# Acto Institucional de Celebración del XXV Aniversario del CEAM

# 9 de Junio de 2016 25 AÑOS DEL CEAM EN LA INVESTIGACIÓN EUROPEA

Karl H. Becker University Wuppertal

El proyecto EUPHORE. The EUPHORE Project

## Content

- Introduction
- The Aim of Outdoor Chambers
- The History of the EUPHORE Project
- The Proposal of the Project
- Building the Chamber Facilities
- Inauguration
- Start of Experimental Work
- Appraisal of the Chamber Studies
- Some Final Remarks

## Introduction

By the discussion within the Working Party 2 of COST 611 and together with EUROTRAC activities the need for an European simulation facility came-up in order to investigate atmospheric chemical processes as close as possible to atmospheric conditions. This kind of studies emerged from laboratory work of European groups working in Departments of Physical Chemistry. It was envisaged that a close cooperation with modelers and meteorologists would be necessary.

The goal was to carry out mechnistic and kinetic studies under controlled atmospheric conditions.

But it should also been mentioned, that some well recognized scientists had a critical view of smog chamber studies.

## **Simple Considerations:**

■ In order to minimize wall effects a volume to surface ratio should be as large as possible. The wall reaction coefficient k<sub>w</sub> is proportional to the inverse of the linear chamber dimension of a spherical reactor. In order to minimize wall effects the volume of a chamber increases with the third power of the linear dimension D:

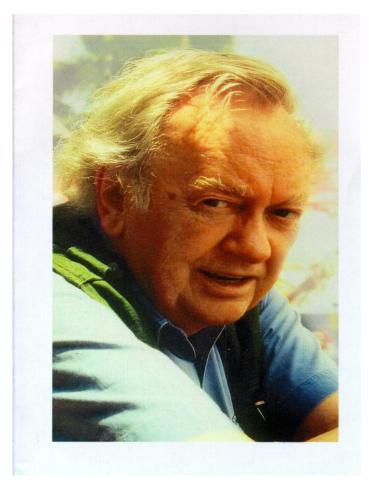
k<sub>w</sub> proportinal to 1/D and V increases with D<sup>3</sup>

Somewhere a compromise leads to a dimension between 9 - 10 m; EUPHORE: 9.20 m

- With a large linear dimension the use of long-path optical detection of chemical species by high sensitivity becomes feasible (DOAS and FTIR).
- Outdoor chambers offer the advantage, that photolysis by an artificial light spectrum is avoided, however, steadily available sunlight is required.

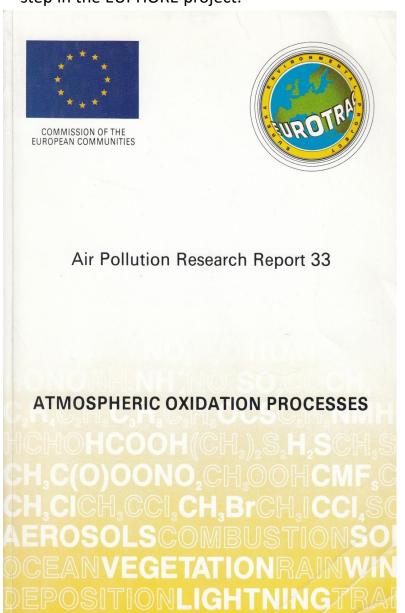
This condition favours smog chambers in Mediterranean areas.

It has to be mentioned that the head of unit in DG12/EU responsible for research on problems in the polluted atmosphere, **Heinz Ott**, was eventually convinced to support an European smog chamber project, in particular in Spain. Without his help the EUPHORE proposal would have faced strong difficulties for getting an approval, especially by opposition from Mediterranean neighbours.



He passed away March 28, 2004

Considering Spain as a favoured place for an outdoor chamber, a workshop in Madrid 1990 can be seen as a first step in the EUPHORE project.



#### COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate-General for Science, Research and Development Environment Research Programme

## Air Pollution Research Report 33

Joint Workshop COST 611/Working Party 2 and EUROTRAC
Atmospheric Oxidation Processes
I. Volatile Biogenic Species (LACTOZ)
II. Heterogeneous Processes of Major Pollutants (HALIPP)
(kinetic and mechanistic studies in the laboratory)

September 25-27, 1990 C.I.E.M.A.T. Avenida Complutense 22 28040 Madrid/Spain

> Edited by K.H. Becker

The proposal has been submitted to the EU in 1992.

#### **EUPHORE**

(European Photoreactor)

A proposal to build and operate an outdoor smog chamber in Valencia for studying mechanisms of photochemical processes and their modelling in the polluted air of different European regions.

K. H. Becker, J. Hjorth, G. Laverdet, M. Millán, U. Platt, G. Toupance, J. Wildt

#### **Project Groups**

#### (1) K.H. Becker / Project Co-ordinator

Institute Physical Chemistry/FB 9, University Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany

Tel.: 49-202-439-2666, Fax: 049-202-439-2505

E-Mail: becker@wcpc1.chemie.uni-wuppertal.de

#### (2) J. Hjorth

Joint Research Centre, Ispra Establishment, Environment Institute, 21020 Ispra, Italy Tel.: 39-332-789076, Fax: 39-332-785837

E-Mail: jens.hjorth@jrc.it

#### (3) G. Laverdet

Laboratoire de Combustion et Systemes Reactifs (CNRS-LCSR), F-45071 Orléans, Cedex 2, France

Tel.: 33-38-515493, Fax: 33-38-642670

E-Mail: laverdet@cnrs-orleans.fr

#### (4) M.M. Millán

CEAM, Parque Technológico, Calle 4, Sector Oeste, 46980 Paterna (Valencia), Spain Tel.: 34-6-1318227, Fax: 34-6-1318190

E-Mail: millan@ceam.es

#### (5) U. Platt

Institute for Environmental Physics, University Heidelberg, Im Neuenheimer Feld, D-69120 Heidelberg, Germany

Tel.: 49-6221-546350, Fax: 49-6221-546405

E-Mail: pl@uphys.uni-heidelberg.de

#### (6) G. Toupance

LISA, URA CNRS 1404, Université Paris 12, Av. Général de Gaulle, 94010 Crétail, France

Tel.: 33-1-45171560, Fax: 33-1-45171564

E-Mail: toupance@p12vx.univ-paris12.fr

#### (7) J. Wildt

Forschungszentrum Jülich GmbH, ICG 2, Postfach 19 13, 52425 Jülich, Germany

Tel.: 49-2461-616532, Fax: 49-2461-615346

E-Mail: j.wildt@kfa-juelich.de

#### Co-workers:

- (1): I. Barnes, K.J. Brockmann, D. Fuchs, H. Geiger, B. Klotz, V. Kriesche, R. Kurtenbach
  - S. Mönninghoff, B. Nozière, I. Patroescu, J. Richling, L. Ruppert, F. Schmidt,
  - L. Thüner, I. Wängberg
- (2): G. Fantechi, N.R. Jensen, G. Restelli
- (3): A. El Boudali, G. Le Bras, A. Mellouki, S. Téton
- (4): J. Bea, M. Martín-Reviejo, K. Wirtz, M. Pons (5): T. Etzkorn, R. Volkamer
- (6): P. Colin, M. Maille
- (7): M. Heitlinger, A. Hofzumahaus, A. Volz-Thomas

#### Guest Scientists:

E. Porter, H. Sidebottom, J. Tracy and J. Wenger, Dublin

## **Executive Summary EU-Project EUPHORE (proposal submitted 1992)**

## Objectives:

Development and evaluation of chemical mechanisms required to model tropospheric ozone on regional and global scales

## Social Benefits:

The development of technical measures to control and avoid disturbances of the photooxidant system by man-made emissions which result in adverse effects on human health, plants and materials in many regions of Europe and can cause global climatic changes

## Methodology:

Construction and operation of a dual outdoor smog chamber facility used in a differential mode with photolytic sources initiated by sunlight for studying the mechanisms of specific chemical systems under variable atmospheric conditions at ambient concentration levels oft the reactants

## **Location:**

Valencia/Spain
Valencia Parc Tecnologic
CEAM

## **Executive Summary EU-Project EUPHORE (submitted 1992)**

## <u>Tasks</u>

- 1. Study of the oxidation mechanisms of biogenic VOC in the presence of different  $NO_X$  concentrations with respect to photooxidant formation
- 2. Study of the oxidation mechanisms of anthropogenically emitted aromatic VOC with respect to photooxidant formation
- Study of the impact of the use of alternative/blended fuels in combustion engines on the expected reduction in photooxidant formation; comparison studies on the photooxidant formation in air enriched by real exhaust emissions from automobile engines
- 4. Study of tropospheric sources and sinks of radicals initiating oxidation processes which control the chemistry of photooxidants and the oxidising capacity of the troposphere
- Determination of data on which the "ozone formation potential" of specific VOC can be based

A very demanding programme for many years with a funding period of the project : January 1993 – December 1995, however, many concomitant EU-projects were actually part of it.

## Second Periodic Report 01/01/94 to 31/12/94

## SUMMARY REPORT OF THE PROJECT

## I. GENERAL OBJECTIVES:

 Development and evaluation of chemical mechanisms required to model tropospheric ozone on regional and global scales

## II. SPECIFIC OBJECTIVES FOR THE REPORTING PERIOD:

- Construction of the laboratory building for the simulation chambers
- Detailed preparations for the construction of the simulation chambers
- Planning of the optical DOAS, FT-IR and TDLS systems
- Selection of the analytical instruments for the simulation chambers
- Construction of a chemical amplifier
- Development of a nighttime chemical mechanism
- Preparatory work on the degradation mechanism of aromatic hydrocarbons and the ozonolysis of alkenes

The types of analytic instruments for the smog chambers, including spectral radiometers, were selected. The Spanish authorities assure the financial support for the analytic instruments in the beginning of 1995. Support has been granted for the following equipment:

- NO/NO<sub>2</sub>-analyser
- 2 FT-IR-spectrometers
- DOAS
- 2 GC (FID/ECD)
- GC-MS-system
- 2 ozone analysers
- HPLC-system
- TDL-system
- Dew point water measurement system
- Gas calibration system
- J(NO<sub>2</sub>) and J(O<sup>1</sup>D) actinometer
- Spectral radiometer
- Meteorological tower

August 1994





October 1994





# Second Periodic Report 01/01/94 to 31/12/94

November 1994





# Second Periodic Report 01/01/94 to 31/12/94

December 1994





December 1994











Inauguration and Opening of EUPHORE by LERMA, the President of the Valencia Regional Government

One week later a government of a different political party came into power.

# Workshop

# Chemical Mechanisms Describing Oxidation Processes in the Troposphere

Palacio Pineda, Valencia April 25-28, 1995

More than 60 participants from Europe, the US and Canada attended the workshop.



Financially Supported by

The international workshop organized by K. H. Becker and M. M. Millián was financially supported by the European Commission, Ford Research Centre Aachen, CEAM and the University Wuppertal





European Commission

ENV4 CT95 6152







## 7<sup>th</sup> Steering Committee Meeting

Hotel Paradores, 22<sup>nd</sup> January 2000, 18 – 20 h

Participants:

G. Angeletti

K. H. Becker

M. Pilling

U. Platt

J. Hjorth

G. Le Bras

M. Millán (excused)

O.J. Nielsen (excused)

H. Sidebottom

K. Wirtz

Guests: I. Barnes, J. Wenger

## Financial situation at CEAM

Financial situation with the chambers: consortium payments / other user payments.

The following payments were made by members of the consortium during 1999:

 Dublin
 10,000 €

 CNRS (France)
 10,000 €

 Heidelberg
 5,000 €

 Ispra
 10,000 €

 Wuppertal
 10,000 €

There was a discussion over the types of projects which used EUPHORE in 1999 and which projects would use the chamber in 2000.

It was established that in 1999 the following projects used EUPHORE: EUROSOLV, HALOBUD, SAMPLER, DIFUSO, TFS, AFS, CNRS, RADICAL.

In 2000 the following projects have the use of EUPHORE specifically written into the project proposals: EL CID (Barnes), EXACT (Pilling), DIFUSO (Wiesen), OSOA and IAAFEE (Nielsen), CNRS (Le Bras), AFS (Barnes).

Workshop has been supported by: German Federal State Ministery for Research Ford Motor Company, Research Center Aachen E. I. du Pont de Nemours, US







# Chemical Behaviour of Aromatic Hydrocarbons in the Troposphere

Hotel Parador de El Saler, El Saler (Valencia), Spain February 27-29, 2000

## Conference Proceedings

Editor: Karl H. Becker

Bergische Universität Gesamthochschule Wuppertal Fachbereich 9 / Physikalische Chemie

Bericht Nr. 53



August 2000

ISSN 1436 - 2198



Back Row: Rainer Volkamer / Markus Kalberer / Ole John Nielsen / Heike Vogel / Bernhard Golding / Sandra Saunders / Bruno Rindone / Michael Jenkin Nicola Carslaw / Harry Geiger / Peter Wiesen / William Carter / Benedikt Schell / Manuel Pons / Michael Pilling / Deborah Luecken Hans Puxbaum / Robert Lesclaux / Klaus Wirtz / Karl Heinz Becker / Cornelius Zetzsch / Tim Wallington

Front Row: Bernhard Vogel / John Pearson / John Wenger / Harvey Jeffries / Bjoern Klotz / Ralf Ackermann / Ralf Kurtenbach / Daniel Kleine / Ian Barnes
Ulrich Platt / Jack Calvert

Prof. Jack Calvert together with Dr. Millán on the roof of EUPHORE



- After the implementation in the fall 1995 the research using EUPHORE started with great enthusiasm.
- A steering committee was established, which coordinated the research activities. Most of its members were leaders of highly recognized Euopean research groups, which were involved in many EU projects at that time, they became also actively involved in using EUPHORE.
- 1995 2000 can be seen as the golden age of laboratory studies on atmospheric chemical processes. EU/COST 611, EUROTRAC and National Programmes provided enough financial support, European groups reached worldwide the top in atmospheric chemistry. After 2000 the golden age came to an end because of obscure reasons.
- Klaus Wirtz was leading the EUPHORE team (4 5 persons), the scientific guidance was provided by members of the steering group: K. H. Becker/I. Barnes, J. Hjorth, G. LeBras, M. Pilling, U. Platt, H. Sidebottom, J. Wenger
- In particular, Howard Sidebottom has to be mentioned as a very active person, who took great responsibility for doing research using EUPHORE.
   Bad news: Howard Sidebottom, a good friend and colleague to many of us here, sadly passed away on Sunday the 29th May 2016. I think we should keep in mind our best memories of this amiable person and excellent scientist.



Prof. Howard Sidebottom passed away a week ago, Sunday May 29th, 2016

- The EUPHPORE studies touched many topics: degradation mechanisms of aromatic hydrocarbons, VOC ozone formation potentials, primary photolysis rates of important atmospheric species, degradition of halocarbons and pesticides, OH, O<sub>3</sub> and NO<sub>3</sub> reactivities and much more. In situ measurements of OH radicals have also been carried out (EUPHORAM) with the result that relative measurements were of equal use without the requirement of the high technical burden.
- After 2000 the strong EU support for research projects disappeared and the use of EUPHORE had to be widened for other users. Some success was obtained by companies supporting EUPHORE projects.
- During a committee meeting a member of EU/DG12 gave the advise to consider the EU infrastructure programme for support. Following that advice resulted in the EUROCHAMP project coordinated by Peter Wiesen.
- EUROCHAMP I and II between 2004-2014 opened a new successful working period, where EUPHORE played a major role.
   The importance of the steering committee disappeared, the coordination took place within EUROCHAMP or for additional projects by the EUPHORE team directly.

- After Klaus Wirtz left CEAM 2005, Amalia took over his responsibilities.
- The present EUPHORE team (a ladies team: a group of 5 young women) has carried out highly recognized studies in cooperation with other European partners and by themselves under supervision of Amalia.
- An impressive number of publications and presentations at relevant meetings are documented. The initiative by CEAM authors for publishing in time in international journals is of extreme importance.
- The coordination of European projects like LIFE PHOTOCITYTEX has also to be considered as a great success of the EUPHORE team.
- Several intercomparison campaigns within EUROCHAMP using EUPHORE were sucessfully carried out by the team; in particular, the FIONA campaign on HONO measurements and the campaign on carbonyl measurements should be mentioned.
- A strong cooperation with research groups in Europe ensured the exchange of new ideas and technical know-how, however, many leaders of the European groups, in this respect, are now retired. A continuation hopefully will be established by a follow-up project of EUROCHAMP coordinated by Jean-Francois Doussin, Paris, where EUPHORE again should play an important role.

## Some suggestions and final remarks:

- In order to attract young persons to work at CEAM the existing cooperation with the local universities should be strengthened.
- A reasonable balance between technological orientated projects, which might make the allocation of financial support easier, and sophisticated research activities, which keeps the EUPHORE team in close contact with the international scientific community, should be considered.
- In the beginning myself and colleagues from Germany, England, France, Ireland etc. probably concentrated research with EUPHORE too much on kinetic and mechanistic studies, which were highly favoured research topics between 1990 -2000. Today such studies are not supported anymore on a larger scale.
- Intercomparison campaigns for analytical instruments applied in field measurements from ground-based ond airborne platforms using EUPHORE worked very successfully.
- It has to be expected that most parts of the EUPHORE facility have to be renewed after 25 years.
  - It is highly appreciated that the ladies group operating EUPHORE kept EUPHORE running for such a long time.
- Spanish institutions should further provide support to strengthen the leadership of the active EUPHORE team in some specific fields of atmopheric research, for which the facility is unique in the world, however, the competion of chamber studies, in particular in Europe, significantly has increased during the last few years.

The very successful work during the last 25 years has been highly recognized in the international community of atmosheric research. Numerous presentations at international meetings and many publications in peer reviewed journals have led to this worldwide recognition.

I wish you all the best that this success will continue or even increase during the coming 25 years. I hope that a next EUROCHAMP project will be approved, where EUPHORE again will play a very important role.

Finally I like to remind you that EUPHORE emerged from the idea of closer European cooperation. Presently more of such ideas are urgently needed in Europe.

At the end I also like to thank on behalf of the European users of EUPHORE the following institutions for their generous support and help during 25 years:

- CEAM
- Generalitat Valencia
- Comisión Interministerial de Ciencia Tecnología (CICYT)
- Secretaria de Estado de Universidades e investigación
- Fundación BANCAIXA

I also have to thank the Ingenieria Diez Cisneros, Valencia, and the Engineer Volker Kriesche, from my team in Wuppertal, for designing and building EUPHORE. Without the help of Volker Kriesche and his assistant Klaus Brockmann the EUPHORE project would not have been possible.

