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**AGACC-II:
Advanced exploitation of Ground-based measurements for Atmospheric Chemistry
and Climate applications - II**

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

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ACRONYMS, ABBREVIATIONS AND UNITS

ACE	Atmospheric Chemistry Experiment
AERONET	AERosol ROBotic NETwork
AGACC	Advanced exploitation of Ground-based measurements for Atmospheric Chemistry and Climate applications
AGAGE	Advanced Global Atmospheric Gases Experiment
ALADIN	Aire Limitée Adaptation dynamique Développement InterNational
AOD	Aerosol Optical Depth
BC	Black Carbon
BIRA-IASB	Belgisch Instituut voor Ruimte-Aeronomie – Institut d'Aéronomie Spatiale de Belgique
BLH	Boundary Layer Height
BRAIN	Belgian Research Action through Interdisciplinary Networks
CBH	Cloud Base Height
CCI	Climate Change Initiative
CFC	ChloroFluoroCarbon
CI	Colour Index
CHIMERE	Name of a multi-scale chemistry-transport model for air quality forecasting and simulation
CIMEL	Commercial provider of sunphotometers
COST	European Cooperation in Science and Technology
CST	Cumulative Sum Technique
CTM	Chemistry-Transport Model
CW-CRDS	Continuous-Wave Cavity Ring-Down Spectroscopy
DOFS	Degrees of freedom
ECMWF	European Center for Medium range Weather Forecasting
EGU	European Geosciences Union
EMPA	Eidgenössische Materialprüfungs- und Forschungsanstalt
ESA	European Space Agency
EU	European Union
EUMETNET	Network of European Meteorological Services
FIR	Far-InfraRed
FP7	Seventh Framework Programme
FTIR	Fourier Transform InfraRed
FTS	Fourier Transform Spectrometer
GCOS	Global Climate Observing System
GFED	Global Fire Emissions Database
GEISA	Gestion et Etude des Informations Spectroscopiques Atmosphériques (Management and Study of Atmospheric Spectroscopic Information)
GEOS	Goddard Earth Observing System
GHG	GreenHouse Gas
GOME	Global Ozone Monitoring Experiment
GWP	Global-Warming Potential
HITRAN	High resolution TRANsmission database
IASI	Infrared Atmospheric Sounding Interferometer
ICOS	Integrated Carbon Observing System
IR	InfraRed
JGR	Journal of Geophysical Research
JQSRT	Journal of Quantitative Spectroscopy and Radiative Transfer
KMI-IRM	Koninklijk Meteorologisch Instituut – Institut Royal Météorologique
LACy	Laboratoire de l'Atmosphère et des Cyclones
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
MAXDOAS	MultiAXis Differential Optical Absorption Spectroscopy
MIR	Mid-InfraRed
mK	milliKaiser (0.001 cm^{-1})
MLH	Mixing Layer Height
MWW	Mann-Whitney-Wilcoxon

NDACC	Network for the Detection of Atmospheric Composition Change
NIR	Near-InfraRed
NORS	Demonstration Network Of ground-based Remote Sensing Observations in support of the Copernicus Atmospheric Service
O3MSAF	Satellite Application Facility on Ozone and Atmospheric Chemistry Monitoring
OC	Organic Carbon
OMI	Ozone Monitoring Instrument
OPAC	Optical Properties of Aerosols and Clouds
PAN	PeroxyAcetyl Nitrates
PBL	Planetary Bounday Layer
PI	Principal Investigator
PICARRO	Commercial provider of greenhouse gas analyzers
PMW	Pettitt-Mann-Whitney
PPM	Primary Particulate Matter
pptv	Parts Per Trillion by Volume
RH	Relative Humidity
SOA	Secondary Organic Aerosols
SSA	Single Scattering Albedo
STCE	Solar-Terrestrial Centre of Excellence
TCCON	Total Carbon Column Observing Network
TDL	Tunable Diode Laser
TOPROF	Towards operational ground based profiling with ceilometers, doppler lidars and microwave radiometers for improving weather forecasts
ULB	Université Libre de Bruxelles
ULg	Université de Liège
UNEP	United Nations Environment Programme
UTINAM	Univers, Transport, Interfaces, Nanostructures, Atmosphère et environnement, Molécules
UV	UltraViolet
VOC	Volatile Organic Compound
WMO	World Meteorological Organization
WOUDC	World Ozone and Ultraviolet Radiation Data Centre
WP	Work Package

1. EXECUTIVE SUMMARY

The overall objective of the project is to advance ground-based remote sensing techniques for studying atmospheric chemistry and climate. The measurements are embedded in international networks, they are complementary to satellite observations and support satellite and model validation. The associated research contributes to current international research agendas.

After this third year of the project, we see that some tasks have already been concluded, with interesting results, and other tasks that requested some preparatory work, are now starting to deliver results. As during the first half of the project, a good collaboration between the partners has taken place.

A first focus of the project is on ground-based solar absorption infrared observations of major greenhouse gases, at the Jungfraujoch (ULg) and at Ile de La Réunion (BIRA-IASB).

At the Jungfraujoch, historic data from grating spectrometers have been joined to present data from Fourier-transform spectrometers (FTS). This required thorough re-analysis of the historic data and checks on data consistency. After the previous successful work on CH₄ and N₂O, the historical data have been analyzed with the objective to also extend the time series of CO₂ column abundances back to the past. Unfortunately, it was found that the available spectra do not allow any extension before 1985, when the first observations with FTS started. Laboratory work on the CO₂ spectroscopy has been initiated.

The greenhouse gas measurements at Ile de La Réunion, now part of the Total Carbon Column Observing Network (TCCON), were continued continuously, apart from some interruptions due to instrumental failures. The acquired data are submitted on a regular basis to the TCCON database. Good progress has been made as to the comparison between quasi-simultaneous CH₄ and CO data at Ile de La Réunion acquired in the frame of NDACC and TCCON, recorded in the mid-infrared and near-infrared spectral domains, respectively. In particular, for CO, the agreement looks very good in general, and for CH₄, the final results will be obtained in 2014. This work has been carried out in collaboration with other NDACC and TCCON partners and reported in the frame of European projects (ESA CCI Greenhouse Gas project for CH₄ and NORS EU FP7 project for CO). The Réunion TCCON data are also included in the EU FP7 project ICOS_Inwire, and will be made available to the ICOS community at latest 3 weeks after acquisition.

Good progress has also been made to retrieve the additional greenhouse gases CF₄ and CCl₄ at the Jungfraujoch. The work on CCl₄ was already published in 2012. In 2013, the final time series for CF₄ has been analysed: annual emissions have been characterized and a very consistent picture was found when comparing to other ground-based, balloon- and space-borne data. CF₄, which has a very long lifetime and a strong warming potential, is still increasing at a rate of order 1%/year. The results have been published and will be included, together with the results on CFC-11, and -12, HCFC-22 and CCl₄, in the next WMO Assessment on Ozone Depletion (2014).

A second focus of the project is the advanced detection of volatile organic compounds (VOCs) at Jungfraujoch (ULg and BIRA-IASB) and Ile de La Réunion (BIRA-IASB), underpinned by laboratory spectrometric work.

The laboratory activities have focused on the most abundant isotopologues of formaldehyde (H₂¹²C¹⁶O), ethane (¹²C₂H₆), and ethylene (¹²C₂H₄). As to H₂CO, HgCdTe detector non-linearities have been identified as the origin of inconsistencies in intensities measured in the tunable diode laser (TDL) spectra (as reported last year) and a correction method is being developed. This correction will soon be effective, allowing the analysis of the H₂CO spectra to proceed.

For C₂H₆, linelists including line positions, intensities and lower state energies and assignments have been generated for the ν_7 and the $\nu_8+\nu_{11}$ bands; additional shape-specific parameters will be added to make them better suitable for atmospheric applications.

The experimental work for the ν_7 band of C₂H₄ has yielded line intensities and self-broadening coefficients. Based hereupon, the corresponding line intensities in HITRAN 2012

have been corrected and the self-broadening coefficients have been included; in other words, an updated HITRAN linelist has been delivered.

At Jungfraujoch, a final time series for methanol (CH_3OH) has been analysed for diurnal and seasonal variations and long-term trends.

The formaldehyde time series has been revised using the 6 microwindow approach developed for Réunion Island. This new time series shows a strong seasonal cycle with a consistent maximum in summer related to biogenic sources and enhanced methane oxidation, which appears to be in good qualitative agreement with collocated MAXDOAS data and model simulations. Also a decreasing trend ($-1.4\% \pm 0.2\%$) is observed.

The FTIR data however appear generally lower than the MAXDOAS and the model (GEOS-chem and IMAGES) data; this discrepancy requires additional investigations.

The HCFC-142b time series for 2000-2012 has been analysed: it is characterized by a strong increase by about 6.5%/yr, which is commensurate with AGAGE observations at Mace Head.

At Réunion Island, preliminary retrievals have been performed for CH_3Cl and C_2H_4 . It is remarkable that the quality of the spectra (signal-to-noise ratio), and therefore of the retrievals, has strongly increased since the installation of the new Bruker 125HR and after adjustment of the measurement settings. This work will be finalized in 2014.

The third objective of AGACC-II is to advance the detection and understanding of aerosol properties. Several instruments for aerosol characterization are now operational at Uccle; the nephelometer will be implemented early 2014. Also retrieval algorithms for the MAXDOAS data have been improved, especially regarding cloud screening methods, and modelling tools are operational.

BIRA-IASB and KMI-IRM are collaborating in the comparisons and interpretation of the data at Uccle. First comparisons concern the aerosol optical depths (AOD), and extinction profiles from the MAXDOAS with mixing layer heights from the ceilometer. Also comparisons between observed and modeled (using CHIMERE and OPAC) single scattering albedos (SSA) and AOD and the establishment of relationships between observed SSA/AOD and the source of the aerosol obtained via back trajectory analyses are ongoing. This study will be finalized in 2014.

A study regarding trends in UV, global radiation, total ozone and AOD at 320 nm, and their mutual correlation has been finalized, and will be published. It has been found that more than 98% of the total variation in UV can be explained by the combination of global radiation (most impacting factor), ozone and AOD.

The retrieval of SSA from Brewer seems to be too sensitive to different retrieval input parameters, and will probably be abandoned.

The fourth target of AGACC-II is the initiation of an atmospheric observatory in Bujumbura, Burundi. After preparatory work in the previous years, a MAXDOAS and a CIMEL sunphotometer have been installed and are now operational. The first results show that the instruments are working well and that the agreements with correlative data, e.g., for formaldehyde, are within their uncertainties. More data will be acquired and more work will be carried out to analyse the data.

The AGACC-II results are well disseminated in the scientific community, especially the NDACC and TCCON communities, the satellite teams and the modeling community, as well as in the community dealing with laboratory spectroscopy for atmospheric applications. But, as mentioned here above, additional outreach actions include, e.g., contributions to the WMO Assessment on Ozone Depletion, to the ICOS community, and to EU and ESA projects in which some partners are involved.

A flyer about the project is ready to be published; the Website is updated regularly. AGACC-II has also contributed to a brochure about the Science for Sustainable Development Programme that will appear in 2014.

2. INTRODUCTION

2.1 Context

The AGACC-II research contributes to international ground-based remote sensing networks and their expansion, in terms of capabilities and in terms of sites. It also contributes to global change research in general. It includes laboratory experiments in support of the remote sensing observations. It combines the expertise in the field of remote sensing and laboratory spectroscopy of the 4 Belgian partners involved in the project, and that of the networks in which the work is embedded. Moreover the partners have strong collaborations with satellite teams and the atmospheric modeling community, for the interpretation of the observations.

The project also intends to start an atmospheric observatory in Africa, in particular in Burundi, and therefore to initiate a collaboration with the University of Bujumbura in Burundi. Africa is an undersampled region; still it is an important source of biogenic compounds and biomass burning products.

2.2 Objectives

1. The first major objective is to improve or expand the measurement capabilities for greenhouse gases (CO_2 , CH_4 and N_2O , as well as CF_4 and CCl_4) with FTIR spectrometers at Jungfraujoch and Ile de La Réunion, to make Ile de La Réunion a site affiliated to the Total Carbon Column Observing Network (TCCON), and to deliver long-term trends of the major greenhouse gases at the Jungfraujoch back to 1976.
2. Secondly, we aim at extending the measurement capabilities of ground-based FTIR spectrometry to various volatile organic compounds (CH_3Cl , CH_3OH , PAN, acetone) and to some CFC-substitutes, and consequently, using also the results for CCl_4 and CF_4 mentioned above, to establish representative CCl_y and CF_y budgets at the Jungfraujoch, including the contributions from the new AGACC-II halocarbons and of the standard FTIR products (CFC-11 and -12, HCFC-22). It is also planned to revise the time series for C_2H_4 , C_2H_6 , H_2CO based on better laboratory data, at Jungfraujoch and Ile de La Réunion.
3. The remote sensing measurements in AGACC-II are of spectrometric nature. As such, they entirely depend on the availability of reference spectroscopic information for the target species, measured in the laboratory. Although such an information exists, its completeness and accuracy for instance do not necessarily meet the requirements of current atmospheric research and may introduce biases in the results obtained and conclusions drawn. Reference spectroscopic information is bound to evolve because it can be very difficult to measure accurately in the laboratory and such activities are intimately linked with technological progress and financial support. A third objective of AGACC-II is to provide improved laboratory spectroscopic data in support of the above objectives 1 and 2.
4. Fourth, we aim at advancing our understanding of aerosol characteristics above Ukkel and to estimate the aerosol direct radiative forcing above Ukkel. Therefore the underlying objectives are
 - to retrieve more information regarding aerosol properties from remote sensing measurements with Brewer and MAXDOAS spectrometers;
 - to deploy a lidar ceilometer at Ukkel;
 - to combine the information from all instruments including those from the CIMEL sunphotometer, for a more comprehensive evaluation of the aerosol properties at Ukkel;
 - to derive information about the aerosol sources by modeling with CHIMERE and backtrajectory studies;
5. The fifth objective is to implement MAXDOAS measurements in Bujumbura (Burundi, Africa) for the measurement of aerosol and ozone precursors (NO_2 , glyoxal, H_2CO , ...) and to study the export of African emissions to the Indian Ocean (Ile de La Réunion).

6. And finally, we want to make sure that the results of the project are disseminated appropriately and that they are integrated in national and international environmental assessments in support of policy makers.

2.3 Expected outcomes

The new data that we aim to obtain in AGACC-II will be very useful for global and regional chemistry-climate models, as they provide means to verify the emission databases and the models that are used for understanding atmospheric processes and biogeochemical cycles, and for forecasting the future state of the atmosphere and climate. Moreover, the laboratory and the field data will be delivered to international databases like the HITRAN and GEISA databases, and the NDACC and TCCON databases, respectively. They will also be integrated in regional and global assessment reports. Some of the results will appeal directly to policy makers: long-term trends of greenhouse gases, aerosol direct radiative forcing above Ukkel, organic chlorine and fluorine budgets... But on the longer term, all the AGACC-II results will be relevant to environmental policies, because monitoring of atmospheric composition changes is a fundamental ingredient of any environmental assessment in support of policy makers.

The proposed research is also embedded in the international research programmes to which the partner institutes contribute and it will involve interactions with the international research community. It will strengthen the role of Belgium in NDACC. Moreover, it enables Belgian researchers to join TCCON, another important international observation network cooperating with NDACC, which will probably be integrated in the near-future in ICOS, the Integrated Carbon Observing System.

3. SCIENTIFIC METHODOLOGY

Overall methodology

In AGACC-II, several ground-based remote sensing observation techniques are further developed, improved and exploited for the study of the Earth atmosphere composition and the link with climate. The progress is mostly situated in the development and improvement of the spectral data analysis algorithms. The targeted techniques are Brewer, MAXDOAS and Fourier transform infrared (FTIR) spectrometry, as well as sunphotometry. An aerosol lidar (ceilometer) has been installed at Ukkel in 2011 and is now operational as well. In addition, we managed to acquire an aethalometer and nephelometer, that are now deployed in Ukkel¹ and maybe, at some time, for a campaign in Bujumbura. Most of the instruments exploited in the project are integrated in global observation networks, like the Network for the Detection of Atmospheric Composition Change (NDACC), the Total Carbon Column Observing Network (TCCON), and AERONET. The observation sites included in the project are Ukkel (50.5°N, 4°E), Jungfraujoch (46.5°N, 8°E), and Ile de La Réunion (21°S, 55°E), and Bujumbura (3°S, 29°E) in Africa where a MAXDOAS spectrometer and a CIMEL were installed successfully in 2013.

The project also includes dedicated laboratory experiments to support the field observations, and modeling exercises (via collaborations) for an enhanced interpretation of the measurements.

Dedicated tasks

WP1. Exploitation of FTIR spectra to derive useful geophysical information for a suite of GHGs (CO₂, CH₄, N₂O, CF₄, CCl₄)

Task 1.1 Produce time series for the major greenhouse gases CH₄, N₂O and CO₂

Task 1.1.1

Within the framework of *task 1.1.1*, it is intended to re-analyze historical observations recorded at the Jungfraujoch station with a high-resolution grating spectrometer in order to extend the total column time series of important GHGs back in time. These observations correspond to narrow spectral intervals in the mid-infrared which were specifically selected to encompass absorption lines of gases of atmospheric interest, among which CH₄ and N₂O. More than ten thousand double-pass grating spectra were recorded from 1977 to 1989.

Over the reporting period, all available observational subsets (various diffraction orders and slit widths were used, resulting in spectral resolution from about 7 to 13 mK) have been investigated to identify suitable lines allowing total column determination of CO₂, a gas which was not a specific target of this pioneering observational effort.

Task 1.1.2

TCCON compliant measurements of CO₂, CH₄, N₂O and CO in St. Denis on Reunion Island started in September 2011. In 2012 the site was recognised as an official part of the TCCON. The past year was very productive for the Reunion site: while no measurements were performed during the months January and February due to a faulty laser tube, there were no significant interruptions in the measurements for the rest of the year until the end of November. In total, the system was not operational for 98 days between January 1 and November 26 2013. Of those 98 days, 56 are due to the laser problem at the beginning of the year. At the end of March there was a problem with a reference switch for the solar

¹ The installation of the nephelometer will occur early 2014.

tracker. The remaining days were mostly lost due to power-cuts and maintenance of the electrical and network systems at the University of Reunion where the instrument is hosted. During the first week of October 2013, the systems of the St. Denis TCCON site were upgraded. A new solar tracker was installed, and the solar-tracking software was upgraded based on the CamTracker principle (Gisi *et al.*). In this system, the camera-image of the sun on the entrance aperture of the spectrometer is analysed in real time to give feedback to the motors of the tracker, this results in a smoother, better tracking of the centre of the Sun, which improves the quality of the acquired interferograms and the resulting spectra. The analysed and quality-checked data from the Reunion TCCON site is regularly uploaded to the TCCON database at Caltech. The Reunion Island TCCON data is freely available to the public three months after acquisition (<http://tccon.ipac.caltech.edu/>). This year, a BRAIN pioneer project was approved in which we aim to calibrate our TCCON measurements with in-situ atmospheric profiles. If successful, this will grant our site a full TCCON status.

Task 1.1.3

This task comprises the comparison of the retrievals in the near- and mid-infrared. Figure 1 shows the X_{gas} results of the CH_4 retrievals from the TCCON (near-infrared) and NDACC (mid-infrared) measurements at St. Denis. Each datapoint in the plot represents the mean value of the measurements during a 6-hour interval.

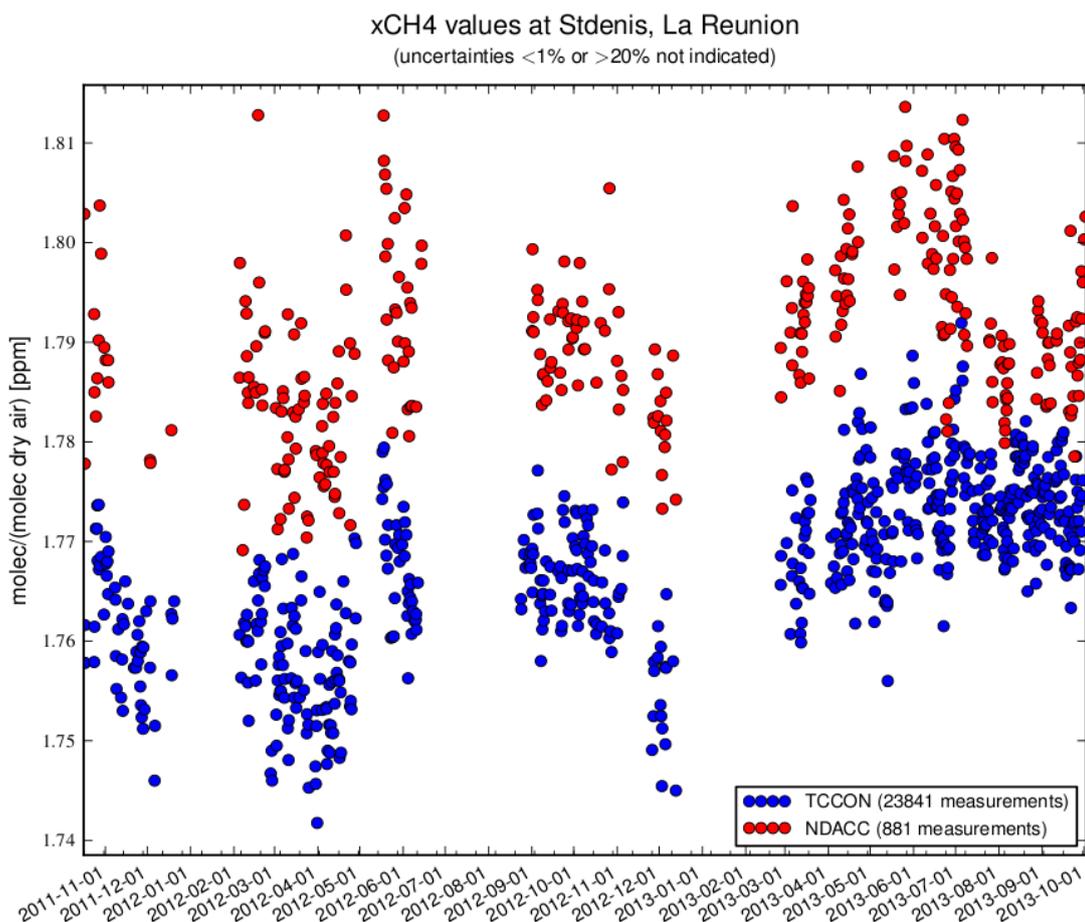


Figure 1: A comparison of the retrievals of X_{CH_4} in the NIR (TCCON) and MIR (NDACC).

Although the same events are captured in the timeseries of the NIR and MIR measurements, there is a bias of 1.3% between the results from the different spectral domains. It should be noted that this bias depends on the NDACC strategy that is used. There are different strategies for CH_4 retrievals in the NDACC, these differ in their choice of microwindows, spectroscopy, modelling of the instrument response and retrieval method. It is principally the choice of microwindows and spectroscopy which has an influence on the results of the retrievals. In Figure 1, a strategy proposed by Frank Hase (based on the strategy proposed

in the discussion of Sussmann *et al.*, 2011) is used for the retrieval; when another strategy is used (proposed by Sussmann *et al.*, 2011), the bias changes to 1.6%.

The choice of microwindows and the spectroscopy of the absorption lines has a clear influence on the bias. In the next year, the MIR spectra will be re-analysed with the latest new version of the SFIT analysis software (SFIT4), which uses updated linelists: HITRAN 2012 and ATM (version 20120409) for CO₂, CH₄ and H₂O.

Task 1.2 Investigate additional greenhouse gases: CCl₄ and CF₄

As to carbon tetrafluoride (CF₄), a very long-lived GHG, a retrieval strategy using ground-based FTIR spectra has been set up for the first time and a complete error budget has been established. The two-decade time series produced earlier in the course of the project was carefully analyzed and the results were compared to other CF₄ data sets derived from in situ sampling and from solar observations performed from balloon or space platforms.

Task 1.3 Provide laboratory spectroscopic data for CO₂ and N₂O if needs emerge

In collaboration with the UTINAM Institute of the Université de Franche Comté in Besançon, an experimental and theoretical study of self broadening, shift and first-order line-mixing coefficients for the $\nu_1+3\nu_2^1$ band of carbon dioxide observed near 3340 cm⁻¹ has been started this year. It relies on ten spectra of pure CO₂ recorded at pressures from 3 to 903 hPa (with 55 meters absorption path and at 293 K), using the FTS available at ULB. A resulting improved description of this spectral absorption region of carbon dioxide is anticipated.

WP2. Volatile Organic Compounds (VOC) and CFC-substitutes in the troposphere

Task 2.1 Methanol (CH₃OH) and other VOCs at Reunion Island and Jungfraujoch

The CH₃OH retrieval strategy has been finalized. Two wide windows are fitted simultaneously (992-1008.3 & 1029-1037 cm⁻¹), providing unprecedented information content. The typical DOFS is equal to 1.8, with vertical sensitivity spanning the 3.6-15 km altitude range. A complete uncertainty budget has been carefully evaluated, including systematic and random contributions. We found e.g. that typical random errors amount to less than 5% for the total columns, to less than 20% for the tropospheric columns. A final data set has been produced and analyzed for the 1995-2012 time period.

Reunion Island:

Retrievals of CH₃OH have been performed and published in the first years of AGACC-II (Vigouroux *et al.*, 2012; Stavrakou *et al.*, 2011).

We have performed tests in order to optimize a retrieval strategy for CH₃Cl at Reunion Island. We use a micro-window around 2967 cm⁻¹, where the main interferences are CH₄, H₂O and isotopologues of H₂O. The spectroscopic signature of CH₃Cl is very weak, so the random error budget due to the signal to noise ratio should be very large. Indeed, a very large scatter is seen in the retrieved total columns. This scatter observed at St-Denis is nicely reduced when the instrumentation has moved from Bruker 120M to Bruker 125HR, due to the better quality of the new spectra, especially since April-May 2013 with the improvement of our settings (6 scans are co-added per spectrum instead of 4). Also the interference with water vapour and methane being smaller at the Maïdo observatory thanks to the higher altitude of the site, the scatter is even smaller there.

However, the interference with methane is an issue, and we want to test very soon the new HITRAN 2012 spectroscopic database to see if we can obtain further improvements in the

retrieval fits with this new spectroscopy. This will be done as soon as the new version of the spectral retrieval software (SFIT4) will be fully ready and implemented.

Task 2.2 Re-analysis of C₂H₄, C₂H₆ and H₂CO data at Jungfraujoch and La Réunion with improved spectroscopic data

Task 2.2.1 Provide improved laboratory spectroscopic data for ethylene (¹²C₂H₄), ethane (¹²C₂H₆) and formaldehyde (H₂¹²C¹⁶O)

Task 2.2.1.a Provide improved laboratory spectroscopic data for H₂¹²C¹⁶O

This contribution aims to derive infrared line intensities for formaldehyde, relying on its partial pressure measured using intensities of far infrared (FIR) pure rotation lines and the accurately known electric dipole moment of H₂CO. A total of six experiments were conducted at 296 K. During each experiment, one high-resolution FT-FIR spectrum of H₂CO was recorded and about 30 IR (around 3.4 μm) spectra of the same sample were simultaneously acquired using a TDL spectrometer. At the end of 2012, we were facing two difficulties: (1) we were unable to identify some IR spectral regions probed by the TDL spectrometer and (2) inconsistent H₂CO line intensities were measured in some TDL spectra (for example, two H₂CO lines observed in the same TDL spectra yielded H₂CO partial pressures differing by as much as 10 %). This year, all the TDL spectral ranges were identified. The inconsistent intensities were found to originate from the non linear response of the HgCdTe detector used to record the TDL spectra, enhanced by a high laser intensity on the detector. We modeled the non linear response of the detector, and are developing a systematic correction procedure to correct all the affected spectra.

Task 2.2.1.b Provide improved laboratory spectroscopic data for ¹²C₂H₆

To try and improve the description of the 3.3 μm region of the ethane spectrum, we carried out last year a rotational analysis focused on the ν₇ band near 2985 cm⁻¹, only relying on the observed positions of R and P branch lines (and Q branch lines when resolved) and information from previous work. This year, we extended this work to the parallel component of the weaker ν₈+ν₁₁ band, observed in the same spectral region near 2954 cm⁻¹, in an attempt to provide an information for the 3.3 μm region as complete as currently possible. We thus go beyond the anticipated outcome of this work. To turn the whole linelist into information useful for atmospheric applications, we refine the line intensity information and add shape-specific parameters.

Task 2.2.1.c Provide improved laboratory spectroscopic data for ¹²C₂H₄

As described in previous reports, the general methodology of this work involves experimental measurements of line positions and intensities at ULB and their theoretical analysis by two French research teams, at the *Université de Reims Champagne Ardenne* and at the *Université de Bourgogne*. Because the modelling of line intensities relies on information (wavefunctions) derived from the analysis of line positions, that part of the work was carried out first. The combined frequency analysis of the ν₁₀, ν₇, ν₄ and ν₁₂ bands, started last year, now includes 11723 line positions measured at ULB or reported earlier (Rotger et al, 2008), reproduced with an overall standard deviation of 0.00036 cm⁻¹. Earlier data (Rusinek et al, 1998; Willaert et al, 2006) are now being included in the analysis. Meanwhile, the intensity measurements performed at ULB have been finalized. More precisely, line intensities have been measured in a total of 9 FTS spectra of pure ethylene for the strong ν₇ band and the very weak ν₁₀ and ν₄ bands of ¹²C₂H₄, respectively located near 949, 826 and 1026 cm⁻¹. Because the self-broadening coefficients are correlated with line intensities and not yet extensively measured (see Flaud et al, 2011 and references therein), the work carried out also involved (unforeseen) extensive measurements of self-broadening coefficients of ethylene lines. The line intensities measured for the ν₇ band were compared with HITRAN 2012, and a correction to be applied to the latter determined. A similar work has been started for the 3 μm spectral region of ethylene (the main bands are ν₉ and ν₁₁ near 3105 and 3012 cm⁻¹, respectively). Although probably not of direct interest in the context of the atmosphere of the Earth but rather for other planets such as Mars, it will also lead to an improvement of spectroscopic parameters for ethylene.

In addition to the planned work, ULB is involved in an unforeseen activity, aiming to measure tropospheric pollutants *in situ* using Continuous-Wave Cavity Ring-Down Spectroscopy (CW-CRDS) [see for example (von Bobruzki et al, 2010) and (Phillips et al, 2013)]. The sensitivity of a home-made CW-CRDS spectrometer was improved (Földes, 2013), as demonstrated by application to the detection of clusters of isotopic water vapor and ammonia with argon (Didriche and Földes, 2013; Didriche et al, 2013). A portable CW-CRDS-based spectrometer is now being developed at ULB. It will be initially dedicated to the detection of trace pollutants in drinking water in Brussels.

Task 2.2.2 H₂CO from Jungfraujoch

Two H₂CO retrieval strategies have been tested for the Jungfraujoch station, where the H₂CO absorption generally does not exceed 1%. The first one focuses on one microwindow (2833.07 – 2833.35 cm⁻¹) only, which is covered by a tunable bandpass optical filter since December 2005. Using a larger diaphragm aperture (1.45 mm) on a narrow spectral range (2810 – 2850 cm⁻¹), it provides solar spectra with very high signal-to-noise ratio helping for the H₂CO fitting. A data set of solar spectra ranging from December 2005 to April 2013 has been produced for comparison with UV-visible preliminary MAX-DOAS results, ACE-FTS v.3 occultation measurements and simulations from GEOS-Chem and IMAGES models.

The second H₂CO retrieval strategy is based on the method implemented by Vigouroux et al. (2009) at Réunion Island, fitting simultaneously 6 microwindows of the 2760 – 2860 cm⁻¹ spectral domain but not covered by the tunable optical filter. Using this approach, an unprecedented 1995 – 2013 H₂CO time series has been produced to initiate comparisons with MAX-DOAS and models data and to provide the first long-term trend of H₂CO.

The species C₂H₄ was not retrieved yet at Reunion Island. Therefore, we have performed tests of the retrieval strategy for this molecule, in order to be ready for its analysis when the new spectroscopic parameters from ULB will be delivered. The spectroscopic signatures are very weak and close to the detection limit. Therefore, as for CH₃Cl, a large scatter is observed in the total columns, due to the large random noise error. This scatter is improved at the Maïdo observatory, due to the better instrumentation (Bruker 125HR) and the lower interferences with other molecules.

The total columns time-series and the seasonal cycle have been compared to the model IMAGES.

Task 2.2.3 Comparison between MAX-DOAS and FTIR data for H₂CO at Jungfraujoch

First comparisons between FTIR and MAX-DOAS data have revealed an underestimation of the H₂CO total columns produced by the single-microwindow FTIR retrieval strategy, especially during summertime, which has been confirmed by further comparisons with ACE-FTS v.3 measurements as well as GEOS-CHEM and IMAGES simulations. However, the multi-windows retrieval approach has provided H₂CO data in good agreement with MAX-DOAS, ACE-FTS and both models. Further tests using the HITRAN 2012 line list parameters (implementing enhanced broadening coefficients of the H₂CO features) have also been performed, leading to much lower total columns, thus significantly degrading the agreement between the FTIR, MAX-DOAS and model time series.

Task 2.3 Retrieval feasibility studies

Task 2.3.1: Feasibility of retrieval of PAN and acetone at Jungfraujoch and La Réunion

Reunion Island: PAN and acetone (new spectroscopy available in HITRAN 2012) will be tested when the new retrieval software SFIT4 will be available, which is very soon.

Task 2.3.2

In the framework of task 2.3.2, we have carefully evaluated the possibility to retrieve HCFC-142b (CH_3CClF_2), a CFC-substitute, from Jungfraujoch spectra, in four candidate windows (900-906, 965-970, 1132-1136 and 1191-1196 cm^{-1}). It turned out that only two domains could be used, the 900-906 and 1191-1196 windows, the two others being affected by strong interferences by CO_2 , O_3 and H_2O . Moreover, systematic and independent fits to both domains have revealed that the adoption of the second interval led to the determination of total columns too large by about a factor of 2, possibly resulting from missing interferences in HITRAN 2008 and/or inconsistent cross section parameters for HCFC-142b. Therefore, the 900-906 feature has been selected to produce a HCFC-142b data set, using all available low sun spectra for the 2000-2012 time frame. Uncertainties on the total columns have been evaluated to <8% and <12% for the total random and systematic contributions. Figure 2 shows the contribution of the interferences (shifted vertically for clarity) as well as the weak HCFC-142b feature (pink trace). The upper panel allows comparing the fitting residuals, in green when including HCFC-142b in the retrieved species, in red when assuming no HCFC-142b in the atmosphere.

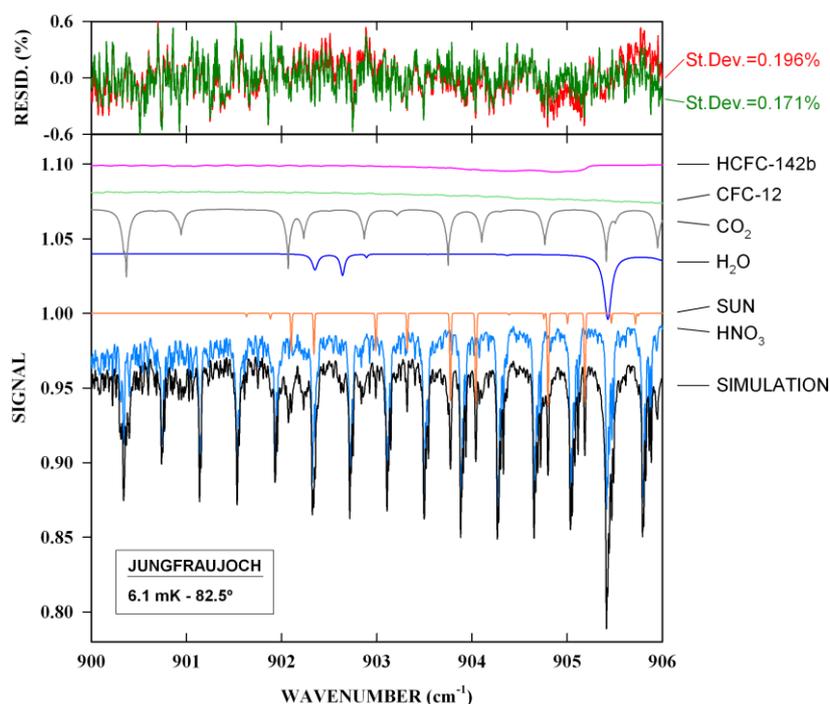


Figure 2: Selected microwindow for the retrieval of HCFC-142b from the Jungfraujoch station.

Task 2.4 Production of the CCl_y and CF_y budgets for Jungfraujoch

Retrieval strategies have been revisited for CFC-11, CFC-12 and HCFC-22, in order to derive some vertical information from the spectra and optimize the total column determinations. Typical DOFS respectively amount to 1.6, 1.9 and 1.5. Final time series have been produced from 2000 onwards. They will be combined next year with the HCFC-142b and either with the CCl_4 or CF_4 weighted contributions to generate CCl_y and CF_y total column budgets.

WP3. Aerosol

Task 3.1 Improve algorithms for aerosol characterization from ground-based spectral measurements

Task 3.1.2 Brewer SSA

As was mentioned in the previous report, the method to retrieve SSA values from Brewer measurements does not perform very well, especially under circumstances with low AOD. It

was decided to look into the sensitivity of the model to different parameters, such as the measured intensity, measured ozone and measured AOD.

The Brewer instruments measure the UV intensity with an average error of about 5%. The difference between the modeled SSA at measured intensity and at an intensity increased/decreased by 5% was therefore analyzed. For ozone, we used the same 5% as uncertainty while for the AOD measurements the absolute uncertainty is 0.08.

Task 3.1.3: Further algorithm developments for retrieval of aerosol properties from MAX-DOAS observations

Retrievals of trace gas columns and aerosol optical depths (AODs) from MAX-DOAS observations are ideally performed under clear-sky conditions. However, MAX-DOAS measurements at Ukkel are often strongly affected by clouds, leading to larger uncertainties on the retrievals. To better characterise data taken under cloudy conditions we developed a cloud-screening method for the MAX-DOAS observations, based on the colour index (CI, the ratio of the intensity of a measured spectrum at 350 nm and 420 nm) of the sky.

Using the CI we define 3 different sky conditions: bad (=full thick cloud cover/extreme aerosols), mediocre (=thin clouds/aerosols) and good (=clear sky). We also flag the presence of broken scattered clouds.

Removing data under bad-sky and broken-cloud conditions results in a better agreement, in both correlation and slope, between the AERONET and MAX-DOAS AOD retrievals (see Figure 3). We find that high MAX-DOAS AODs are removed, as they are now identified as due to clouds (Blue crosses in Figure 3 Left).

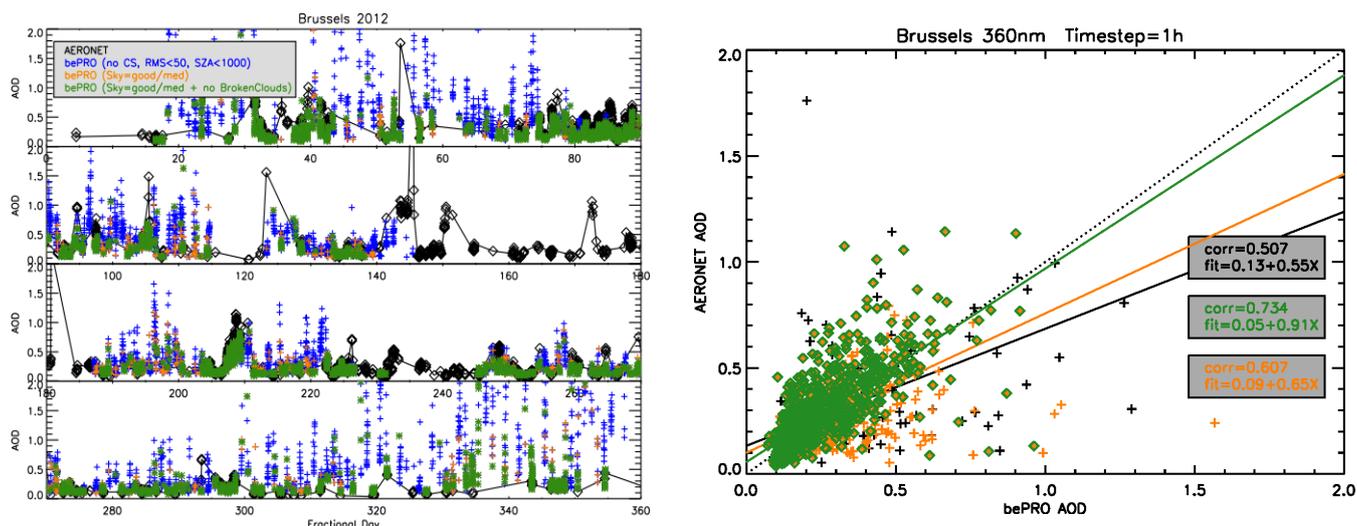


Figure 3 Left: Comparison of AOD retrieved by applying the bePRO profiling tool (Clémer et al. 2010) to mini MAX-DOAS O_4 measurements at Ukkel and co-located AERONET data. In black the AERONET data, blue the non-cloud-screened MAX-DOAS data, orange the cloud-screened data under good/mediocre conditions, green the good/mediocre data with additional removal of data hindered by broken clouds. **Right:** Corresponding correlation between MAX-DOAS and AERONET AODs. In black the non-cloud-screened MAX-DOAS data, green and orange are defined the same as in the left figure.

It should be also noted that we further compared our cloud-screening method with results from cloud-cover fractions derived from thermal infrared measurements performed by BIRA, and find a good agreement.

Task 3.2 Aerosol measurements at Ukkel

Task 3.2.1 Routine Brewer and sunphotometer

The data of the two Brewer instruments are continuously stored and regularly checked and the AOD time series from both Brewers is kept up to date.

The analysis of the simultaneous time series of the erythemal UV dose, global solar radiation, total ozone and AOD has been further extended. Next to a linear trend analysis of the monthly anomalies, the trends in the extremes are studied together with the frequency distribution of the daily values in order to investigate whether there is a shift in the distribution of the daily values from the first decade (1991-2000) to the second decade (2001-2010). The extreme values are calculated by determining the lowest and highest measured value for each month. Change points are determined for each time series and a multiple linear regression technique was applied in order to determine the influence of global radiation, total ozone and AOD on the variation in UV. Data from 1991 to 2006 were used to construct the regression model and the model was validated against the 2007-2011 data. The results of our analysis are compared with literature and show a good agreement in most cases. A paper with this analysis is currently in preparation.

Task 3.2.2 Aerosol lidar

The mixing layer height (MLH) algorithm (developed during the previous year) has been validated by comparing the MLH retrieved by the LIDAR-ceilometer with the MLH retrieved from radio-soundings and with the boundary layer height (BLH) directly computed by the ECMWF and ALARO7 models. The comparison was made at daily and monthly temporal scale for the Uccle data set from May 2011 to January 2013. Under specific atmospheric conditions, the algorithm fails to retrieve a MLH similar with the values from the other remote sensing retrieval techniques. Therefore, several MLH quality control flags were developed, to automatically detect the failure of the MLH retrieval algorithm. The quality criteria on the MLH observations are crucial for the use of MLH in near real time.

In the frame of the development of a coordinated system for the LIDAR observation in Europe, KMI-IRM is involved in two major European projects. In EUMETNET, KMI-IRM participates in the E-PROFILE program to develop an operational LIDAR ceilometer network by the exchange of LIDAR-ceilometer backscatter data in a standard format and the maintenance of an archive of communicated data and metadata for all systems connected to the networks. KMI-IRM also participates in a COST Action: TOPROF. The aim of this action is to coordinate the operation of many ceilometers installed across Europe, in order to build a network and to provide quality controlled and calibrated observations of aerosols in the lowest few kilometers of the atmosphere to national meteorological services in near real time.

Task 3.3 Aerosol data interpretation

Task 3.3.1 Comprehensive data set of aerosol optical properties

Both KMI-IRM and BIRA-IASB have instruments at their disposal to measure optical properties of aerosols.

KMI-IRM has purchased two new instruments (on an external budget allocated to BIRA-IASB and KMI-IRM). The aethalometer, which measures the absorption coefficient of aerosol particles, has been installed in May 2013 and has been running since then. Due to some technical issues, the nephelometer, which gives information on the scattering properties of aerosols, is yet to be installed. We expect the issues to be solved in the near future and we plan to install the instrument in the beginning of 2014.

The measurements of the different instruments can be combined to build an extensive data set of aerosol optical properties at Uccle. Comparisons between measurements of different instruments have already been made - e.g., AOD from Brewer spectrophotometers, Cimel sunphotometer and MAXDOAS. Discussions and exchanges of data between both institutes have been intensified.

Aerosol optical depths (AODs) and vertical extinction profiles have been retrieved at 360 nm by applying the bePRO profiling algorithm developed at BIRA-IASB (Clémer et al., 2010) to mini-MAX-DOAS O₄ measurements at Ukkel, and compared to co-located AERONET data after applying the cloud-screening method (see Task 3.1.3). This has been done for the entire time series, ranging from 2011 up to now.

In general, good agreement. in both value and variation, is found between bePRO and AERONET AODs, especially after removal of data taken under non-clear-sky conditions (see Figure 3 Left).

The retrieved aerosol extinction profiles at Ukkel show a marked diurnal cycle, with typically the aerosol layer extending to higher altitudes during the morning and evening, and a settling down of the aerosols during midday (see Figure 4). We are currently investigating the origin of this feature, looking for links with meteorological and/or traffic conditions.

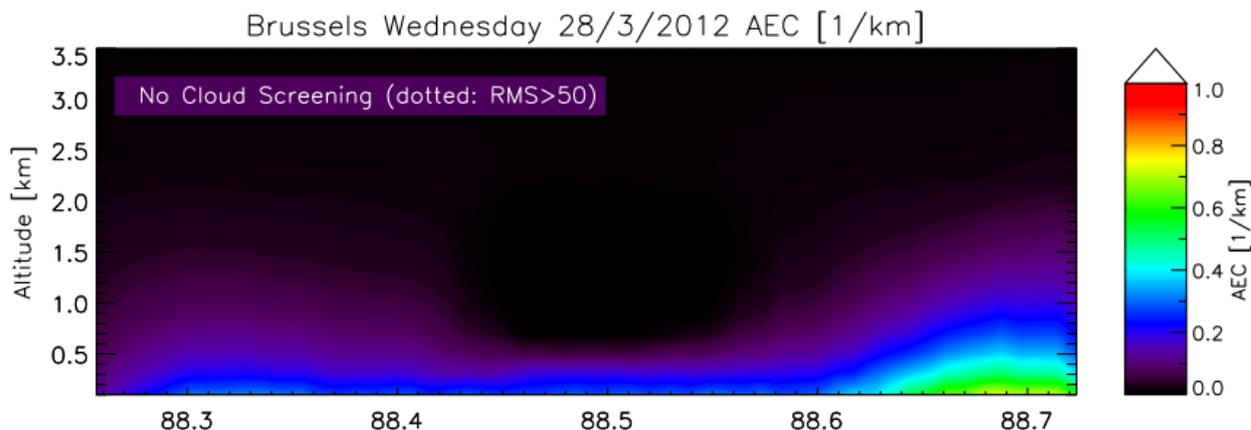


Figure 4: The MAX-DOAS aerosol extinction coefficient (AEC) vertical profile at Ukkel on 28/3/2012. This observed diurnal cycle of the extinction profile is found frequently for the Ukkel data.

With these new AOD and extinction profile data sets, the seasonal and diurnal variations of the aerosol content and vertical distribution in Ukkel will be investigated in further detail. By combining with additional information derived by other instruments (Brewer, nephelometer, aethalometer, ceilometer) operated at the station by KMI-IRM, we will further study the observed aerosol characteristics, and their influence on and by meteorological conditions such as clouds and/or the boundary layer height.

Recently, an extensive comparison of all available data obtained by BIRA-IASB and KMI-IRM in this workpackage has been initiated. We compare in detail the retrieved aerosol extinction profiles (BIRA-IASB) with backscatter cloud profiles and mixing layer height values from lidar measurements (KMI-IRM). We find that in general cloud screening from BIRA-IASB corresponds to the backscatter profiles derived at KMI-IRM (see Figure 5). Also, we often see a clear correlation between the height of the aerosol layer and the mixing layer height. Both institutes are currently collaborating to investigate the observed trends in aerosol profiles, backscatter profiles and mixing layer height.

Also related to WP3, it should be noted that tropospheric NO₂ columns derived from MAX-DOAS measurements in Ukkel have been used to validate satellite observations, in particular GOME-2 data within the framework of the O3MSAF (<http://cdop.aeronomie.be>).

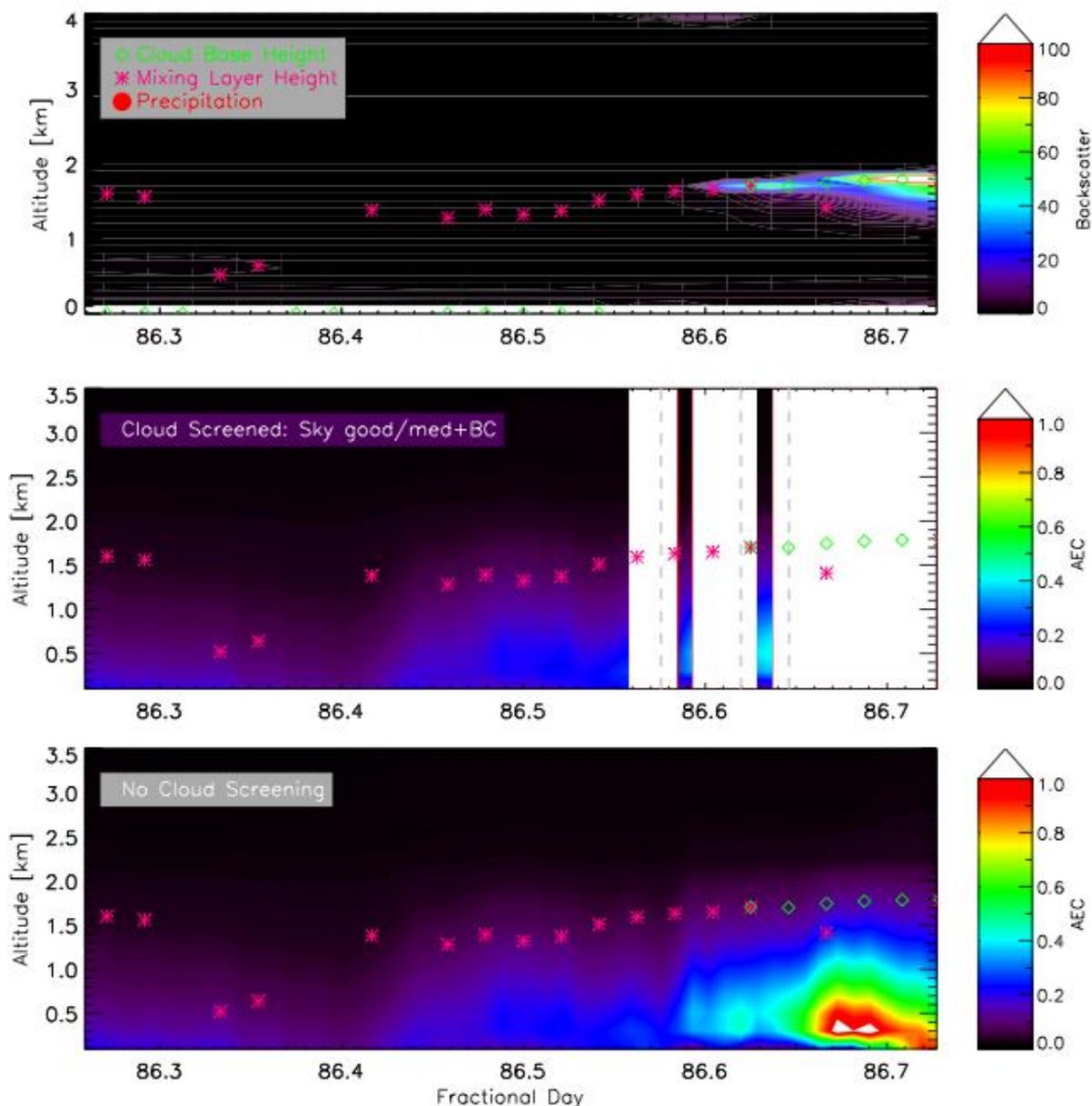


Figure 5: Comparison of the retrieved aerosol extinction profiles (km^{-1}) and cloud screening from BIRA-IASB (middle and bottom plot), with backscatter profiles and mixing layer height derived by KMI-IRM (top plot) for day 86 (March 27) 2013. Top: Backscatter lidar profile with the estimated cloud base heights (green) and mixing layer height (magenta). Middle: Aerosol extinction profiles retrieved by applying the bePRO-profiling tool to MAX-DOAS measurements. Bottom: Cloud-screened aerosol profiles. For comparison, we also plot the cloud base height and mixing layer height derived from lidar measurements in the middle and bottom plot. There is no precipitation on that day.

Task 3.3.2 Aerosol modeling with CHIMERE

The chemical transport model CHIMERE (Vautard et al. 2007) was used to model the composition of the aerosol mixture at Uccle. The model provides the chemical composition of aerosol particles in $\mu\text{g}/\text{m}^3$ up to a height of 5.5km and uses different aerosol components (Salt, HNO_3 , H_2SO_4 , NH_3 , Organic Carbon (OC), Black Carbon (BC), Primary Particulate Matter (PPM), Secondary Organic Aerosols (SOA) and DUST). In order to be able to use the output of CHIMERE as input for the OPAC software package, some changes were needed. First, the output in mass density ($\mu\text{g}/\text{m}^3$) had to be converted to number density (particles/ cm^3). Second, since the OPAC software package uses different aerosol categories, the CHIMERE components (in red) needed to be attributed to the OPAC categories (in green). This is done as follows:

BC => Soot

Dust => Mineral coarse mode
NH₃+H₂SO₄+HNO₃ => Soluble
OC + PPM + SOA => Insoluble
Salt => Seasalt coarse mode

OPAC also needs the mixing layer height (MLH) as input. The MLH values are taken either from balloon soundings or from the ALADIN model output. The OPAC software package provides optical properties of atmospheric particulate matter for 61 wavelengths (between 0.25 and 40µm) and for 8 values of relative humidity (RH) (0, 50, 70, 80, 90, 95, 98 and 99%). We will use the resulting optical properties calculated for the RH class closest to the observed RH values from our synoptical station.

Both the Aerosol Optical Depth (AOD) and the Single Scattering Albedo (SSA) were modeled for 11UT at Uccle for a period from 01/01/1991 to 31/12/2010. For some days during that period, no MLH or RH data were available. For these days, the model still provided an AOD and SSA value, but these values were excluded from the results. In total, 4421 AOD and SSA values remained.

Task 3.3.3 Aerosol sources from backtrajectories

Backtrajectory analysis (with the APTRA model) is used to determine the origin of the observed air masses. For a period from 01/01/1990 to 31/12/2010, 7671 trajectories were calculated. Cluster analysis was used to divide the trajectories into different clusters. The measured AOD and SSA were compared between the different clusters.

4. INTERMEDIARY RESULTS

WP1. Exploitation of FTIR spectra to derive useful geophysical information for a suite of GHGs (CO₂, CH₄, N₂O, CF₄, CCl₄)

Task 1.1 Produce time series for the major greenhouse gases CH₄, N₂O and CO₂

Table 1 lists the intervals which include at least an exploitable CO₂ line for its total column retrieval from the grating spectra. It immediately appears that the earlier relevant observation was recorded in November 1983, but this interval spans a weak CO₂ line and a reliable retrieval is far from obvious. All other windows have been systematically recorded from 1985 onwards, i.e. after the start of regular operation of the homemade FTS. Therefore and unfortunately, their exploitation would not allow us to extend the Jungfrauoch CO₂ total column time series back in time.

Spectral range (cm ⁻¹)	Time period	# days (spectra)	Comment
2481.3-2484.9	11/1983 – 07/1985	24 (61)	Weak feature
2437.2-2442.1	08/1985 – 10/1989	119 (789)	
2416.0-2419.9	10/1985 – 09/1989	93 (1016)	
2386.8-2394.3	10/1985 – 09/1989	74 (412)	

Table 1: Available spectral ranges and time periods for the retrieval of CO₂ from grating observations at Jungfrauoch.

Task 1.2 Investigate additional greenhouse gases: CCl₄ and CF₄

For CF₄, the analysis of our final time series indicates that two regimes have characterized its recent accumulation in the atmosphere, with corresponding annual emissions evaluated at 15.8 and 11.1 Gg, for 1989-1997 and 1998-2012, respectively. This reduction is attributed to efforts of the Aluminum industry to limit its emissions despite increasing Al production. However, CF₄ is still on the rise at a rate of ~1%/yr and this is a serious issue considering its very long lifetime and large global warming potential. Comparisons with results obtained in situ by the AGAGE network (including at the Jungfrauoch station), or from balloon- or space- platforms have shown a very consistent picture for the CF₄ atmospheric build up over the last 30 years, when accounting for the uncertainties associated to the various techniques involved. More information can be found in Mahieu et al. (2013a). Such trend and emission determinations are key elements to support decision makers, and we would like to point out that our results have been solicited for inclusion in the next edition of the WMO assessment on ozone depletion, together with those for CFC-11, -12, HCFC-22 and CCl₄.

Task 1.3 Provide laboratory spectroscopic data for CO₂ and N₂O if needs emerge

We measured first-order line-mixing coefficients for Q-branch lines and self broadening and shift parameters for R-, P- and Q-branch lines of the $\nu_1+3\nu_2^1$ band of carbon dioxide, using a Voigt lineshape model and line positions and intensities from HITRAN 2008 and 2012. These preliminary results seem to indicate that more sophisticated lineshape models are needed, and put forward some differences between these two versions of the HITRAN database.

WP2. Volatile Organic Compounds (VOC) and CFC-substitutes in the troposphere

Task 2.1 Methanol (CH₃OH) and other VOCs at Reunion Island and Jungfrauoch.

a) Reunion Island

See Vigouroux et al. (2012), Stavrou et al. (2011) and AGACC-II previous report for results on CH₃OH.

Some preliminary retrievals have been performed for CH₃Cl. As mentioned previously, the scatter due to the large random error in the total columns is very large at the period when the Bruker 120M instrument was used (2009-2011) at St-Denis, as shown in Figure 6. It is improved by the use of the Bruker 125HR at St-Denis and Maïdo, and it is even better at Maïdo where the influence of interfering species is reduced.

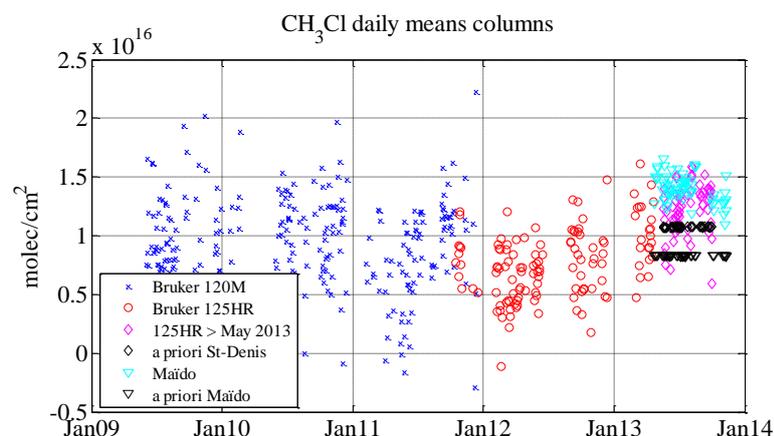


Figure 6: CH₃Cl daily means total columns at St-Denis (blue for Bruker 120M data, red for Bruker 125HR data and magenta for Bruker 125HR data after May 2013) and at Maïdo (cyan). The black symbols indicate the a priori values for St Denis (circles) and Maïdo (triangles).

The lifetime of CH₃Cl in the troposphere is more than 1 year, therefore the observed large scatter is not due to natural variability, but indeed to the too large random noise. In Figure 7, we show the seasonal cycle derived from our measurements. In the left panel, we see the different seasonal cycles obtained at the two stations. We still need to understand this difference, and try to avoid it in future improved retrievals. At present, the seasonal cycles provided in the literature for the Southern Hemisphere are quite contrasted. Indeed the seasonal cycle from AURA satellite measurements at 150hPa altitude in the 15°S-30°S region shows a maximum in December-January, with an amplitude of about 30% (Santee et al., JGR, in press), while surface measurements have a maximum in March and August at Samoa (14°S), but with an amplitude lower than 5%; and a maximum in July-August in Tasmania (40°S), with an amplitude of about 10%.

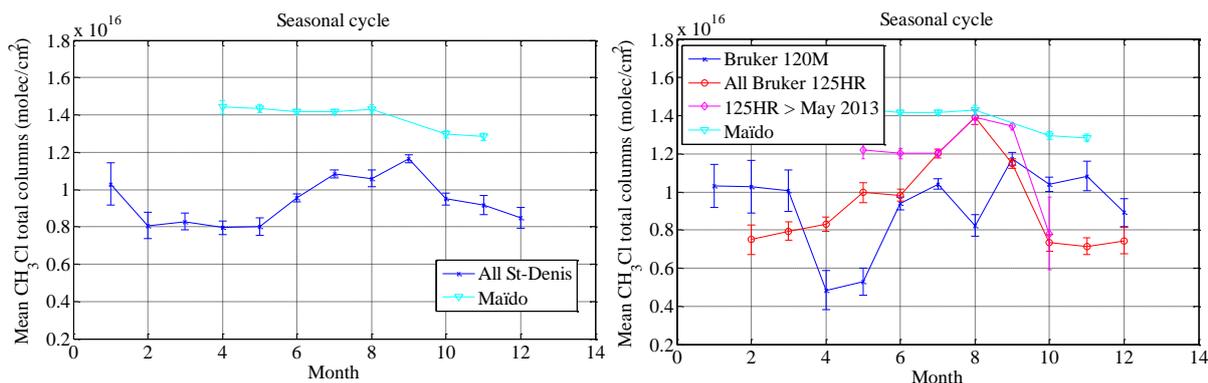


Figure 7: Seasonal cycle of CH₃Cl total columns at Reunion Island. Same legend as in Fig. 6.

Also the total columns at Maïdo should be lower than at St-Denis, due to the higher altitude of the site. We see from Figure 6 and Figure 7 that the comparisons between St-Denis and Maïdo improve when we look only at the Bruker 125HR data after May 2013 (in magenta). We have to explore if this is due to a decreased systematic error (e. g. due to interfering species) when the random noise is reduced, or if the 2013 CH₃Cl values are indeed higher compared to other years. For the latter, we would need the help of a chemistry-transport model.

The data retrieved from the Bruker 120M seem not exploitable at present. We will concentrate on the St-Denis and Maïdo Bruker 125HR time-series, and try to optimize these data. Especially we want to use the new HITRAN 2012 spectroscopic database.

b) Jungfraujoch

A final methanol time series has been produced, allowing characterizing the short and long-term variations of this species at northern mid-latitudes. The trend analysis does not reveal a long-term change but a strong seasonal modulation with peak-to-peak amplitude of ~130%. The diurnal cycle has also been analyzed, showing significant variations characterized by maximum columns at noontime from fall to spring, in contrast with summer (no clear signal during the day), when the CH₃OH variability and columns are by far the largest. Finally, in situ campaign-type measurements performed at the Jungfraujoch in 2005 have been compared with our lower-tropospheric data. First investigations suggest a reasonable agreement, with similar seasonal pattern and data variability for both subsets. It is also clear that significantly higher concentrations are associated to air masses originating from the South, where substantial emissions from biogenic sources occur. A manuscript is in preparation, but first results can be found in Bader et al. (2013)

Task 2.2 Re-analysis of C₂H₄, C₂H₆ and H₂CO data at Jungfraujoch and La Réunion with improved spectroscopic data

Task 2.2.1 Provide improved laboratory spectroscopic data for ¹²C₂H₄, ¹²C₂H₆ and H₂¹²C¹⁶O

Task 2.2.1.a Provide improved laboratory spectroscopic data for H₂¹²C¹⁶O

To overcome the two difficulties faced at the end of last year, we redid all the treatments to linearize (generate a proper wavenumber scale for) the raw TDL spectra to make sure that no error was done in that treatment. By comparison of the TDL spectra thus linearized with FTS spectra of the whole ν_1 and ν_5 band system (2500–3200 cm⁻¹) recorded last year, we identified all the IR regions probed by the TDL spectrometer. They are: 2911.5–2912.2 cm⁻¹ (probed in 2 different experiments), 2916.4–2917.2 cm⁻¹, 2928.3–2929.2 cm⁻¹ (probed in 2 different experiments) and 2940.6–2941.4 cm⁻¹. As explained in section 3, we found that the inconsistent intensities measured last year in TDL spectra resulted from the non linear response of the HgCdTe detector used to record these spectra. We modelled the non linear response of the detector, and are developing a systematic correction procedure to apply to all the affected spectra. No results are therefore available for H₂CO at the moment.

Task 2.2.1.b Provide improved laboratory spectroscopic data for ¹²C₂H₆

The linelist generated last year for the ν_7 band was extended with a linelist for the parallel component of the $\nu_8+\nu_{11}$ band, observed near 2954 cm⁻¹. It was built using 429 lines reported earlier (Pine and Lafferty, 1982), of which 33 unassigned lines have been assigned, to which 129 newly assigned lines were added. The linelist thus generated for both bands contains observed line positions and intensities, lower state energies and assignments. To turn this linelist into information useful for atmospheric applications, we refine the line intensity information and add shape-specific parameters taken from the literature.

Task 2.2.1.c Provide improved laboratory spectroscopic data for ¹²C₂H₄

Simultaneous fits of 6 FTS spectra of pure ethylene, at pressures from 1.6 to 101 hPa, were carried out to measure the intensities and self-broadening coefficients of 1221 ν_7 band lines of ¹²C₂H₄. This is the first time that such an extensive information is measured for that band.

Among the 6 spectra finally included in the analysis are 3 FTS spectra of pure C₂H₄ at pressures of 25, 51 and 101 hPa, recorded this year. Such higher pressure spectra were indeed needed to allow precise measurements of self-broadening coefficients of C₂H₄ lines, simultaneously with their intensities. As a result, the experimental work carried out this year yielded the anticipated line intensities, as well as unforeseen self-broadening coefficients of ethylene lines. As already mentioned in previous reports, discrepancies with the line intensities available in HITRAN (Rothman et al, 2012), varying linearly with wavenumber, are observed. As Fig. 1 shows, line intensities measured in this work are larger than HITRAN by about 8 % at 860 cm⁻¹ and approximately agree with HITRAN at 1080 cm⁻¹. The observed discrepancies are within the stated uncertainty of the line intensities in HITRAN (5–10%). We believe that they come from an incomplete modelling of the rotational dependence of the line intensities in HITRAN provided by the model used at the time to generate them (Rusinek et al, 1998; A. Fayt, private communication). Relying on the comparison shown in Fig. 1, the line intensities for the ν_7 band of ¹²C₂H₄ in HITRAN 2012 were corrected. We estimated that the uncertainties on these corrected line intensities are in the 2–5% range. We included in the updated HITRAN linelist self broadening coefficients calculated with expressions determined using the 1221 self-broadening coefficients that we measured this year. This updated HITRAN linelist constitutes deliverable D2.3, thus obtained on schedule.

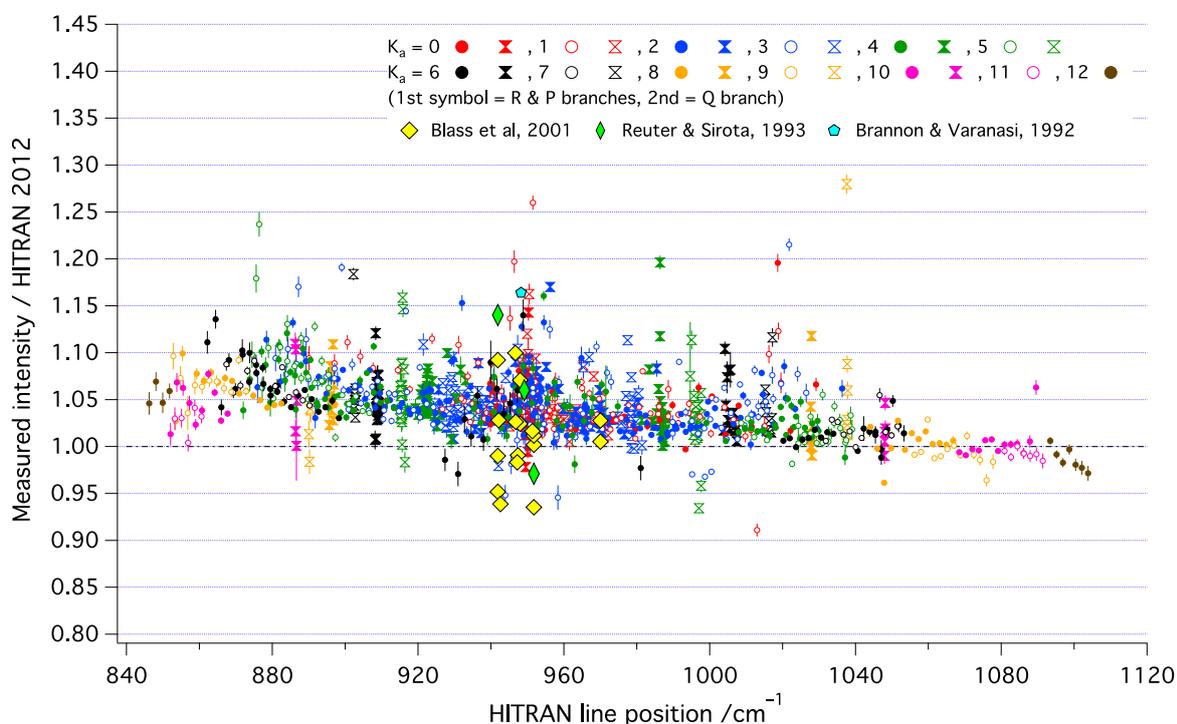


Figure 8: Ratio of line intensities measured in this work for the ν_7 band of ¹²C₂H₄ and in the literature with those available in HITRAN 2012 (K_a is a rotational quantum number). Note that the line intensities in HITRAN were generated by scaling calculated relative intensities (Rusinek et al, 1998) with some average of the intensities reported in (Blass et al, 2001).

Task 2.2.2: re-analysis of the time-series of C₂H₄, C₂H₆ and H₂CO at Jungfraujoch and Réunion

Reunion Island:

As for CH₃Cl, the very weak absorption signature of C₂H₄ leads to a large scatter in the retrieved total columns (Figure 9). The main C₂H₄ signature is at the edge of a strong CO₂ line (around 949.5 cm⁻¹).

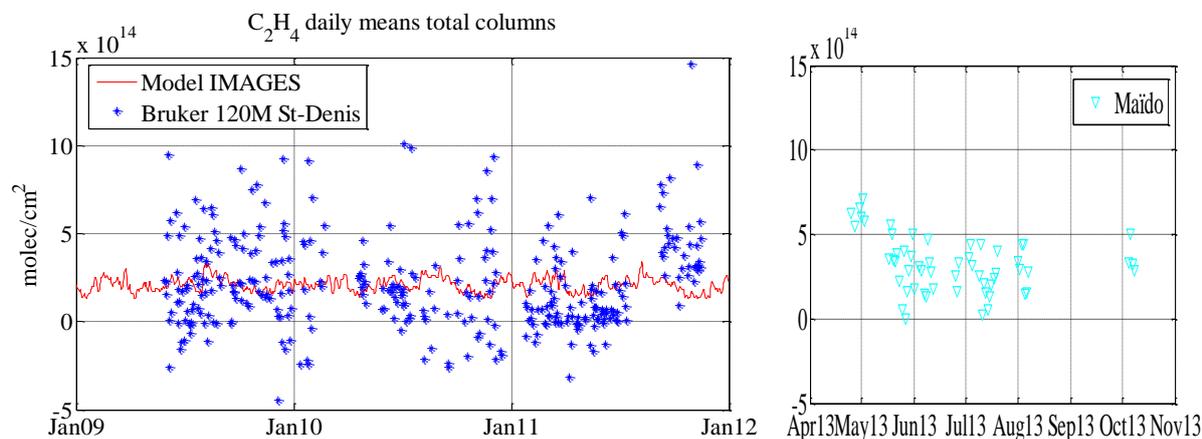


Figure 9: C₂H₄ daily means total columns at St-Denis (blue) and at Maïdo (cyan). Model IMAGES simulations are shown in red for the 2009-2011 period.

We compare in Figure 10, the seasonal cycles obtained at St-Denis and Maïdo, and with the model IMAGES. IMAGES and the seasonal cycle at St-Denis are in reasonable agreement, except for the September-November period, which is a period of biomass burning in Madagascar. Some biomass burning sources (fires from agriculture) are still missing in the GFED3 inventory used by IMAGES, and will be included in the next GFED4 inventory. We will make new comparisons when this will be implemented in IMAGES. Also, it can be noted that at Reunion Island in November 2010 and 2011, some local fires took place, which is also not taken into account in the model. The seasonal cycle from June to November is in agreement between St-Denis and Maïdo, but not in April and May. We have only a few measurements for Maïdo. One needs at least another complete year of observations at Maïdo to have a better picture. As for CH₃Cl, the columns at Maïdo are not lower than at St-Denis as they should be, therefore a large systematic error, which could be due to interfering species, is expected. Further work is needed to quantify this error, and if possible to reduce it and improve our C₂H₄ products.

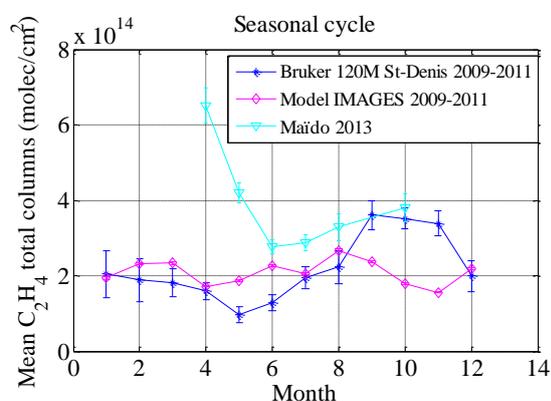


Figure 10: Seasonal cycle of C₂H₄ total columns at Reunion Island.

At Jungfraujoch, the 6-microwindow retrieval strategy has been used to produce a H₂CO long-term time series covering the 1995 – 2013 period. This data set (Figure 11) indicates strong intra-annual variations characterized by the largest columns and variability during summertime and by regular minimum and compact columns in winter. The larger columns are consistent with the main H₂CO sources in summer (biogenic sources and methane oxidation); forthcoming models simulations will help to investigate this issue. The trend analysis also reveals a significant long-term decrease of $-1.424 \pm 0.227 \text{ \% year}^{-1}$. Further works are still required to identify the causes of the negative trend of the H₂CO columns.

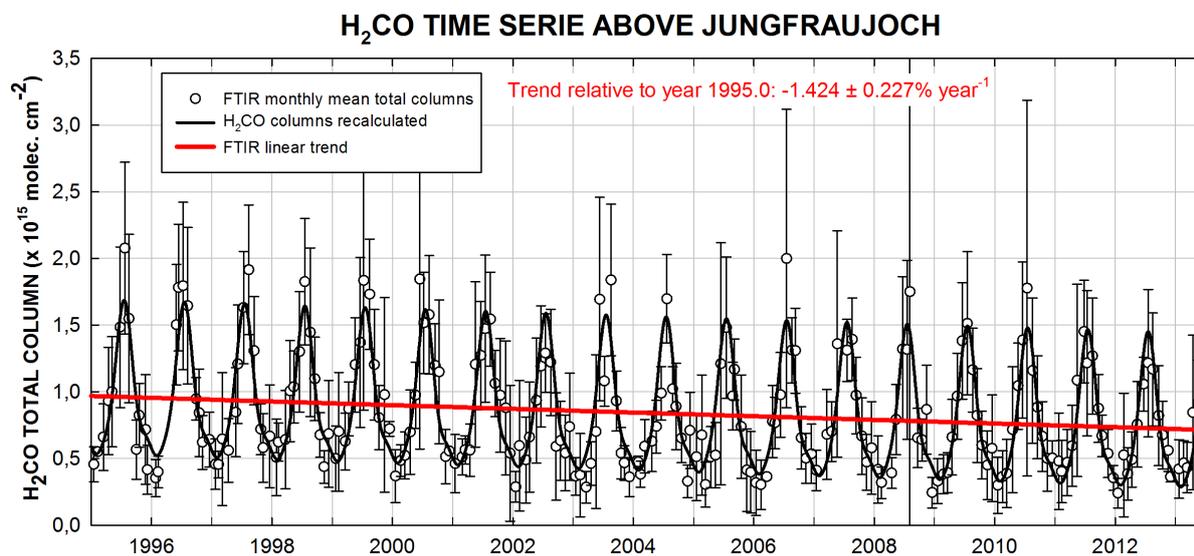


Figure 11: Long-term FTIR time series of formaldehyde above Jungfraujoch.

Task 2.2.3 comparison between FTIR and MAX-DOAS and with model simulations.

The mean seasonal cycle of total H₂CO column above Jungfraujoch deduced from the FTIR retrieval of the 2010 – 2012 observations data set is presented in Figure 12, showing maximum abundance in summer (July), minimum in winter. As shown previously, higher standard deviations of the monthly averaged total columns can be observed during summertime. The FTIR results show a mean seasonal cycle consistent throughout the year with UV-visible MAX-DOAS observations, but systematically lower total H₂CO abundances. MAX-DOAS total H₂CO columns have been retrieved by using the OEM-based profiling tool bePRO (Clémer et al., 2010; Hendrick et al., 2013). A cloud screening method has been also applied to the data in order to reject cloudy scans since the quality of the MAX-DOAS retrieval can be significantly affected by the presence of clouds (see Task 3.1.3). In Figure 12, FTIR data are also compared with H₂CO partial columns above 3.5km produced by GEOS-CHEM 4° x 5° and IMAGES 2.5° x 2.5° simulations. The comparison reveals FTIR and MAX-DOAS seasonal cycles in phase with the models data, as well as simulated H₂CO abundances in agreement with MAX-DOAS results, especially in summer. Finally, IMAGES shows a seasonal amplitude that is weaker than the observed one; GEOS-CHEM presents a seasonal amplitude that is similar to the observed one. For example, the correlation over the 2007 – 2012 period between the FTIR and GEOS-CHEM monthly mean columns is 0.89 (and 0.69 for the daily mean columns).

Task 2.3 Retrieval feasibility studies

The 2000-2012 total column data set of HCFC-142b is characterized by a strong increase, from about 1.6 to 2.8 x10¹⁴ molec./cm² over 13 years, i.e. a relative rate of change of 6.5%/yr. This is commensurate with the trend derived by the AGAGE network at Mace Head (53°N). Comparison of surface mixing ratio suggests that the FTIR data are lower by 5% on average, i.e. well below the systematic uncertainty upper limit of 12% evaluated in our study (Mahieu et al., 2013b).

2010-2012 SEASONAL CYCLE AT JUNGFRAUJOCH

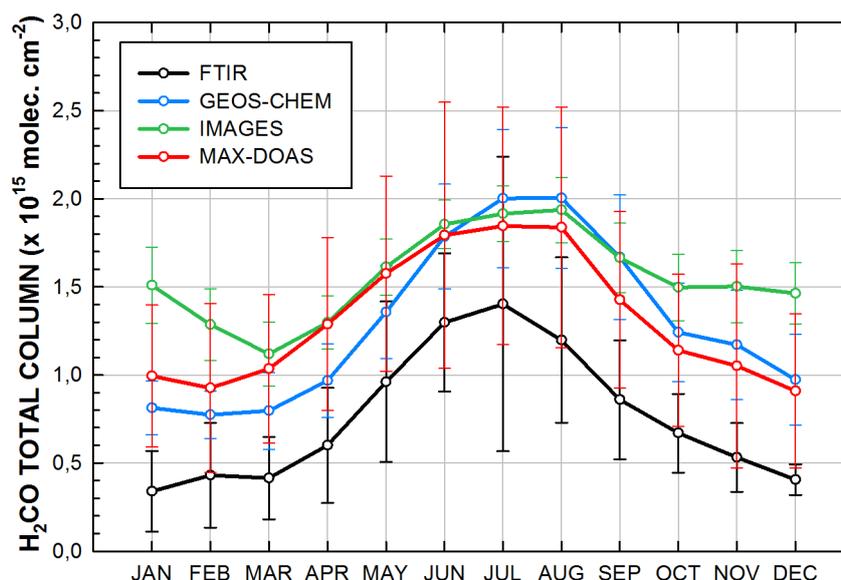


Figure 12: Preliminary comparisons between mean seasonal cycles from FTIR and MAX-DOAS observations, GEOS-Chem and IMAGES model simulations.

WP3. Aerosol

Task 3.1 Improve algorithms for aerosol characterization from ground-based spectral measurements

Task 3.1.2 Brewer SSA

The sensitivity of the SSA retrieval algorithm to different input parameters was tested. The results for the modeled SSA at 320nm can be found in Table 2. These results show that the modeled SSA values are very sensitive to the uncertainties in the input parameters.

	Minimum absolute difference	Maximum absolute difference	Minimum % difference	Maximum % difference
Intensity +5%	0.02	0.22	2.20%	181.82%
Intensity -5%	-0.03	-0.25	-3.30%	-91.43%
Ozone + 5%	0.01	0.16	1.10%	103.23%
Ozone -5%	0.01	-0.14	1.49%	-90.91%
AOD + 0.08	0.01	0.41	1.10%	336.36%
AOD -0.08	-0.01	-0.45	-1.01%	-92.63%

Table 2: Absolute and relative differences between modeled SSA values caused by changes in input parameters

Due to the high sensitivity of the model to the input parameters, it is not feasible to use the model (at least not in its current form) for SSA retrieval.

Task 3.2 Aerosol measurements at Ukkel

Task 3.2.1 Routine Brewer and sunphotometer

At Uccle, simultaneous measurements of erythemal UV dose, global solar radiation, total ozone column and Aerosol Optical Depth (AOD) at 320.1nm are available for a long time period of 21 years (1991-2011), which allows us to study their mutual relationship. The erythemal UV dose, total ozone column and AOD are retrieved from the Brewer spectrophotometer measurements at Uccle. Global radiation measurements are provided by pyranometers. A change point analysis has been performed to determine significant change points in the time series of UV, global radiation, ozone and AOD. There are different tests

that can be used to detect a change point in a time series. Here we used the combination of three tests: the non-parametric Pettitt-Mann-Whitney (PMW) test (based on the ranks of the values in the sequence), the Mann-Whitney-Wilcoxon (MWW) test (a rank sum test) and the Cumulative Sum Technique (CST). The details of these tests are described in Hoppe & Kiely (1999). The change points in this study were detected by all three tests and only the change points that exceeded the 90% confidence level were retained. Significant change points were detected in the monthly anomalies time series of erythemal UV dose, total ozone and AOD. For UV and ozone, the change points occur around the same time period (February/March 1998) (see Figure 14 for ozone time series). The change point in AOD was observed around June 1996.

We also studied the frequency distribution of UV radiation, global radiation, total ozone and AOD at 320nm. Only for ozone there is a clear shift in the frequency distribution (Figure 13) of the daily ozone values. The entire curve of the frequency distribution is shifted which means that both the minimum and maximum values of the distribution have increased between the two decades. After a period with lower ozone values in the beginning of the 1990s, ozone seems to start recovering from the late 1990s. This is also clear from Figure 14 which shows a lower ozone mean before 1998.

Using all daily values from 1991 to 2006, the following regression equation describes the relation between UV, global radiation, total ozone and AOD:

$$UV = 81.82 * AOD - 3.07 * OZON + 0.61 * RAD + \varepsilon$$

with UV: erythemal UV dose (W/m^2); RAD: global radiation (W/m^2); OZON: total ozone column (DU); AOD: AOD at 320nm. The adjusted R^2 value of the multiple regression is 0.98, which means that global radiation, ozone and AOD together explain 98% of the variation in daily UV. Of these parameters, global radiation has the biggest influence on UV. The regression equation between the modeled and measured erythemal UV values ($f(x) = 0.96x + 57.85$) and the correlation coefficient (0.96) reveal the good agreement between model and reality. However, in some cases, negative UV doses were modeled, which is a sign that the model does not always give realistic results. Therefore, we decided to perform the multiple regression analysis on a seasonal scale and hence derive regression coefficients for each season. For all seasons, more than 98% of the total variation in UV is explained by the combination of global radiation, ozone and AOD. Changes in the variation of global radiation are again the most important and the influence of the variation in ozone and AOD is much smaller. We conclude that the seasonal models perform well in estimating the measured UV values. The correlation between the modeled and measured values varies between 0.84 (in winter) and 0.96 (in autumn). Each model has a tendency to underestimate the measured values. The summer model performs best with an absolute mean model error of only 7.31%.

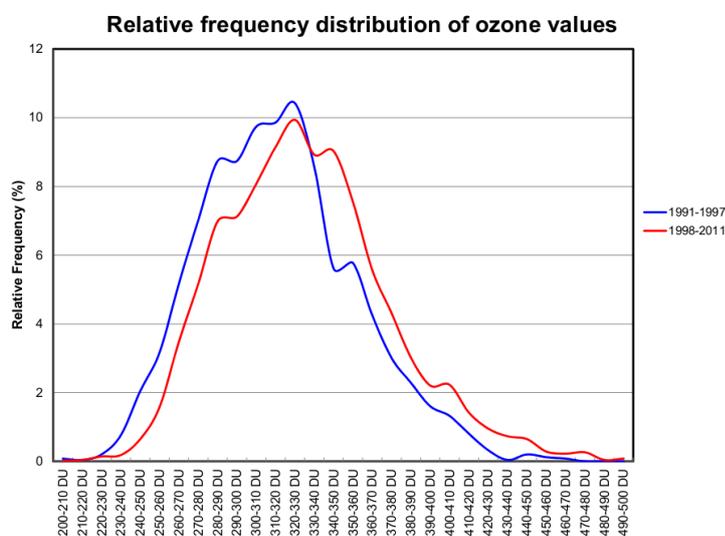


Figure 13: Relative frequency distribution of daily ozone values before and after the change point: 1991-1997 (in blue) and 1998-2011 (in red)

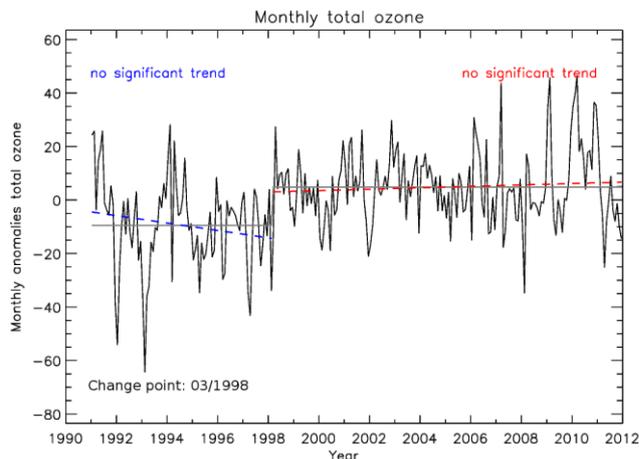


Figure 14: Time series of monthly mean ozone anomalies with the detected change point in 1998.

Task 3.2.2 Aerosol lidar

Figure 15 shows an example of a plot with the MLH determined from the LIDAR-ceilometer, compared with ALARO7, ECMWF and radiosounding values. The LIDAR-ceilometer MLH values are all quality-flagged and their quality flag values are equal to either 1 (=weak quality) or 2 (=good quality).

Task 3.3 Aerosol data interpretation

Task 3.3.1 Comprehensive data set of aerosol optical properties

First results of the intercomparison between the different instruments of KMI-IRM and BIRA are expected by the end of 2013 and a comprehensive analysis of the data set will take place in 2014 (when the nephelometer is operational).

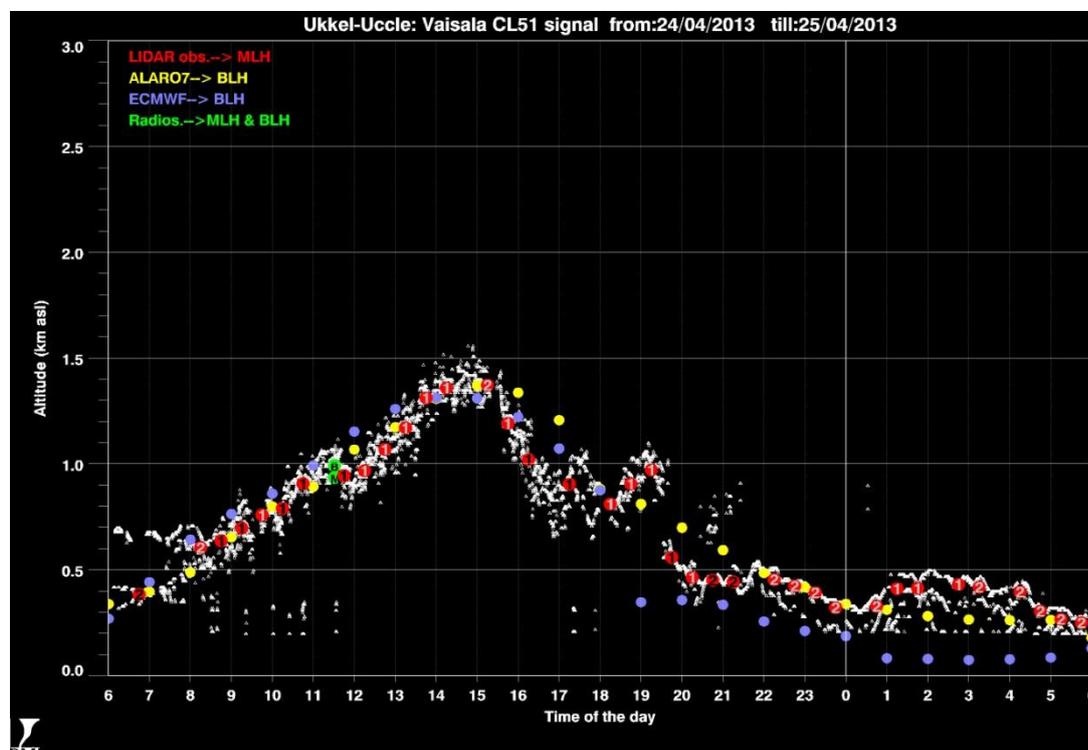


Figure 15: Example of 24 hours of MLH retrieved from LIDAR measurements by the algorithm at Uccle between 120 and 3000m (white points represent individual MLH values, red points represent the averaged values (over half an hour)). Within the red points there is a number that corresponds to the MLH quality evaluation. The MLH measurements are compared with the Boundary Layer Height (BLH = MLH + entrainment zone) computed by ALARO7 (yellow points)

and by ECMWF (blue points) and with the MLH and the BLH retrieved from the temperature profile measured by the radiosounding of Uccle when it is available (green points).

Task 3.3.2 Aerosol modeling with CHIMERE

We compared the modeled AOD and SSA values with the available measurements (closest to 11UT) from the Brewer spectrophotometer and the Cimel sunphotometer at Uccle. The correlation coefficients between the modeled and measured values (closest in wavelength) are shown in Table 3. This shows that the first attempt to model the AOD with CHIMERE and OPAC was already rather successful with a correlation of 0.54 between the AOD from OPAC and Cimel at 500nm. For SSA however, the agreement between modeled and 'measured' values is very poor (correlation of 0.04).

	Modeled	Measured	Correlation
AOD	OPAC 300nm	Brewer 306nm	0.34
	OPAC 350nm	Brewer 340nm	0.41
	OPAC 500nm	Cimel 500nm	0.54
SSA	OPAC 450nm	Cimel 440nm	0.04

Table 3: Correlation coefficients between the modeled and measured AOD and SSA

We also looked into the influence of the different input parameters on the modeled AOD and SSA values (correlation coefficients in Table 4). It seems that the relative humidity (RH) class and the amount of soot are of significant influence for the modeled SSA. From Figure 16 it can be seen that the lower the RH class, the higher the range of modeled SSA values with the SSA values having the tendency to be lower at lower RH class values. The relation between the amount of soot particles and the SSA is also clear (Figure 17). The more soot particles in an aerosol mixture, the lower the SSA, which is normal as soot particles are absorbing. For AOD, the correlation with the MLH and the amount of water soluble particles is the highest. An increase in both parameters is characterized by an increase of AOD.

	OPAC SSA 350nm	OPAC AOD 350nm
RH class	0.68	0.08
MLH	-0.34	0.36
Seasalt	-0.39	0.27
Water soluble	0.39	0.59
Mineral	-0.27	0.29
Insoluble	-0.03	0.00
Soot	-0.6	-0.03

Table 4: Correlation coefficients between the modeled AOD/SSA and the different input parameters

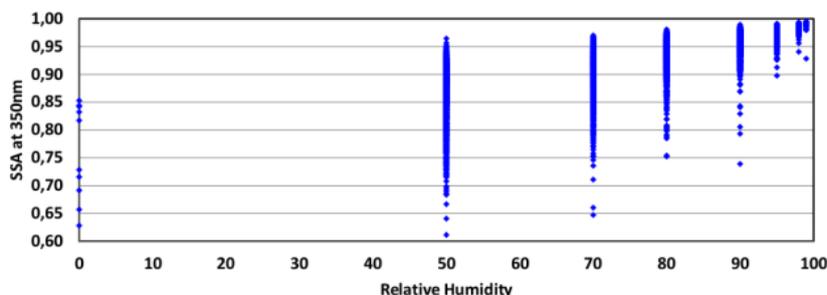


Figure 16: modeled SSA at 350nm in function of the relative humidity class

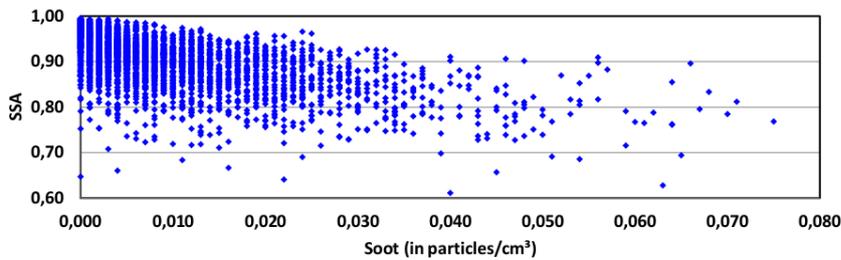


Figure 17: modeled SSA at 350nm in function of the amount of soot particles

Task 3.3.3 Aerosol sources from backtrajectories

The cluster analysis divided the trajectories between 1990 and 2010 into 12 different clusters. Figure 18 shows the distribution of the measured Brewer AOD values (at 320nm) and the modeled OPAC SSA values (at 350nm) over the different clusters. If we look into the properties of each cluster, it is clear that AOD and SSA are influenced by the origin of the air masses. Air coming from clean zones (eg. from W-NW regions, clusters 4 and 7 in Figure 19) is characterized by lower AOD and higher SSA values, whereas local air masses (cluster 8 in Figure 19) show higher AOD and lower SSA.

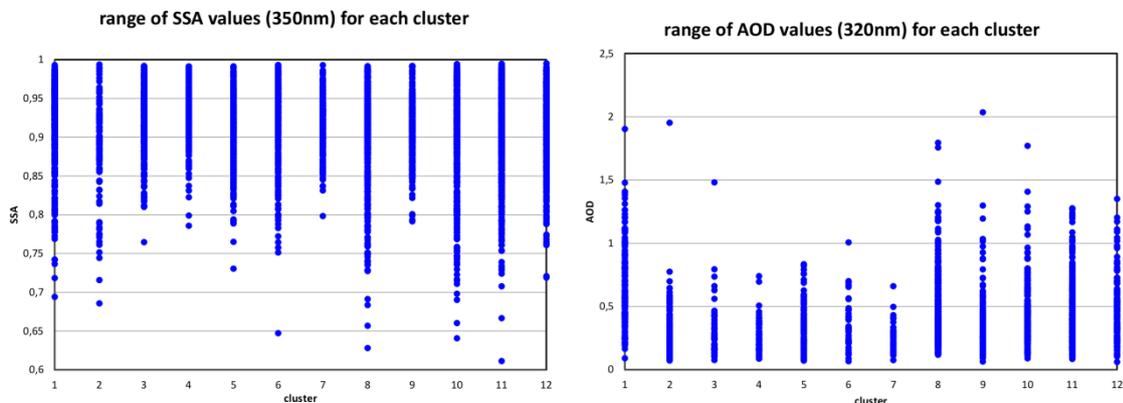
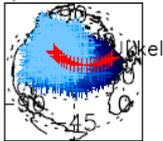
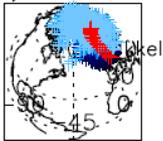


Figure 18: Range of AOD and SSA values for the clustered trajectories

3D back trajectory for the 950 hPa level, cluster4



3D back trajectory for the 950 hPa level, cluster7



3D back trajectory for the 950 hPa level, cluster8

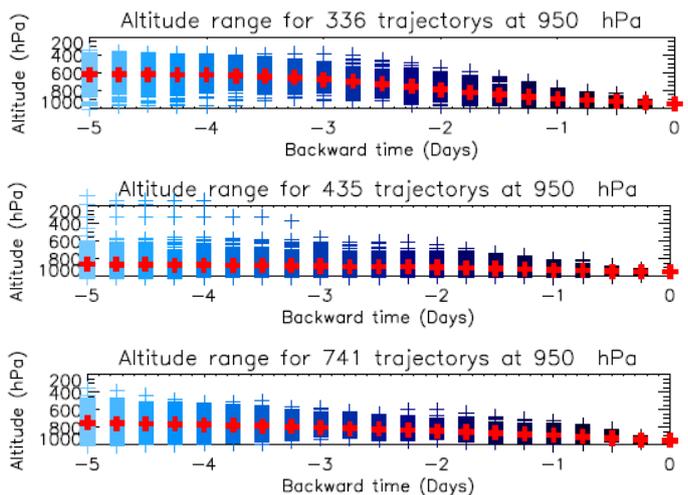
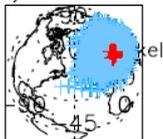


Figure 19: Detail of clusters 4, 7 and 8. The blue points represent each individual trajectory (and its height in the right-hand figure), the red points represent the mean of the trajectory (and the mean height in the right-hand figure).

WP4. African emissions

The main objective of this workpackage is to study African emissions by means of complementary observations from the ground and from space. Current satellite observations indicate large uncertainties on these emissions which motivates the need for additional

measurements, using reference high precision instrumentation from the ground. We report on the installation of a scientific grade high performance MAXDOAS instrument in Bujumbura (Burundi), to monitor aerosol and several key atmospheric trace gases such as formaldehyde, nitrogen dioxide, glyoxal, ozone and sulphur dioxide.

Task 4.1. Installation of MAXDOAS instrument in Burundi (Bujumbura)

In 2013, the MAXDOAS instrument developed and assembled in late 2012 has been finalized and calibrated. This work was performed in part during the training period of Eugène Nzendako, a physicist from the University of Burundi. The training of M. Nzendako ended in February 2013. During his stay at BIRA, he contributed to the preparation and testing of the instrument including its initial calibration. He was also trained to the usage of the various control and evaluation software packages. In the period from March to late April 2013, the instrument was finalized and fully calibrated. Before its installation in Bujumbura, it was deployed in the international MADCAT intercomparison campaign which was organized at the Max Planck Institute of Mainz in June - July 2013. This campaign allowed for a complete verification and validation of the instrument against similar systems. This led to the identification of an instrumental problem which could be fixed during the summer period at BIRA-IASB. The final calibration and preparation of the instrument and the organisation of its transfer to Burundi (customs) took place in the September-October period. The instrument was finally installed in Bujumbura in the course of November 2013 (see Figure 20), together with a commercial CIMEL sunphotometer for accurate aerosol optical depth measurements as part of the AERONET network. Both systems are operational since 25 November 2013. Raw data (spectra) are transferred to BIRA on daily basis at night using a dedicated internet line. The overall system is highly securised by means of a dedicated room build on purpose to host the instrumentation. Also the MAXDOAS optical head and the CIMEL system installed on the roof of the building are protected by several levels of fences, one of which is visible on Figure 20. In order to cope with the regular power failures (typically several times a day), the whole system is connected to a high capacity battery system allowing for autonomous operation of the instruments even during prolonged power failures (up to several hours).



Figure 20: MAXDOAS instrument installed on the roof of the Physics Department building of the University of Burundi, in Bujumbura (3°S, 30°E).

Task 4.2. Data analysis for trace gases and aerosols

The instruments are completely automated using a software developed at BIRA-IASB, which controls the different devices (sun tracker, filter wheel, CCD), the sequence of measurements (elevation angles, dark currents), automatically adjust the integration time according to ambient light level, etc. The overall system can be remotely controlled from BIRA which allows to support the local operator (E. Nzendako) in case of problems or failures. Data are downloaded daily by ftp and raw data are stored at BIRA for further processing. An automated processing chain has also been developed at BIRA which also

includes a facility for rapid quality control of the results by means of a local web page. First results confirm that the instrument performs nominally. The spectral signatures from all target species (NO₂, HCHO, O₃, H₂O, O₄, etc) are detected with high S/N ratio according to specifications. Figure 21 shows typical fitting results for HCHO and NO₂.

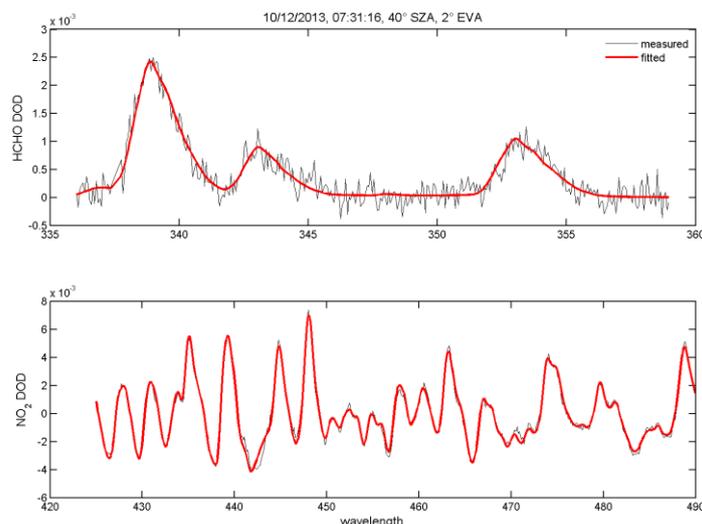


Figure 21: Typical DOAS fit results for HCHO and NO₂ obtained on 10 December 2013. The spectral signatures of both molecules are clearly detected with nominal S/N ratio.

First analysis have been performed for HCHO and initial comparisons with GOME-2 and OMI satellite measurements, as well as with results from Three Dimensional Chemical Transport Model (3D-CTM) simulations have been conducted. Although comparison statistics are still poor (considering the short measurement period available), results displayed in Figure 22 are encouraging and suggest that MAXDOAS and satellite measurements agree within their combined uncertainties.

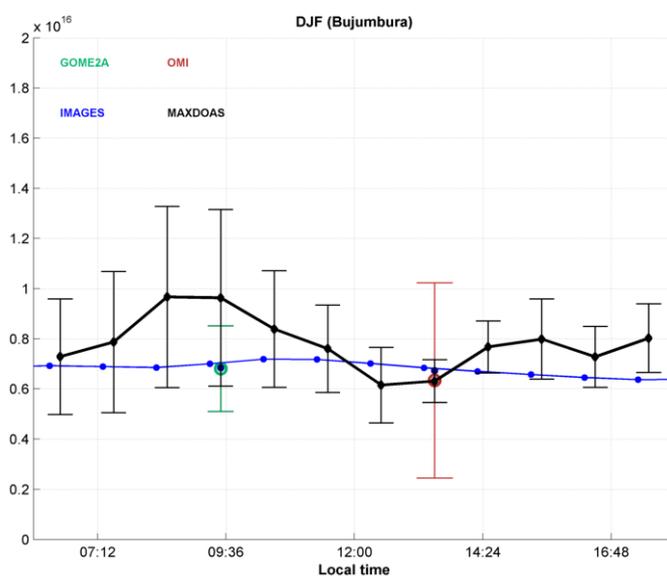


Figure 22: Average diurnal variation of the HCHO vertical column density as measured by the Bujumbura MAXDOAS instrument (black lines), simulated by the 3D-CTM IMAGES and measured by the GOME-2 and OMI satellite instruments (green and red circles respectively). All measurements agree within their combined error bars.

More work is needed however to refine the MAXDOAS analysis as well as the methodology of comparison with satellite measurements, considering e.g. the different vertical sensitivities of both measuring systems. Such comparison must also be extended to other species, and

the overall data sets need to be studied for their variability, impact of local sources, etc. This work will be conducted during the next phase of the project in 2014.

WP5. Outreach

Outreach activities have included:

- Publications and communications at symposia and workshops → see Section 9
- Delivery of data to databases : GEISA, HITRAN for spectroscopic laboratory data and NDACC, TCCON for geophysical data; delivery of TCCON data of Ile de La Réunion to the ICOS community has been prepared and will start in 2014.
- Collaboration with modelers (IMAGES, KASIMA, SLIMCAT, GEOSchem): AGACC-II provides data in support of model verification and process studies.
- Collaborations with in-situ data providers (e.g., EMPA at the Jungfraujoch, the AGAGE network) for exchange of data and understanding.
- Support to validation of /comparison with satellite data (IASI, GOME-2, OMI, ACE-FTS, ...)
- Use of the data in other international projects, like the ESA Greenhouse Gas CCI project, the EU FP7 NORS project, etc.
- Positioning in NDACC (M. De Mazière has been elected NDACC co-chair at the NDACC SC meeting in October 2013, for a 3-years term) & TCCON and ICOS
- C. Vigouroux authored an article in the 2013 NDACC Newsletter, building on the results on VOC in the biomass burning seasons obtained at La Reunion in AGACC-II
- Web pages: <http://agacc.aeronomie.be>
- An AGACC-II Flyer
- An article in Science Connection is planned in 2014
Contribution to the brochure on the Science for Sustainable Development Programme
- Work carried out in AGACC-II will be included in the 2014 WMO Scientific Assessment on Ozone Depletion.
- The expertise acquired by the AGACC partners has been valorized, e.g., in the fact that they are contributing strongly to the international SI²N initiative about the evaluation of long-term trends in the ozone vertical distribution. The results will also be included in the 2014 WMO Scientific Assessment on Ozone Depletion.

5. PRELIMINARY CONCLUSIONS AND RECOMMENDATIONS

Laboratory spectroscopy data

In the frame of task 1.3, we have started an experimental and theoretical study of line-shape-specific parameters for the $\nu_1+3\nu_2^1$ band of CO_2 near 3340 cm^{-1} . Task 2.2.1.c devoted to the improvement of reference spectroscopic information for $^{12}\text{C}_2\text{H}_4$ has been completed on schedule. We found that line intensities measured within this project for the ν_7 band are larger than HITRAN by about 8 % at 860 cm^{-1} and approximately agree with HITRAN at 1080 cm^{-1} . The observed discrepancies are within the stated uncertainty of the line intensities in HITRAN (5–10%). We believe that they come from the incomplete character of the theoretical model used to generate the line intensities in HITRAN. We generated an updated linelist (in HITRAN format), in which these discrepancies are removed. We estimated that the uncertainties on the corrected line intensities are in the 2–5% range. In addition, this updated linelist provides for the first time self-broadening coefficients for all the bands (uncertainty = 5–10%). Indeed, the self-broadening coefficients in HITRAN 2012 are only rough guesses (HITRAN error code = 0: “unreported or unavailable”). Task 2.2.1.b devoted to the improvement of reference spectroscopic information for C_2H_6 is progressing well. We are building a linelist for the $3.3\text{ }\mu\text{m}$ spectral region that will include line-by-line parameters for the Q branches of the ν_7 band, as anticipated. In addition, parameters for the weaker R and P branch lines of the ν_7 band and for lines of the nearby parallel component of the $\nu_8+\nu_{11}$ band will also be available. Difficulties we faced with task 2.2.1.a devoted to the improvement of reference spectroscopic information H_2CO are essentially solved; a systematic procedure to correct TDL spectra affected by detector non-linearities is being developed. As tasks 1.3, 2.2.1.b and 2.2.1.a are still ongoing, it is too early to provide recommendations for the related reference spectroscopic information.

Atmospheric composition data at Jungfraujoch and Ile de La Réunion.

The strength of the solar infrared absorption measurements with FTS for remote sensing of the atmospheric composition has again been confirmed in the 3rd year of the project: the detection capability of additional species, like methylchloride at Ile de La Réunion, HCFC-142b and methanol at Jungfraujoch, has been demonstrated. Time series have been retrieved for a number of species that play a role in the global warming problem and the total chlorine and fluorine budgets, e.g., CF_4 . The importance of good reference spectroscopic parameters, high-quality and continuous records of observations (spectral data) and adequate retrieval algorithms and strategies has again been acknowledged. The confrontation of the data with complementary measurements from satellite and in-situ surface observations and with model simulations is the best way to guarantee progress in the understanding of the atmospheric processes and long-term evolution. Another important aspect is the consistency between observations made with different techniques, like the FTIR versus MAXDOAS measurements of formaldehyde at the Jungfraujoch, or the methane concentrations observed in different infrared spectral ranges: it is important, in particular for the satellite and modelling communities, to get a clear view on the uncertainties associated with the data.

The data are essential ingredients in assessments of the atmospheric state, like the WMO scientific Assessment of ozone depletion.

In 2014, a special effort will be devoted to the submission of all the new data, after proper consolidation, to the international databases.

Also, the time series of high-precision greenhouse gases at Ile de La Réunion is growing, and will be better exploited in 2014.

Aerosol observations and their interpretation

The preparatory work on instruments and data retrieval algorithms is now leading to a set of complementary data of aerosol properties above Uccle that provides promising opportunities to learn more about the aerosol distribution in the atmosphere, their optical properties, their origin, their impact on the radiative budget, etc.

The combination of CHIMERE and OPAC to model aerosol optical properties (such as AOD and SSA) also looks promising for the future. The modeled AOD values already show a good correlation with the measured values. However, the modeled SSA values compare very poorly to the CIMEL SSA values. It would be interesting to look into the possibility of making some alterations to the OPAC software package in order to get more accurate modeled values. If it is possible to improve the model, we could use the modeled AOD (and/or SSA values) in the UV index forecast program.

First analysis of the results of the back-trajectory analysis showed that the air masses over Uccle can be divided into 12 clusters. Between these clusters, differences in AOD and (modeled) SSA have been clearly seen. A more detailed analysis is planned and will give us more insights into the relation between AOD/SSA and the origin of the air masses above Uccle.

The more in-depth analysis of the data in 2014 is expected to lead to more insight in the aerosol occurrence and their impact on the radiation budget above Uccle. The analysis method will probably be applicable to other sites with similar observational capabilities.

African emissions

We have succeeded in setting up the planned instrumentation for an atmospheric observatory in Bujumbura, Burundi, namely a MAXDOAS instrument and a CIMEL sunphotometer. Several precautions had to be taken for securing the instruments and for avoiding too frequent interruptions of the measurements due to local electricity interruptions. At present, one scientist at the University, who was trained at BIRA-IASB, is in charge of supporting the operation of the instruments and he will be collaborating for the exploitation of the data. We are looking for more scientific collaborations with the local students and scientists.

The first data that have been acquired look very promising for solving some of the uncertainties that are still inherent in the satellite observations over the location, e.g., regarding the diurnal cycle of formaldehyde. The continuation of the observations and of the data analysis in 2014 will certainly give us more insight in the local emissions and chemistry and transport phenomena.

6. FUTURE PROSPECTS AND PLANNING

Laboratory spectroscopy data

The following activities will be carried out for tasks 1.3 and 2.2.1.a-c, devoted to the improvement of reference spectroscopic data for H₂CO, C₂H₆ and C₂H₄:

- We will finalize the measurements of improved line parameters for R-, P- and Q-branch lines of the $\nu_1+3\nu_2^1$ band of carbon dioxide. An article describing that work will be prepared.
- We will correct the TDL spectra of H₂CO affected by detector non linearities using the procedure currently being developed, and finalize the analysis of the FIR and IR spectra. This work will lead to the absolute intensity of the H₂CO IR lines probed by the TDL spectrometer. These line intensities will then be compared with HITRAN 2012 (Rothman et al, 2012) and used to “calibrate” the line intensities available therein. The quality of the modeling of the whole ν_1 and ν_5 band system (2500–3200 cm⁻¹) using the improved linelist (deliverable D2.5) will be assessed using the FTS spectra recorded, with particular attention to the regions used to probe H₂CO in the terrestrial atmosphere (Vigouroux et al, 2009). Deliverable D2.5 will then be sent to the ULg partner for validation with atmospheric spectra.
- We will finalize the linelist for the ν_7 band and the parallel component of the $\nu_8+\nu_{11}$ band of ethane (deliverable D2.4). It will include line positions, intensities, lower state energies and assignments. This information will be complemented with literature data for the air- and self-broadening and shift coefficients. The quality of this linelist will be assessed using laboratory spectra, and will then be sent to the ULg partner for validation with atmospheric spectra. An article describing this work will be written and submitted to a peer-reviewed journal.
- The completed work of task 2.2.1.c will be reported in an article to be published in a peer-reviewed journal. Deliverable D2.3 (the HITRAN 2012 linelist with corrected line intensities for the ν_7 band of ¹²C₂H₄ and new self broadening coefficients for all the bands) will be provided with it, as supplementary material. It has been sent to the ULg partner for validation with atmospheric spectra. The frequency analysis performed using the French model will be completed. The line intensities measured at ULB for the ν_7 , ν_{10} and ν_4 bands and reported earlier for the ν_{12} band (Rotger et al, 2008) will then be fitted using wavefunctions derived from this frequency analysis to determine parameters of the dipole moment function of ethylene. This work will result in another linelist, providing extensive and consistent reference information for the 4 bands observed at 10 μ m. An article describing that effort will be prepared.

Atmospheric composition data at Jungfraujoch and Ile de La Réunion.

The development of retrieval strategies will be finalised and consolidated time series will be analysed and disseminated. The final retrieval strategies and scientific results will be published. The consistency between data from different instruments / retrievals will be further investigated and improved where possible.

Also the impact of the updated spectroscopic reference data will be verified and time series for C₂H₆, C₂H₄ and H₂CO will be updated accordingly.

By the end of 2014 we will have acquired about 3 years of TCCON data and we will make a first geophysical analysis.

Aerosol observations and their interpretation.

A calibration campaign is planned for both Brewers in 2014. A paper with the results of the linear trend analysis, change point analysis and multiple linear trend analysis of erythemal UV dose, global solar radiation, total ozone and AOD at 320nm will be published.

In 2014, three new LIDAR-ceilometers (Vaisala CL51) will be installed at Zeebrugge, Diepenbeek and Humain. The near-real time dissemination of the backscatter profiles, the cloud base height detection, the MLH detection and the quality control flagging will be continued and expanded with the new stations.

The LIDAR-ceilometer network of Belgium will be integrated into the future European network which will be developed within the frame of the E-PROFILE program of EUMETNET and of the TOPROF COST-action. Together with the metadata, the LIDAR-ceilometer backscatter data (past and near-real time) will be made available in a standard format for the European network users. Data from the LIDAR-ceilometer at Uccle will be used to test calibration algorithms for a working group of TOPROF.

Due to some technical issues, the installation and operational use of the nephelometer has been delayed. We expect the problems to be solved soon and the installation is now planned for the beginning of 2014. When all instruments (of both KMI-IRM and BIRA-IASB) are running simultaneously, the entire data set of aerosol data at Uccle will be analyzed.

We will look into the possibility of making changes to the OPAC software package in order to be able to get more accurate results for the modeled AOD and SSA values. For instance, since the results seem to depend much on the used RH class, it would be interesting if we could find a way to use the actual measured RH value instead of a RH class. We will also continue with the analysis of the modeled AOD and SSA and with the comparison with measured values.

The correlation between the source regions of the aerosols and the observed AOD and SSA and their relation with meteorological conditions will be further investigated. Possible changes in AOD/SSA within certain clusters are to be investigated as are differences in the frequency of certain clusters. An attempt will be made to assign tendencies in AOD/SSA to either the origin of air masses (and meteorological conditions) or to changes in the emissions.

The full data set of aerosol properties at Ukkel will then be studied in the most comprehensive way and the impact of the aerosol on the radiative budget will be evaluated.

African emissions

The atmospheric monitoring in Bujumbura with MAXDOAS and CIMEL instruments will be continued and the resulting timeseries that will nominally cover about 1 year of data by the end of 2014 will be analysed as good as possible. This will include a characterisation of the variability of key tropospheric gases such as NO₂, HCHO, glyoxal, SO₂, O₃ and aerosols. These will be related to known natural emissions from vegetation, biomass burning and volcanoes as well as to anthropogenic emissions. Data will be used to assess the quality of satellite measurements of tropospheric gases in Central Africa, as well as to assess the output from three-dimensional chemical transport models such as the IMAGES model developed at BIRA. In particular the possibility to monitor the diurnal variation of the trace gases will be used to assess the consistency of multiple satellite data sets measuring at different local times. If feasible, signatures of transport of African emissions towards Ile de La Réunion will be investigated using the data at Bujumbura and at Ile de La Réunion and FLEXPART modelling.

Outreach

AGACC-II partners will continue to present their efforts and results to the international scientific community and to user groups, like the NDACC and TCCON communities, the Brewer User Group, etc. For example, methodologies developed in AGACC-II have a good chance to be 'copied' by other NDACC teams; this stimulates collaborative work on data from several sites.

Trend and emission determinations are key elements to support decision makers, and we would like to point out that AGACC-II results for CF₄ have been solicited for inclusion in the next edition of the WMO assessment on ozone depletion, together with those for CFC-11, -12, HCFC-22 and CCl₄.

In 2014, more focus will be put on dissemination of the data to databases.

Starting in 2014, BIRA-IASB will contribute the St. Denis TCCON data to the ICOS-INWIRE project. As part of the timely delivery, the data will become publicly available within 3 weeks after acquisition.

A workshop with the follow-up committee members and policy makers together with other projects in the Science for Sustainable Development Programme is an option that will be considered.

7. FOLLOW-UP COMMITTEE

The role of the Follow-Up Committee has been essentially to interact with the partners by asking appropriate questions, and making useful remarks, comments, and suggestions, during the annual meetings.

In addition, there is a strong interaction with J.-F. Müller because of his contributions with model results and useful insights in the tropospheric chemistry processes.

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9. PUBLICATIONS

9.1 Publications of the teams

9.1.1 Peer review

BIRA-IASB

Hase, F., Drouin, B. J., Roehl, C. M., Toon, G. C., Wennberg, P. O., Wunch, D., Blumenstock, T., Desmet, F., Feist, D. G., Heikkinen, P., De Mazière, M., Rettinger, M., Robinson, J., Schneider, M., Sherlock, V., Sussmann, R., Té, Y., Warneke, T., and Weinzierl, C.: Calibration of sealed HCl cells used for TCCON instrumental line shape monitoring, *Atmos. Meas. Tech. Discuss.*, 6, 7185-7215, doi:10.5194/amtd-6-7185-2013, 2013. (See Annex, publication No. 1)

Hassler, B., Petropavlovskikh, I., Staehelin, J., August, T., Bhartia, P. K., Clerbaux, C., Degenstein, D., Mazière, M. De, Dinelli, B. M., Dudhia, A., Dufour, G., Frith, S. M., Froidevaux, L., Godin-Beekmann, S., Granville, J., Harris, N. R. P., Hoppel, K., Hubert, D., Kasai, Y., Kurylo, M. J., Kyrölä, E., Lambert, J.-C., Levelt, P. F., McElroy, C. T., McPeters, R. D., Munro, R., Nakajima, H., Parrish, A., Raspollini, P., Remsberg, E. E., Rosenlof, K. H., Rozanov, A., Sano, T., Sasano, Y., Shiotani, M., Smit, H. G. J., Stiller, G., Tamminen, J., Tarasick, D. W., Urban, J., van der A, R. J., Veefkind, J. P., Vigouroux, C., von Clarmann, T., von Savigny, C., Walker, K. A., Weber, M., Wild, J., and Zawodny, J.: SI2N overview paper: ozone profile measurements: techniques, uncertainties and availability, *Atmos. Meas. Tech. Discuss.*, 6, 9857-9938, doi:10.5194/amtd-6-9857-2013, 2013. (See Annex, publication No. 2)

Hendrick, F., J.-F. Müller, K. Clémer, M. De Mazière, C. Fayt, C. Hermans, T. Stavrou, T. Vlemmix, P. Wang, and M. Van Roozendaal, Four Years of Ground-based MAX-DOAS Observations of HONO and NO₂ in the Beijing Area, *Atmos. Chem. Phys. Discuss.*, 13, 10621-10660, 2013. (See Annex, publication No. 3)

Pinardi, G., M. Van Roozendaal, N. Abuhassan, C. Adams, A. Cede, K. Clémer, C. Fayt, U. Frieß, M. Gil, J. Herman, C. Hermans, F. Hendrick, H. Irie, A. Merlaud, M. Navarro Comas, E. Peters, A. J. M. Piters, O. Puentedura, A. Richter, A. Schönhardt, R. Shaiganfar, E. Spinei, K. Strong, H. Takashima, M. Vrekoussis, T. Wagner, F. Wittrock, and S. Yilmaz, MAXDOAS formaldehyde slant column measurements during CINDI: intercomparison and analysis improvement, *Atmos. Meas. Tech.*, 6, 167-185, 2013. (See Annex, publication No. 4)

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Lattanzi F., C. di Lauro, J. Vander Auwera, "Toward the understanding of the high resolution infrared spectrum of C₂H₆ near 3.3 μm", *Journal of Molecular Spectroscopy* 267 (2011) 71-79. (See Annex, publication No. 6)

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ULg

Mahieu, E., R. Zander, G.C. Toon, M.K. Vollmer, S. Reimann, J. Mühle, W. Bader, B. Bovy, B. Lejeune, C. Servais, P. Demoulin, G. Roland, P.F. Bernath, C.D. Boone, K.A. Walker, and P. Duchatelet, Spectrometric monitoring of atmospheric carbon tetrafluoride (CF₄) above the Jungfraujoch station since 1989: evidence of continued increase but at a slowing rate, *Atmos. Meas. Tech. Discuss.*, 6, 7535-7563, 2013a. (See Annex, publication No. 10)

9.1.2 Others

Theses

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Vigouroux, C.: Ground-based FTIR measurements of volatile organic compounds: precious data for model and satellite validation, NDACC newsletter, vol. 5, September 2013. <http://www.ndsc.ncep.noaa.gov/news/archives/> (See Annex, publication No. 11)

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De Smedt, I., M. Van Roozendaal, T. Danckaert, T. Vlemmix, G. Pinardi, F. Hendrick, H. Yu, T. Stavrou, J.-F. Müller, On the formaldehyde diurnal variation as observed with GOME-2 and OMI, ground-based measurements and model simulations, Oral presentation at the 6th International DOAS Workshop, Boulder, USA, 12-14 August 2013.

Desmet Filip, Christian Hermans, Corinne Vigouroux, Bavo Langerock, Francis Scolas, Nicolas Kumps, Martine De Mazière, Jean-Marc Metzger, Thierry Gaudou, Jean-Luc Baray: Poster: Reunion Island Site Report. NDACC IRWG/TCCON Meeting, June 10 – 14, 2013, Abashiri, Hokkaido, Japan.

Gielen, C., M. Van Roozendaal, F. Hendrick, C. Fayt, C. Hermans, G. Pinardi, and T. Vlemmix, Development of a cloud-screening method for MAX-DOAS observations, Poster presentation at the General Assembly of the European Geosciences Union, Vienna, Austria, 07-12 April 2013.

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Hendrick, F., J.-F. Müller, M. De Mazière, C. Fayt, C. Hermans, T. Stavrou, P. Wang, and M. Van Roozendaal, Four Years of Ground-based MAX-DOAS Observations of HONO and NO₂ in the Beijing Area, Oral presentation at the General Assembly of the European Geosciences Union, Vienna, Austria, 07-12 April 2013.

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Pinardi, G., Huan Yu, F. Hendrick, F. Tack, J. Granville, J.-C. Lambert, and M. Van Roozendael, End-to-end validation of total and tropospheric NO₂ columns from atmospheric composition satellite sensors, Poster presentation at the ESA ACVE conference, Frascati, Italy, 13-15 March 2013.

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Vigouroux C., M. De Mazière, P. Demoulin, C. Servais, T. Blumenstock, F. Hase, R. Kohlhepp, S. Barthlott, O. García, M. Schneider, J. Mellqvist, G. Person, M. Palm, J. Notholt, J. Hannigan, M. Coffey: Ozone tropospheric and stratospheric trends (1995-2012) at six ground-based FTIR stations (28°N to 79°N), poster presentation, EGU 2013 General Assembly, 7-12 April, Vienna, Austria, 2013.

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Warneke T., N. Deutscher, J. Notholt and TCCON partners, Recent developments in ground based measurements of greenhouse gases, Oral Presentation at ICOS-INWIRE KickOff meeting, Paris, January 2013.

Desmet F., C. Hermans, C. Vigouroux, B. Langerock, M. De Mazière, TCCON Measurements at Reunion Island, Oral presentation at ICOS-INWIRE KickOff meeting, Paris, January 2013.

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KMI-IRM

De Bock, V., Delcloo, A., Mangold, A. and De Backer, H., "Modeling of aerosol optical properties with CHIMERE and OPAC and validation with Brewer and Cimel measurements at Brussels, Belgium", European Aerosol Conference 2013, Prague, Czech Republic, 1-6 September 2013. (See Annex, publication No. 12)

Laffineur Q., De Backer H., Delcloo A., Nemeghaire J., and Debal. F., "Quality control on the retrieval of mixing layer height by LIDAR-ceilometer", European Geoscience Union General Assembly 2013, Vienna, 7-12 April 2013. (See Annex, publication No. 13)

ULB

Bourgeois M.-T., M. Rotger, M. Tudorie, J. Vander Auwera, V. Boudon, "*Frequency analysis of the 10 μm region of the ethylene spectrum using the D_{2h} top data system*", oral presentation (RI09), 68th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, USA, 17-21 June 2013.

Bourgeois M.-T., M. Rotger, M. Tudorie, J. Vander Auwera, V. Boudon, "*Frequency analysis of the 10 μm region of the ethylene spectrum using the D_{2h} top data system*", poster presentation (B21), 23rd Colloquium on High Resolution Molecular Spectroscopy, Budapest, Hungary, 25-30 August 2013.

Daneshvar L., T. Földes, S. Léonis, J. Buldyreva, J. Vander Auwera, "*Infrared absorption by pure CO_2 near 3300 cm^{-1} : measurements of collisional broadening and shift coefficients and analysis of line-mixing effects at subatmospheric pressures*", poster presentation (D3), 23rd Colloquium on High Resolution Molecular Spectroscopy, Budapest, Hungary, 25-30 August 2013.

ULg

Bader, W., E. Mahieu, B. Bovy, B. Lejeune, P. Demoulin, C. Servais, and J.J. Harrison, Evolution of methanol (CH_3OH) above the Jungfraujoch station (46.5°N): variability, seasonal modulation and long-term trend, poster presentation at the "*EGU 2013 General Assembly*", 07-12 April 2013, Vienna, Austria, 2013. (See Annex, publication No. 14)

Kolonjari, F., K.A. Walker, E. Mahieu, R.L. Batchelor, P.F. Bernath, C.D. Boone, S. Conway, L. Dan, D. Griffin, A. Harrett, Y. Kasai, A. Kagawa, R. Lindenmaier, K. Strong, and C. Whaley, Validation of ACE-FTS measurements of CFC-11, CFC-12 and HCFC-22 using ground-based FTIRs, poster presentation at the "*AGU Fall Meeting 2013*", 09-13 December 2013, San Fransisco, CA, USA, 2013.

Mahieu, E., S. O'Doherty, S. Reimann, M. Vollmer, W. Bader, B. Bovy, B. Lejeune, P. Demoulin, G. Roland, C. Servais, and R. Zander, First retrievals of HCFC-142b from ground-based high-resolution FTIR solar observations: application to high-altitude Jungfraujoch spectra, poster presentation at the "*EGU 2013 General Assembly*", 07-12 April 2013, Vienna, Austria, 2013b. (See Annex, publication No. 15)

9.2 Co-publications

9.2.2 Not peer review

BIRA-ULB-ULg

Duflot, V., Hurtmans, D., Clarisse, L., R'honi, Y., Vigouroux, C., De Mazière, M., Mahieu, E., Servais, C., Clerbaux, C., and Coheur, P.-F.: Measurements of hydrogen cyanide (HCN) and acetylene (C₂H₂) from the Infrared Atmospheric Sounding Interferometer (IASI), *Atmos. Meas. Tech.*, 6, 917-925, doi:10.5194/amt-6-917-2013, 2013. (See Annex, publication No. 16)

BIRA-ULg

Mahieu, E., B. Bovy, W. Bader, P. Demoulin, B. Franco, B. Lejeune, C. Servais, and C. Vigouroux, Overview of the geophysical data derived from long-term FTIR monitoring at the Jungfraujoch NDACC site (46.5°N), poster presented at the 6th International GEOS-Chem Meeting, 6-9 May 2013, Harvard University, Cambridge, MA, 2013c. (See Annex, publication No. 17)