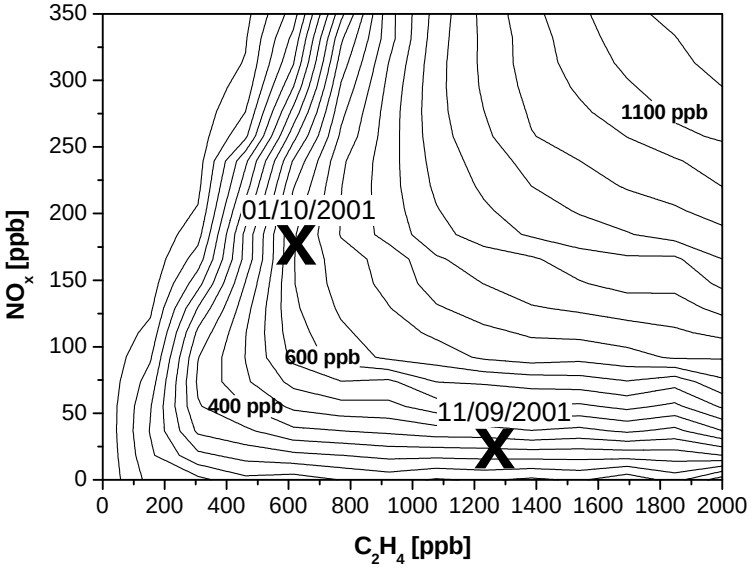
JRA2
WP4 Development of chemical modelling techniques

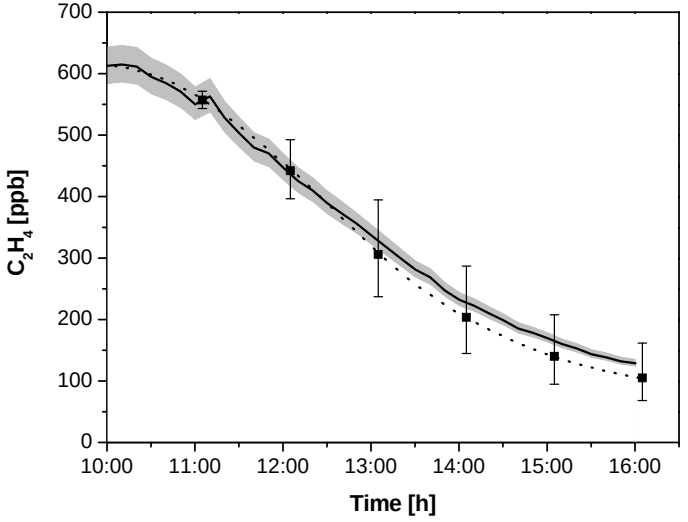
Statistical analysis of chamber data

- Developed methods based on screening methods, Monte Carlo analysis, and sensitivity analysis and applied to experiments at EUPHORE. Works well for small systems, with comparatively small mechanisms and with parameter uncertainties that are known or can be estimated.
- Useful particularly for chamber parameter determinations and for instrument development and testing. Juelich methods applied to EUPHORE
- Difficult to apply to larger systems. Too many parameters, even when reduced by sensitivity analysis and screening
- Adopted new approach based on evaluation of the MCM by chamber partners

Workpackage 4
Development of statistical tests and sensitivity analysis mechanisms

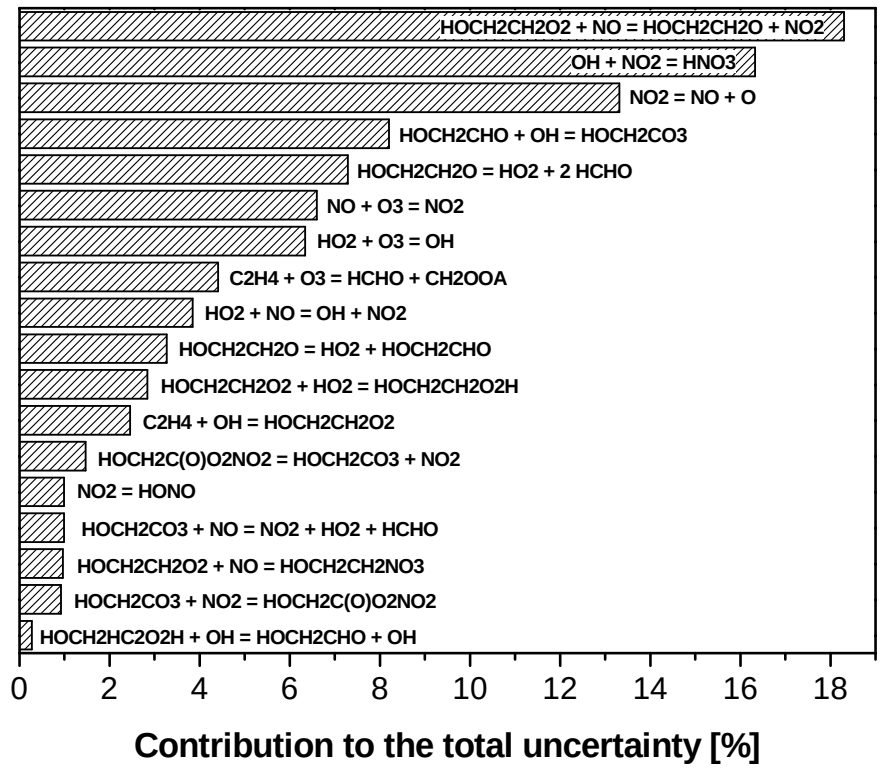
- Testing of approach on ethene/air/NOx
- MCM simulation to calculate ozone isopleths and hence determine NOx and VOC limiting conditions for experiments
- Monte Carlo analysis to determine overall model uncertainty (model – points, experiment continuous line with shading giving uncertainty.

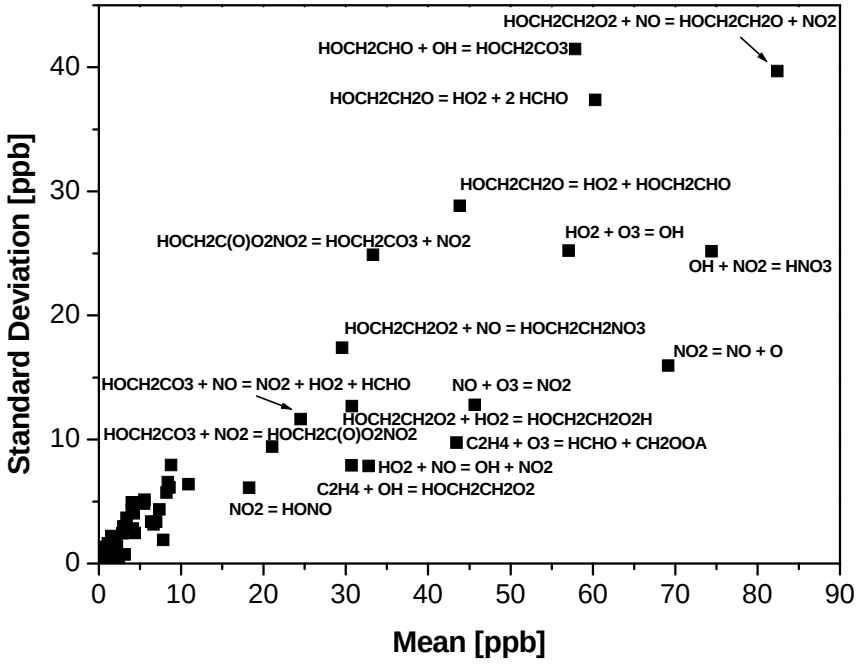




Examples of methodology. Ethene oxidation, low NO_x

- Sensitivity analysis – contribution of reactions to model uncertainty





- Screening approach Morris one at a time (MOAT) method – identifies key reactions and speeds up application of full Monte Carlo analysis

Community testing of MCM with chamber data

New approach proposed at Orleans meeting.

- MCM available for use with chamber experiments; standard box model. Can tailor to different chambers.
- Test mechanisms against chamber data – make comparisons available in standard format.
- Include experimental uncertainties in comparison.
- Assess possible sources of discrepancies through community discussion using web.
- Build up database of experiment / mechanism comparisons, + review of discrepancies and potential explanations.
- Initiated through a 'Training' meeting for MCM in Leeds in January 2007 as part of EUROCHAMP

Eurochamp MCM workshop University of Leeds, January 18th – 19th, 2007

- Aim: to provide hands-on experience of using the MCM in support of chamber studies.
- short background lectures and tutorials, plus exercises using the MCM.
- 10 partner attendees (+ 6 from Leeds). Each was provided with a PC, with FACSIMILE to facilitate easy use of the MCM.
- Interactions started immediately – students from LISA and from Wuppertal stayed on in Leeds for further experience.
- Tutorials mounted on web. Process facilitated Leeds understanding of requirements for use of MCM and website.

LISA

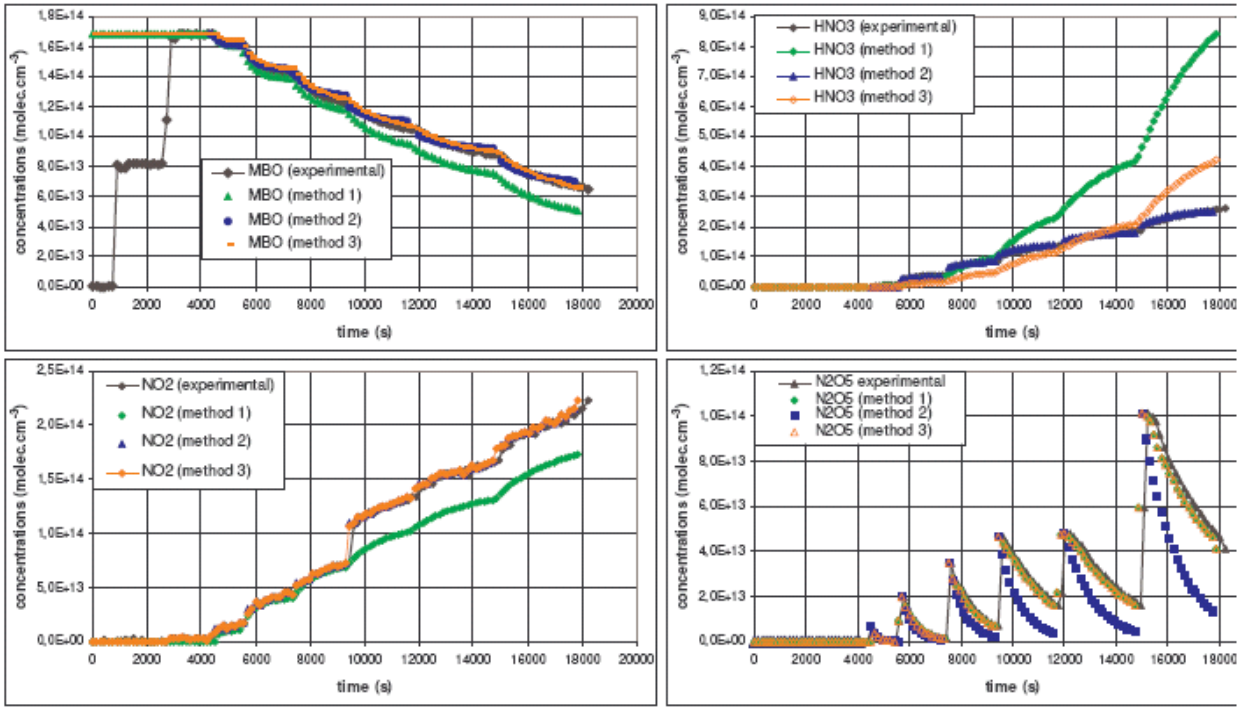


Figure 1: Data of one of the studied experiment on MBO+NO_3, and three different ways of modelling them with the MCM and FACSIMILE. In the model 1, N_2O_5 is constrained while NO_2 is kept free ; in the model 2, N_2O_5 is kept free while NO_2 is constrained ; in the model 3, both N_2O_5 and NO_2 are constrained.

	Acetone	2-nitrooxy acetaldehyde	Formaldehyde	HMPR	Sum of all hydro--peroxydes	Sum of all Nitrates	reference
Experimental yield	53.2% (63 ±6)% (68.7 ±7.1)%	not measured (67 ±8)% not measured	3.7% (2±2)% 0%	3.7% ? 0%	not measured not measured not measured	113.8% 71±12% 13±1%	this work *Noda et al. 2000* *Fantechi et al. 1998a*
Modelled yield	31.2%	33.8%	18.5%	18.8%	21.8%	78.5%	this work
Modelled yield (when the internal addition pathway is canceled)	47.5%	44.0%	0%	0%	30.3%	96.0%	this work

Table 1: yields of the products of the reaction MBO+NO_3, obtained during both chamber experiments and modelling sessions.

Generic box model

- MCM, for historical reasons, is based on the FACSIMILE integrator, that is expensive commercial code. Inhibits uptake of the MCM.
- Leeds developed a generic box model, with a freeware integrator, that is carefully designed for chamber applications.
- Uses MCM mechanism extraction facilities
- Uses CVODE (http://www.llnl.gov/CASC/sundials/) to solve system of ODEs
- Graphical user interface being developed by CEAM
- Work will continue in EUROCHAMP 2: code rewritten in more stable form by software engineer, will be run and maintained on a server at Leeds – and source code also available. Work on GUI will continue.

Graphical user interface to generic box model (CEAM)

- Being developed in C using the GTK+ library and Anjuta for Linux as programming environment
- Easy incorporation of experimental variables, chemical mechanism, photolysis frequencies, model parameters, etc. Will give graphical comparison between modeled and experimental results. Experimental results will be included in the program with the .edf format