X_{observed} \right)^{2}$$

This is done using a Marquardt-Levenberg (Marquardt, 1963) algorithm for optimisation.

• Designing new RAMS-grid configuration to allow for a fine resolution grid around Cabauw. The complete RAMS configuration is tabulated in Table 5.2.

	Grid #1	Grid #2	Grid #3		
dx, dy	18 km (50 x 54)	6 km (62 x 62)	3 km (149 x 149)		
dt	20 s	6.7 s	6.7 s		
dz	100 stretching from 50 to 750 m (35 levels)				
Topography DEM USGS (~1 km resolution)					
Landuse PELCOM (Mücher et al., 2001)			al., 2001)		
Radiation		Harrington (1997)			
land surface model		SWAPS-C			
Diffusion Mellor/Yamada (Mellor and Yamada, 1982)		Yamada, 1982)			
nudging time scale	lateral 1800 s				
Convection	Convection Full microphysics package (Flatau et al., 1989)				

 Table 5.2
 Configuration of RAMS/SWAPS setup used in the CHIOTTO-simulation

5.4.2 Results

With the configuration shown in Table 5.2 RAMS/SWAPS has been used to simulate the regional climate around Cabauw from 5 to 15 May 2005. To validate the model various observations are used from the following sites: Haarweg (<u>http://www.met.wau.nl/</u>haarwegdata/), Loobos, Langerak and Cabauw (CarboEurope/CHIOTTO-sites). The main focus here will be on the carbon exchange processes. The variables which are used to drive the HYPACT model have also been checked but these results are not shown here. It suffices to say that the comparison between model and observations gives enough confidence to use the dynamics of the simulation for the simulations with HYPACT.

Figure 5.5 shows the time series of the Net Ecosystem Exchange (μ mol m⁻² s⁻¹) for both Cabauw (upper) and Loobos (lower). The black dots represent the observation and the grey line represents the output of RAMS/SWAPS. The model simulates the CO2 exchange reasonably well for both forest (Loobos) and grass (Cabauw). However, the large uptake of the grass at Cabauw at the end of the simulation is not simulated well by the model. The model has a minimum net ecosystem exchange of approximately -7 μ mol m⁻² s⁻¹, whereas the measurements reach values of -30 μ mol m⁻² s⁻¹. It needs to be remarked that the data used are only roughly quality checked.

The next step in this validation is a modelling experiment using HYPACT with the output data from RAMS for the same period, to determine and quantify the contribution of each land use type in the grid. In the current model setup (Eulerian approach used in RAMS/SWAPS) it has already been noted that a change in wind direction and/or weather type can have a big influence on the concentration simulated for Cabauw tower.

As particle emission, CO_2 -fluxes are used which are simulated by RAMS so that gridcells which emit large CO_2 quantities will be represented rightly in the HYPACT simulation. To do this an hourly spatial flux representation, derived from RAMS results, had to be transformed into an emission map. Next to an emission map, it is also necessary to mark the particles with the landuse it originates from. In the vicinity of the Cabauw tower three main land use categories can be distinguished: forest, grass and urban areas. The analyses shown will therefore only focus on particles originating from these categories. A clear difference between the land use classes is that both forest and grass emit two different types of particles, namely one originating from positive carbon-fluxes (respiration) and the other originating from negative carbon-fluxes (uptake). Urban areas only emit positive particles.



Figure 5.5 Net ecosystem exchange (μ mol m⁻² s⁻¹) for Cabauw (left panel) and Loobos (right panel). Black squares: observations (hourly), grey line: model



Figure 5.6 Vertical profiles of CO₂ concentration [ppm] at Cabauw. Left panel shows an instantaneous profile at 6 May 2005 2 PM UTC; Right panel shows a 48 hours average (5 and 6 May). Colours in both panels are the same: black – urban contribution, green – grass contribution, yellow – forest contribution

Figure 5.6 shows the amount of particles, translated into a concentration in ppm, which are transported into an area around the Cabauw tower. The contributions of the three land use classes are clearly seen. In both the instantaneous profile and the averaged profile the contribution of the particles originating from the urban areas around Cabauw is largest for the whole profile, only during daytime the contribution of the surrounding grass is significant near the surface. Figure 5.7 shows the contribution of the land use classes to the concentration for two levels at Cabauw. It can be seen that Cabauw detects a significant amount of particles coming from urban areas: 16 ppm (50 m) and 10 ppm (200 m). Analyses (not shown here) relate this contribution to the urban areas north and west of Cabauw, mainly from the cities of Amsterdam, The Hague and Rotterdam. The contribution from forest areas is negligible in Figure 5.2 and Figure 5.3 which is a result of the prevailing wind direction. During the first days of the simulated period a west-northwesterly current was present over The Netherlands. In this direction no forest is present and therefore the contribution of forests to the concentration simulated at Cabauw is near zero. In the course of the simulation this changed and the contribution of forest is apparent. Figure 5.8, finally, shows an almost complete picture of the footprint of the Cabauw tower for the simulated period. This figure shows the contribution of each land use pixel to the concentration at Cabauw. The lighter the colour the smaller the contribution. From this figure it can be clearly seen that no contribution from the southern part of The Netherlands was simulated due to a dominant northerly component in the wind during the simulated period.



Figure 5.7 Time series of CO_2 concentration [ppm] at Cabauw for 5 - 7 May 2005. Left panel shows the time series at 50 m height; Right panel shows the time series at 200 m height. Colours in both panels are the same: black – urban contribution, green – forest contribution, yellow – grass contribution

From the results shown from RAMS and HYPACT-simulations it can be concluded that the usage of HYPACT is a good tool next to RAMS to have the full package of Eulerian and Lagrangian modelling. RAMS simulations showed good agreement with observations for various sites. For the simulated period it can be concluded that contributions to the concentration in Cabauw mainly stem from urban emissions from the surrounding cities. Also the analysis (graph not presented here) shows clear variations in the footprint with height related to wind direction changes following the Ekman spiral.

Comparing Figure 5.8 to the footprint graph presented in the 1st year report, shows marked differences which to a small extent are caused by the contrast in methodology (analytical footprint model based on plume analogies vs. Lagrangian particle dispersion). More importantly the differences reflect a difference in footprint between fluxes and concentrations, the latter always being larger than the former. Also in the lagrangian approach the source strength variations within the footprint immediately show up and its effect on concentration anomalies along the tall tower can be attributed to these straightforwardly.

Thus the Lagrangian simulations showed that it is possible to quantify the contribution of certain land use types to the concentration at Cabauw and allows for a novel, more quantitative analysis of the footprint concept.



Figure 5.8 Simulated footprint for 5-15 May 2005. Yellow – Red: footprint urban pixels, lightblue – darkblue: footprint grass pixels, lightgreen – darkgreen: footprint forest pixels

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Appendix A Recommend equipment list

For the old and new towers the newly bought equipment and instrumentation will be harmonised as far as possible, at least for as far as the equipment will be (partly) bought from the project budget. Here follows a list of recommended hardware.

It is still possible to deviate from this list, but then the alternative must be equal or better in specifications. If a group wants to deviate from the list, a written detailed request has to be made to the CHIOTTO coordinator. After discussion on the pro and cons of the requested alternative with at least the involved work-package leader a decision will be made.

A.1 Tubing

Dekoron Dekabon type 1300

Remarks: 1. 12 mm outside diameter on towers to pumps

- 2. ¹/₄ inch diameter inside laboratories
- 3. O₂ measurements require <u>no</u> T-junctions
 - 4. Lots of local distributors, depending on your country. Just do a Google search.
 - 5. GC-quality stainless steel tubing should also be used inside the container where appropriate.

6. In NO CASES (for GC, CO₂, or O_2/N_2 measurements) should any plastic tubing be used.

A.2 Cryo coolers

Kinetics Thermal Systems Vapor Trap VT490 (4 litre alcohol bath) This American company recently got a European distributor (along with a large price increase!):

DHS Europe

http://www.kineticseurope.com

- Remarks: 1. Must install a small fan on top to prevent condensation which could kill the cryo cooler (has happened to us in the past).
 - 2. Do not buy any of the expensive and impractical lids. Instead, you must make your own custom lid.
 - 3. Cost estimate: 4,600€4. If you would like a bigger alcohol bath to put additional traps in, they also sell an 8 litre model, the VT890, for only a small price increase. (However, I do not know how much bigger the diameter of the cold bath is).

A.3 GC System

Agilent HP 6890

G1540N 6890N GC

- Opt 210 FID incl EPC (equipped with FID jet 18789-80070)
- Opt 231 µECD
- Opt 307 Ni-cat (methanizer)
- Opt 301 3 additional EPC-channels
- Opt 500 LAN-Interface card
- Opt ??? additional inlet flow module

- G1530-60660 Aux Zone/VLV box cable
- G1530- 60590 cable for external events cable (2 are needed)
- G2075AA Chemstation software licence

http://we.home.agilent.com

Remarks:

- 1. A paper containing GC Instrument setup suggestions (columns, flows,
 - temperatures, detector settings) will be writtenby Martina Schmidt. 2. We discussed in Paris that the new micro-ECD detector was reported to not be good (experience of the AGAGE group). New information (from CMDL and Doug Worthy) suggests that in fact it is fine. Therefore this is no longer a concern.
- 3. Cost estimate: 23,000€
- 4. Price does not include many other parts needed to operate the GC, for example Valco valves, gas generators and purifiers, and a computer.
- 5. Agilent offer a computer with the system. Our experience suggests that you should NOT buy this, since it costs more than double what you can get from any computer supplier.

A.4 Pumps

Pumps are critical only if placed before, and inline with, detectors or analysers. Then use: KNF Neuberger

- N05 or N010 models
- Specify: aluminium pump head; teflon valve plate; teflon-coated Viton diaphragm
- Requires homemade improvement to the pump head. Contact Andrew Manning for technical drawings
- For higher flowrates (>approx. 10 Lpm), get N828 model
- If buying DC motor model, be sure to get brushless version
- <u>http://www.knf.com/</u>
- Although there are several European distributors (see above web page), you may have to go to the American company to get the N05 or N010 models.
- There are some new KNF pumps which look very promising, but they have not been thoroughly tested for CO₂ contamination at this time. Therefore at this time we can only recommend this difficult-to-get model which requires a homemade improvement.

A.5 (Sample height selection) valves

Valco Instruments Company

http://www.vici.com

Remark: Multiport valves need to be checked periodically for leakages. Often such leakages are subtle and can go unnoticed. Be warned!!

A.6 CO₂ concentration (gradients)

Siemens Ultramat 6E http://www.sea.siemens.com/ia/product/aiultra6e.html Li-cor 6252/6262/7000 http://env.licor.com

We do not have enough information to recommend between the Siemens and the LiCor. The LiCor has a much smaller cell (9 mL compared to about 100 mL), but the Siemens is a much better engineered analyser, and has very good flushing characteristics, despite the large cell volume.

For the different LiCors:

- The 6252 is definitely better (and cheaper) than the 6262. And we have been told by the German distributor that although the 6252 is no longer being made, there are still several in stock which can be bought.
- Comparing the 6252 (or 6262) with the 7000, Andrew reported in Paris a rumour that • CMDL did not like the 7000, even though in theory it should be much better. Since Paris, we received more recent information from CMDL which stated: 'the 7000 is a little better than the 6262 in terms of signal to noise, and the efficiency to flush the sample cell is quite a bit better'. The 7000 is quite a lot more expensive, however.

Cost estimates: LiCor 6252 = 11,530 Euro (quote given in 2003) LiCor 6262 = 15,000 Euro (approximate)LiCor 7000 = 17,300 Euro (quote March 2003) Siemens Ultramat ??

A.7 Rn

University of Heidelberg or CNRS custom Rn monitors. Franz Conen (UEDIN) will provide info on Australian Rn monitors.

A.8 Zero Air generator for GC

Parker Balston 75-83 http://www.parker.com/balston/ags Cost Estimate: 1,200 Euro

A.9 Hydrogen generator for GC

Parker Balston A9150

http://www.parker.com/balston/ags 1) You can also purchase the same model from other suppliers, for example

Remarks:

Alltech or Supelco.

2) Cost Estimate: 5,800 Euro

3) You also need a Deionised Water supply for the H₂ generator. If you can not regularly provide deionised water to your tower site, you can purchase a deionised water generator system, also from Parker, model number 72-230 DI; cost estimate 1,300 Euro

A.10 N₂ generator for GC

Parker Balston 76-92 Ultra Pure Nitrogen Generator

Cost Estimate: 8,000 Euro

This is the make and model which Doug Worthy recommended, and is definitely much better than the make MPI-BGC have experience with (Domnic Hunter). However, Parker Balston also sell a:

76-94 Ultra Pure Nitrogen Generator

The only difference is that this model includes a catalyst for removing hydrocarbons. The cost is about 900 Euros more. Unfortunately no one has experience about how good this catalyst is. For the same increase in cost, you can buy an 'Aeronex' gas purifier (see below), which several of us have very good experiences with. HOWEVER, the Aeronex will only remove NMHCs, leaving a big question about possible interferences from methane. http://www.parker.com/balston/ags

A.11 Remarks on gas generators:

- 1. N_2 and H_2 generators are not compulsory for a CHIOTTO GC system. The other option is to use cylinders of N_2 and H_2 supplied by a commercial company.
- 2. In the case of H_2 , however, for an unattended system, it may be a safety concern or even requirement to have cylinders of H_2 on site. In this case, having an H_2 generator is a very good idea.
- 3. You can also buy Zero Air from cylinders supplied by a commercial company. However, in this case, the Zero Air generator is so cheap (approx 1200 Euro), that we recommend in all cases to buy one of these.
- 4. No matter whether you use a generator or commercially supplied cylinders, we highly recommend the use of gas purifiers see below.

A.12 Gas Purifiers

Aeronex (for N_2 carrier gas cleanup: SS-400KGC-I-4S) (can also be purchased from Supelco) <u>http://www.aeronex.com</u>

Supelco

Remarks:

http://www.sigmaaldrich.com/Brands/Supelco_Home.html

- 1. Aeronex does not require heating, so is preferred, and has been shown to have excellent clean-up characteristics. However, take note that none of the Aeronex models will cleanup methane.
 - 2. The model above is to cleanup an N_2 carrier gas. If you want to cleanup the CH_4/Ar carrier gas, purchase a different model from the same company. Contact Martina Schmidt for specifications.
 - 3. Cost Estimate: 900 Euro

A.13 GC Data Acquisition

Chemstation is included in the Agilent HP6890 package above.

If you prefer, you may ask for this option to be excluded from the package, and purchase PeakSimple instead. (€2500 inclusive USB hardware).

A.14 CO analyser:

- Martina recommends using an HP6890 FID with methaniser, as listed under the GC specs.
- A complete system therefore would comprise of a single GC, with an FID providing CH_4 and CO, and an ECD providing N_2O and SF_6 . This system requires a separate analyser for CO_2 measurements, which is the recommendation for the CHIOTTO group anyway, that we must use an NDIR analyser for CO_2 measurements.

Appendix B CALIBRATION PROTOCOL

B.1 Philosophy of the calibration protocol

To achieve the precision and accuracy goals established for the CHIOTTO project, a detailed calibration protocol has been designed for the tall towers in our network. This protocol has been arrived at after much discussion, both within the CHIOTTO consortium, and with our international colleagues, some of whom have several decades of experience in high precision atmospheric measurements. This document outlines our calibration protocol. For additional details or clarifications, please contact Andrew Manning at Max Planck Institute for Biogeochemistry (amanning@bgc-jena.mpg.de).

B.2 Standard cylinder calibration system

Each tower will receive from MPI-BGC seven 50-Litre Luxfer aluminium high pressure gas cylinders, and an associated seven two-stage cylinder regulators (Scott Specialty Gases). Four of these cylinders are designated as **Working Secondary Standards (WSSes)** and three are designated as **Longterm Secondary Standards (LSSes)**. All seven cylinders sent to each tower will be assigned concentration values at MPI-BGC for each of the trace gases that will be measured at each tower (shown in Table B.1 B.1).

	0	1				
	CO_2	CH_4	СО	N_2O	SF_6	O_2/N_2
Angus, Scotland	Х	Х		Х	Х	
Bialystok, Poland	Х	Х	Х	Х	Х	Х
Cabauw, Netherlands	Х	Х	Х	Х	Х	
Florence, Italy	Х	Х		Х	Х	
Hegyhatsal, Hungary	Х	Х	Х	Х	Х	
Norunda, Sweden	Х	Х				
Orleans, France	Х	Х	Х	Х	Х	
Ochsenkopf, Germany	Х	Х		Х	Х	Х

Table B.1'X' denotes which gas species are measured at which towers

The WSSes are used for **daily calibration** of each analyser at each tower. For example, at many towers this means that the same cylinders will be used to calibrate a LiCor CO₂ analyser as well as to calibrate a GC for other gases such as CH₄, CO, N₂O, and SF₆. Despite such heavy usage, all WSS cylinders are estimated to last for 18-30 months before being depleted and needing replacement. The four WSSes will span a range in concentration in each gas species to be measured. These concentration ranges (which must be supplied by the institute responsible for each tower to MPI-BGC) will be adapted for the expected conditions present at each tower, taking into account expected diurnal and seasonal variability in each gas. In this manner, each analyser will be calibrated for the full range of concentration values reported from the tower, with no extrapolation of calibration curves necessary.

The LSSes should be analysed on each analyser at each tower on a frequency of **once every two weeks.** For some towers, where logistical demands preclude such a high frequency of LSS calibration, we recommend a minimum frequency of once every two months. These LSSes provide a check on the WSSes. In particular, they are able to show if one of the WSSes is misbehaving with respect to the others, and they are able to show if there is a change over time in WSS concentrations. For example, in many cases, drift observed in trace gas concentration in a cylinder can be attributed to the slow decrease in pressure in the cylinder over time as air is taken out of it. Thus, the LSSes, which will last about 20 years before being depleted, will be able to show up any such drift occurring in the WSSes which are depleted at a rate more than ten times faster than the LSSes. Each time that LSSes are analysed, the WSS calibration scale will be reassessed, and potentially adjusted, if such an adjustment is deemed necessary.

B.3 Zero tanks

In the case of LiCor calibration, an additional cylinder is needed, called the **Zero Tank**. A LiCor calibration curve is a quadratic relationship of mV output signal versus CO_2 concentration, of the form:

 CO_2 concentration (ppm) = $amV^2 + bmV + c$.

Each time the four WSSes are analysed on the LiCor (once per day), new values are defined for a, b, and c based on a least squares regression fit. Because of the analytical characteristics of the LiCor analyser, the zero coefficient, the c parameter in the above equation, is particularly susceptible to variability. Therefore, each tower should have a Zero Tank, which is analysed on the LiCor at higher frequency than the WSS daily calibration, and which should be used to provide updated values to the c parameter in the above equation. The frequency with which this Zero Tank should be run depends on the individual tower setup of their LiCor. For those towers which will have no active temperature control of their LiCor analyser, a frequency of at least once every two hours is highly recommended. For those towers which have active temperature control for their LiCor (of the order of $\pm 0.2^{\circ}$ C or better), it will be sufficient to run a Zero Tank check once every 12 hours. In the most infrequent case, each tower should run a Zero Tank check at least halfway between successive daily calibrations. (Note that this Zero Tank is not provided by MPI-BGC, because its concentration need not be accurately known). Note that Zero Tank does **not** mean that this cylinder should have zero CO₂ concentration. On the contrary, improved precision will be achieved if this cylinder has CO_2 concentration close to ambient levels.

B.4 Target tanks

The WSSes, LSSes, and Zero Tank cylinders discussed thus far are all used to actively define or adjust the calibration scales used at each tower. The next step of the CHIOTTO calibration protocol is **not** concerned with **defining** the calibration scale, but rather is used as a **warning system**, to indicate whether or not the analyser system is functioning according to the prescribed precision goals. This involves a cylinder called the **Target Tank**. The Target Tank, which should be used with all analysers at the tower, should be analysed at a frequency similar to the frequency of analysis for the LiCor Zero Tank (in other words, this depends somewhat on the laboratory conditions at each tower). As with the Zero Tank, the lowest frequency of analysis of the Target Tank should be every 12 hours. If the concentration calculated by the system for the Target Tank is outside prescribed limits for any gas species, then a warning flag should be raised indicating that all subsequent data are suspect. As with the Zero Tank, the Target Tank concentrations need not be accurately known, and this cylinder is not provided by MPI-BGC. It is most desirably if the Target Tank and Zero Tank be two independent calibration cylinders. However, for towers where this is not possible, or creates undue hardship, it is permitted to combine these two functions into a single cylinder.

B.5 Concentration assignment

Establishing WSSes, LSSes, Zero Tanks and Target Tanks at each tower in the manner described above aims to achieve a very high level of internal consistency of calibration of each analyser at each tower. Thus it is directly concerned with achieving the precision goals for

CHIOTTO, as shown in column two of Table 1.1. In addition to these precision goals, each tower is not an island, and thus data derived from any tower must be directly comparable to data derived from any other tower. The accuracy we are striving for in such a comparison is shown in the accuracy goals for CHIOTTO. To achieve these accuracy goals, we have developed a 3-step process.

First, all WSSes and LSSes initially sent to each tower will be assigned concentration values by MPI-BGC. These assignations will be traceable to WMO standards (for the trace gas species where such standards exist). This traceability is achieved because we have primary secondary standards (PSSes) in our labs which were purchased directly from the WMO-certified standard laboratories (NOAA/CMDL, in the case of CO_2 and CH_4). In addition, Pieter Tans of NOAA/CMDL has given MPI-BGC provisional permission to transfer these WMO scales from our PSSes to the WSSes and LSSes which we supply to each tower. This is a very generous offer from Pieter which we are very thankful for. Thus, in the beginning of operation, each tower will have a strong link to the official WMO calibration scales. In addition, at the end of a WSS's lifetime, and before all air has been depleted from the cylinder, it will be returned to MPI-BGC and reanalysed against the PSS cylinders. In this manner, the drift in concentration in the WSS cylinder can be quantified. It is important to realise, however, that this procedure only provides information about the average drift over the lifetime of the cylinder.



Figure B.1 Example of rotation of TSSes between the 8 towers in the CHIOTTO network. Numbers denote week number when the cylinder should arrive at the next tower in the sequence. Each set of three TSSes travels twice a year within a subset of the CHIOTTO towers

B.6 Travelling standards

We next need a method to maintain this link through time, and also to ensure the intercomparability of all towers as time progresses as well as initially (supplying all towers with cylinders from the same central laboratory, in itself, is not sufficient to ensure that each tower is initially reporting concentration data on identical scales – there are analytical artefacts that could be present at a tower, corrupting its scale). Thus we have an additional set of six Luxfer high pressure cylinders called **Travelling Secondary Standards (TSSes)**. These six cylinders will rotate in two sets of three between the towers, as shown in Figure B.1. The purpose of these cylinders is to directly compare the calibration scales at all towers with each other. Because each tower will only receive these cylinders two times per year, it would be dangerous to adjust a tower's concentration scale based on results from the TSS analyses, simply because these analyses are so infrequent. Instead, data derived from the TSS analyses will be used as diagnostic information about the relative performance of the tower, in comparison to all others. Whenever TSSes are analysed on a tower system, a full WSS/LSS calibration should also be done on the same day.

B.7 Flask intercomparisons

The third method to ensure CHIOTTO achieves its intra-tower accuracy goals involves collecting periodic flask measurements from all towers, and analysing them in two or three central laboratories. A separate protocol is required to establish such flask measurements, and this has not yet been agreed upon within the CHIOTTO consortium. We have decided to focus first on establishing all measurement equipment at all towers, and establishing the calibration protocol outlined in this document. The next step, which should come towards the end of the second year of the CHIOTTO project, will be to establish a flask collection and intercomparison programme, keeping in mind, and making full use of the fact that some towers are already collecting flask samples in independent programmes.

B.8 Calibration Analysis Guidelines

The procedure used for measuring a calibration gas on an analyser will vary somewhat between towers, between different analysers, and for different calibration gases. Provided here are some general guidelines which can be considered as a **minimum** for the procedures used at each CHIOTTO tower.

- Whenever a new calibration cylinder is introduced to the system, or whenever a regulator has been removed and reattached to a cylinder, the regulator must be 'pressure-flushed' 4 times. This means filling the regulator to the cylinder pressure, closing the cylinder, emptying all air from the regulator, and repeating, 4 times. Finally, the regulator should be left at cylinder pressure, awaiting its next analysis.
- Every calibration gas (WSS, LSS, TSS, Target Tank, Zero Tank) requires flushing of the cylinder regulator before measurement. The volume of air that should be flushed is a function of the regulator type, the field site conditions, and how long since the regulator was previously flushed. The following recommendations are for the Scott Specialty Gases regulators supplied to the CHIOTTO consortium. WSSes should have a minimum of 3 Litres of air flushed through the regulator before analysis. Since most analysis systems employ a flowrate of about 100 mL/min, this would require 30 minutes of flushing at this flowrate for each WSS. Therefore, it is advisable to have a plumbing system that allows for fast flushing (say 500 mL/min) through a different outlet, then introducing the WSS to the analyser system at the reduced flowrate.
- LSSes, because their regulators have been sitting static unused for a longer time, should have a minimum of 10 Litres flushing. (Please do not remove the regulators from the LSSes between subsequent analyses each tower is provided with 3 dedicated regulators for the 3 LSS cylinders. In addition, please leave the regulator at cylinder pressure continuously).
- Flushing required for Target and Zero Tanks depends on how frequently they are employed. For example, if used every two hours, 0.5 Litres of flushing should be sufficient, whereas if used only two times per day, 2 Litres of flushing should be employed.

- Analysis times of each calibration gas is dependent on analyser type. For a LiCor, between 5 and 10 minutes of analysis should be sufficient (for all calibration gas types). The precision of the measurement (on a 5 minute average) should be in the vicinity of 0.05 ppm for CO₂. For GC measurements, analysis times are fixed by the GC analysis cycle. The flushing time of the sample loops (not to be confused with regulator flushing) depends on the size of the sample loops.
- For GC analysis, each measurement of a calibration gas (WSS, LSS, TSS, Target and Zero Tank) should consist of typically 3 sample aliquots which are then averaged. In some cases such as for LSS and TSS calibrations which are only done on an infrequent basis, if would be advisable to measure more than 3 sample aliquots.
- Most calibration gases should be replaced before they run completely empty. For example, WSS cylinders should be replaced when they reach a pressure of 25 bar. LSSes, for which pressure-related drift is a more serious issue, should be replaced at 40 bar of pressure.

Appendix C Database format and upload protocol

C.1 File Upload Procedure

Provided Data

- Measurement heights shall be stated as above ground level. The site description on the other hand will contain surface height above sea level and from this the measurement height above sea level can be calculated.
- Height will be stored up to a precision of 0.1 m. If more precise is provided it will be rounded in the upload procedure into the database.
- Timestamps will be stored up to a precision of one second. Timestamps should always be in standard time, not daylight savings time.
- Timestamps can be complemented within the data file by additional columns for the startand end-time of averaging intervals (this is because at some sites, different gases will have different averaging intervals, and sometimes these averaging intervals will change for one gas at different times). If, however, these timestamps are always equal for a site, the interval can instead be stated in the measurement description, with only one timestamp column in the data files.
- Latitude and longitude coordinates will be stored in decimal notation and will allow four decimal places.

C.2 Quality Flags

Based on the opinions and feelings expressed during our discussions at previous CHIOTTO meetings, we have decided that there will be a rough data quality flag that says only if data are good, bad, or questionable (for example, columns containing either '0', '1', or '2', or 'G', 'B', or 'Q'). This judgment must be provided in each file for each species (i.e. gas) and for each timestamp.

Other more specific flags can be provided too, and are especially useful for the 'questionable' values. Since it is unlikely that there can be a CHIOTTO-wide standard to be agreed upon, these may be site-specific. Their meaning would have to be explained within the database under the measurement or site description since users who deal with 'questionable' values would want to be able to interpret these flags.

C.3 Constraints for Data Files

- 1. Standardized filenames e.g. 'OXK090_20030124CON.dat'. The file name must always have the same pattern for the same data series. In this case 'OXK090_??????CON.dat' could be the pattern for Ochsenkopf (OXK) concentration time series (CON) for 90 meter height (090). The date varies and documents the creation date of the file. Site name, measurement height and date are necessary elements of the name. Up to three letters before the extension may be freely used for further discrimination of files.
- 2. Each file shall have a unique file name. That means that all files for one time series must have another date in their name. In case that more than one file is produced per day I would propose to use different extensions (here 'dat') to allow distinct names.
- 3. Concentration data from different heights shall be provided in different files. While the height is specified in the precision of 1 m in the filename it can be stated up to a precision of 0.1 m in the measurement description.
- 4. Except for file header, only data rows allowed.
- 5. The file header shall somewhere contain a version number or name that specifies the file format. Whenever the file format changes, this version number shall change, too.
- 6. Use only and exactly one measurement timestamp per row. Additional secondary timestamps may however be used (e.g. for indicating the measurement interval).
- 7. All data rows within one file must have identical columns.
- 8. Data quality flags: basic flags for a whole row or for portions of a row shall always be provided having three possible values: good (0), questionable (1), bad (2). Other site specific flags may be used additionally.
- 9. Different Date/Time formats are okay, and therefore please let us know the formats you use.
- 10. All timestamps should be provided in UTC or local time (without light saving time). When using local time the difference to UTC must be communicated to us so that the upload procedure can calculate UTC from the timestamps in your files. Timestamps should always be in standard time, not daylight savings time. Timestamps will be stored up to a precision of one second.



Figure C.1

Illustration of the upload process

File-Upload-Description

Data set: Ochsenkopf CHIOTTO measurement				
Separator: " "				
Time: DDMONYYYY HH:MI:SS, Column 1, Column 2				
Location: "OXK", Height = Column3("S1" => 30, "S2" => 100), Unit = m				
Column 4: Species = O2, Variable = conc. delta_avg, Unit = %*10^4, NULL = -99999				
Column 5: Species = O2, Variable = conc. delta_sigma, Unit = %*10^4, NULL = -99999				
Column 6: Species = O2, Variable = conc. delta_avg, Unit = ppmequiv, NULL = -99999				
Column 7: Species = O2, Variable = conc. delta_sigma, Unit = ppmequiv, NULL = -99999				
Column 8: Species = O2, Variable = conc. delta_avg, Unit = permeg, NULL = -99999				
Column 9: Species = O2, Variable = conc. delta_sigma, Unit = permeg, NULL = -99999				
Column 10: Species = CO2, Variable = conc. avg, Unit = mV, NULL = -99999				
Column 11: Species = CO2, Variable = conc. sigma, Unit = mV, NULL = -99999				
Column 12: Species = CO2, Variable = conc. avg, Unit = ppm, NULL = -99999				
Column 13: Species = CO2, Variable = conc. sigma, Unit = ppm, NULL = -99999				
01DEC2002 00:06:59 S1 -24.400 1.100 -72.40 2.40 -411.86 8.50 48.17 1.10 383.34 2.60				
01DEC2002 00:08:59 S1 -32.375 1.100 -77.06 2.40 -440.63 8.80 44.89 1.10 382.86 2.60				
01DEC2002 00:11:59 S1 -22.762 1.100 -71.44 2.40 -406.06 8.80 48.25 1.10 383.35 2.60				
01DEC2002 00:13:59 S1 -16.500 1.100 -67.78 2.40 -384.71 8.60 44.11 1.10 382.75 2.60				
01DEC2002 00:15:59 S1 -19.900 1.100 -69.77 2.40 -397.31 8.70 40.92 1.10 382.28 2.60				

•A row of data is divided into one row per variable. The grouping is done by the time and location columns.

For an import some preparations are necessary:

- It would make implementation easier if we could have a small set of different file definitions. To have only one format over all sites seems unrealistic.
- Instead of having one upload script for each format it is a better solution to have a fileupload description for each format that can be interpreted by an upload script that has to be implemented only once. The file-upload-description can be altered if the format changes (e.g. new variables are included).
- This slide illustrates how such a description looks like. In this case the measured values are attached to the description. But it is also possible to have it in a separate file. The following things are described:
- Data set is the means for putting the data into the right place of the metadata.
- Separator is the sign separating the values
- For time and location format, fixed values and translations have to be described.
- For variables the column, species, name, unit and missing value (null) are described.
- Quality flags are treated like variables. They can describe the quality for a species or for all species at a site.
- Flags can be inserted automatically during uploading a file. Additionally flags can be inserted manually. Automatic and manual flags shall be distinguishable from each other.
- Standardization of flags and their values is of great help for reading data.
- Status is the result of assessing the values and their origin. In some cases it can be set automatically, in other cases this must be done manually.

C.4 Example of a File Upload Description

Example of File Contents

01DEC2002 00:06:59 S1 -24.400 1.10 -72.40 2.40 -411.86 6.50 48.17 1.10 383.34 0.83 0020 01DEC2002 00:08:59 S1 -32.375 1.10 -77.06 2.40 -440.63 4.80 44.89 1.10 382.86 0.81 0120

01DEC2002 00:11:59 S1 -22.762 1.10 -71.44 2.40 -406.06 3.80 48.25 1.10 383.35 0.15 0120 01DEC2002 00:13:59 S1 -16.500 1.10 -67.78 2.40 -384.71 3.60 44.11 1.10 382.75 0.29 0100 01DEC2002 00:15:59 S1 -19.900 1.10 -69.77 2.40 -397.31 5.70 40.92 1.10 382.28 0.34 0000

Descriptor Type Part/Variable Item Unit/Format Missing Value

Column Separator: ' '

Decimal Separator: '.'

Column 1: TimeStamp; Date; DDMMMYYYY

Column 2: TimeStamp; Time; HH:MM:SS

Column 4: Variable; OXK.CT-Ox.O2.conc_delta_avg[%*10^4]; %*10^4; -99999

Column 5: Variable; OXK.CT-Ox.O2.conc_delta_sigma[%*10^4]; %*10^4; -99999

Column 6: Variable; OXK.CT-Ox.O2.conc_delta_avg[ppmequiv]; ppmequiv; -99999

Column 7: Variable; OXK.CT-Ox.O2.conc_delta_sigma[ppmequiv]; ppmequiv; -99999

Column 8: Variable; OXK.CT-Ox.O2.conc_delta avg[permeg]; permeg; -99999

Column 9: Variable; OXK.CT-Ox.O2.conc_delta_sigma[permeg]; permeg; -99999

Column 10: Variable; OXK.CT-Li.CO2.conc_avg[mV]; mV; -99999

Column 11: Variable; OXK.CT-Li.CO2.conc sigma[mV]; mV; -99999

Column 12: Variable; OXK.CT-Li.CO2.conc avg[ppm]; ppm; -99999

Column 13: Variable; OXK.CT-Li.CO2.conc_sigma[ppm]; ppm; -99999

Column 14.1: Flag; OXK.CT-Ox.O2.Analyzer_Quality

Column 14.1: Flag; OXK.CT-Li.CO2.Analyzer_Quality

Column 14.2: Flag; OXK.CT-Ox.O2.Concentration_Quality

Column 14.3: Flag; OXK.CT-Li.CO2.Concentration_Quality

Column 14.4: Flag; OXK.CT.Lab_Quality

Three letter code for each tower (Use CMDL code if available):

Cabauw	CBW
Edinburgh	TTA
Florence	FIR
Hegyhatsal	HUN
Bialystok	BIK
Norunda	NOR
Ochsenkopf	OXK
Orleans	ORL

Appendix D Report of the CHIOTTO final workshop

SRTCA, Amsterdam, March 9 and 10, 2006



Figure D.1 Photograph of the participants taken during the workshop

D.1 List and summary of the presentations

Welcome message by Alex Vermeulen

Introduction by Alex Vermeulen

The meeting started of with an overview by the coordinator of the CHIOTTO project, its roots and history, objectives, means and achievements. The project started November 2002 and will end April 2006. Major achievement of the project is the design, construction and implementation of 8 automated, very high precision, continuous greenhouse gas observation systems at tall towers distributed over Europe. Major hurdles have been overcome in equipment availability, supplier delivery delays and logistical problems with tower owners. 7 towers are now delivering the envisaged continuous data stream as foreseen, one tower will become operational before the end of the project.

The project objectives proved to be overly optimistic and the agreed update of the precision requirements, common instrumentation setup and calibration and intercomparison protocols, agreed upon after the start of the project, required from every partner an enormous extra effort, originally not foreseen. But in the end the overall result stands out, so that by the end of 2006 a rich dataset for CO_2 and non- CO_2 greenhouse gas concentrations over Europe will become available to the scientific community.

D.2 Session 1 : The CHIOTTO project

Report of Hegyhatsal, Laszlo Haszpra, HMS (HU)

The GC system has been installed at Hegyhatsal in January 2006. Also the low level flux measurements have been restarted after replacing the broken old system. CO_2 concentration

profiles have continued during the whole project. Finally the telecom company could deliver the promised data line for remote control to replace the slow GSM connection. Now work has started for near-real time atomatic data transmission. The new web-site introduces better communication to the public and the scientific community.

Report of Ochsenkopf, Rona Thompson, MPI-BGC (D)

All systems at Ochsenkopf required and have got a major overhaul in this project. Work has finished for the CO_2 and O_2 systems, that now function very well. There is very good correlation between O_2 and CO_2 levels, results confirm the expected significant contribution from fossil fuels to these signals in winter time. In the final month the improved GC system will be placed at Ochsenkopf, together with temperature control for Licor and Oxzilla for further improved accuracy.

Report of Cabauw, Alex Vermeulen, ECN (NL)

Also at Cabauw all systems were improved in this project. All new instrumentation was installed at the tower in November 2004. After a startup phase of a few months now all measurements run well with very good data coverage, except for CO. The old setup continued to be operational until April 2004. The first ICP was performed for Cabauw at January 2006. All data has been submitted to the CHIOTTO and CE-IP database. Data is updated near real-time to the lab and the web-site.

Report of Angus, John Moncrieff, UEDIN (UK)

Angus Tall tower became fully operational August 2005. ²²²Rn measurements are available already since 2003. The measurement performance is well within the precision targets. CO₂ measurements will be improved further before the end of the project. Problems with failures of the cryogenic water trap caused some data loss. First ICP performed February 2006.

Report of Orleans, Cyril Messager, CNRS (F)

All instrumentation is ready for installation at Orleans by March 2006. Tower owner now finally agreed on contract. Measurements now have been performed at Gif, precision of all systems is up to par.

Report of Bialystok, Elena Popa, MPI-BGC (D)

Bialystok Tall Tower is operational since July 2005. The system was improved further by a new PC and removal of the rotameters. ECD has been polluted by problem of carrier-gas. Concentrations measured look consistent, comparison with flask measurements also ok. First intercomparison was performed in November 2005.

Report of Firenze, Paolo Stefani, UNITUS (I)

Tower became operational in September 2005. Absolute values of GC concentrations and precisions still need to be improved. Unfortunately the tower will have to be abandoned. A new location is found near Orvieto.

Report of Norunda, Anders Lindroth, LUND (S)

The TDL system now is operating in eddy correlation mode. Significant and consistent emissions are found from the forest site, indicating indeed some 'Keppler' fluxes of CH_4 from growing woody material.

Report of La Muela, Josép Morguí, BARC (ES)

La Muela tower was equipped December 2005. Tubing will have to be redone March 2006. Problems with stability of Licor 7000 measurements due to introduction of zero gas.

The CHIOTTO quality control program, Martina Schmidt, LSCE (F)

Tall towers are also part of network of CE-IP. The ICP and other quality programs of these projects will be merged and developed further. New in the CHIOTTO approach were the

common measurement setup, equipment list, production of common high purity and high precision calibration gases and a frequent intercomparison scheme. Implementation took longer than expected, but now more than 70 cylinders have been produced by MPI-BGC. These ideas have evolved and are and will be developed further in e.g. TACOS and CE-IP. Most partners followed harmonisation standards. First intercomparison campaign has started, ending within the project timeline.

D.3 Session 2 : (Inverse) model studies for CO₂

Regional Scale Simulations of CO2- Comparison with Measurements at CHIOTTO Towers, Ute Karstens, MPI-BGC (D)

REMO model simulations were shown for CO_2 and compared with the tall tower measurements at Cabauw and Hegyhatsal. Correspondance is better for winter than summer. CASA biogenic fluxes perform better than SIB, but for HEG large anomalous uptakes are found around noon. Better performance for lower levels of the towers (r^2 up to 0.63). Diurnal cycle captured relatively well, unless IER fossil fuel emissions are used. Low correlations for mean daytime values of concentration. At Cabauw signal is determined for 50% by biosphere, for Hegyhatsal this is considerably more.

Results from the WLEF tall tower, Wisconsin, Ken Davis, PSU (USA)

An overview was given of the history of the US tall tower program starting 1992 and its results until now. Will tall tower concentrations bridge the gap in time and space between flux upscaling and inverse model downscaling? Cheas project around WLEF tower as testbed in very heterogeneuous forest system. WLEF tower data shows a major source of CO_2 , flux towers show net sink, interannual variability is large. Respiratory fluxes seem to make the difference, not seen at flux towers, but seen in tall tower in fluxes and concentrations. Regional upscaling results with independent methods seem to agree well, but uncertainties still big. Virtual Tall Tower concept tested further for midday obs only, more tall tower vertical data is needed for gradient functions. Tall tower data useful, better with additional flux data and accompanying flux sites: ring of towers.

Regional Inversions Using SiB-RAMS, Scott Denning, CSU (USA)

A very high resolution (1 km) simulation with SIB flux model coupled to RAMS for period of 10 days show the coherent structures of CO_2 in the PBL, combining transport with fluxes, both driven by meteorology and landuse/vegetation. Simulation agrees more or less with observation. Problems of upscaling high res. flux measurement results in continental scale inversion, the local measurements reduce uncertainties for only very small regions. Ring of tower show coherent structures in obs. Here high res inversion show weak constraints of obs on inversion result. How to specify temporal and spatial correlation patterns for flux observations to improve error reduction in inversion? Delphi says: 'The atmospheric data are not sufficiently dense to constrain fluxes without them'

Towards an estimate of daily European CO2 fluxes at model resolution by inversion of atmospheric transport, Leo Rivier (replacing Claire Carouge), LSCE (F)

High resolution (0.5 degree) CO_2 simulation for 2001 using LMDZ, in Europe daily (ORCHIDEE) fluxes, otherwise monthly. Different temporal and spatial correlation patterns were tested, spatial aggregation to 400x400 km, temporal aggregation to 10 days. Using tall tower sites flux error reduction for Europe around 30%. Data selection on obs has significant impact of inverted flux field. More obs are needed to contrain problem. Transport error and fossil fuel flux field most important for possible biases. Will improve PBL scheme and use more data.

Uncertainties in regional scale inversions using tower data, Christoph Gerbig, MPI-BGC (D)

The LPDM model STILT was applied to several measurements from aircraft (COBRA) and towers (Harvard forest). Uncertainties in model and parameters (5 ppm expressed in CO_2 conc) outweigh measurement errors. To infer fluxes from (inverse) models emphasis should be on more data, and model improvement, specifically to reduce transport errors and to reduce errors in the PBL (improved z_i). Should add ceilometers to (flux) tower sites. Vertical profiles over the American continent show that CO_2 variability is found mainly in the PBL.

Comparing forward COMET model results with tall tower CO2 measurements, Gerben Pieterse, ECN (NL)

COMET trajectory two-layer model applied to Cabauw and Hegyhatsal data for CO_2 . $r^2 0.72$ for Cabauw 2002 using in-line SWAT model (MLBC), soil respiration still missing. MLBC CO_2 plant module performs well, illustration for 2003 summer drought in SE France. Comparison with Euroflux sites reasonable. Model will join TRANSCOM comparison.

Title?, Manuel Gloor, Uni Leeds (UK)

Of course there are blobs of greenhouse gases in the atmosphere, there is also long range coherence. Problem is that inversions are still inherently unstable. Can be circumvented by doing budget studies measuring in- and outbound flows (airplane obs): no inversion needed. Example for NACP campaigns. Also in this approach problems with advection or flows trough lid of the box (minor).

Source sink discrimination within the footprint of the Cabauw tower, Herbert ter Maat, Alterra (NL)

RAMS simulation with nested grids, highest res 2 km. Use HYPACT LPDM within RAMS at highest res. Hourly fluxes from CO₂ from SWAPS-C and EDGAR FT scaled down in time and space using pop. dens + statistics. Flux and concentration footprint of Cabauw per hour. CO₂ flux, LE underestimated, H overestimated. Windspeed factor 2-3 higher than obs. CO₂ diurnal variation at CBW (May) ~7 ppm. Simulations suggest that Cabauw is for this period mainly influenced by fossil fuel emissions.

The NOAA/ESRL Tall Tower Trace Gas Observing Network: Scientific Objectives and Network Design, Arlyn Andrews, NOAA ESRL (USA)

An overview was given of the NCAP and NOAA's tall tower program, status and plans. Now 3 tall towers, 2 are planned for 2006, 7 more before 2009. Unfortunately a major budget cut for 2006. Experiment to see how footprint gets affected when network gets less dense, STILT model with SiB fluxes+Takahashi+Fossil. NEE concentration response on towers 0-20 ppm. Transport causes day-to-day variation in daytime concentrations. Agreement between modeled and measured depends on flow pattern and source region. Sensitivity to sources is sometimes lost quick, low coherence, at other times larger sensistivities persist for several days, convection processes? More analysis of current data needed and underway, remaining questions concern measurement setup: how tall should we get, what's the optimal horizontal spacing, how to gain from multi-component obs.

Tall tower measurements in global CO_2 inversions, Christan Rödenbeck, MPI-BGC (D)

Comparisons of CHIOTTO data with forward simulations from the TransCom-Continuous model comparison (version 5.0) were shown. The ability of present-day atmospheric models (in particular global models) to simulate tall tower concentrations may be improved by a careful data selection. Strategies are still inconclusive, however, and will need to be specific for each site. Inappropriate selection may even deteriorate model-data mismatch. Further, a recent study was presented according to which systematic measurement errors are only a minor source of errors in present-day global inversions.

D.4 Session 3 : (Inverse) model studies for non CO₂ greenhouse gases

Allistair Manning, UKMO (UK)

NAME model runs on high res RACMO model meteorology.10 day backward particles. Baseline detection on concentration record by air origin filter and statistical filter (outlier removal), line-fit on the background. No a priori emissions, using 1995-2005 Macehead data+6 GAW stations. Simulated annealing for source area emission estimate. Macehead only: No emission reduction for CH_4 detected in period 1995-2005! Using other station give highly varying results, depending which ones you add and how you try to correct/mask for local influences. Emission estimate for Europe ranges from 9-18 Mt/y.

Peter Bergamaschi, JRC Ispra (I)

New TM5 (1 by 1 degree zoom) forward calculations for 2005 using Schauinsland and Cabauw. Good agreement between obs and model for all levels, also for NOAA flask sites. Pallas 2002 en 2005 indicate smaller emissions than inventory for Finnish wetlands. For synoptic events at Cabauw TM5 shows significant influences on concentration of UK, France, Germany. For some summer events at Schauinsland positive offset of measurements (50-100 ppb), OH field or remote wetland emissions in free troposphere air? Downward bottom-up emission trend again not confirmed by updated TM5 inverse results.

Doris Folini, EMPA (CH)

Interpretation of Junkfraujoch data by LM-LPDM (Meteo Swiss) model, driven by 7 km res. meteo fields of Meteo Swiss. Model height JFJ: 2600 (real: 3600). 75 million particles for footprint analysis per a year (25000 per 3 hour), 3 days backwards. Test with CO emissions (EMEP, not regridded completely ok). R^2 =0.4. Wintertime is better R^2 =0.6-0.8. Sampling height should be taken variable. Footprint JFJ covers CH, Eastern France, Northern Italy. Inversion results (simulated annealing) not yet conclusive, method works.

Alex Vermeulen, ECN (NL)

COMET model put to test, performance for methane at Cabauw for year of hourly obs: R2=0.72. Daytime better performance R2=0.84. Periods of several weeks with R2>0.9. Performance improves with averaging time. Performance lower for mixing layer transition times (8-10 UTC) and some summer months of 2002 (less obs available). COMET model insensitive to assumptions on reservoir layer height and radius of region of influence around trajectory (as long as bigger than 20 km and smaller than 60 km at arrival). SVD inversion with automatic source aggregation allows for inverted fluxes at highest spatial resolution depending on the footprint density for a region. More stations give added value for spatial resolution and emission uncertainty. Now wait for the first full year of real data for emission estimates...

D.5 General questions, issues and topics raised

Do we need more measurements and which type will this have to be?

How to choose/balance between surface, surface flux, tall tower and airplane measurements? Can we compromise on the measurement precision as the models are/will not be good enough

anyway?

Is the expected natural variability of the concentration signal not much higher than our precision requirements?

What are the model improvements needed to better match the observation scales in time and space, do we have to capture all local scale variability or do the measurements not pick this up also?

We seem to agree that model transport errors should be reduced anyhow, anyway soon and that most importantly the description of the PBL in models is top priority, matched with observations (ceilometers/radiosondes).

How and/or do we have to take care of local scale variability? Is this really relevant for atmospheric inversions?

All agree that tall tower measurements are an important part of any observation system, deploying its data is still difficult as the models are just not good enough yet. But improvements are possible, but there are quite some roads to follow.

The combination of tall towers with concentration and flux measurements and nearby surface flux towers can be of great value. More studies are needed. Transcontinental cooperation and using each others data in the different models seems worthwhile.

What is the added value of additional tracers?

There seems to be more consistency and structure in atmospheric data than can be reproduced by the current models.

Model intercomparison is crucial for model improvements.

D.6 Actions

In the discussion at the end of the meeting we mainly discussed on how to carry on after CHIOTTO ends, now the Manometer proposal has failed and support from GEOMON IP (if it runs) is quite minimal.

- The CHIOTTO partners will write a sound scientific report within the deadline and we will write at least two articles on CHIOTTO and its achievements.
- Anyway the CHIOTTO partners will meet during small CEIP Tall Tower Meetings at CEIP (Atmosphere) events for the years to come.
- The coordinator will make up a Memorandum of Understanding (MoU) that CHIOTTO partners can sign in which they agree to continue the cooperation and the sharing of measurement data between the groups like after the finishing of the CHIOTTO project. This is particularly useful for the non-CO₂ data, as the CO₂ and CO data is part of the CE-IP. We can use the CHIOTTO database at MPI and the discussion forum at <u>www.chiotto.org</u> that will both be continued and supported.
- Anders Lindroth will work together with the other PI's on a scientific proposal for ESF targeted at the continuation and use of the tall tower data in modelling
- We agreed to join forces in defining future FP7 project proposal(s) and possibly a NoE later this year in order to get more support for continuing the measurements and to deploy the datasets gathered.

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D.7 List of participants of the CHIOTTO final workshop, March 26, A'dam

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