Use of high-volume outdoor smog chamber photo-reactors for studying physical and chemical atmospheric aerosol formation and composition

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Abstract. The atmospheric particulate matter has a large impact on climate, biosphere behaviour and human health. Its study is complex because of large number of species are present at low concentrations and the continuous time evolution, being not easily separable from meteorology, and transport processes. Closed systems have been proposed by isolating specific reactions, pollutants or products and controlling the oxidizing environment. High volume simulation chambers, such as EUropean PHOtoREactor (EUPHORE), are an essential tool used to simulate atmospheric photochemical reactions. This communication describes the last results about the reactivity of prominent atmospheric pollutants and the subsequent particulate matter formation. Specific experiments focused on organic aerosols have been developed at the EUPHORE photo-reactor. The use of on-line instrumentation, supported by off-line techniques, has provided well-defined reaction profiles, physical properties, and up to 300 different species are determined in particulate matter. The application fields include the degradation of anthropogenic and biogenic pollutants, and pesticides under several atmospheric conditions, studying their contribution on the formation of secondary organic aerosols (SOA). The studies performed at the EUPHORE have improved the mechanistic studies of atmospheric degradation processes and the knowledge about the chemical and physical properties of atmospheric particulate matter formed during these processes.

1. Introduction

Environmental air pollution is generally classified as photochemical smog pollution, biomass burning, coal combustion and other, according to the source of contamination [1]. Photochemical smog is a mixture of primary and secondary pollutants that are formed by the irradiation of primary pollutants with UV light (290–400 nm). Indeed, gaseous species lead to a variety of secondary oxidized products – ozone (O3), aldehydes, ketones, carboxylic acids, peroxyacetyl nitrates, organic aerosols, etc... –, many of them being often more harmful than their precursors. Furthermore, atmospheric organic matter undergoes progressive oxidation during its chemical transformations, to yield products, generally oxygenated, that have sufficiently low vapour pressures to partition themselves between gas and aerosol phases [2]. These phase change processes affect the atmospheric aerosol by nucleation or by condensation of particles. Moreover, chemical transformations can also occur in the condensed phase. All these processes – in gas and in particulate phase – are susceptible to modify the physicochemical properties in a short time and affected by different conditions.
Since, in the ambient, it is difficult to separate the chemistry from meteorology, advection, dispersion, and other transport processes. Then, closed systems have been developed by isolating specific compounds of interest and controlling the oxidizing environment. The smog chamber facility is an essential tool used to simulate atmospheric photochemical reaction processes by irradiating primary pollutants and oxidants inside the chamber. Originally, smog chamber experiments were essentially focused on the understanding and developing of atmospheric oxidation mechanisms in the gas phase. Later, these facilities were also used to investigate processes concerning secondary organic aerosol (SOA) formation as well as concerning the physicochemical properties of aerosols [3].

However, environmental chambers are not without uncertainties in characterization and background effects depending of volume, light source, design, control of temperature, filling air system, etc [4]. In consequence, background chemicals, off-gassing materials and memory effects may complicate the chemical composition of the studied mixture and hence the reliability of the data [5]. This paper describes the design, analytical instrumentation and environmental applications of EUPHORE smog chamber developed to minimize reactor effects in studies of VOC reactivity, to increase knowledge about the chemical and physical characterization of degradation products in particulate phase. EUPHOPE is a large a Teflon – fluoropolymer - facility designed to carry out experiments under a great S/V ratio, realistic natural sunlight irradiation and purification developed air system. EUPHORE has been be used for studying degradation studies of aromatic hydrocarbons [2], biogenic compounds [6], mixture of pollutants [7], pesticides [8], such as an intercomparison platform, etc…that made these facilities ones of the most important and representative in the scientific community.

2. Experimental Section

2.1 Facility Description

Each simulation chamber (there are two identical smog chambers) consists of a half-spherical Teflon bag with a volume of 200 m$^3$, a diameter of 7 m, and a surface-to-volume ratio of 1 m$^{-1}$. The chambers were made of a fluoropolymer foil that has a transmission up to 80% of the solar radiation, in the wavelength of 280 – 640 nm. To compensate heating of the outdoor chamber by solar radiation, the chamber floor panels are cooled by a home-made refrigeration system. For mixing the air, two larges fans are installed at the bottom of the chamber with an air throughput of 4000 m$^3$ h$^{-1}$ that permits an homogenous air distribution in height as well as in area. Moreover, each chamber is filled with purified air from an air purification system which included absorption driers (type HEA 1400, Zander, Essen, Germany) with a molecular sieve (ECO 30%, MOL 70% Sogimair, Barcelona, Spain), providing air that had non-detectable hydrocarbons, NOx and particles (aerosol background of 0.010 ± 0.005 µg m$^{-3}$).
2.2 Aerosol Instrumentation

Aerosol Generator. The aerosol atomizer (TSI Model 9306) generates submicron aerosols. The mean particle size of the generated aerosol can be varied between 0.02 μm and 0.3 μm by atomizing a solution. More usually solutions employed are NaCl, (NH₄)₂SO₄, etc, at different concentration levels to generate different mass concentrations into the chamber. Combined with the aerosol generator, an aerosol neutralizer of Kr has been installed to reduce the number of charged particles generated.

Tapered element oscillating monitor (TEOM). This instrument model 1400a, was supplied by Ruppercht and Patashnick Co. Inc, (Albany, NY, USA). It is employed to measure real-time aerosol mass concentrations with a 1 min scan rate and PM1 sampling head. The particles are collected on a replaceable 0.5 cm diameter filter, incorporated in a microbalance that is free to oscillate. This sensor causes a flow of air, regulated by a thermal mass flow controller, through a filter placed in a holder which vibrates at its natural frequency of oscillation. The frequency changes proportionally with the deposited mass because the particles are collected on that filter progressively (transducer mass). It was work-operated with a sampling flow of 3 L min⁻¹ and an operating temperature ranging between 25ºC and 50ºC.

Scanning mobility particle sizer (SMPS). This instrument model 3080 (TSI), measures size distributions in the 11 – 982 nm diameter range in real time with a 5 min scan rate. This system consists of a differential mobility analyzer (DMA), model 3081, and a condensation particle counter (CPC), model 3075A. The SMPS instrument is based on the principal of the mobility of a charged particle in an electric field. Sheath and aerosol sampling flows were 3 L min⁻¹ and 0.30 L min⁻¹, respectively. Aerosol volume concentrations were converted to aerosol mass concentrations by assuming a density of 1 g cm⁻³, spherical shapes and multi-charge correction for the condensed organic material. The correction of aerosol wall losses was performed by fitting the decrease of the integrated particle number concentrations over time to an exponential decay function after closure of the chamber to sunlight for each experiment.

Filter sampling system. It was also integrated in the smog chamber for off-line aerosol monitoring. This system consists of a filter holder (Millipore, Billerica, MA, USA) with a pre-heated 47 mm-
diameter glass fiber filter. The sampling was performed at a flow of 60 L min\(^{-1}\), when maximum aerosol formation was reached.

Moreover, methodologies for the determination of polycyclic aromatic compounds (PAHs), pesticides and hydroxycarbonyl compounds in particulate matter have been developed using a gas chromatograph – mass spectrometry (GC-MS). A TRACE-DSQ II instrument system was used (Thermo Fisher Scientific Co., Waltham, MA, USA).

2.3 Protocol experiments

Set-up experiments. Since reactor walls could be a source of gas and/or particles, due to the off-gassing of compounds, preliminary tests are required before each run. For that, a chamber blank experiment has to be performed to assure the absence of possible artifacts. First, the high-volume chamber must be flushed almost for 24 h with purified air. Secondly, the chamber must to be exposed to darkness to characterize the artifacts and to the sunlight to characterize the background levels.

Walls effect characterization. It is fundamental to understand the impact of reactor walls on gas-phase reactivity and particulate matter formation. The dilution is determined using SF\(_6\) [9] as an non-reactive gas tracer. To address particles deposition wall loss, it is assumed a first order kinetics and the loss rate constant is dependent of particle size. Then, it is necessary to calculate loss coefficient for every measured size bin of the particle distribution as function of time [10].

Photolysis. The photolysis experiments are performed over approximately three hours in the middle of the day. To study the pure photolysis and to prevent any reaction with OH radicals, an excess of OH scavenger is added to the system.

Ozonolysis. The rate coefficient for the reaction of O\(_3\) with precursor is determined by monitoring the loss of O\(_3\) in the presence of a measured excess concentration of precursor, left in darkness for around 3 hours.

Photo-oxidations. The rate coefficient for the reaction of OH radicals with precursor is determined using a conventional relative rate method in which the concentrations of precursor and the reference compound are followed as function of time. There are several methods to induce OH generation: H\(_2\)O\(_2\) photolysis - in the absence of NO\(_x\) -, the classic initial addition of NO and HONO photolysis - in the presence of NO\(_x\) -. The slowest, although roughly constant, OH generation is derived from the photolysis of H\(_2\)O\(_2\) (6.04×10^{-6} \text{ s}^{-1}). For the photo-oxidation experiments in the presence of NO\(_x\), the radical source in the initial-NO experiments came from a heterogeneous reaction of NO\(_2\) on the chamber wall [11], promoting a slower OH generation and a lower SOA production. Finally, in the photo-oxidation in the presence of NO\(_x\), nitrous acid is added to introduce OH and NO\(_x\) by its photolysis. The rapid photolysis of HONO (1.44×10^{-3} \text{ s}^{-1}) promoted a burst generation of OH which was continued by the radicals produced through recycling via NO\(_x)/\text{HO}_x\) chemistry.

Study of degradation products. The experiments carried out for the physical and chemical characterization products are: photolysis, photo-oxidation in the presence or in the absence of nitrogen oxides and ozonolysis.

2.4 Experimental procedure

All degradation experiments were carried out by duplicate with a high reproducibility in the precursor consumption and degradation products formation. The experiments were under dry conditions - < 2\% RH - or wet conditions adding pure water via sprayer - up to 55\% - . The experiments were carried out in the absence. Precursors were introduced in the photo-reactor via heated air stream. The vapor pass through a FEP-Teflon transfer line and then injected into the chamber. Regarding the induced routes, H\(_2\)O\(_2\) is introduced in the chamber with a sprayer, NO or NO\(_2\) is added at 20 ppbV min\(^{-1}\) from an NO or NO\(_2\) calibration bottle (99.999 % of 5000 ppm) and HONO was generated by a liquid-phase reaction between a 0.5 % NaNO\(_2\) solution and a 30 % H\(_2\)SO\(_4\) solution and transferred directly into the chamber via a stream of purified air. Ozone is added via a stream of gas produced in an ozonizer that converts O\(_2\) in O\(_3\).
Firstly, background data from all the instrumentation implied in the experiments is taken. The immediately analysis of this data informed us the state of the chamber initial conditions to continue or in the opposite case to abort the experiment. Later, all the reactants were introduced into the chamber and mixed with high power fans for 10 min before exposing them to sunlight. After that, all the instrumentation takes a sample to have the information of the mixture studied just before to start the degradation process. When all the samples were taken, the sunlight exposure was conducted or ozone was generated until the formation of secondary products in the gas phase or aerosol mass concentration reached the steady-state. Subsequently, the home was closed and the measurements continued for at least one hour to observe the aerosol decay behavior. Finally, particles were collected at maximum aerosol formation.

Figure 2. Time table of general experiment protocol.

3. Results

3.1 Aromatic hydrocarbons

Benzene is a major aromatic hydrocarbon air pollutant with an emission rate of 11 Tg year-1, and it plays a critical role in atmospheric chemistry. Atmospheric studies on benzene acquired greater relevance when this volatile organic compound (VOC) became established as a petrol additive, thus increasing its direct emission. Also, it is the only one aromatic hydrocarbon which ambient level is legislated - European Directive 2000/ 69/EC -. An example of experiment with benzene is herein showed. The experiments consisted of the photo-decomposition of benzene (1500 ppbV) under dry conditions in the absence of inorganic seed aerosol. The main gaseous products were phenol, ozone, catechol, formic acid, nitric acid and formaldehyde. Other minority gases were glyoxal, maleic anhydride, 4-nitrophenol and 2-nitrophenol (0.1-20 ppbV). Also, a significant amount of aerosol was obtained. In NOx-absence experiments, the beginning of aerosol nucleation required a sunlight exposition time around 2h, while for initial-NO conditions, the delay was around 1h, being the existence of a delay (or induction period) between the start of oxidation and SOA formation has also been observed for other aromatic hydrocarbons. Under the addition of HONO, aerosols were formed immediately after the exposition of the pollutant to sunlight radiation. Aerosol yields between 2 – 14%
were obtained and all results indicated that the SOA formation process is NOx-dependent (see Figure 3).

![Figure 3](image3.png)

**Figure 3.** Particulate matter formation as function of precursor consumption under different NOx conditions.

### 3.2 Biogenic compounds

The emission of terpenes from vegetation is a major source of reactive organic species in the atmosphere with a rate in the order of 1014 g yr⁻¹ on a global scale. Monoterpenes are important biogenic pollutants and play an important role in night-time atmospheric chemistry. Measurements performed in the last decade indicate that biogenic VOCs give the largest contribution to secondary organic aerosol formation. α-pinene, β-pinene and limonene are the most abundant terpenes [12]. In particular, the global production of SOA from the oxidation of biogenic compounds was estimated to be higher than 10 Tg yr⁻¹. For that, the use of smog chambers as EUPHORE has a significant relevance since so the decay of terpenes so the formation of degradation products can be followed with a high time resolution and high precision and accuracy. Figure 4 shows the typical profile of ozonolysis experiment comparing the three main emitted monoterpenes.

![Figure 4](image4.png)

**Figure 4.** SMPS aerosol concentration profiles as a function of time.
The maximum mass concentrations (and aerosol yield) were 210 µg m⁻³ (21 %), 125 µg m⁻³ (14 %) and 250 µg m⁻³ (65 %), from α-pinene, β-pinene and limonene, respectively. These results agree with previously reported studies investigating SOA products from ozonolysis reactions of biogenic precursors in different-volume reaction chambers or SOA models [13]. The reproducibility of the aerosol formation obtained from replicates of ozonolysis experiments was also confirmed. The inter-day relative standard deviations of aerosol measurements were 5.0 %, 4.1 % and 1.8 % for α-pinene, β-pinene and limonene reactions, respectively. The main particulate matter products of a-pinene ozonolysis were pinic acid, pinonaldehyde, pinonic acid, norpinonic acid and hydroxyxpinonic acid. The main products of b-pinene were norpinone, pinonic acid, pinic acid, 2-hydroxynorpinone, norpinonic acid and norpinic acid. Finally, the main products of limonene were limononaldehyde, limononic acid, 7-OH-limonoaldehyde and keto-limononaldehyde.

3.2 Pesticides

Pesticides are extensively used in agriculture, gardening and a variety of other household applications. Its intensive use led to ubiquitous contamination of exposed and remoted areas, not only water or soil, but also in the atmosphere. However, studies of the gas-phase degradation of pesticides are problematic because of their low vapor pressures. One advantage of EUPHORE facilities is that compounds can be introduced into the chamber. Figure 5 shows an example of experimental data collected from degradation experiment of chlorpyrifos.

![Figure 5. Experimental data collected for the photo-oxidation of chlorpyrifos.](image)

The main degradation products were 3,5,6-trichloropyridine-2,4-diol, ethyl dihydrogen phosphate, o-ethyl o-(3,5,6-trichloro-4-hydroxypyridin-2-y1) hydrogen phosphoro-thioate, ethyl 2-oxoethyl hydrogen phosphate, 3,5,6-trichloropyridin-2-yl dihydrogen phosphate and, o -(3,5,6-trichloropyridin-2-yl) dihydrogen phosphorothioate.

4. Discussion and conclusion
The EUPHORE facility was designed to bring new insights on atmospheric photochemistry by providing new, precise and comprehensive data relevant to gas phase chemistry as well as to aerosol chemistry and physics at lower simulated pollutant concentrations. The data set from this chamber has been widely applied.

Furthermore, secondary aerosol yield studies from a known chemical system has shown good reproducibility and good agreement with previous studies indicating that this chamber is also well suited for studies of secondary aerosol formation and demonstrates our ability to accurately and precisely measure SOA formation potentials.

EUPHORE chamber is now integrating experimental simulations that will permit a significantly better integration of multiphase processes in more atmospherically representative conditions.

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