



FOREGROUND ACHIEVED

WP2/ Networking Activity N1: Raw Data Analysis, Data Intercomparison and Quality Assurance. Lead partner FZJ

The effort within WP2 was directed toward organizing comprehensive intercomparison campaigns for testing and validating instruments and methods developed by the EUROCHAMP-2 beneficiaries against external applications.

Intercomparison campaigns:

- ◆ Formal Intercomparisons of Observations of Nitrous Acid (FIONA): in May 2010 a formal comparison of *instrumentation for measurements of HONO* was performed at EUPHORE (beneficiary no. 3 CEAM). William Bloss from U. Birmingham acted as referee. Seventeen instruments using 11 different detection methods participated to FIONA: seven Eurochamp-2 groups and 10 external groups were supported under the TA scheme (TA activity 0014, see short report for details¹).

The campaign was very successful, with many days of intercomparison of a wide range of instruments accounting for a wide range of scenarios (urban and semi-rural). The majority of the instruments could successfully follow the wide dynamic range, which was explored for HONO. However, some setbacks occurred due to malfunctions that were observed later in the campaign. A large set of data was collected regarding the primary target - HONO - and additionally some instruments delivered data regarding NO₂ detection. The outcomes of the FIONA campaign were partly reported at conferences during 2011-2013 and used in instrument development and modelling.

- ◆ FAGE intercomparison at SAPHIR (beneficiary no. 2 FZJ): two FAGE (Fluorescence Assay by Gas Expansion) instrument for OH and HO₂ measurements (SAPHIR vs. University Lille, France) were compared. In general a very good agreement was found for the new instrument (Lille) with the existing instrument (FZJ) for OH, while more deviation between the two was found for HO₂ (TA 0016).

- ◆ Instrument comparison for the measurement of glyoxal (GLY), methyl-glyoxal (MGLY), and nitrogen dioxide (NO₂) in July 2011: a comprehensive campaign was conducted at EUPHORE (CEAM) and the results compared with ones obtained in an atmospheric simulation chamber in USA (NCAR Boulder, CO US). Six instruments from five research groups from Europe and USA were presented at CEAM (partly supported by TA 0054). The experimental conditions were chosen to cover the tropospheric environments from *clean* to *pollute*, and influence of potential interferences.

Dr. Maria T. Baeza Romero (presently at Universidad Castilla la Mancha, ES) did act as a referee. The final analysis of this activity will take some more time but preliminary results proved that the initial objectives were achieved.

- ◆ Comparison of several off-line and spectroscopic techniques for the analysis of carbonylic compounds at CEAM: the feasibility of the *microfluidic derivatisation technique* was assessed in quantification of α -dicarbonyls formed during the photo-oxidation of isoprene in the EUPHORE chamber was assessed vs. various established techniques. Good correlations

¹ A list of campaigns supported under the transnational access scheme in EUROCHAMP-2 and the short reports provided by users can be found at: http://www.eurochamp.org/transnational_access/.



were found between *microfluidic measurements* and Fourier Transform Infra Red (FTIR, $r = 0.844$), Band Cavity Enhanced Absorption Spectroscopy (BBCEAS, $r = 0.749$), solid phase micro extraction (SPME, $r = 0.787$), and a photochemical chamber box modelling calculation ($r = 0.890$) in GLY measurements.

♦ AQUAVIT2 - Intercomparison of atmospheric hygrometers at the AIDA chamber (KIT): Seventeen different groups from 6 countries participated with 36 different instruments and more than 50 scientists to the AquaVIT 2 campaign (April 2013). The results are foreseen for publication 2014 in the Atmospheric Measurement Techniques journal.

While the data analysis is still ongoing it can already be stated that the AquaVIT 2 water vapor intercomparison was a technical success with respect to measurement accuracy and instrument calibration and validation.

At present (December 2013), the data is still kept confidential by the referees of the intercomparison. Eventually the results of AquaVit2 are going to be published 2014 in Atmospheric Measurement Techniques (AMT).

Quality assurance

Since decisions are in many cases based on the results of measurements, the results of measurements performed in different laboratories and by different instruments must be comparable and reliable. A part of the effort in WP2 was focused on: 1) assuring that a test method is fit for the intended purpose, 2) establishing traceability of the results to stated references and 3) estimate the uncertainty of measurement.

However within research, as performed by the Eurochamp members, the scope for comparison may vary. In order to achieve results that are comparable and suitable for inclusion in the EUROCHAMP database there is as well a need of a common quality protocol. Therefore, based on comparative exercises within the consortium a Protocol for calculations of measurement uncertainties within the consortium was issued.

The comparative exercises within the EUROCHAMP infrastructure included intercomparison of ozone instruments using traceable calibration (beneficiary no. 10 – SP), characterisation of potential interference in chemiluminescence measurements of ambient atmospheric NO_x in the presence of alkenes (beneficiary no. 3 – CEAM), the series of OH radical measurements by LIF and DOAS performed at SAPHIR (beneficiary no. 2 – FZJ) in 2011, 2012 and 2013.



WP3/ Networking Activity N2: Central Database of Environmental Chamber Studies and Central Spectroscopic Databases. Lead partner CEAM

The main objectives in WP3 are:

- To maintain, further promote and improve a www-based database on environmental chambers studies, which was initially created within the EUROCHAMP project², with the aim of providing different services to the project participants, the atmospheric chemistry research community and other stakeholders.
- to further explore and develop specific products for communities such as modellers, initially mainly for use within the project, but later to offer the products in the public domain (i.e. issues related to metadata for modelling studies).
- to incorporate new modules with reference databases of mass spectra database of derivatives from PFBHA, BSTFA, etc.; IR spectra, and spectroscopy related software tools for UV-Vis and IR.

The Environmental Chamber Studies Database (EUROCHAMP DB) provides a practical tool for the optimisation of the resources invested in research and help to advance the knowledge acquired by atmospheric scientists.

The activities performed over the whole duration of the project in fulfilment of the above objectives comprise:

- surveillance of quality and quantity of data sets submitted by the partners,
- establishing a database policy regarding administration and use rights, security and controlling measures,
- continuous development of the database to accommodate new features and respond to the feedback received from users.

The format used for the reference spectra is JCAMP-DX as agreed in the workshop hosted by CEAM: EUROCHAMP-2 Database and spectroscopic tools workshop (October 20th-21st, 2010, Valencia, ES).

The database policy was established 2009 and it regulates the different access levels for users, intern and extern to the Consortium. The access to the database content is provided upon registration (individual users and institutions), but *guest* visits (read only) are also allowed.

Statistics on data sets uploads by partners and *visits* were provided with each periodic progress report.

The development of the database comprises two aspects: 1) new modules to better sort the information (i.e. reference spectra modules) and 2) new tools to operate with the content of the database.

Under first aspect modules for mass spectra of derivatives from PFBHA³ and BSTFA⁴ and FTIR reference spectra were created together with a user interface including data introduction, data retrieval and security features.

² <http://eurochamp-database.es/>

³ Pentafluorobenzyl)hydroxylamine hydrochloride

⁴ N,O-Bis(trimethylsilyl)trifluoroacetamide



As new tools for the EUROCHAMP database (not for *guest*) were created:

- a search tool that allows the comparison of different mass spectra in JCAMP-DX files, in the GCMS database of derivatives,
- *IR-Spec* that facilitates the work with Infrared spectra collected by different instruments;
- *Main_polwin* is a home-made software developed at CEAM for the automatic analysis of FTIR samples although it allows to work also with UV spectra. The program is distributed for free upon request.

An “ask the experts” forum was created for the database registered users. Users can read and write messages, create threads of discussion related to database, atmospheric chemistry, smog chamber, gas and aerosol modelling, linked databases such as NIST, LEEDS MCM etc.⁵

The majority end users to benefit from the EUROCHAMP database are *modellers*. An intercomparison exercise, using datasets from the EUROCHAMP DB, was performed with participation of modellers from KIT (Karlsruhe, DE), ETH (Zurich, CH), and Imperial College of London (UK) in 2011. The results were discussed at the “Workshop On Modelling Chamber Aerosols” (12-14.04.2011, Manchester, UK) and lead to a further development.

Thus a unique format (edf format, based in ASCII format) makes it possible to incorporate the data in the different models. A graphical interface, based on the *AtChem* model developed by the University of Leeds (output in edf format), allow modelling experiments carried out in different chambers and comparison with experimental results.

The statistic data on use/visits are encouraging with respect to the usefulness of the EUROCHAMP database for the scientific community.

The consortium decided at the final project meeting (Wuppertal, 28-29.12.2013) that:

- the database will be maintained for at last 5 years after the termination of EUROCHAMP-2;
- the data sets should continue to be improved (in quantity and quality);
- it should be proved if the users acknowledge using the DB in publications.

⁵ http://eurochamp-database.es/Data_Base.htm through the link “discussion forum”.



WP5. Improved Analytical Methods for Organic Compounds. Lead partner UCC

The work in WP5 focused on the improvement and development of on-line and off-line techniques for measurement of organic species in both gas and particle phases. Particular emphasis was placed on techniques for the detection of oxygenated volatile organic compounds (OVOC) because of their wide variety and complexity. The main outcome of this work package is the delivery of improved tools to provide researchers with enhanced capability to address key issues such as the identity of “missing” reaction products, the development and testing of chemical mechanisms and the formation and composition of secondary organic aerosol (SOA).

Objectives

The following objectives for this work package were fully achieved:

- To develop and optimize the use of a range of new and emerging techniques for the on-line measurement of organic compounds in the gas and particle phases.
- To improve and extend the existing methods available for off-line measurement of organic compounds.
- To investigate the suitability of alternative techniques for measurement of organic aerosol produced in simulation chamber experiments.
- To improve the quality and quantity of techniques available for the measurement of organic compounds within the research infrastructure.

On-line gas phase measurement techniques

ICARE-CNRS optimised a portable gas chromatograph with photoionization detection (GC-PID) to facilitate its use for laboratory studies. Efforts were focussed on making it robust and easy to use, as well as improving its sensitivity and capability for on line analysis of a variety of organic compounds used and produced in simulation chamber experiments. This instrument, shown below in Figure 5.1, does not require the use of any chemical reactants to run, only air is needed as a carrier gas. Its installation and optimisation has greatly improved the measurement capabilities of the facility.

BUW developed a novel approach for the on-line detection of VOCs using Atmospheric Pressure Laser Ionization – Mass Spectrometry (APLI-MS). The inlet of a Bruker Esquire 6000 mass spectrometer was modified to accommodate a new linear flow unit which results in a significant increase of the ionization volume compared to other APLI systems commonly in use. In addition, a small UV solid state laser was employed as the radiation source which has a performance level comparable to that of an excimer laser used in current APLI-MS applications, but has the added benefits of smaller size, reduced signal noise, and lower purchase cost. The entire setup was successfully applied in several experiments of the OH radical initiated degradation of aromatic hydrocarbons and other compounds. The range of analyzable degradation products was extended further by employing two new approaches, atmospheric pressure electron capture ionization (APECI) and dopant assisted APLI. Using the latter technique, multiple oxygenated ring-opened products were observable as their quasi-molecular ions in the positive MS mode.

TROPOS worked on optimisation of the sampling method and instrumental operational parameters for online analysis of VOCs using both a gas chromatograph- mass spectrometer (GC-MS) and a proton transfer reaction mass spectrometer (PTR-MS) connected to the LEAK chamber. UBT also developed an on-line VOC sampling system based on a gas chromatograph with flame ionization detection (GC-FID) coupled to a modified cold-trap injector.



The combined efforts of CNRS-ICARE, BUW, IfT and UBT enabled considerable progress to be made on the installation and development of analytical systems for on-line measurements of organic compounds in the individual chambers and also within the research infrastructure as a whole.

Off-line gas phase measurement techniques

CEAM successfully developed a technique for the collection and analysis of gaseous carbonyl compounds using solid phase microextraction (SPME) with on-fibre derivatization coupled to GC-MS or GC-FID. This technique was optimized by developing standardized calibration procedures, the synthesis of commercially unavailable carbonyls and performing inter-calibrations with FTIR spectroscopy and Differential Optical Absorption Spectroscopy (DOAS). Efforts were focussed on quantitative measurements of the unsaturated dicarbonyls produced from the atmospheric oxidation of aromatic hydrocarbons. The technique was also successfully used in several intercomparison campaigns carried out at the EUPHORE chambers in 2011 and 2012 (Pang et al., 2014⁶).

TROPOS worked on improvements to denuder-filter sampling techniques for the identification and quantification of carbonyl compounds in chamber experiments. Two different denuder sampling techniques were compared for the analysis of gaseous carbonyl compounds formed in the atmospheric oxidation of monoterpenes, isoprene and aromatic hydrocarbons. A detailed coating protocol for XAD-4 resin and the combination of XAD-4 and 2,4-dinitrophenylhydrazine (DNPH) was also developed. Two research papers based on this work have been published (Kahnt et al., 2011, Böge et al., 2013).

Novel techniques to measure polyfunctional OVOC, containing many hydroxyl, carbonyl or carboxyl groups were also developed and tested by **PARIS12**. The original approach, which combined the use of multiple derivatization agents with an automated VOC sampler, proved to be problematic since it exhibited significant memory effects which resulted in artifacts and caused the detection limits to be increased. A second technique based on the use of classical TenaxTA sorption cartridges but modified by impregnation with a derivatizing solution was much more successful. In this method, sampling can be performed using a normal autosampler connected to a GC-MS instrument. The technique has shown very good sensitivity, allowing for quantification of polyfunctional OVOC down to ppt level. Successful applications during chamber experiments and in the field have been performed and reported in the literature (Rossignol et al., 2012, Sassine et al., 2014).

The development of these off-line techniques has been a particularly important part of WP5 since they involve the use of relatively simple sampling technology coupled with analysis using standard instruments such as GC-MS and LC-MS, which are available in most laboratories in the EUROCHAMP consortium. The benefits to the whole infrastructure, and indeed the larger research community, are clear.

On-line particle phase measurement techniques

UCC successfully used an aerosol time-of-flight mass spectrometer (ATOFMS) to monitor the formation of oligomers in SOA generated from the photooxidation of naphthalene under a variety of reaction conditions. It was shown that sufficient naphthalene starting concentrations (300-500 ppbV) must be used to ensure growth of SOA to sizes large enough to be detected by the ATOFMS. Careful data pre-processing must also be performed to remove background particles and ensure detection of larger oligomers. The high intensity desorption/ionization UV laser used by the ATOFMS results in excessive fragmentation and molecular information is thus difficult to obtain. Nevertheless, operation at low laser power is useful for certain

⁶ All references are publications emerged from activities in EUROCHAMP-2, s. section dissemination,



highly absorbing species and this approach proved to be valuable in identifying dimers in SOA produced from the direct photolysis of 1-nitronaphthalene (Healy et al., 2012). Furthermore, the real-time monitoring capabilities mean that the instrument is suited for chamber experiments where systematic study of reaction variables is explored.

PSI characterized SOA produced from the emissions of three different anthropogenic sources: a log wood burner, a Euro 2 diesel car and a two-stroke Euro 2 scooter. High-resolution mass spectra were obtained using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) and compared to SOA from α -pinene. As shown in figure 5.2, the spectra could be separated using principal component analysis (PCA). This means that at least for fresh SOA there is some possibility to separate it according to the precursors. However, with increasing aging time this differentiation will become impossible, as the differences will essentially disappear (Heringa et al., 2012).

PSI also tested a new lens for the inlet system of the aerosol mass spectrometer, which allows for particles up to 2.5 μm to be measured. This turned out to be important for measurements at high concentrations where the particles become increasingly bigger; in addition, bacteria could also be measured with this new lens (Wolf et al., in preparation). A method for the determination of peroxides with significantly improved detection limits was also developed and optimized. With this method it could be shown that under low NO_x conditions high concentrations are formed during initial SOA formation, which then are gradually decomposed with increasing aging time (Mertes et al., 2012).

FZJ and **IfT** investigated the use of the HR-TOF-AMS instrument for a variety of other applications in chamber studies. Some tests were more successful than others, e.g. it was demonstrated that detection of organosulfates in SOA was more difficult than anticipated while, on the other hand, the HR-TOF-MS was capable of clearly separating non-deuterated fragment ions from their partly and fully deuterated counterparts in SOA.

Overall, considerable progress has been made in assessing the various ways in which aerosol mass spectrometers can be applied to characterization of organic aerosol in chamber studies. In particular, operating conditions have been optimised for on-line analysis of SOA generated from biogenic and anthropogenic precursors. The infrastructure has also benefitted from the development of new approaches for understanding the large amounts of data produced by these powerful instruments.

Off-line particle phase measurement techniques

PARIS12 developed the supercritical fluid extraction (SFE) GC-MS technique for analysis of OVOC present in filter samples of SOA making the analysis more automatic and hence more reproducible and less time/manpower consuming. Large efforts were made to adapt the SFE-GC-MS techniques to organosulfates and oligomers. Nevertheless, due to the chemical nature of the derivatization reactions and the use of GC-MS which is inherent to the techniques, it was demonstrated that this was not technically feasible. On another hand, the SFE-GC-MS method for analysis of OVOC was improved greatly and this very sensitive technique was successfully compared with UPLC-MS².

SP explored the use of Time-of-Flight Secondary Ion Mass spectrometry (ToF-SIMS) for determination of the organic compounds present in SOA generated in simulation chamber experiments. Despite extensive experimentation, a very high level of ion fragmentation was observed inhibiting molecular identification. An alternative method, namely direct thermal extraction GC-FID/MS was found to be more successful in identifying species contained in SOA from biogenic and anthropogenic compounds. The FID signal was used for quantification and the MS for identification by matching the experimental mass spectra against the NIST mass spectral library. A mass spectral library of identified and unidentified oxygenated products was developed from the experimental results.



WP6: Improved analytical methods for inorganic trace gases and radicals. Lead partner PARIS12

This work package aims at improving the existing analytical/mathematical methods or developing new analytical methods to fulfill the following objectives:

- To reach a better detection limit and reliability for the measurement of the atmospheric oxidizing radicals OH, NO₃ and Cl
- To further enhance the capability in the detection of transient radicals (RO₂ and HO₂) in simulation chambers
- To improve time resolution and detection limit in the detection of HONO
- To provide sensitive in situ trace gas detection also in the presence of aerosol particles
- To develop automatic methods for the standardization and reliability of the spectral data analysis

Direct measurements of radicals and very low concentrations of gases during simulation chamber experiments are still a challenging task. Highly sensitive spectroscopic techniques dedicated to chamber reactive mixtures characterization have been the subject of research of many Eurochamp-2 partners. These techniques offer non-extractive passive measurements combined with high spatial and temporal resolution which are particularly well adapted to chamber measurements.

During EUROCHAMP-2 in agreement with the objectives of the work-package various system or methodologies have been developed to enhance the infrastructures capabilities

Cavity Spectroscopies

Among the new techniques, a very sensitive method, the Cavity-Enhanced Absorption Spectroscopy (CEAS), has been developed. This technique is based on high-reflectivity mirrors leading to optical path lengths of up to a few kilometres. Its application to the measurement of radicals or stable species exhibiting structured absorption spectra in the UV range at the ppt level has already been demonstrated. Existing Cavity Ring Down (CRD) system techniques were tested against DOAS in the NO₃-N₂O₅ intercomparisons campaign through EUROCHAMP. All the cavities developed through this work-package aim at detecting low levels of nitrate radical.

At ULEEDS the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) has been provided with a cavity ring down (CRD) instrument for the detection of NO₃. The system was tested by directly measuring the rates of reaction of NO₃ with a series of aldehydes and the results were found to be in agreement with published data. The CRD facility involved the installation of new mirror mounts in HIRAC and development of new data acquisition code as ring-down data were recorded at 200 Hz, with a significant improvement in signal/noise for the same acquisition time, compared to typical values of ~ 10 Hz. Although the focus in Eurochamp-2 was NO₃ detection, replacement of the mirrors and the use of an alternative probe wavelength, would allow for the detection of other atmospherically relevant species such as glyoxal.

One of the goals of this task was to develop, install, and test incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) instrumentation in the CRAC atmospheric chambers (UCC), and to extend its applicability to multiple target species. One such cavity was permanently installed on the 4 m³ CRAC chamber, and a second, two-channel system has been installed on a semi-permanent basis on another, smaller chamber at UCC. A multi-



channel IBBCEAS system was also temporarily deployed in the **UBT** chamber as part of this project. Early work focused on NO_3 , the primary driver of nocturnal oxidation chemistry, which absorbs from 660 – 670 nm. The NO_3 performance characteristics of our instrument were compared with other optical cavity systems during the study. Moreover, we extended the measurement range to different spectral regions, which has significantly enhanced the utility of the method for chamber studies. Other target molecules included I_2 (520 – 560 nm), NO_2 (420 – 460 nm), HONO (340 – 380 nm), and nitroaromatics (320 – 400 nm). An important recent focus has been on using IBBCEAS instrumentation for quantifying aerosol extinction in the near-ultraviolet so as to characterize the optical properties of particles and hence to characterise their impact on radiative transfer and climate forcing. A test case for such particle measurements was a study of the photo-oxidation of several small nitroaromatic compounds.

Tuneable Diode Laser Spectroscopy

KIT developed sensitive tuneable diode laser direct absorption techniques for in situ water vapour detection in the presence of clouds and aerosols. The water vapour measurements inside the AIDA simulation chamber (APicT: 24-288 m and SP-APicT: 4.1 m) were significantly improved with new fibre couplings avoiding water absorption from outside the chamber and with a new single optical path system extending the dynamic measurement range to: <1-12000 ppmv. By combining water vapour data with total water concentrations which are measured in a closed path cell APeT (30.3 m) by extractive sampling from AIDA condensed water contents (total water – water vapour) can be obtained with ~1 Hz. Two new instruments were installed to measure water isotopes (HDO , H_2^{16}O , H_2^{18}O) in the gas- and condensed phase of AIDA. A 2.7 μm TDL spectrometer ISO-APicT (24-288 m optical path) with a high sensitivity to measure gas phase water isotopes in situ and a 1.4 μm OF-CEAS spectrometer (54 km optical path) to measure total and (via virtual impactor) condensed phase water isotopes by extractive sampling. The performance of these instruments was validated by comparison with about 30 other hygrometers including transfer standards to the national water standard (PTB) during an international intercomparison campaign (AquaVIT2) in April 2013. All deliverables: technical drawings of the tuneable diode laser systems, list of performance data, intercomparisons and publication of the results were achieved in time.

The TDLAS technique for the detection and measurement of NO_3 has been developed at **CNRS-ICARE** laboratory. The system based on an ECDL source coupled to a homemade multi-pass absorption cell. The instrument response and reliability for the detection of NO_3 has been confirmed by measuring the reported spectrum of NO_3 in this range 658-665 nm, which was found in good agreement with the recommended one. A detection limit of 100 pptv for one second integration has been achieved using the photolysis method to measure the reference without NO_3 . Ozone interference has been observed while using high concentrations of ozone for the generation of the NO_3 . NO_2 and other compounds used in the studies such as propanal, pentanal and propene do not have any interference with the NO_3 detection. However, there are still problems remaining regarding the stability of the signal and the source making the longer period measurements difficult. Owing to these problems, kinetic measurements did not yield satisfactory data. These have to be resolved before going for the kinetic and field measurements. Future work will focus mainly to improve the stability of the system.

Fluorescence Techniques

The Fluorescence Assay by Gas Expansion (FAGE) instrument developed for field measurements in Leeds has been applied to a chamber (**ULEEDS**), in order to observe OH and HO_2 radicals in-situ. The main focus of the work was on the use of HIRAC to develop



new calibration techniques for the detection of OH and HO₂ by the FAGE technique and investigate possible interferences. Recent observations of high HO_x concentrations in low NO_x, high biogenic VOC environments have called into question both our understanding of oxidation of VOCs but also the reliability of the FAGE technique. Our investigations show that interference on the HO₂ channel should be minimal for instruments with short residence times. Alternative calibration methods for both OH and HO₂ confirm the accuracy of the previous calibration methods and validate previous aircraft based measurements where the pressure dependence of the signal had only been indirectly accounted for.

The newly developed OH lifetime measurement instrument at **FZJ** has been applied in combination with laser-induced fluorescence (LIF) detection of HO_x radicals in simulation experiments in the SAPHIR chamber. The measurements' goal was the investigation of day- and night-time chemistry of volatile organic compounds (VOCs) and to quantify the influence of the background reactivity observed in the clean chamber. Within this task we focused on the OH initiated degradation of isoprene and its degradation products methyl vinyl ketone and methacrolein under low NO concentration. This work comprised five isoprene degradation experiments and was finished very successfully. The results are described in the respective deliverable.

Mass spectrometry techniques

The Ion Molecule Reaction Mass Spectrometry (IRMS) system developed by **CNRS** to detect HO_x and RO₂ has been calibrated toward a better characterisation of the interferences in the chemical conversion reactor, in the presence of high NO_x concentrations and in the presence of VOCs. The IRMS instrument is based on the measurements by chemical conversion of the radicals in air in the presence or absence of NO, and in the presence of SO₂, and detection of HSO₄⁻ ion formed by reaction of NO₃⁻ with H₂SO₄ produced, it allows the measurement of HO_x (OH, HO₂) and RO₂ radicals. Experiments have been carried out to test the influence of high NO_x and organic concentrations on the IRMS instrument performance. The OH and RO₂ radicals were generated by illuminating gas mixtures in the presence of different initial concentrations of NO, NO₂, O₃ and C₃H₆. Standard calibration procedure using H₂O photolysis in a flow reactor was verified by comparing measured OH and that derived from the consumption rate of toluene in the simulation chamber. A series of experiments will be carried out to investigate the HO_x behavior during the atmospheric oxidation of biogenic VOCs.

PARIS12 has studied the performance of direct mass spectrometry, by directly connecting a new quadrupole to the CESAM photo-reactor. Good sensitivity has been achieved by averaging large numbers of spectra (up to 5 min of averaging time). The new mass spectrometer has been successfully connected to the CESAM chamber. Our tests have illustrated the difference of sensitivity between SEM and Faraday detector: the signal-to-noise ratio is improved by three to four orders of magnitude by the use of SEM. For example, the detection limits for toluene was found ca. 5 ppm and 5 ppb, for the faraday detector and the SEM respectively over a 1 minutes averaging time. Improvement can be made by systematically testing the use of various critical orifice, by optimizing the ion volume around the ionization filament (use of a gas tight crossbeam ions source for example) and by using chemical ionization to reduce fragmentation of the analytes. While its performance cannot compete with PTR-MS technology, it can be helpful in monitoring moderately diluted species and for species, which are not detectable with PTR-MS (proton affinity lower than water).



Chemical conversion techniques

At **BUW** the LOPAP instrument built initially for NO₂ detection was developed to variants that allows measurement of PAN-like species (e.g. PAN = peroxyacetyl nitrate, PPN = peroxypropionyl nitrate and PBzN = peroxybenzoyl nitrate) and selective detection of ozone in the atmosphere.

As opposed to the straightforward determination of PAHs, amines are difficult to monitor at low quantities by gas chromatography. In order to detect microgram quantities from air samples, the amines must be derivatized prior to GC-MS analysis. This reduces peak tailing and eliminates injector-amine interactions that are well-known for causing high detection limits.

Determination of volatile amines content by derivatization and GC-MS. The amines are derivatized according to a protocol described by Ugland et al, using ethylchloroformate and pyridine. The use of chloroformates as derivatizing reagents is well investigated, the reaction is quick, and it works when water is present. Primary and secondary amines are added to the chloroformate as shown below, resulting in the desired carbamate. Pyridine or sodium hydroxide solution is added to neutralize the formed hydrochloric acid. The emission of volatile amines was studied in **SP** portable micro-chamber FLEC (Field and Laboratory Emission Cell). A modified method to the ISO standard was used for determination of emissions from the samples⁷.

Radical clock technique

The **PSI** group has developed and published an independent radical clock method based on the convenient detection of butanol-D₉ by PTR-MS. This is a relative method, based on a known rate constant for the reaction of OH with butanol-D₉ which has the advantage of no interfering background for the deuterated compound.

The indirect method of monitoring a set of hydrocarbons with known OH-reactivity by gas chromatography has been developed in at **UBT**, and the hydrocarbons are selected to cover a certain range of reactivities against OH and Cl, even more so a range of reactivity ratio k_{OH}/k_{Cl} (toluene and several lower alkanes, useful to distinguish between OH and Cl).

A total of 20 successful smog chamber runs have been performed at room temperature to investigate the reaction of OH with aerosol-borne terbuthylazine (a semi-volatile herbicide). This corresponds to 20 time profiles of OH radicals determined from time profiles of 4 hydrocarbons each. The agreement of the 4 independent time profiles of OH is an excellent quality check of the data.

The two methods (developed at PSI and UBT) were successfully intercompared during a TA campaign at the LOTASC Teflon chamber with Sasho Gligorovski (University of Provence, TA 0073 and 0090)

Improved data analysis system

Spectroscopic techniques are widely used at many simulation chambers sites. They are in-situ and non-destructive techniques and hence allow collecting information on the reacting mixtures without any perturbation of the chemistry going on. They are very efficient in the characterization of complex mixtures both the reactants involved and the reaction products but also both for organic and inorganic species. Nevertheless, its use implies the

⁷ ISO 16000-10:2006: Indoor air -- Part 10: Determination of the emission of volatile organic compounds from building products and furnishing -- Emission test cell method



deconvolution of complex mixture spectra into pure compounds contribution. The data analysis methods used affects directly the reliability of the measurements.

In this task two main results were obtained: i) the provision of dedicated software to be distributed among the partners for a higher efficiencies/reliability of the FTIR data analysis and ii) the comparison of the various deconvolution methods (including the widespread cumbersome method based on a manual process).

UCPH is using a non-linear least-squares spectral fitting algorithm, the Multi Atmospheric Layer Transmission software (MALT). The UCPH spectral fitting program is a simple high quality tool for fitting infrared spectra from chamber experiments. The program can use high quality line parameters from the HITRAN database (U. S. Air Force/Harvard-Smithsonian), in addition to standard absorption spectra such as those available in the EUROCHAMP-2 FTIR database. The program builds on the analysis tool Multi Atmospheric Layer Transmission (MALT). However we have found that the text interface for this program can be a barrier for many users: to achieve a good fit the various parameters need to be finely tuned, e.g. initial concentrations, pressure, temperature, resolution, apodization, field of view, path length, source files, etc. The parameters are then optimized using a least square method. Therefore, a GUI front end has been written for MALT using Python and the graphical library wx-widgets. The combination of python and wx-widgets was chosen because it is able to run on all common operating systems (Linux, MacOS, and Windows);, the programs are free and easy to install and use. The main interface covers the parameters that are most important for achieving a good fit. The program works very well, fulfilling the stated objectives and improving productivity.

PARIS12 has developed during Eurochamp-1 a Array Basic ® GRAMS® software based on matrix algebra and as a main task of this WP, **CEAM** has developed a home-made software at CEAM (Main_polwin) for the automatic analysis of FTIR samples under MathLab®. It has been developed on the based on classic linear square fitting routines basis, but modified to improve the filtering process to remove baseline and also broad absorptions of unknown compounds. The filter method is based on splitting the spectral range in overlapping windows, where low degree polynomials are adjusted to remove the baseline. The software is aimed for improving the quality of the data and therefore the obtaining of important information: kinetic constants, fate, products of reaction, etc... Main_polwin has been successfully tested on the analysis of complex gas mixtures where different gases interfere each other. This experience was performed comparing the software against two other programs and the manual subtraction method presenting very good results. It has been used in the analysis of the IR samples at the EUPHORE chamber. The program is distributed for free upon request to the author and it allows working also with UV spectra, provided that the format is the correct one. Finally, **ULEEDS** has also worked on the upgrading of their FTIR software for analysis of complex spectra.

A large intercomparison exercise has been organized between CEAM (Main_Polwin), UCPH (Malt), PARIS12 (Matrix_deconvolution) and BUW (Manual subtraction). It has allowed us to test the various software developed through Eurochamp-2 (CEAM, UCPH, PARIS12). The outcome was a much better appreciation of the biases and artifact related with the different mathematic approaches.



WP7: Improved experimental techniques for generation and characterization of physical particle properties. Lead partner TROPOS

When performing experiments concerning aerosol particles' hygroscopic growth, CCN activation, ice formation, and chemical transformation experiments, provision of aerosol particles with well-defined size, mass, shape and composition is crucial. WP7's objectives are:

- To provide techniques for generating aerosol particles with well defined physical properties for performing particle ageing, transformation and freezing experiments.
- To provide techniques for the characterization of aerosol particles in such experiments concerning their physical and chemical properties of interest.

PSI performed experiments with highly monodisperse aerosols using the electrospray technique. These seed aerosols were then coated with secondary organic aerosol, and closure between chemical composition (measured with an aerosol mass spectrometer, AMS) and hygroscopic growth (measured with a hygroscopicity tandem differential mobility analyzer, HTDMA) was achieved (Meyer et al., 2009). Using combined AMS and HTDMA measurements we were also able to show that there is a correlation between the hygroscopicity of SOA particles and the O:C ratio (Duplissy et al., 2011).

Moreover, PSI performed extensive measurements of hygroscopicity and volatility in order to follow the aging of secondary organic aerosol formed by oxidation of α -pinene (Tritscher et al., 2011a, Donahue et al., 2012). The same two techniques were also applied to follow the aging of diesel exhaust (Tritscher et al., 2011b) or wood combustion exhaust (Martin et al., 2013). Moreover, the effect of photochemical ageing on the ice nucleation properties of diesel and wood burning particles was investigated (Chou et al., 2013).

Often, it is argued that smog chamber experiments are not representative of the ambient atmosphere since the degree of oxidation in SOA produced in smog chamber experiments is typically substantially lower than in the ambient atmosphere. However, PSI could show in dedicated experiments that for low SOA loadings and sufficiently high OH exposures (see WP8 for the method used for the measurement of the OH exposure) the SOA is very similar to the one of the ambient atmosphere, indicating that smog chamber experiments can indeed be designed such that they are representative of the ambient atmosphere (Pfaffenberger et al., 2013).

Summarizing, PSI developed and applied tandem differential methods for the characterization of hygroscopicity and volatility and applied these techniques to a wide variety of smogchamber experiments. Moreover, smogchamber experiments could be shown to be representative of ambient conditions, which greatly advances the importance and relevance of such smogchamber experiments.

PARIS12 has investigated the characterization of synthetic cloud in simulation chamber. The first step has consisted in developing stable protocols to generate cloud ensemble of significant lifetime. Two different protocols were developed, one based upon the saturation of the chamber atmosphere by adding water vapour, the other by pseudo-adiabatic expansion of a nearly saturated gas mixture. Then two devices have been developed or adapted to characterize droplet ensemble both systems are based on the same physical principles: light scattering by droplets. One system based on a laser diode at 650 nm was set-up in the chamber allowing a photodiode to collect the light in-situ scattered. The other, is based on the



use of an external optical particle sizer connected to the chamber and fed with water complex refraction index to retrieved droplet size distribution from 0.3 to 40 μm .

PARIS12 has developed a new HTDMA which was used for the investigation the ageing of aerosol such as ammonium sulfate and α -pinene ozonolysis SOA. The combination of HTDMA with in-situ humidification probed with an SMPS modified for the measurement of wet particle has shone a new light on the hygroscopic behavior of particles.

PARIS12 has carried out experiment over up to 15 hours of ageing on the SOA arising from α -pinene ozonolysis. During these experiments a combination of HTDMA, AMS, SMPS (modified to probe wet aerosol), aethalometer, nephelometer and FTIR instruments have been used. Complementary results have led to a more comprehensive picture of aerosol behavior during ageing in the presence/absence of light, ozone and water.

UCPH performed experiments on laboratory and chamber generated aerosol particles using two different CCNCs: a Continuous Flow CCN counter from Droplet Measurement Technologies and a static thermal diffusion counter developed and built at the University of Wyoming (CCNC-100B). Two types of particles were studied: 1) particles of well defined chemical composition and 2) chamber generated aerosol particles featuring complex and to a large extend unknown chemical composition. In both cases great care has to be taken when designing experiments and interpreting results when semi-volatile components are present. In particular attention has to be paid to the possibility of evaporation of volatile components inside the CF-CCNC when operated at high temperatures.

TROPOS has developed several devices for generating mono disperse coated particles and, together with UMAN developed a technique for the reproducible generation of mixed *organic/salt solution particles* simulating primary marine bubble bursting seaspray particles. The technique employs recycling of briny organic containing water (either synthetically produced using marine algal exudates or real seawater) into water jets falling back onto the water surface. Modification of the existing flow system has shown the tank to be capable of generating a realistic bubble distribution and resulting aerosol population at sufficient numbers to produce reasonable loading for the chambers. Four publications have resulted from the technique and its application (Fuentes et al., 2010, Wex et al., 2010).

At UBT, a fast aerosol injection device was built to feed aerosol into chamber, using three commercially available *ultra-sonic nebulizers* (Quick-Ohm, QUV-HEV FT25/16-A). The set-up consists of three quartz-metal membranes connected to a glass tube, which can be filled with the aerosol solution. The vibrating membranes (1.63 MHz) generate polydisperse aerosol, whose distribution maximum is dependent, inter alia, on the concentration of the solute/suspension. Since the chamber filling process is usually carried out at low temperatures (between 0°C and -25°C, depending on freezing properties of the particles), the warm aerosol solution was injected at the bottom of the chamber in order to reach a well-mixed and large volume quickly. The chamber was cooled down before with air, containing high relative humidity in order to coat the chamber walls with ice. Then the chamber was evacuated, leading to a cooling by a near-adiabatic process.

Reproducible ice nucleation temperatures of a fast-generated aerosol are clearly the main benefits of the *ultra-sonic nebulizer set-up*. The set-up allowed a spectacular observation on washing water of birch pollen during a TA campaign that took place at UBT in autumn 2010, Pummer et al., 2011 (TA 0041, H. Grothe, TU Wien, AT).



WP8: Improved experimental approaches in the design of experiments. Lead partner PSI

The discrepancy between experimental and model results suggests either higher than expected SOA yields or unmeasured precursors that together could be even more important for SOA formation than the measured compounds. The project includes a number of new approaches to address the shortcomings in aerosol yields.

Objectives

- To provide the experimental data for decreasing the gap between experimental data and model SOA predictions
- To extend the types of smog chamber experiments to more representative VOC/NO_x ratios, more realistic seed aerosols and a wider temperature range
- To characterize turbulence effects

Non-conventional SOA precursors

As part of this task, **UCC** performed a series of simulation chamber studies to show that direct photolysis of substituted aromatic compounds (up 30 % of VOC in urban atmosphere) is a previously unidentified source of SOA. Experiments were performed on a number of aromatic aldehydes and indicate that the photolysis of *o*-tolualdehyde, 2,3-, 2,4- 2,5- and 2,6-dimethylbenzaldehyde may contribute to SOA formation in the atmospheric degradation of their parent compounds (*o*-xylene and trimethylbenzenes). Direct photolysis of nitroaromatics is rapid and also produces SOA with yields as high as 70%. This work is one of the first studies to identify SOA as a product of the direct photolysis of a volatile organic compound. These reaction systems are considerably less complex than those employing OH, NO₃ or O₃ to initiate the oxidation of VOCs and could provide useful information on SOA formation processes and further detail to feed into the aromatic oxidation mechanisms being developed in WP 10.

PARIS12 has investigated the potential of the use long chain alkane (e.g. dodecane) as non-conventional study. Extensive study of SOA yields as a function of temperature, together with polyfunctional species measurement in both gas- and aerosol phases have been conducted. These study confirm the interest of these precursors: firstly because they may be a significant part of unburnt volatile organic species from car emission and secondly because they provide apparently simple systems to compare outcome of chambers experiments with the results of explicit modeling runs.

PSI investigated the SOA formation from a number of different precursors, i.e., α -pinene (Pfaffenberger et al., 2013), wood combustion exhaust (Heringa et al., 2011), diesel car exhaust (Chirico et al., 2010), gasoline car exhaust (Platt et al., 2013), as well as scooter exhaust (Platt et al., submitted). These experiments were either performed at the PSI stationary smog chamber (e.g., by taking off the front wheels of a diesel car and running it at a constant 'speed' of 60 km/h, (Chirico et al., 2010)), or with a novel mobile smog chamber which was attached to the exhaust of the test bench at the Joint research Institute in Ispra (Platt et al., 2013).

PARIS12 has investigated a new protocol to sustain a significant OH level in NO_x containing system without reaching too high NO_x and remain at reasonable NO level during very long ageing experiments. Usually oxidation in simulation chambers leads to a fast consumption of NO and a rise of NO₂ which induce a decrease in the efficiency of OH production. To sustain the OH level during all the experiment a small flow of diluted NO in N₂ was added to the



reacting mixture. Calculations from VOC decay corrected from possible ozonolysis show that this protocol allows keeping an OH level in the chamber between 1.5×10^{-6} and 3.5×10^{-6} radicals/cm³ for more than 10 hours. After an initiation time, the level of NO during ageing experiments was always below 1 ppb.

Improved methods for traditional oxidant addition

A method for introduction of the nitrate (NO₃) radical into simulation chambers has been developed and tested at UCC. The NO₃ radical is produced from the reaction of ozone with nitrogen dioxide whilst flowing through a custom-made S-shaped pyrex tube. Since ozone can react with unsaturated hydrocarbons, it is often preferable to ensure that NO₂ is in excess. This can be achieved by variation of the flow rates of both gases (but mainly NO₂) to produce a slightly brown gas mixture at the exit of the tube. Under these conditions, the NO₃ radical can react further with NO₂ to produce N₂O₅, which effectively acts a temporary reservoir for NO₃ and its formation helps to ensure that the concentration of the radical is maintained in the chamber for longer periods. Overall, this is a simple method for generation of NO₃ radicals that requires minimal preparation and can be used at short notice. The main alternative involves the synthesis of N₂O₅, which is time-consuming and requires specialist skills, a custom-built glass line and cold storage facilities for N₂O₅.

In smog chamber experiments the time after turning on the lights is often used. However, this does not allow to compare different chamber experiments. For this, the OH exposure (OH concentration integrated over the time) would need to be known, however, measurement of the OH concentration is not straightforward. A simple alternative method (OH clock) is to use a compound that reacts only with OH such that its decay can be related to the OH concentration, and that exhibits unique peaks that can be measured unequivocally with a proton transfer reaction mass spectrometer. Fully deuterated butanol (d9-butanol) has been found by PSI to be such a compound (Barmet et al., 2012), and has since then successfully been used in many different smog chamber experiments.

PSI optimized HONO injection to perform photooxidation experiments under high and low NO_x conditions. This was tested in the case of α-pinene photooxidation. In these experiments we also varied the humidity and the pH of the seed aerosol to investigate conditions more representative for ambient processes. These experiments yielded information on the uptake of organics on inorganic seeds and on what determines the absorptive aerosol mass (Pfaffenberger et al., in preparation).

A new method for the production of OH radicals in simulation chambers under low NO_x has been developed at the TROPOS smog chamber LEAK. OH radicals are generated by the photolysis of hydrogen peroxide (H₂O₂) at 254 nm. Hydrogen peroxide is injected into the chamber using a peristaltic pump and a bypass air flow of 5 L/min. The main advantage is that H₂O₂ is continuously added into the chamber and consumed via photolysis. This method offers a continuous and stable OH source without side products.

Improvement of seeded SOA formation experiments

PSI investigated the use of complex mixtures of inorganic and organic components as seed aerosols. In one case these seed aerosols consisted of ammonium sulfate and fulvic acid, where the concentrations of fulvic acid and of the formed secondary organic aerosol were successfully discriminated by performing positive matrix factorization on the aerosol mass spectrometer data (Kampf et al., 2013). In another case, mixtures of hydrogen bisulfate and SOA of trimethylbenzene was used to investigate the formation and uptake of SOA from ¹³C labeled methane. In this case, the amount of ¹³C labeled SOA from methane was determined by isotope ratio mass spectrometry (Barmet et al., in preparation).



Improved procedures for assessment of temperature dependence of SOA formation

The **TROPOS** BBF (Institute for Tropospheric Research Biomass Burning Facility) was built to study i: the behaviour of biomass burning aerosols in the course of atmospheric processing and ii: to generate more realistic seed particles for studying SOA formation from different organic precursors. The TROPOS BBF allows the generation of particles, which contains a mixture of inorganic compounds as well as organic and elemental carbon. The ratio of the constituents can be changed in a wide range using different fuels, by changing the oven or by using different combustion conditions. The TROPOS BBF was used to study the processing of combustion aerosols by ozone, hydroxy- and nitrate radicals.

The CESAM (**PARIS12**) simulation chamber has been provided with a temperature control system involving high power cryo-cooling system. This system is now allowing the temperature of the chamber to remain stable (even under irradiation) from -10°C and 60°C . Thank to this system and to adequate protocol, the temperature dependence of n-dodecane + OH secondary aerosol yield was successfully studied.



WP9: Development of techniques and exchange of experience for studying surface reactions in simulation chambers. Lead partner CNRS

The atmospheric transformation of air pollutants on various surfaces plays an important role for the issue of ambient and indoor air quality. Urban and indoor environments provide huge surface area to interact with gaseous pollutants. The study of the interferences of surfaces on the oxidizing capacity of the atmosphere is a very original approach and the use of simulation chambers to assess the chemical impact of massive solid surfaces on air quality is fairly new. Simulation chambers are the most direct way for investigating the effectiveness of photocatalytic material on de-pollution, the potential feedback from surface chemistry to air composition in order to draw chemical mechanisms for modelling purposes. Nevertheless, the smog chamber approach is not artefact-free as the chamber themselves exhibit surfaces with potential chemical reactivity (the walls).

Photo-catalytic self-cleaning and “de-polluting” materials

PARIS12 has investigated the possibility of the use of simulation chamber to investigate the depolluting efficiency of TiO_2 containing material. A suitable protocol based on a set of comparison between experiment without material, without non-active material and with active material have been developed. This protocol has been applied for the study of commercial self-cleaning glass (activeTM Pilkinton®) and of TiO_2 containing cement-base coating (TX ActiveTM Italcementi©). NO_x abatement, HONO recycling, O_3 formation and destruction have been studied. A set of pseudo-first order kinetic rate has been determined.

Inter-comparison of chambers using the same material and protocol

In this project, **CNRS-ICARE**, **LISA** and **SP** have developed methodologies for the definition of suitable techniques allowing to efficiently characterizing atmospheric urban/indoor air chemistry using simulation chamber experiments (). The defined methodologies have been applied to perform an intercomparison between complementary chambers. This was done through the investigation of (i) how the TiO_2 coating technology could affect the smog production mechanisms through a study of the NO_x /propene/air/light systems as models of this complex chemistry (CNRS, LISA) and (ii) the uptake of ozone on surfaces of indoor/building materials (SP).

In the first type of studies, propene was chosen as a model because it is a highly reactive volatile organic compound (VOC) involved in the formation of ground-level and tropospheric ozone and therefore in photochemical smog. The chemical system NO_x /propene/air has been well investigated in atmospheric simulation chambers and the reaction mechanism leading to the formation of aldehydes, PAN and other oxidation products is well characterised. The experiments were conducted in three different simulation chambers with different characteristics at ICARE and LISA. Comparable sets of experiments were carried out using both standard glass and TiO_2 -coated glass plates (Pilkington ActivTM) in order to assess the effect of photo-activated surfaces on the heterogeneous chemistry of NO_x . All experiments were conducted at ambient temperature (293 ± 5 K), atmospheric pressure and under dry (<1% RH) and humid conditions (45% RH) as the increased availability of adsorbed water molecules is expected to enhance the reactivity of the photocatalytic material towards nitrogen oxides. The concentration of a range of compounds in the gas phase was measured using FTIR, NO_x , O_3 and HONO analyser. The data were then fed into a model adapted from the MCM v.3 mechanism, in which the various heterogeneous kinetic parameters were adjusted to simulate and to reproduce the concentration profiles measured experimentally.



Various qualitative conclusions have been drawn from the model based analysis of the experimental results regarding the impact of photocatalytic material on smog chemistry:

- The same chemistry is observed in different chambers despite their different characteristics.
- An increase in the process rate affecting all species involved: The reactants lifetimes are significantly reduced and the products reach their concentration maxima much earlier.
- The overall chemical budget remains unaffected, with two notable exceptions: A net loss in NO_x, in line with the advertised capability of self-cleaning glass to act as a sink for nitrogen oxides; and the formation of significant amounts of HONO. Because of the photolabile nature of nitrous acid, this has potential implications in terms of re-noxification as well as increased atmospheric oxidative capacity since the photocatalytic material thus acts as an OH source. Nevertheless, the ability of HONO to be released in the gas phase is probably strongly dependent on the acidity of the media and further work is needed for other substrate (in particular basic substrate as cement). This latter impact on the concentration of atmospheric oxidative species is counter-balanced by the lower total amount of O₃ formed over the course of propene oxidation, which points to the ability of TiO₂-coated glass to act as ozone sink. However, this assertion has to be mitigated by the fact that the irreversible seclusion of a significant fraction of NO_x in the condensed phase renders it ultimately unavailable for ozone formation, which is not the case for standard glass.

These results show that the photocatalytic effect of TiO₂ can affect the oxidative capacity of the gas phase composition. However, these effects seem to be non-linear and the NO/NO₂/HONO system, which is the heart of the ozone production scheme, is strongly affected. The consumption of NO and propene is accelerated in presence of TiO₂ coated materials. In the same time, a HONO production was observed on TiO₂ coated a surface which was around 4 times higher than the one observed on standard urban surfaces in the same conditions. This suggests that this photo-induced nitrous acid production on self-cleaning surfaces could have a potentially significant impact on the chemistry of the lower troposphere leading to changes in the HO_x and NO_x budget all day long. On the other hand, we demonstrate that the TiO₂ coated surfaces reduce the photochemical production of ozone.

The protocol developed has been disseminated between **PARIS12** and **CNRS-ICARE**. Similar experiments have been conducted in both type of chamber (stainless steel for PARIS12 and Teflon film for CNRS-IRCARE). These experiments turned out to lead to compatible results and the benefits of the use of different chamber to better “subtract” the wall effect of chambers has been emphasized.

The uptake of ozone on surfaces of indoor/building materials was studied in the **SP** portable micro-chamber (FLEC). A procedure used previously has been used and extended to multiple exposure of the sample to ozone. A modified method to the ISO standard was used for determination of VOC emission from the samples (ISO 16000-10:2006: Indoor air – Part 10: Determination of the emission of VOCs from building products and furnishing – Emission test cell method). The sample was conditioned at 23 °C and 50% RH with purified air at a flow of 100 mL/minute. After the conditioning, the surface was exposed to 100 ppb of ozone in the flow of 1000 mL/min until a steady-state condition with respect to ozone removal was reached. Emission of volatile organic compounds and small aldehydes was determined before and after the ozonation step. VOC were sampled on Tenax adsorbent tubes, which were analyzed after being thermally desorbed into a gas chromatograph with both flame ionization and mass selective detectors for identification and quantification. The aldehydes were sampled on DNPH-coated C18 cartridges, eluted with acetonitrile and analyzed by liquid chromatography with UV detection.

Indoor (wood, polishes, paints) material / Ozone Deposition Theory for Indoor Materials
Determination of differences in ozone transport limited deposition velocities for chambers



ranging from 35 cm³ to 8 m³ was performed by **SP**. Previous indoor ozone deposition experiments have assumed: Separation of ozone surface resistance and transport resistance; Measured surface resistance is material specific and constant when measured across multiple chambers. There is a need for verification of the theory. Two materials were examined for their range of reaction probabilities: vinyl flooring and office paper. Paper is typically thought of as a transport limited (rt) material, while vinyl flooring is a surface limited (rs) material. New Tarkett iQ Eminent vinyl flooring was acquired from a remodeling project (homogeneous single layered vinyl flooring, 2 mm thick, phthalate free). Paper samples were from two reams of new MultiCopy Original white office paper (80 g/m², 210x297 mm, chlorine free). The materials were stored in a conditioning room (24 °C and 50% RH) for at least one week prior to testing. Five chamber sizes were examined in this study. The chambers range in volume from 35 mL to 22 m³. The FLEC and 30 L chambers are cylindrical, while the remaining chambers are rectangular. Except for the FLEC, the chambers had internal mixing fans. The sample area of materials in all other chambers was adjusted so that the area specific airflow rate was as constant as possible throughout all experiments.



WP10: Development of Common Techniques for the Use of Chamber Measurements in Model Development and Evaluation - Gas Phase Processes. Lead partner ULEEDS

Computational models are used extensively to understand and quantify the impacts of emissions on air quality on local, regional, and global scales and the effects of human activities on the global climate system. Chemistry is included in these models using chemical mechanisms that describe the oxidation of volatile organic compounds emitted to the troposphere. The mechanisms are complex and require experimental and theoretical data on the large numbers of component chemical reactions, including products formed and rate coefficients. Chamber measurements have long provided a rich source of mechanistic data and a means of evaluating the component chemical mechanisms. The master chemical mechanism (MCM), provided via a website at ULEEDS (<http://mcm.leeds.ac.uk/MCM/>), has provided a focus for this work within EUROCHAMP2.

Database for oxygenated compounds An accurate representation of atmospheric chemistry depends on the provision of reaction rate data, which is primarily provided from laboratory experiments carried out across the world. The ERADB makes a large range of kinetic data available to the scientific community in an online database. The database was created and is maintained on a website at the ICARE-CNRS through the support of Eurochamp among others.

The ERADB database (<http://www.era-orleans.org/eradb/index.php>) is complementary to the existing databases IUPAC, NIST, NASA/JPL It provides a compilation of recent kinetic data on gas phase reactions of oxygenated volatile organic compounds with OH, NO₃, O₃, Cl and Br.

A new search method has been incorporated which allows searching by a number of criteria, including name, formula, SMILES string and CAS number. A graphical representation in Arrhenius form is now available, and there are direct web links to individual papers. Access to the site is assessed through Google analytics. Typically there are hundreds of visits per month, from across the world.

Evaluation of mechanisms through model experiment comparisons. Chamber-based experiments on a wide range of volatile organic compounds lie at the heart of JRA2. These experiments have provided important rate and mechanistic data and key information for and approaches to mechanism development based on chamber experiments. The following sections provide a summary of examples from work in this component of EUROCHAMP2.

Chamber experiments at BUW have extended quite significantly the kinetic databases for the reactions of OH radicals, Cl atoms and O₃ with alkyl benzenes, methoxylated benzenes, benzoquinones, fluoroacetates, unsaturated ketones and saturated and unsaturated straight-chain esters. For specific compounds the temperature dependence of the rate coefficients has been determined. Product studies for mechanism elucidation have been performed for the reaction of OH radicals and Cl atoms with alkyl benzenes, benzoquinones and alkyl esters. Many of the studies have been performed in the presence and absence of NO_x to establish photooxidation mechanism for both high and low NO_x conditions. In many cases distinct changes in the product distributions were observed with and without NO_x. These changes were particularly stark for the reactions of OH and Cl with unsaturated esters and highlight the necessity of more product studies at different NO_x levels. The work on aromatic hydrocarbons performed by BUW demonstrates that the ipso addition pathway for the reaction of OH radicals with alkyl benzenes, discussed quite recently in the literature, is negligible. Convincing evidence was also found in studies of the reactions of OH radicals with alkyl benzenes for the existence the channel to form a ring-opened epoxy compound.



First-time product studies on the photooxidation mechanisms of benzoquinones have shown that vicinal triones are major products.

UCC have performed a series of experiments on the photolysis of aromatic aldehydes and nitroaromatics in the CRAC1 indoor chamber and also using natural sunlight at the outdoor EUPHORE chamber. Detailed studies have been performed on *o*-tolualdehyde and the resulting kinetic and mechanistic data are suitably well constrained for inclusion in the Master Chemical Mechanism. Similar studies have been carried out on phthalaldehyde and 1-nitronaphthalene, two oxidation products of naphthalene. The atmospheric oxidation of isoprene under low NO_x conditions has also been investigated in collaboration with colleagues at Tokyo Metropolitan University, Japan. The chamber experiments used FTIR spectroscopy to detect a wide range of species, and a technique to measure the OH reactivity – the lifetime for OH in the system. The experiments demonstrate that the MCM provides a poor representation of a number of species at low NO_x, including HCHO, CO and HCOOH. The OH reactivity differs from that calculated from measured OH sinks by up to 40%. The data provide a means of developing an improved mechanism for the degradation of this important biogenic compound.

3. 3-Methyl-1,2,3-tricarboxylic acid (MBTCA), terpenylic acid and diaterpenylic acid acetate were identified in secondary organic aerosol (SOA) from α -pinene photooxidation or ozonolysis. These compounds display interesting structural features: MBTCA has a high O:C ratio, terpenylic acid contains a lactone ring in its structure and diaterpenylic acid acetate possesses an ester functional group. The reaction mechanisms leading to these products are still unknown. Because the direct observation of pinonic acid oxidation in a smog chamber would be difficult due to its relatively low volatility, PSI have used a model compound possessing the substructure of interest instead: cyclobutyl methyl ketone (CMK). From its oxidation, several organic acids could be measured with ion chromatography (IC) coupled to a mass spectrometer (MS). Succinic acid, the analogous product of MBTCA is formed at molar yields of 2 to 5 %. Butyrolactone, an analogue of terpenylic acid, is detected as butanoic acid, due to hydrolysis in the sampling device. A monocarboxylic acid with nominal mass 146 was detected in the absence of nitrogen oxides (NO_x) and could be the analogous product of diaterpenylic acid acetate. Because these compounds are primary products of the CMK oxidation, reaction mechanisms capable of adding one or two carboxylic functional groups without formation of stable intermediate products need to be formulated (Praplan et al., 2012).

To make different experiments from the same chamber and similar experiments from different chambers comparable a useful metric is needed. Such a metric is the photochemical age or OH-clock. PSI tested fully deuterated butanol (d₉-butanol) to determine the OH-clock in each experiment. Its reaction rate constant was determined at PSI. The primary kinetic isotope effect (KIE) was found to be 2.5, which is in line with the fundamental primary KIE derived for H-abstractions by OH with a minimal reaction barrier height.

PARIS12 has developed an auxiliary mechanism to describe the wall effect on the NO_x chemistry. This auxiliary mechanism has been successfully applied in both NO_x/air/light system and propene/NO_x/air/light system. Comparison between MCM extraction for propene and chamber simulation have led to very good agreement (Wang et al, 2011).

Tools for mechanism development using chamber experiments. A number of new tools have been developed in EUROCHAMP2 to facilitate the use of chamber experiments to evaluate and extend the master chemical mechanism and other mechanisms. These developments are based on comparisons between chamber measurements of, for example, time dependent species concentrations with model simulations based on mechanisms from the MCM. These predictions require extraction of current mechanisms from the MCM website (***) and numerical integration of the rate equations derived from those mechanisms under conditions appropriate to the chamber experiments.



Numerical integrator – AtChem. A purpose-built numerical integrator has been developed to facilitate the comparisons. The integrator is available on the MCM website, which provides a service, with model runs from external sites (EUROCHAMP labs and elsewhere) being run on a server at ULEEDS. In addition, advanced graphical user interface for AtChem has been developed at CEAM to facilitate local use of the integrator. Both versions of AtChem, together with mechanisms from the MCM, provide a computer model that can be used across all chambers for the evaluation of chemical mechanisms for the atmospheric oxidation of VOCs. A number of post-processing tools have been developed to facilitate model – measurement comparisons and are available at the MCM website and can also be used with the CEAM GUI.

Electronic lab notebook (ELN). An electronic lab notebook has been developed that provides an environment in which chamber / model comparisons, and related mechanism developments, can be carried out. The ELN is a structured environment and records changes made to mechanisms in the development of an improved mechanism, and reasons for those changes; it utilizes the MCM and AtChem. The ELN provides a means of storing, searching, retrieving and assessing the large amount of information needed to understand and reconstruct the mechanism development process. At present the ELN is designed to be run on user computers, but a service mode, using a remote server (at ULEEDS) is under investigation. The ELN provides a basis for a searchable database for model / experiment comparisons

Condensed mechanism – CRIMECH. The MCM is very large and there is often a need for a much smaller mechanism with a lower computational overhead. The lumped mechanism, CRIMECH, developed by M E Jenkin, has been mounted on the MCM website (see the website for details). It can be used with both AtChem and the ELN in chamber experiment / model intercomparisons.



WP11, Aerosol Process Modelling (thermodynamics, particle formation, transformation, ageing, multiphase chemical reaction). Lead partner UMAN

The overall aim of WP11 is to develop the two-way interaction between aerosol models and aerosol investigations in chambers. The reasoning for WP11 were:

There was no explicit model of aerosol processes analogous to the MCM for gases (see WP10).

There was no consensus about the most appropriate methodology, nor was there a generic framework, to reasonably model the relevant processes contributing to the aerosol evolution observed in chamber experiments.

A Common aerosol microphysical framework to enable simulation of aerosol distribution evolution in different chambers has been built.

The generic code is based on a moving-centre sectional aerosol dynamics representation developed to carry a multicomponent gas-aerosol partitioning module delivered within the EU EUCAARI integrated project. It is capable of addressing the broad features of aerosol evolution common to all experiments, requiring bespoke tuning for each chamber and for specific classes of experiments. The code is now available to all partners along with documentation and recommendations for suitable customisation for the chambers (experimental protocol for size dependent wall losses etc.). This model architecture, lacking a transport framework, is most suitable for those chambers that conduct batch simulations, though direct comparison with the aerosol dynamics modules into the model systems for those chambers with strong transients (e.g. AIDA) or deliberately imposed gradients (e.g. LACIS) in experimental conditions is possible.

The “Workshop on modelling of chamber aerosols”, hosted by **UMAN** (12-14.04.2011), provided a number of key recommendations concerning the assessment of experimental design strategy and protocol for optimum evaluation of aerosol modelling tools. As the multicomponent aerosol model framework has continued developing, the data and experimental constraint requirements have been more clearly identified. Data on the most appropriate chamber experiments has been mined and collated from the Manchester and EUROCHAMP2 databases and used in the model evaluation. This is leading to identification of gaps in the measurement data and attempts to reconcile the model requirements with data availability.

At **TROPOS** the evaluation of multiphase processing experiments against appropriate models of aerosol transformation was performed. The work performed focused at the extension of the aqueous phase organic oxidation scheme in the multiphase mechanism MCMv3.1-CAPRAM 3.0i. Therefore, a protocol was designed for the automated mechanism self-generation with a modified version of GECKO-A based on evaluated kinetic data and rate prediction methods from the literature.

The quality of the generated mechanisms and model results was evaluated by comparison with chamber experiments especially designed for this assessment process.

The development of a combined computational fluid and particle dynamics model FLUENT/FPM was made at **TROPOS**. With FLUENT/FPM (fine particle model) a model is available for describing coupled fluid and aerosol dynamical processes in other chambers. E.g., the model has already been, and will be also in the future applied for modeling applications in the framework of the climate change related CLOUD-project at CERN.



KIT did improve the COSIMA aerosol model to allow a description of the influence of aerosol dynamics, structural changes, and heterogeneous chemistry on physical properties of aerosol particles by combination of dedicated experimental data and targeted theoretical developments. The COSIMA aerosol dynamic model was extended regarding SOA chemistry and fractal dynamics. This includes especially the kinetics of SOA formation (combination with the master chemical mechanism and explicit treatment of nucleation), prediction of SOA yields, the dynamical behaviour of SOA particles, and ageing of organic aerosol by condensation/evaporation, composition change, and by reactions with reactive radical species. The fractal dynamics module now accounts for the size dependence of hydrodynamic interactions and screening of aggregate particles (e.g. fresh soot), resulting in reduced mobilities of small clusters compared to conventional fractal scaling approaches. Description of the dynamic restructuring of fractal like aggregates was made possible.

KIT improved and validated the cloud models MAID and ACPIM describing heterogeneous ice nucleation for mineral dust aerosol by development of new parameterisations and comparison with simulation chamber data. Various ice nucleation parameterizations have been implemented into MAID and compared to ice cloud experiments in AIDA. The ACPIM model was extended with the newly developed deterministic surface-area-dependent ice nucleation parameterization by Niemand et al. (2012). A large number of ice nucleation studies in the AIDA chamber were compared to model calculations for 6 different dust samples over a wide range of experimental conditions allowing to deduce and validate the surface-area-dependent ice nucleation parameterisation.

Ageing & Multiphase Reactions

A number of cross-chamber activities have contributed to the investigations of **aerosol ageing**. The Multiple Chamber Aerosol Chemical Aging Study (MUCHACHAS) was initiated by Neil Donahue (Carnegie Mellon University, US) and was supported by EUROCHAMP-2 TA activities. Experiments were performed in the chambers of **FZJ** (SAPHIR), **KIT** (AIDA), **PSI**, and **CMU**, and tested the hypothesis that hydroxyl radical (OH) aging significantly increases the levels of first-generation secondary organic aerosol (SOA). Details can be found in Salo et al. 2011 and Donahue et al. 2012.

UCPH investigated the evaporative behavior of submicron, aerosol particles containing SOA components (in the 50-200 nm diameter range) using a modified Tandem Differential Mobility Analyser system (TDMA) including a 3.5 m long laminar flow reactor. Detailed studies of mixed organic/inorganic particles provided new insight into the influence of inorganic aerosol constituents on thermodynamic properties of the organic aerosol components.

Characterization of turbulence effects in simulation chambers

TROPOS designed and a three-dimensional hotwire anemometer and cold-wire temperature measurements to be used for point measurements inside AIDA chamber.

KIT did provide a better understanding of the dynamics in the AIDA simulation chamber by employing a computational fluid dynamic model (ANSYS CFX 12.0). The AIDA chamber geometry was converted into a CFD model and coupled fields of gas velocity, temperature, and water vapour inside the AIDA chamber were simulated for typical expansion experiments and compared to measured data. The degree of homogeneity inside the aerosol vessel, the role of inner structures, and the 3D vortex from the mixing fan were evaluated. All deliverables were achieved in time.