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Characterization and testing of a new environmental chamber designed for emission aging studies

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Abstract

A 29 m³ Teflon chamber, designed for aging studies of combustion aerosols, at the University of Eastern Finland is described and characterized. The chamber belongs to a research facility, called Ilmari, where small-scale combustion devices, a dynamometer for vehicle exhaust studies, dilution systems, the chamber, as well as cell and animal exposure devices are side by side under the same roof. The small surface-to-volume ratio of the chamber enables reasonably long experiment times, with particle wall loss rate constants of 0.088, 0.080, 0.045, and 0.040 h⁻¹ for polydisperse, 50, 100, and 200 nm monodisperse aerosols, respectively. The NO₂ photolysis rate can be adjusted from zero to 0.62 min⁻¹. The irradiance spectrum is centered at 365 nm and the maximum irradiance, produced by 160 blacklight lamps, is 29.7 W m⁻², which corresponds to the UV irradiance in Central Finland at noon on a sunny day in the midsummer. The temperature inside the chamber is uniform and can be kept at 25±1°C when half of the blacklights are on. The chamber is kept in an overpressure with a moving top frame,

- ¹⁵ which prevents sample dilution and contamination from entering the chamber during an experiment. The functionality of the chamber was tested with oxidation experiments of toluene, resulting in secondary organic aerosol (SOA) yields of 33–44 %, depending on the initial conditions, such as the NO_x concentration. The highest gaseous oxidation product yields of 14.4–19.5 % were detected with ions corresponding to 2-butenedial (m/z 73.029) and 4-oxo-2-pentenal (m/z 99.044). Overall, reasonable yields of SOA
- and gaseous reaction products, comparable to those obtained in other laboratories, were obtained.

1 Introduction

The atmospheric aerosols undergo changes in their physicochemical properties, such as size and chemical composition, during their residence in the atmosphere. These changes are due to aerosol dynamic processes, such as coagulation, condensation



and evaporation, and photochemical reactions with atmospheric oxidants. During the aging a substantial amount of secondary organic aerosol (SOA) is formed, which is further oxidized with increasing aging time (e.g., Ziemann and Atkinson, 2012; Hallquist et al., 2009). This may lead to significant changes, e.g., in the health and climate relevant properties of the atmospheric aerosols.

The transformation processes have been studied extensively and for decades in environmental chambers with different designs (Wang et al., 2014; Platt et al., 2013; Hallquist et al., 2009, and references therein). The most used chamber materials are glass, stainless steel, and Teflon. The glass and stainless steel walls are rigid so the chambers have a fixed volume, whereas a thin heat-sealable Teflon film enables the construction of a collapsible bag, whose volume decreases as the sample is taken out. Teflon is also advantageous, because it is inert and withstands the mechanical stress when the chamber frequently collapses and expands.

The rigid walls are advantageous in experiments which are carried out at a pressure that is much different from the ambient pressure. However, when sample is taken out, the concentrations in the chamber dilute, which affects, e.g., the reaction rates in the chamber. In collapsible bags, the concentrations are not diluted during sampling, unless there are inward leaks through the walls. This can be prevented by keeping the bag at a slight overpressure, so the flow through the possible cracks is rather outwards than inwards.

When photochemical reactions are to be studied, the chamber material must let through the relevant ultraviolet irradiation, such as sunlight in outdoor chambers or blacklight in indoor chambers. For Teflon films the penetration is high, whereas for glass, excluding quartz glass, the penetration is weaker.

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In addition to chambers, the oxidation due to the aging processes can be done in flow reactors (e.g., Keller and Burtscher, 2012; Lambe et al., 2011), where the aerosol is aged fast in an environment with a high concentration of oxidants. This enables achieving chamber-equivalent photochemical age of several hours in seconds. The short residence time reduces wall losses, although the transition efficiency, especially



for nanoparticles, is low, which is a considerable fact if new particle formation is studied (Keller and Burtscher, 2012). Another advantage of a flow reactor is its relatively small size and portability. Also mobile environmental chambers, such as the one described by Platt et al. (2013), can be brought close to the emission sources, such as vegetation or stacks or tailpipes.

The chambers and flow reactors offer, in general, a fairly inexpensive method to investigate the properties of an aging aerosol, compared to, e.g., aircraft or balloon measurements along the trajectory of the air parcel in the atmosphere. Furthermore, the conditions, such as the temperature, humidity, and the composition of the parent aerosol, precursors and oxidants in the chamber can be controlled. A drawback of an environmental chamber, compared to atmospheric measurements, is that the chamber walls act as a sink for the studied aerosol, as a part of the aerosol particles and gaseous compounds are lost to the chamber walls due to deposition and chemical reactions (e.g., McMurry and Grosjean, 1985). The wall losses can, however, be corrected afterwards but they restrict the experiment duration. Contaminants can also penetrate through the walls into the chamber, or the species deposited on the walls in

previous experiments may be released. Therefore, the chamber must be cleaned as well as possible between the experiments.

In this paper, the environmental chamber at Ilmari, an on-line aerosol exposure unit at the University of Eastern Finland (UEF), is described for the first time. The technical details of the chamber are given and discussed, and hopefully can help persons when planning new chambers in their work. In Ilmari the main focus is in studying the toxicological effects of both fresh primary and aged, combustion derived aerosols. The emission sources, the chamber, and the exposure units are side by side under the same roof, which is an advantage due to relatively short transport lines.

Results from the first test runs with the mixture of toluene, ozone, and nitrous acid (HONO), serving as a hydroxyl radical (OH) precursor, under the influence of UV radiation from blacklights, are presented and discussed, in order to test the functionality of the chamber for SOA formation studies.



2 Methods

2.1 The environmental chamber

The chamber at Ilmari, sketched in Fig. 1, is manufactured by Foiltec GmbH, Germany, of a 125 μm thick fluorinated ethylene propylene resin (Teflon[®] FEP). Its shape is a rect-angular prism and it measures 3.5 m (length) × 3.5 m (width) × 2.4 m (height). Thus, its nominal volume and surface area are, when full, 29.4 m³ and 58.1 m², respectively. The surface-to-volume ratio for a chamber is a parameter that describes, for example, the degree of wall effects. The higher the ratio, the more frequently the aerosol contacts the walls. In prismatic or nearly cubical chambers, the surface-to-volume ratio is inversely proportional to its volume. For example, values of 3.0 in a 8 m³ chamber and of 1.4 in a 90 m³ chamber have been reported (Platt et al., 2013; Carter et al., 2005). In our chamber the surface-to-volume ratio is 2.0, which equals to the surface-to-volume ratio of several other 27–30 m³ chambers (Wang et al., 2014; Paulsen et al., 2005; Cocker

et al., 2001).
 The chamber is a collapsible bag, which is attached to a moving top frame. There are counterweights attached to the top frame by a steel wire, which goes over four low-friction rollers. The rollers are attached to the supporting frame around the chamber. All frames are made of an aluminium profile, whose cross section is 30 mm × 30 mm. The chamber is electrically insulated from the surroundings by letting the framework stand
 on rubber feet and by preventing the chamber walls from touching the surrounding objects.

The pressure inside the chamber can be controlled by adding or removing extra weights on the moving top frame. In normal operation the combined weight of the chamber bag, the moving frame, and the extra weights is slightly more than that of

the counterweights, so the top frame pushes the chamber bag and maintains an overpressure in the chamber. The typical overpressure inside the chamber is around 10 Pa, when the chamber is full. The overpressure decreases when sample is taken out of the chamber, because the weight of the chamber is increasingly supported by the bottom

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grid as the chamber is collapsed. The pressure difference between the chamber and the surroundings (the experimental hall) is measured by a MicaFlex MF-PD pressure difference sensor (Mikor Instuments Ltd., Finland), whose operating range is from -50 to 50 Pa with an accuracy of ± 1.0 Pa.

- ⁵ The chamber is located in a thermally insulated enclosure, whose inner dimensions are 4.3 m (width) × 4.6 m (length) × 3.1 m (height). Two arrays of blacklight lamps (Sylvania F36/T8 BLB 36 W) are placed between the enclosure wall and the chamber, on two opposite sides. There are altogether 160 lamps, which can be switched on in 18 different combination, thereby enabling the adjustment of the output irradiance in almost
- a continuous manner. The inner walls of the enclosure are covered by aluminium plates (floor) or foil (walls and ceiling) in order to enhance and equalize the UV radiation. The spectral irradiance inside the enclosure was measured with a portable spectroradiometer (Optronic OL756), equipped with a dome window for semi-spatial irradiance measurements. The measured wavelength range was 250–800 nm with a bandwidth
- ¹⁵ of 1 nm. The total irradiance was calculated by integrating the spectral irradiance over the measured wavelength range.

The temperature of the enclosure is controlled by a thermostated air-conditioner (Argo AW 764 CL3), whose maximum cooling power is 6.5 kW. The desired temperature can be preset in the range of 16–25 °C. The temperature in the chamber is mea-

- ²⁰ sured at nine points in order to monitor possible temperature gradients in the chamber. In the middle of the chamber there is a combined temperature and humidity probe (Vaisala HMP 60; -40 to 60 °C and 0 to 100 %RH) and a diffusion type carbon dioxide (CO₂) sensor (Vaisala GMP 343; 0 to 1000 ppm). Near each corner (20 cm from the corner) there are altogether eight K-type thermocouples.
- ²⁵ The inlet and outlet ports (Swagelok[®]) are attached to an aluminium plate (diameter 0.5 m, thickness 5 mm) in the bottom face of the chamber. Stainless steel sampling lines having 6, 10 and 25 mm outer diameter are attached to the ports. The ends of the lines are at 1.0 m height from the chamber bottom (inside the chamber) and 0.5 m below the chamber (outside). Manual control valves are used to open and close



separate lines. Maintenance work inside the chamber is possible when a $0.5 \,\text{m} \times 0.5 \,\text{m}$ aluminium plate in the bottom face is removed.

The data from the sensors are acquired by National Instrument DAQ modules (NI9207 and NI9213) and transferred wirelessly to a PC, where they are stored in a database with a time resolution of 1 s by using a Datain data fusion system (Kuava Ltd., Finland).

2.2 Characterization of the chamber

2.2.1 Aerosol wall losses

Ammoniumsulphate ($(NH_4)_2SO_4$) particles were produced from a 1 g L⁻¹ solution of (NH_4)₂SO₄ in water by using a constant output atomizer (TSI 3076), a silica gel diffusion dryer and a Kr-85 bipolar diffusion charger. The neutralized aerosol was injected either directly into the chamber, filled with purified air, as a polydisperse sample (for 30 min at a flow rate of 3.0 L min⁻¹) or through a size-selective differential mobility analyser (TSI 3081 DMA) as monodisperse samples (for 2 h at the flow rate of 1.9 L min⁻¹).

- ¹⁵ The number median diameter and geometric standard deviation of the polydisperse samples were 70 nm and 1.8, respectively, and the mobility equivalent diameters of the monodisperse samples were 50, 100, and 200 nm. It must be noted that a fraction of the particles exiting the DMA are larger than the selected size, possessing multiple elementary charges and therefore the same electrical mobility. The fraction of the
- ²⁰ multiply charged particles is estimated to be 4 % for the 50 nm, 14 % for the 100 nm, and 27 % for the 200 nm monodisperse aerosol (Wiedensohler, 1988). The number of multiply charged particles were subtracted from the total number concentration of the monodisperse samples in the aerosol wall loss analysis.

The particle size distribution (14–750 nm) in the chamber was monitored, during the injection and the experiments that lasted 13–24 h, with a scanning mobility particle sizer (SMPS; TSI 3081 DMA + 3775 CPC) with a time resolution of 5 min. The total



particle number concentration was obtained by integrating the size distribution over the particle size.

Provided that the aerosol in the chamber is well mixed, a coefficient for the wall loss rate, β_i (s⁻¹), can be defined from (Crump et al., 1983)

5 $dN_i/dt = -\beta_i N_i$,

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where N_i is the number concentration (cm⁻³) of particles of size class *i* in the chamber. The coefficient β_i for each size class was obtained by integrating Eq. (1), which gives $-\ln(N_i/N_{i,0}) = \beta_i t$, and then by performing a linear fit to the data (t, $\ln(N_i/N_{i,0})$), where $N_{i,0}$ is the initial number concentration (cm⁻³) of size class *i*.

2.2.2 NO₂ photolysis rate

The photolysis rate of nitrogen dioxide (j_{NO_2}) was determined in order to characterise the photochemical potential of the blacklights for the cases when 54 (1/3 of all), 108 (2/3 of all), or 160 (all) lamps were switched on. The NO₂, NO, and O₃ concentrations

- ¹⁵ in the chamber were monitored with a trace-level chemiluminescence NO–NO₂–NO_x analyser (Thermo 42i-TL) and an UV photometric ozone analyser (Thermo 49i). NO₂ was injected from a gas cylinder into the chamber which had been flushed with purified air, produced from indoor air with an oil-free compressor with a ballast tank and an air purifier with methane reactors (Model 737-250, Aadco Instruments Inc., USA).
- The system produces air with less than 1 ppb of ozone, methane, hydrocarbons, NO, NO_x, H₂S, SO₂, COS, CO, CO₂, SF₆ and fluorocarbons at the nominal flow rate of 250 L min⁻¹. After 5 min for equilibration, all blacklights were switched on. The photolysis of NO₂ leads to formation of NO and O₃, which in turn react with each other and produce NO₂, and after some time, an equilibrium is established. The NO₂ photolysis rate can be calculated from the equilibrium concentrations [NO] (ppb), [O₃] (ppb), and [NO₂] (ppb) as

 $j_{NO_2} = k[NO][O_3]/[NO_2],$

(1)

(2)

where $k = 1.8 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ is the rate constant of the reaction between O₃ and NO at 298 K (Seinfeld and Pandis, 2006). Similar equilibria were sought for the cases when only 2/3 or 1/3 of the lamps were switched on, in order to find out the effect of irradiance on the NO₂ photolysis rate. Since the equilibrium holds only in the presence of the UV lights, the gas concentrations start changing immediately when they enter the dark sampling line to the gas analysers. In our case, the residence time between the chamber and the analysers was 0.8 s, and therefore, the gas concentrations were corrected based on the reaction between O₃ and NO.

2.2.3 Inter-experiment cleaning of the chamber

- ¹⁰ The following procedure is used to clean the chamber between the experiments. First, the aerosol from the chamber is sucked fast by the help of a blower until the chamber has collapsed (pressure difference –5 Pa). Then the chamber is filled with purified and ozonised air with a high humidity (> 90 %RH). The dry purified air was conditioned with a Model FC125-240-5MP-02 (Perma Pure LLC., USA) humidifier, where the humidity of the air flowing through is controlled by the temperature of the deionised water on the other side of 240 pieces of Nafion[®] membrane tubes which allow water molecules to pass from the water stream into the air flow. During the filling stage of the chamber cleaning the water temperature in the humidifier was 35 °C. The ozone was generated by irradiating a part of the dry purified air with a high-energy UV lamp
- at 253 nm, filtered with a high-efficiency particulate absorption (HEPA) filter and mixed with the humid air before transporting into the chamber. The temperature, relative humidity, overpressure, and ozone concentration in the chamber were monitored with the instruments described in Sects. 2.1 and 2.2.2, and necessary adjustments were made in order to keep the RH above 90 % and ozone concentration above 1 ppm. When the
- chamber reached its full volume, an outlet port was opened and all blacklight lamps were switched on in order to "bake" the chamber walls and to remove the impurities from the chamber. The baking and flushing phase was continued for 2 h, after which



all blacklights and ozone generation were switched off and the chamber was flushed overnight with purified air, whose relative humidity was set to the value to be used in the next experiment. Before each experiment the purity of the chamber was tested by switching all blacklights on and monitoring the particle number concentration in the chamber with a condensation particle counter (TSI 3022A CPC). If the number concentration did not increase and stayed below 100 cm⁻³ for 20 min, the chamber was considered clean.

2.3 Test runs with toluene/O₃/OH under the influence of UV

Four experiments with toluene (C₇H₈) in the presence of OH radicals and ozone and
 under the influence of the blacklights were carried out. First, ozone was injected into the chamber (the ozone generation is described in Sect. 2.2.3) until a desired concentration was achieved. After a short stabilization time, HONO was produced by titrating sodiumnitrite (NaNO₂) solution (1 wt-%) into sulphuric acid (H₂SO₄) solution (10 wt-%) in a glass flask equipped with a magnetic stirrer, based on the method developed by Taira and Kanda (1990). The gaseous HONO was carried by a purified air flow of 3.0 L min⁻¹ into the chamber. The HONO concentration, and the consequential OH concentration, in the chamber was adjusted by the amount of the NaNO₂ and the injec-

tion time. The mixing of HONO was monitored from the NO_2 concentration calculated by the NO-NO_x analyser as the difference between NO_x and NO concentrations, because the instrument reduces HONO to NO in a similar manner to the conversion of NO₂ (Taira and Kanda, 1990). The titration also produces NO and NO₂, whose con-

- centrations depend on the carrier gas flow rate. At the flow rate of $3.0 \,\mathrm{L\,min^{-1}}$ in our experiments, however, the fractions of NO and NO₂ can be considered negligible (Taira and Kanda, 1990).
- ²⁵ When the HONO concentration in the chamber had stabilized, liquid toluene (Sigma-Aldrich, > 99.9%) was injected with a syringe through a septum into a 6 mm stainless steel tube where it mixed with purified air, flowing into the chamber at the flow rate of $100 L min^{-1}$. The high flow rate was used to enhance the evaporation of the toluene.



The toluene concentration and the oxidation products in the chamber were monitored using a high-resolution proton transfer reaction mass spectrometer (PTR-TOF 8000, Ionicon Analytik, Innsbruck, Austria). Sample air from the chamber stainless steel inlet port was introduced to the PTR drift tube via a 1.5 m long heated (60 °C) PEEK tubing (inner diameter 1 mm) at a flow rate of 160 mL min⁻¹. PTR-MS was operated under

- ⁵ (inner diameter 1 mm) at a flow rate of 160 mL min⁻¹. PTR-MS was operated under controlled conditions (2.3 mbar drift tube pressure, 600 V drift tube voltage and 60 °C temperature). The raw PTR-MS data were post-processed by PTR-MS Viewer 3.1.0.18 program (Ionicon Analytic). Concentrations in parts per billion (ppb) were calculated by the program using a standard reaction rate constant of 2 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹.
- After stabilization and mixing of the components, the blacklights were switched on. During the irradiation HONO efficiently photolyzes to form OH and NO. The initial OH radical concentration was estimated from the first-order decay of toluene observed in the PTR-MS. A reaction rate constant of 5.6 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ was used for the OH-toluene reaction (Calvert et al., 2002). It must be noted that OH radical formation through the HONO photochemistry produces easily a high concentration of NO, which is known to suppress SOA formation (Ng et al., 2007). If the presence of
- NO needs to be avoided, a different generation method for OH radicals, such as the photochemical decomposition of hydrogen peroxide (H_2O_2) , should be used.

The concentration of selected reaction products of toluene with OH were monitored

- ²⁰ with the PTR-MS. The selected reaction products were CH_3O^+ (*m/z* 31.018), $C_2H_5O^+$ (*m/z* 45.034), $C_3H_7O^+$ (*m/z* 59.049), $C_3H_5O_2^+$ (*m/z* 73.029), $C_4H_5O_2^+$ (*m/z* 85.029), $C_4H_3O_3^+$ (*m/z* 99.008), $C_5H_7O_2^+$ (*m/z* 99.044), $C_7H_7O^+$ (*m/z* 107.049) and $C_7H_9O^+$ (*m/z* 109.065). They were selected based on toluene photooxidation reactions provided by the Master Chemical Mechanism (MCM) model (Wagner et al., 2003; Gómes
- Alvarez et al., 2007). Molar yields of gas phase oxidation products were calculated as the slope of the linear regression between the amounts of the product and of reacted toluene. Possible secondary reactions with ozone and OH radicals, showing as decreasing concentrations of the products after the initial maximum, were not included in the yield calculations.



The SOA yield, *Y*, was calculated as the ratio of the formed mass, ΔM_o (µg m⁻³), to the reacted toluene (a volatile organic compound, VOC) mass, ΔVOC (µg m⁻³), in the course of the experiment, as

 $Y = \Delta M_{\rm o} / \Delta \text{VOC}.$

The formed mass was estimated from the wall loss corrected total aerosol volume, calculated from the SMPS data, and by assuming a density of 1400 kg m^{-3} for the produced SOA (Ng et al., 2007).

3 Results

10 3.1 Particle wall loss rates

The particle wall loss rate constants β in Eq. (1) for 50, 100, and 200 nm monodisperse particles with an initial number concentration of 1690, 840, and 340 cm⁻³, were 0.080, 0.045, and 0.040 h⁻¹, respectively (Fig. 2). These wall loss rates are only 18–33% of those observed by Wang et al. (2014) in a 30 m³ chamber. One possible reason for the difference is that the chamber in Ilmari has no mixing fans which could enhance the wall deposition by increasing turbulence inside the chamber. Furthermore, Wang et al. used excerpts of polydisperse aerosol, while our rates were determined for almost pure monodisperse aerosol (including up to 27% of larger, multiply charged particles), for which the coagulation rate is smaller than for polydisperse aerosols with the same number concentration (e.g., Seinfeld and Pandis, 2006). Also, at the number concentrations in our experiments the effect of coagulation is only minor or negligible at the

time scales of our experiments (maximum duration 40 h), as discussed, e.g., by Cocker et al. (2001).

The wall loss rate for polydisperse aerosol was faster in the beginning and levelled off to $0.088 h^{-1}$ in 10 h (Fig. 2). In the beginning of the experiment the particle number concentration was 12700 cm⁻³, so coagulation has more significance in reducing the



(3)

number concentration. Also, smaller particles deposit faster onto the chamber walls. Figure 3 illustrates these effects: the median of the particle size increases from the initial 50 nm to 65 nm in 10 h. After this, no growth of particles but only decrease in concentration is observed.

- The polydisperse aerosol number loss rate in our chamber is comparable to those 5 in, e.g., the Guangzhou (30 m³), PSI (27 m³), and the California Institute of Technology (28 m^3) chambers with loss rates of 0.17 h^{-1} , $0.209 \pm 0.018 \text{ h}^{-1}$, and $0.09 - 0.18 \text{ h}^{-1}$, respectively (Wang et al., 2014; Paulsen et al., 2005; Cocker et al., 2001). The particle half-life in our chamber is 8-17 h, which is remarkably longer than, e.g., the 2.8 ± 0.8 h in the PSI mobile chamber (Platt et al., 2013). The longer half-life arises from a smaller 10 surface-to-volume ratio, which is 2.0 m^{-1} in our chamber, as compared to 3.0 m^{-1} in the PSI mobile chamber. Also, as it can be seen in our measurements, the loss rate is highly dependent on particle size, and the overall decrease rate of the total number concentration depends on the size distribution of the inspected aerosol, which makes
- an exact comparison difficult. 15

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3.2 Blacklight lamps and NO₂ photolysis rate

The blacklight lamps irradiate a spectrum that is centered at 365 nm with a half-width of 16 nm (Fig. 4). The spectrum is skewed to the longer wavelengths because of cutting the deeper ultraviolet radiation due to safety regulations for the lamps, which are originally intended for use in public areas, like discotheques. However, the irradiation is in the range for many important photochemical reactions, such as NO₂ photolysis and OH radical formation from HONO (Seinfeld and Pandis, 2006).

The integral irradiances at the UV region ($\lambda < 400$ nm) with the set of 1/3, 2/3, and all blacklights switched on were 9.8, 14.7, and 29.7 W m⁻², respectively. The maximum and 1/3 UV irradiances correspond approximately the UV irradiances of 24.8 W m⁻² 25 and 11.0 W m⁻², measured in Kuopio at noon in July on sunny and cloudy weather, respectively (Fig. 4).



The NO₂ photolysis rate (Eq. 2), at these irradiances were 0.0037, 0.0058, and 0.0103 s^{-1} (or 0.22, 0.35, and 0.62 min⁻¹ or 13.2, 20.8, and 37.1 h^{-1}), respectively. The correction due to dark reactions of ozone and NO in the sampling line was less than 1.4% for each compound and irradiance. The maximum NO₂ photolysis rate in our chamber is comparable to those reported in other indoor photoreactors, such as the rate of 0.12 min⁻¹ in the 27 m³ chamber at the Paul Scherrer Institute (Paulsen et al., 2005), 0.19 min⁻¹ in the 90 m³ environmental chamber at the University of California, Riverside (Carter et al., 2005), 1.5 min⁻¹ in the 28 m³ chamber at the California Institute of Technology (Cocker et al., 2001), and $8.0 \pm 0.7 \times 10^{-3} \text{ s}^{-1}$ in the mobile environmental chamber of the PSI (Platt et al., 2013).

3.3 Temperature control and distribution

The air conditioning is capable of keeping the temperature below 25 °C and within 1 °C when at most half of the blacklights are on. With more lights on, the current cooling capacity is nor sufficient and the temperature inside the chamber may rise significantly. This is important because the equilibria of the semivolatile species between the gas and particle phase are usually exponentially temperature-dependent. Furthermore, condensation in the sampling lines is possible when a warmer sample enters colder sampling lines, at least in experiments with a high relative humidity in the chamber.

²⁰ The temperature inside the chamber was quite uniformly distributed. When the lights were off, the temperatures in each corner were within 0.5 °C. The difference was greater when the lights were on, being 0.9 °C at maximum. The differences are unlikely to cause, e.g., thermal diffusion into a certain direction, or thermophoretic effects.

3.4 Toluene experiments

²⁵ The initial concentrations of ozone, HONO, toluene, and NO_x in the chamber in each experiment are given in Table 1. The NO_x in the chamber originates mostly from the



injected HONO, because both NO and NO_2 concentration were less than 0.6 ppb before HONO injection in each experiment.

After switching the blacklights on the NO from the decomposition of HONO was converted rapidly into NO_2 because there was always ozone present in the chamber.

- ⁵ The NO₂ decomposed into NO and O, which, in turn, produced ozone. There was a net production of ozone, and the ozone was seen to accumulate into the chamber. For example, the maximum ozone concentration was 95 ppb in experiment T130910 (Fig. 5).
- The SOA volume (and mass) increased under the influence of UV radiation (Fig. 6).
 Since no seed aerosol was used, the SOA particles were not detected until they had grown larger than 14 nm, the lower detection limit of the SMPS, approximately 10 min after the lights had been switched on. Over time, the SOA volume concentrations levelled off and reached 12.5, 10.8, and 5.0 µm³ cm⁻³ in 295, 195, and 93 min in the experiments T130910, T130911, and T130912, respectively. The corresponding SOA mass concentration and toluene consumption, and the SOA yield, calculated by using Eq. (3), are given in Table 2.

The SOA yields (0.33–0.44; Table 2) were 7–48 % higher than those obtained by Ng et al. (2007) in the seeded, low-NO_x experiments, even though SOA yield is known to be lower without seed particles (Kroll et al., 2007) and NO_x is known to suppress
SOA formation (Ng et al., 2007). Furthermore, in our experiments the *k* in Eq. (2) was 0.31 min⁻¹, which is approximately 40 % of that in the experiments by Ng et al. (2007, *k* = 0.75 min⁻¹), and hence the yield should be lower because of its proportional dependence on the light intensity (Warren et al., 2008). Huang et al. (2013) obtained a SOA yield of approximately 0.1 when no seed particles were present and 0.2–0.4
when seed particles were present, depending on the seed particle material. It must be noted that Ng et al. (2007), Kroll et al. (2007) and Huang et al. (2013) carried out their experiments in dry conditions (RH 4–7% or 15%) while in our experiments the RH in the chamber was 54–79%. This may have enhanced the SOA yields, because a higher humidity is known to increase the SOA yield remarkably (Zhou et al., 2011; Keller and



Burtscher, 2012). Also, a part of the vapors are lost to the chamber walls, which is more intense in the absence of seed particles (Zhang et al., 2014; Kokkola et al., 2014).

A time series of selected product ion concentrations in experiment T130910 is illustrated in Fig. 7, where the typical first generation oxidation products with m/z of

- ⁵ 73.029 (e.g. methylglyoxal), 85.029 (e.g. 2-butenedial), 99.044 (e.g. 4-oxo-2-pentenal), 107.049 (e.g. benzaldehyde), and 109.065 (e.g. cresol) can be distinguished from the rapid increase in the beginning and a decrease after their consumption exceeds their production (peak concentration at approximately 30 min). The concentration of the second generation oxidation products with m/z of 31.018 (formaldehyde), 45.034 (ac-
- to etaldehyde), 59.049 (acetone), and 99.008 (e.g. 2,5-furandione) increases slowly and is still increasing after 300 min of UV exposure. The formation mechanism of these OH initiated oxidation products of toluene have been discussed in earlier studies (Forstner et al., 1997; Wagner et al., 2003; Gómes Alvarez et al., 2007). Glyoxal (m/z 59.013) has also been confirmed as one of the main photooxidation products of toluene (e.g.
- ¹⁵ Smith et al., 1998). We could not distinguish glyoxal in the current study with PTR-MS because the signal interfered with near acetone peak (*m*/*z* 59.049). However, due to the high sensitivity of PTR-MS we were able to detect traces of nitro compounds which were formed during the further oxidation reactions with OH and NO₂. For example, after 30 min of UV exposure traces of possible secondary oxidation products *m*/*z* ²⁰ 154.05 (C₇H₈NO₃⁺) were detected. The compound was tentatively identified as methyl nitrophenol.

The yields for the selected gas phase oxidation products in the experiments T130909–130911 are given in Table 3. The variation in the yields might be explained by differences between the initial conditions of the chamber experiments. Similar to other

studies (Smith et al., 1998; Gómes Alvarez et al., 2007), the highest formation yields were detected for m/z of 73.029 (15.4–19.5%) and m/z of 99.044 (14.4–19.5%) ions which have the same molecular composition as methyl glyoxal and 4-oxo-2-pentenal, respectively. In the studies of Smith et al. (1998) and Gómes Alvarez et al. (2007), a yield of 16.7–37% for methyl glyoxal and a yield of 3.1–13.8% for 4-oxo-2-pentenal



were observed. Gómes Alvarez et al. (2007) measured a yield of 13 % for 2-butenedial, which is comparable to that for the ion with m/z of 85.029 (4.1–7.6%) in our measurements. Smith et al. (1998) reported similar yield for benzaldehyde, but a twice lower yield for cresol with 6% and 17.9%, respectively.

⁵ The oxidation products of toluene can be found in both gaseous and particulate phases, as reported by earlier research (Forstner et al., 1997; Sato et al., 2007; White et al., 2014). Our analysis did not include a detailed chemical analysis of the particulate phase, and therefore the yields in Table 3 can be underestimations.

4 Conclusions

¹⁰ The functionality of the new environmental chamber at the Ilmari research facility was tested for secondary product formation both in particle and gas phase. The observed yields of SOA and gaseous first and second generation reaction products were reasonable and comparable to those obtained in other laboratories. However, direct comparison is complicated, because the yields depend greatly on conditions and initial con-¹⁵ centrations. For quantitative verification of the yields, calculations with a photooxidation reaction model, such as the MCM, would be needed.

The wall loss rates of aerosol particles on the chamber walls are small enough, because of the low surface-to-volume ratio, to enable experiments with duration of several hours. The particle half-life in the chamber at Ilmari is comparable or somewhat longer

than those in other laboratories. The movable top of the chamber enables maintaining an overpressure in the chamber during the experiments, which prevents dilution of the sample in the chamber and contaminants from entering the chamber.

The conditions in the chamber can be kept constant with the current setup when half of the available lights are used. One of the next steps in developing the chamber facility

²⁵ is to increase the cooling power of the air conditioner in order to keep the temperature in the chamber in control also when the full set of blacklights is going to be used.



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Table 1. Initial concentrations and conditions in the test runs with toluene. $[NO_2]_{HONO}$ is the apparent NO₂ concentration calculated by the analyzer after HONO injection. *N* is the initial particle number concentration.

Run	[O ₃] (ppb)	$[NO_2]_{HONO}$ (ppb)	[Toluene] (ppb)	[NO _x] (ppb)	[OH]×10 ⁷ (cm ⁻³)	<i>T</i> (°C)	RH (%)	<i>N</i> (cm ⁻³)
T130909	48.5	18.8	24.7	19.1	2.3	22.2	54.0	N/A
T130910	53.8	20.1	25.3	22.4	2.1	20.4	65.0	56
T130911	55.2	12.6	26.2	11.9	1.5	22.6	67.9	44
T130912	29.8	128.4	18.2	131.2	N/A	19.3	79.2	10

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Table 2. Formed SOA mass (ΔM_{o}), reacted toluene mass (ΔVOC) and SOA yield (*Y*) in the test runs with toluene.

Run	$\Delta M_{\rm o}~(\mu { m g~m^{-3}})$	$\Delta VOC \ (\mu g \ m^{-3})$	Y
T130909	N/A	28.8	N/A
T130910	17.5	39.7	0.44
T130911	15.1	39.3	0.38
T130912	7.0	21.1	0.33

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Table 3. Gas phase oxidation product yields from oxidation of toluene on percent basis.

Run	<i>m/z</i> 31.018	<i>m/z</i> 45.034	<i>m/z</i> 59.049	<i>m/z</i> 73.029	<i>m/z</i> 85.029	<i>m/z</i> 99.008	<i>m/z</i> 99.044	<i>m/z</i> 107.049	<i>m/z</i> 109.065
T130909	5.5	14.6	11.8	5.3	0.5	1.3	9.5	7.5	7.2
T130910	6.4	18.3	11.3	15.4	4.1	2.7	14.4	7.8	8.6
T130911	5.9	22.5	13.7	19.5	7.6	7.6	19.5	8.4	9.3
T130912	N/A	N/A							



Figure 1. The schematics of the Ilmari chamber facilities.





Figure 2. The logarithmic relative number concentration as a function of time of 50, 100, and 200 nm monodisperse and polydisperse ammoniumsulphate aerosols. The equations for the linear fittings are $\ln(N/N_0) = -0.0803t + 0.0078 (50 \text{ nm})$, $\ln(N/N_0) = -0.0445t + 0.0128 (100 \text{ nm})$, $\ln(N/N_0) = -0.0403t - 0.0722 (200 \text{ nm})$, and $\ln(N/N_0) = -0.0875t + 0.8878$ (polydisperse, after 10 h).











Figure 4. The spectral irradiance of the blacklight lamps at Ilmari and those measured at ground level in Kuopio at noon in July on a sunny and cloudy weather.











Figure 6. The evolution of **(a)** aerosol number concentration, **(b)** median diameter, and **(c)** calculated volume concentration (corrected for wall losses) in the chamber in the experiment T130910.





Figure 7. The evolution of the concentrations of toluene (m/z 93.070) and selected oxidation products in the chamber in the experiment T130910. Tentatively identified oxidation products: m/z 73.029 (methyl glyoxal), m/z 85.029 (2-butenedial), m/z 99.044 (4-oxo-2-pentenal), m/z 107.049 (benzaldehyde), m/z 109.065 (cresol), m/z 99.008 (2,5-furandione), m/z 31.018 (formaldehyde), m/z 45.034 (acetaldehyde), and m/z 59.049 (acetone).

