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# Investigation of RH effect on uncommon limonene ozonolysis products and SOA formation in indoor air with real time measurement techniques



Chemosphere

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### HIGHLIGHTS

### G R A P H I C A L A B S T R A C T

- Specific, uncommon limonene ozonolysis products are formed under dry and humid conditions.
- Increased RH increases particle mass concentration regardless initial terpene concentration.
- Increased RH causes decrease in particle number concentration for experiments with low initial terpene concentration.
- RH influence on particle number concentration is unclear for experimental with high initial terpene concentration.
- Substrate concentration influences SOA formation, particle concentration and size distribution over time.



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### ABSTRACT

Scientific interest in SOA influence on indoor air quality increases since last 20 years. It is well known, that particles of nano-sized diameter pose a threat for human health causing, among others: eye, upper airway irritation, inflammatory response in cells, worsening asthma, hypertension, diabetes, and central nervous dysfunction. Terpenes are reactive VOCs, commonly emitted in indoor air and considered to be SOA precursors by oxidation reactions. The aim of this study was to investigate the relative humidity influence on i) formation of limonene ozonolysis products and ii) SOA formation process – especially the first steps of it. We managed to determine 4 uncommon limonene ozonolysis products (m/z: 43, 83, 99 and 110) appearing in the PTR-TOF-MS mass spectra with the same frequency as well-known formaldehyde, acetone, acetic acid and formic acid. We also detected m/z 75 and m/z 115 formed under dry conditions and m/z 111 and m/z 125 formed under humid conditions. Detected masss to the measured one and the isotope distribution. SMPS data analysis allowed us to conclude that RH around 40% increases particle number concentration are inconsistent. Under low initial terpene concentration, RH around 40% decreases particle number concentration. However, for high initial

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limonene concentration, RH around 40% caused increase in particle number concentration. Obtained results allowed to conclude, that i) RH influences both particle number and particle mass concentration, ii) initial substrate concentration influences SOA formation altering the RH effect, iii) comparison of results and drawing conclusions is difficult due to different experimental protocols in the literature and due to the number of factors influencing SOA formation initiated by terpene oxidation.

#### 1. Introduction

People in indoor environment are exposed to various pollutants present in either gas (volatile organic compounds VOCs), condensed (aerosols) or solid (dust) phase. Those pollutants can cause some serious health problems like lung cancer (Burnett et al., 2014), neuro-degenerative disorders (Moulton and Yang, 2012) or birth defects (Padula et al., 2013). Among before mentioned pollutants, ozone and terpenes are very abundant indoors and their reactions drive most of the indoor air chemistry. Ozone is most commonly present indoors due to outdoor-to-indoor transport (Weschler, 2000; Sabersky et al., 1973) however it may have some indoor sources like photocopies (Destaillats et al., 2008; Lee et al., 2001) or ozone generators (Britigan et al., 2006; Waring et al., 2008). Average concentration of limonene in indoor air equals few to dozen ppbv (Derbez et al., 2018; Godwin and Batterman, 2007), sometimes it may reach up to 50 ppbv (Weisel et al., 2005). Incidental limonene concentration increases to few hundreds and higher (Singer and BK Coleman, 2006) are characteristic for indoor environment due to residents activities such as cleaning, cooking, application of air fresheners and other scented products. Ozone concentration in indoor air depends on its outdoor concentration, hence it is challenging to put a defined value on it (Allen et al., 1978; Weschler, 2000; Nazaroff and Cass, 1986). However, to present some idea about ozone concentration values in indoor air one may refer to literature data claiming indoor ozone concentration varies from several to several dozen ppbv (Nazaroff and Weschler, 2022; Salonen et al., 2018; Weschler et al., 1994). Different concentration levels of terpenes, oxidants and other VOCs, different availability of sunlight as well as different humidity levels and its variations causes indoor terpene oxidation pathways not identical to those occurring in atmospheric air. For that reason, terpene oxidation reactions leading to SOA formation in indoor air are still investigated.

Due to their structure, monoterpenes are highly reactive, therefore in indoor environment abundant in ozone they quickly undergo oxidation reactions resulting in a variety of different compounds such as radicals, highly volatile organic compounds, semi volatile organic compounds/ individuals, carboxylic acids, peroxides, reactive intermediate products, all of them leading to secondary organic aerosol (SOA) formation (Kroll and Seinfeld, 2008).

For now, only first few steps of limonene ozonolysis mechanism are known for sure and these are: i) initial ozone attack on limonene double bond, ii) formation of four excited Criegee Intermediates (CIs), iii) formation of other reactive species and stable products like limonaketone, limononic acid, limonalic acid, limononaldehyde, formaldehyde, acetone, formic acid, acetic acid, and various other stable and reactive species (Destaillats et al., 2006; Lamorena and Lee, 2008; Leungsakul et al., 2005). Currently, during SOA formation experiments, mostly well-known limonene oxidation products, such as formaldehyde (m/z31), formic acid (m/z 47), acetone (m/z 59), acetic acid (m/z 61), limonaketone (m/z 139), limononaldehyde (m/z 169) are monitored (Pytel et al., 2002; Gallimore et al. 2017a,b). However, there surely are some other oxidation products, that may influence SOA formation process, which may result in common discrepancies in research results.

SOA formation is guided mostly by nucleation – formation of nanosized clusters composed of semi-volatile compounds present in gas phase, and condensation of those clusters onto pre-existing particles. Coagulation is responsible for aggregation of particles causing increase in particles diameter with simultaneous decrease of particle number concentration (Hallquist et al., 2009; Kavouras and Stephanou, 2002; Kroll and Seinfeld, 2008; Westervelt et al., 2013).

Indoor aerosol can be defined as ultrafine (<0.1  $\mu m$ ), fine (0.1–2.5  $\mu m$ ) or coarse (>2.5  $\mu m$ ) (Kohanski et al., 2020).

Terpene chemistry and SOA formation processes indoors depend on multiple factors, such as availability of substrates, presence/absence of other reactive species and particles, light availability, temperature, and humidity. Temperature and humidity have a crucial role especially in atmospheric terpene and SOA chemistry, since those factors guide the cloud formation processes, and hence the climate changes (He et al., 2018; Thalman et al., 2017; Xu et al., 2016). Water content influences distribution of products from ozonolysis of unsaturated compounds such as monoterpenes, by reactions with CIs or other processes which are still under investigation (Chen et al., 2021; Jonsson et al., 2006; Zhang et al., 2011).

Currently, there are still contrary results concerning water content influence on aerosol formation. Asa et al. found increase in particles mass concentration under high RH conditions and vast other research also reports significant growth of SOA mass under wet conditions (Bonn et al., 2002; Cocker et al., 2001; Jonsson et al., 2006; Tillmann et al., 2010). Zhang et al. reported that SOA mass concentration under high RH conditions have decreased after reaching its maximum growth, and few explanations were suggested: wall loss of particles, evaporation of semivolatile and volatile compounds back into the gas phase, formation of organic peroxides that quickly photolyzed or evaporation of organic material by heterogeneous oxidation of aerosol (Zhang et al., 2011). Literature data are even less consistent regarding RH influence on SOA number concentration. Asa et al. reported an increase in SOA number concentration under high RH conditions, similarly like Chen et al. which claimed that higher RH promotes SOA formation by transformation of first generation oxidation products into lower volatility products (Chen et al., 2021; Jonsson et al., 2006). These results are in conflict with other studies claiming that SOA number concentration is increased in dry conditions (Von Hessberg et al., 2009; Waring and Siegel, 2013; Zhang et al., 2011), possibly due to water vapor inhibition of stabilized Criegee Intermediates formation, which is correlated with nucleation potential (Bonn et al., 2002). Current literature data on RH influence on oxidation products and SOA formation are inconsistent mostly due to different experimental conditions: substrates type and initial concentrations, presence/absence, and type of OH scavenger, presence/absence of nitrogen oxides and presence/absence of seed particles. Jonsson et al. (2008a) claimed that the application of OH scavenger and its type can have significant influence on the RH-dependence studies, which was also confirmed in another study (Jonsson et al., 2008b).

The aim of this research was to investigate the influence of dry (RH 4%) and humid (RH 46%) conditions on limonene ozonolysis induced SOA formation in terms of indoor air quality. Application of PTR-TOF-MS allowed to investigate limonene ozonolysis with a particular emphasis on compounds that are not commonly described in literature, yet are characteristic for limonene ozonolysis. Investigated compounds are characterized by short lifetime, which suggest their high reactivity and quick transfer from gas to particle phase. Application of SMPS allowed to investigate SOA formation process and further SOA concentration and size distribution changes over the 30 min of the experiment. Study of the particle phase was also done with respect to high and low RH level. Experiments were conducted without application of OH scavenger, nor seed particles and analyze obtained results in terms of indoor air quality.

### 2. Materials and methods

A series of limonene ozonolysis experiments were performed in  $0.125 \text{ m}^3$  reaction chamber composed of 4 highly polished stainless steel and 2 polycarbonate walls. 4 stainless steel walls are welded together, whereas 2 polycarbonate walls are removable and while attached by screws the walls are also sealed with silicone seals, hence whole chamber is tightly closed during the measurement. Inside the chamber there is a fan placed in the middle of the ground wall of the chamber, facing up. Chamber also contains stainless steel capillaries to introduce substrates in and to sample the mixture out from the inside center of the chamber. All experiments were carried out in a steady-state. Chamber setup is presented in Fig. 1.

Applied chemical reagents and gases:

- (R)-(+)-limonene (Sigma Aldrich, 97%)
- Mg(NO<sub>3</sub>)<sub>2</sub> (POCH, analytical quality)
- Oxygen (Air Liquide, 99,99%)
- Zero air/purified air

Gas-phase composition and oxidation products concentration were monitored by proton-Transfer-Reaction Mass Spectrometer (PTR-TOF-MS 1000 Ultra, Ionicon, Austria), with  $H_3O^+$  ionization, E/N = 103 Td, drift and inlet temperature 70 °C, drift voltage 520 V, drift pressure 2.59 bar, sampling velocity 1.5 cm<sup>3</sup>/min, sampling time 10s. PTR-TOF-MS records mass spectra of all ions within the range 14-280 m/z. All signal intensity changes for those ions are recorded during the measurement. All measured ion signals were corrected for PTR transmission similarly as was done and described in detail in another study (Hansela et al., 1995). Ionicon VOC MIX 2018 standard gaseous mixture (containing 6 different VOCs: *m/z* 42 (acetonitrile), *m/z* 59 (acetone), *m/z* 79 (benzene), m/z 93 (toluene), m/z 107 (ethylbenzene), m/z 113 (chlorobenzene), and m/z 147 (dichlorobenzene) and m/z 21 (hydronium ion)) was applied to set transmission rate. Measurement cycle was set to 10s. IoniTOF 3.0 (Ionicon, Austria) software was applied to gather the PTR data, while PTR-MS Viewer 3.4.2 (Ionicon, Austria) software was used for setting fitfunction, correction of mass calibration, averaging spectra fragments in selected time spans, subtraction of selected spectra fragments, determination of chemical formula of selected ions, export of selected ion signals and signals gathered in defined spectra fragments.

Meanwhile, condensed phase were studied with Scanning Mobility Particle Sizer (SMPS, Model 3938 with Model 3789 water-based CPC, TSI, USA). Sheath flow was 7 dm<sup>3</sup>/min, aerosol flow 0.7 dm<sup>3</sup>/min, measurement cycle covered 50 s of sampling and 10 s of purge which resulted in measured particle size range of 9.56–349.12 nm. Application of SMPS allowed to measure particle number concentration and calculate particle mass concentration using aerosol density. According to literature, limonene derived aerosol has density  $1.2-1.4 \text{ g/cm}^3$  (Chen et al., 2017; Pei et al., 2018; Saathoff et al., 2009), however in this study we used aerosol density equal 1 g/cm<sup>3</sup> due to the fact that this study is a continuation of our previous study (Pytel et al., 2020) and we wanted to maintain the same calculation parameters.

Aerosol Instrument Manager (TSI, USA) software was applied to gather and export the data, while Statistica (StatSoft, Polska) software was used to create graphs representing SOA concentration and size distribution changes over time. Purified air was generated by passing ambient air through the compressor and then through Zero Air Generator (Zero Gas Supply NGA 19S, MCZ Umwelttechnik GmbH, Germany)). Zero Air Generator purifies the air via (in following order) filtering, drying, catalytic reactions, molecular sieving and activated charcoal filtering. Purified air was used to clean the chamber after each experiment and to control the RH inside the chamber. Temperature and RH were monitored during cleaning and experiments by thermohigrometer Testo® coupled with dedicated "Testo Smart" application.

Limonene was chosen among all other monoterpenes due to its abundance in indoor air, but also due to structure containing two double bonds, which is responsible for faster reaction with ozone comparing to e.g., α-pinene which is commonly found in indoor air as well (Atkinson, 1994). Ozone was chosen as an oxidant by similar reasons - it's the most abundant oxidant present in indoor air (Weschler, 2000; Salvador et al., 2019). Experiments were performed under room temperature 22  $\pm$  2 °C. No UV source was placed inside the chamber. Before each experiment the chamber interior was cleaned with deionized water damped cloth and flushed with 12 l min-<sup>1</sup> purified air. Each cleaning was monitored by PTR-TOF-MS and SMPS to make sure that after the cleaning limonene concentration is less than 0.4 ppbv and total particle umber concentration is no more than few particles/cm<sup>3</sup>. Experiments were conducted under dry and humid (wet) conditions, since very low RH simplifies terpene ozonolysis process and SOA formation whereas humid conditions mimic the real indoor air humidity conditions. In dry experiments, after cleaning the chamber, RH was around 3-5%. For humid experiments, purified air was firstly passed through the bubbler with saturated solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, then directed into the chamber, which resulted in measured RH in a range 44-47%, which is recommended for indoor spaces.

Once the chamber was cleaned and RH set, the zero air inlet was cutoff. Introduction of (R)-(+)-limonene into the chamber was done by placing a vial filled with liquid limonene standard into small, homemade steel emission chamber that was constantly heated to 30 °C and flushed by a constant stream of purified air which outlet was connected to the reaction chamber. After reaching desired concentration, connection between emission and reaction chambers was cut-off. Next step was ozone introduction into the chamber. Ozone was generated by passing the oxygen through DexXer GL-3189A ozone generator. Oxygen was



Fig. 1. Schematic of experimental setup.

applied instead of air to avoid formation of nitrogen oxides that influence particle formation via limonene ozonolysis (Chen et al., 2017; Nøjgaard et al., 2006). Generator yield was determined by titration with 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in the presence of KI and starch and estimated to be 14 mg O<sub>3</sub>/l. Stream splitting was applied to achieve desired ozone concentration in the chamber. Ozone was always introduced into the chamber in 4th min of the measurement. Ozone introduction was instantaneous, after ozone introduction the ozone inlet was cut-off. All the substrates were introduced into the chamber directly below the fan (Fig. 1), which was on during all experiments to ensure uniform distribution and experimental conditions stability in whole chamber volume.

In presented experiments ozone was always introduced in a concentration ensuring total consumption of the terpene to minimize involvement of any other reactions. Dry and humid experiments were conducted for "low" substrate concentration - limonene 22–28 ppbv and O<sub>3</sub> 110–117 ppbv, and "high" substrate concentration - limonene 119–125 ppbv and O<sub>3</sub> 282–287 ppbv. Experiments were conducted for 4 different conditions variations: (i) RH low and terpene concentration low, (ii) RH low and terpene concentration high, (iii) RH high and terpene concentration high and (iv) RH high and terpene concentration low. Each measurement was done for 30 min (chamber background with terpenes was monitored during first 3 min of the measurement) since we are focusing on the very first steps of SOA formation.

The difficulty in investigation of terpene ozonolysis reaction concerns the fact that OH radical is produced by Criegee Intermediate from hydroperoxide channel (Anglada et al., 2002; Aschmann et al., 2002). The OH produced will induce secondary reactions (degradation) with either the precursor or the products. Not using an OH scavenger results in more organic material converted due to OH reactions with the precursor and its products. It has been proved that SOA formation yield is the highest when no OH scavenger is applied (Gong et al., 2018; Jonsson et al., 2008a,b). This is the reason why scientists decide to apply OH scavenger such as cyclohexane, 2-butanol or CO. However, it has been discovered that the type of applied OH scavenger influences the amount of SOA produced (Atkinson and Arey, 2003; Chew, A. A., & Atkinson, 1996; Jenkin, 2004; Zhang, S., Du, L., Yang, Z., Tchinda, N. T., Li, J., & Li, 2023). Moreover, the goal of this study is to investigate the RH influence on terpene ozonolysis initiated SOA formation and it was discovered that the OH scavenger or the products of its reactions can react with Criegee Intermediate and diminish the role of RH (Jonsson et al., 2008a). Therefore, no OH scavenger was used in this study. In our experiments we applied excess ozone to ensure complete limonene consumption and also minimizes the OH effect on limonene ozonolysis (Gong et al., 2018). Also, by not using OH scavenger we wanted to mimic the indoor conditions and keep the system simple to investigate the limonene ozonolysis, which is the process that initiates gas phase transformations leading to SOA formation. No seed aerosol was applied in the experiments since our goal was to observe first moments of new SOA particles formation. Terpene oxidation and SOA formation processes are fast and even small discrepancies in starting reagent concentrations or trace amounts of SOA in the chamber before experiment may influence the process and hence the obtained results. Therefore, to confirm repeatability of measurements, all experiments were repeated 3-5 times a day and several times on different days. In this study the experiments were relatively short - lasting 30 min and the chamber was flushed and cleaned between each experiment. Additionally the chamber was made with stainless steel and inner walls were highly polished to minimize the porosity of the material and thus minimize adsorption on the walls. In our experiments we did not determine the wall loss and this parameter was not included in results analysis.

### 3. Results

Application of two real-time measurement techniques, PTR-TOF-MS and SMPS, allowed to investigate both, gas and particle phase, during limonene ozonolysis induced SOA formation experiments. Presentation of the results in the following chapter always begins with experiments carried out under dry conditions, followed by those carried out under humid conditions. Experiments carried out under dry conditions do not represent indoor air environment. However, dry experiments represent a simplified environment, which facilitates investigation of processes that undergoes during limonene ozonolysis induced SOA formation. Comparison of the experiments in which only one parameter (RH) was changed, facilitates analysis of the results gathered during those experiments.

### 3.1. Finding uncommon, short-lived limonene ozonolysis products and investigation of RH influence on their appearance

PTR-TOF-MS was applied to investigate gas phase during limonene ozonolysis experiments. Our goal was to investigate ions that appeared right after ozone introduction into the chamber filled with limonene, hence, compounds formed at the very beginning of the oxidation process.

Spectra analyzed in this chapter were gathered while initial concentration of limonene and ozone were 119–125 ppbv and 282–287 ppbv respectively. Despite high substrate concentrations (in terms of indoor air), the signal intensities of some of limonene oxidation products are relatively low, indicating that those species were formed in a relatively small amounts, and/or that they undergone further chemistry very rapidly – faster than PTR-TOF-MS scan time of 10s.

Proposed by the authors of present study, procedure of gas phase investigation is presented in Supplement Fig. 1. Application of PTR-TOF-MS and this procedure allowed to find 43 different ions that appear with different frequency among experiments under dry and wet conditions. Next step of results analysis was to establish the frequency of 43 selected ions appearance during experiments. In the following chapter, only ions with 100% appearance frequency, which means that ions appeared in all conducted experiments - with high substrate concentration, under dry and humid conditions, are discussed. However, ions with 91–95% appearance frequency are also mentioned.

Among found ions, there are those characteristic and well-known for limonene ozonolysis, such as m/z 139 (limona ketone (4-acetyl-1methyl-1-cyclohexene)) which is considered to be an indicator in limonene ozonolysis indicated SOA formation process (Rösch et al., 2017) and also m/z 31 (formaldehyde), m/z 47 (formic acid), m/z 59 (acetone) and m/z 61 (acetic acid). Those ions were observed in all our experiments under both, dry and wet conditions. Currently, there is a lot of literature considering before mentioned compounds, and we also published a paper in this subject in 2020 (Pytel et al., 2020). In this study we are focusing on finding other limonene oxidation products appearing with 100% frequency and analyzing the dependence between their formation and different RH level. For our knowledge, uncommon limonene ozonolysis products discussed in this paper are very rarely highlighted in the literature, especially with respect to different RH level. Formula of detected compounds was determined with probability >70 % and the probability is derived from the deviation of the exact mass to the measured one and the isotope distribution. To determine the chemical structure of those products it is necessary to apply another, off-line analytical method, such as GC-TOF-MS, GC-MS/MS or UPLC/ESI-Q-TOF-MS. Since we did not apply any off-line analytical method, we use only mass (m/z) and chemical formula of uncommon limonene ozonolysis products. In PTR-TOF-MS results analysis we use signal intensity in counts per second [cps]. Signal intensity can be used as abundance since, according to PTR-TOF-MS manual, it can be directly used to calculate concentration of gas phase analyte.

Applied proposed searching procedure (Supplement Fig. 1) followed by appearance frequency analysis allowed to find 4 uncommon ions appearing with 100% frequency, in all dry and humid experiments: m/z43 (C<sub>2</sub>H<sub>2</sub>O), m/z 83 (C<sub>6</sub>H<sub>10</sub>), m/z 99 (C<sub>6</sub>H<sub>10</sub>O) and m/z 101 (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>). Other ions, with a little lower, but still high appearance frequency of 90–95% under dry and wet conditions were also found: m/z 71 (C<sub>4</sub>H<sub>6</sub>O 91% frequency), m/z 73 (C<sub>4</sub>H<sub>8</sub>O 95% frequency) and m/z 113 (C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>) 95% frequency). In the following results analysis we will focus only on the ions with 100% appearance frequency.

Uncommon limonene ozonolysis products found under dry and wet conditions with no clear RH influence on ions signal intensity.

Mass spectra of 4 uncommon limonene ozonolysis products appearing with 100% frequency under dry and humid conditions are presented in Fig. 2. One may notice some differences in signal intensities for given ion between dry and humid conditions. Signal intensity for m/z 43 is greater for about 20% under dry conditions than under humid conditions. For m/z 83 and m/z 101 signal intensity is greater under humid conditions than under dry conditions for around 28% and 35% respectively. For m/z 99 signal intensity difference between dry and humid conditions is smaller, being greater under dry conditions by 9%. For m/z43, m/z 83, m/z 101 and m/z 99 we did not observe repeatability of RH influence, therefore, we assume that those ions are characteristic for both dry and wet conditions.

Uncommon limonene ozonolysis products found under dry and humid conditions with respect to RH influence on ions signal intensity.

Since the experiments were done in dry and wet conditions, we analyzed data also in this regard. We found two ions m/z 75 (C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>)

m/z 43

m/z 83

h.

m/z 99

m/z

m/z 101

m/z

82.4 82.6 82.8 83 83.2 83.4 83.6 2

m/z

2.58132

Signal intensity [cps]

2.25-

2

1.75-

1.5

1.25

0.75 0.5-

0.25-

0.619424

0.4

0.3

0.2

0.1

0.382193

[cps]

intensity

Signal intensity [cps]

0.35

0.3

0.25

0.2

0.15 Signal i

0.1 0.05

1.57225

97.27 97.5

1.4

1.2

1

0.8

0.6

0.4 0.2 DRY

cond

Markey, Hilling and

DRY

81.65 81.8

[cps] 0.5

Signal intensity

42.67 427 42,75 42.8 42.85 42.9 42.95 43 43.05 42 1 43.15

DRY

DRY

and m/z 115 (C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>), that appear under dry and humid conditions, however only under dry conditions their appearance frequency is 100% and their signal intensity is repetitively higher under dry conditions. Mass spectra of m/z 75 ad m/z 115 were gathered under dry and humid conditions, which is presented in Fig. 3. According to Fig. 3, one can notice that for the m/z 75 the difference in signal intensity is quite noticeable, suggesting that low RH favor the formation of  $C_3H_6O_2$ (signal intensity 1,18 cps), whereas under wet conditions almost none of this compound is formed (signal intensity around 0 cps). Signal of m/z115 is still visible under humid conditions, however it is higher under dry conditions (by 0.18 cps), also suggesting that low RH favors the formation of C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>.

We also found ions appearing under dry and humid conditions, however with 100% appearance frequency and higher signal intensity only under humid conditions and these ions are m/z 111 (C<sub>7</sub>H<sub>10</sub>O) and m/z 125 (C<sub>8</sub>H<sub>12</sub>O). Mass spectra for m/z 111 and m/z 125 were gathered as well under dry and humid conditions to compare the signal intensities under different RH conditions which is depicted in Fig. 4. In case of m/z111 (C7H10O) it is difficult to determine favoring conditions since difference in signal intensities are very small (0.15 cps), however still suggesting that C<sub>7</sub>H<sub>10</sub>O is more likely formed under dry conditions. For

m/z 43

42.9

m/z 83

42.8 m/z

82.5

m/z

m/z

82.75

m/z 99

m/z 101

43.1 42.2

83.5

83.25



intensity [cps]

Signal

2.0461

1.8

1.6 [cps]

1.2.

0.8 signal

0.4-

0.2

42 2642 3

1

0.8-

0.5-

0.4-0.3-

0.2 0.1

0.35807

sdo 0.25

intensity 0.2

Signal 0.1

Alle a by be de

0.3

0.15

0.05

2.2

2.5

2

1.5

81.37 81.5

WET

WET

[cps] 0.9

Signal intensity 0.7-0.6WET

42.4 42.9 42.6 42

81.7

WET

cor

mtensity

### 5



Fig. 3. PTR-TOF-MS mass spectra of m/z 75 and m/z 115 gathered under dry and wet conditions.

m/z 125 the signal intensity under humid conditions is higher by 0.45 cps, also suggesting that  $C_8H_{12}O$  is more likely formed under humid conditions. For ions described above and especially for small differences in signal intensities for ions m/z 115, m/z 111 and m/z 125, analysis of exported numerical data were also conducted. Analysis of numerical data is more precise than visual observation, and it confirmed repeatability of results and allowed to make the above conclusions.

To compare our results we carried out literature research and found papers describing experiments similar to ours. For example, in 2010 PTR-MS with quadrupole mass spectrometer was applied by Ishizuka et al. (2010) to identify secondary oxidation products created by limonene oznolysis. Authors in the study indicate 8 different secondary oxidation products, among which m/z 99 and m/z 101 are confirmed by our study, unfortunately authors did not suggest the chemical formula of these products. Norgaard et al., in 2013 (Nørgaard et al., 2013) applied Low Temperature Plasma ionization Mass Spectrometry for detection of limonene ozonolysis products. In this study authors determined 18 different compounds ranging from 6 to 60 carbon atoms ( $C_6$  to  $C_{60}$ ) by comparing collision induced dissociation (CID) spectra with an authentic standards, however we did not confirmed any of those compounds in our study. Norgaard et al. determined also another 7 compounds ranging from C<sub>5</sub> to C<sub>30</sub> by comparing CID spectra to other studies of Norgaard et al. (Nørgaard et al., 2008) and Vibenholt et al. (2009), yet only m/z 115 is in accordance with our study. This accordance is only partial since our proposed formula for m/z 115 is C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>, whereas Norgaard et al. (Nørgaard et al., 2013) assigned it as C<sub>5</sub>H<sub>7</sub>O<sub>3</sub>. In another study by Gallimore et al., where PTR-TOF-MS was applied for health-relevant limonene oxidation products determination, authors determined 6 different limonene ozonolysis products in the mass range

m/z 30–170, among which we confirmed these well-known m/z 31 and m/z 47, however also m/z 75 was confirmed by our study. Formula for m/z 75 proposed by Gallimore et al. is  $C_3H_6O_2$ , which also is in accordance with our findings. Application of Extractive Electrospray Ionization Mass Spectrometry allowed authors to detect yet other oxidation products of ions in the range m/z 170–261, which does not coincide with ions detected in this study in the range m/z 43–125 (Gallimore et al. 2017a,b).

Only 4 ions m/z 75, m/z 99, m/z 101 and m/z 115 described in this study were confirmed by other studies, which indicates that limonene ozonolysis, especially its very first steps, is not well studied yet. All discrepancies and lack of data may be caused by different experimental conditions, which influence monoterpene oxidation and SOA formation significantly, which is confirmed by numerous studies, including this one, showing RH influence on some of limonene ozonolysis products formation. Furthermore, application of different mass spectrometry techniques can also result in some discrepancies.

### 3.2. RH influence on SOA formation

The goal of this study was also to observe RH influence on limonene ozonolysis induced SOA formation. PTR-TOF-MS and SMPS data were collected at the same time, however, SMPS sampling time was 1 min versus 10 s sampling time of PTR-TOF-MS. SMPS sampling time could not be set for less than 1 min, since it would result in shifting the range of measured particle dimeter towards the larger particles. Due to different sampling times applied in PTR-TOF-MS and SMPS we could not directly combine the results from those two devices. SMPS results were analyzed in terms of RH influence on particle number (particles/cm<sup>3</sup>) and



Fig. 4. PTR-TOF-MS mass spectra of m/z 111 and m/z 125 gathered under dry and wet conditions.

concentration mass ( $\mu g/m^3$ ).

### 3.2.1. SOA formation experiments with low substrate concentration under low RH conditions

Experiments were firstly carried out for low substrate concentration (limonene ~25 ppbv, ozone ~114 ppbv) and low RH (~4% - dry conditions) to simplify the and to be alble to observe the changes caused by increased RH in following experiments. For low terpene concentration experiments, particle number and mass concentrations values are too low to be able to represent them for all measured particle sizes as a contour plots. Therefore, particle number and mass concentrations changes in time will be represented only for a sum of all measured particle sizes as a linear plots – total particle number and total particle mass concentrations.

Analyzing data presented in Fig. 5 one may notice that total particle number concentration was significantly increasing from the 7th minute of the measurement, which is 3rd minute after ozone introduction, up to the 15th minute of the measurement reaching its maximum around 2500 particles/cm<sup>3</sup>, which indicated the occurrence of nucleation and new particle formation. Once total particle number concentration reached maximum it was followed by stabilization up to the 20th min of the measurement and subsequent, slight and constant decrease to around 1800 particles/cm<sup>3</sup>. Total particle mass concentration was constantly increasing during the experiment, reaching around  $0.4 \,\mu$ g/m<sup>3</sup> at the end. Analysis of numerical data allowed to establish maximum particle number (Supplement Table 1) concentration in a range 13 000–14 000 particles/cm<sup>3</sup> for a particles of diameter around 47 nm and maximum particle mass concentration (Supplement Table 2) in a range 0.07–0.08  $\mu$ g/m<sup>3</sup> for particles of diameter around 325 nm.

3.2.2. SOA formation experiments with low substrate concentration under high RH conditions

Changing RH from low to high, which is more typical for indoor environment, resulted in significant changes in limonene ozonolysis induced SOA formation. Analyzing data presented in Fig. 5, there is a slight particle number concentration increase visible between 8th and 14th min, yet it is too small in comparison to concentration variation during the measurement, therefore one would not consider it a proof of particle formation process. Other repetition of the experiment, (Supplement Fig. 2) shows slight particle number concentration increase over a time of measurement, however it is even less noticeable than in Fig. 5. Also, there is no visible moment of total particle number concentration becoming constant or decreasing as it was visible in experiments carried out under dry conditions. For experiments carried out in this conditions total particle number concentration was around 250-400 particles/cm<sup>3</sup> which is lower than in experiments under dry conditions. Total particle mass concentration slightly increases over time, similarly as total particle number concentration. Some experiments repetitions showed such small total particle mass concentration variations during the measurement that one could consider it constant (Supplement Fig. 2). Total particle mass concentration was around 0.8  $\mu$ g/m<sup>3</sup> for all the experiments carried out under low substrate concentration and high RH, which is higher than in experiments under low RH. This suggest a greater proportion of particles with larger diameter. Comparing total particle number concentration values under dry and wet conditions, the values under dry conditions are greater than under wet conditions. This is opposite to the particle mass concentration values, which were greater under wet conditions. Observation of particle number concentration changes under wet conditions becomes more difficult, since even small changes in the reaction chamber environment (such as slightly different initial particle number concentration) may influence the result in greater extend, which will be more visible while particle number



otal particle mass concentration  $[\mu g/m^3]$ Total particle number concentration 0.70 350.00 0.60 300.00 particles/cm<sup>2</sup>] 0.50 250.00 0.40 200.00 0.30 150.00 0.20 100.00 0.10 50.00 0.00 0.00 0 5 10 15 20 25 30 35 Time [min]

Number concentration
Mass concentration

Fig. 5. Total particle number concentration and total particle mass concentration changes over time during experiments under low substrate concentration, dry and humid conditions.

concentration is relatively low. This explains the small discrepancies between experiment repetitions and proves that water content strongly influences SOA formation, especially under low substrate concentration. Analysis of numerical data allowed to establish that maximum particle number (Supplement Table 3) concentration was in a range 3200–3300 particles/cm<sup>3</sup> for particles of diameter around 10 nm, whereas the greatest particle mass concentration (Supplement Table 4) was in a range 0.09–0.1  $\mu$ g/m<sup>3</sup> for particles of diameter around 320 nm.

According to the obtained results for low terpene concentration experiments, changing experimental conditions from dry to wet decreased maximum particle number concentration  $\sim$ 4 times among all the experiments. Under dry conditions, the highest particle number concentration was observed for particles of bigger diameter ( $\sim$ 47 nm) than under humid conditions ( $\sim$ 10 nm), therefore the whole particle size distribution was shifted towards smaller particles. Changing experimental conditions from dry to wet resulted also in maximum particle mass concentration increase  $\sim$ 1.5 times. The greatest value of particle mass found similarly, at particles of  $\sim$ 320 nm diameter.

## 3.2.3. SOA formation experiments with high substrate concentration under low RH conditions

As it was mentioned earlier, human activity like using air fresheners, cleaning agents, perfumes, scented candles, essential oils, herbs, and similar every-day use scented products causes temporary increases of monoterpene concentration in indoor air. Therefore, a set of experiments was also carried out to mimic this temporal monoterpene concentration increases in indoor environment. Similarly as in case of low substrate concentration, experiments were firstly conducted under dry conditions (RH  $\sim$ 4%).

The results of total particle mass and number concentration changes over time for high terpene concentration and dry conditions are depicted in Fig. 6. The increase in both total particle number and total particle mass concentration is clearly visible right after ozone introduction into the chamber in 4th min of measurement. Total particle number concentration reaches its maximum of 100 000-150 000 particles/cm<sup>3</sup> within 2 min after ozone introduction, which is much faster than in case of low terpene concentration (for which it took  $\sim$ 7 min). After reaching the maximum, total particle number concentration starts to gradually decrease until the end of the experiment, reaching the value of 20 000-40 000 particles/cm<sup>3</sup>. Total particle mass concentration as well starts to increase right after ozone introduction; however, the increase is a bit slower than total particle number concentration. Total particle mass concentration reaches its maximum of 7–12  $\mu$ g/m<sup>3</sup> within around 7 min. The maximum remains constant for around 5 min, then begins to gradually drop until the end of the measurement reaching 4–6  $\mu$ g/m<sup>3</sup>. The immediate increase of total particle number concentration perfectly depicts the new particle formation process. Total particle mass concentration increase overlays the few minutes of constant total particle number concentration (around 3 min right after rapid increase), which

> 0.31

< 0.31

< 0.26

< 0.21

< 0.16

< 0 11

0.06

< 0.01



Fig. 6. Particle number and mass concentration changes over time as a total concentration and with respect to particle size during experiments under high substrate concentration and dry conditions.

2.75E5

1.75E5

< 75000

indicated the condensation process.

Application of high substrate concentration resulted in higher particle number and mass concentration values, which allowed to present data more precisely - with respect to particle sizes, in contour plots -Fig. 6. According to the results presented in Fig. 6, one may observe particle number concentration increase that initiates in 4th - 5th min and is sharply visible around 5th - 7th min. Increase lasts up to the 13th -15th minute of the measurement, when particle number concentration begins to drop. Particle mass concentration increase starts around a minute later than increase in particle number concentration. While particle number concentration began to be the greatest at 9th minute of the measurement (for particles of diameter 43.32-55.73 nm), one can observe the beginning of particle mass concentration increase. As the particle number concentration begins to decrease, particle mass concentration still has high/moderate values since particles that are present inside the chamber are relatively big, having diameter 43.32-90 nm. Contour plots clearly indicate new particle formation and nucleation processes at the beginning of the measurement, followed by condensation and coagulation observed since around the middle of the measurement time. Similarly as in previous experiments, analysis of numerical data presented in Fig. 6 allowed to establish that maximum particle number concentration was in a range 500 000-650 000 parti $cles/cm^3$  for particles in a range 50–55 nm and the highest particle mass concentration was in the range 0.4–0.6  $\mu$ g/m<sup>3</sup> for particles of diameter around 60 nm.

15 17 19 21 23 25 27

Time [min]

3.2.4. SOA formation experiments with high substrate concentration under high RH conditions

Similarly as in case of low substrate concentration experiments, we

also conducted experiments with higher RH for high substrate concentration experiments to mimic the temporal terpene concentration increases in indoor environment. According to Fig. 7, the highest value of total particle number concentration is 900 000–1 000 000 particles/cm<sup>3</sup>, which is greater in comparison to dry conditions -  $\sim$ 125 000 particles/ cm<sup>3</sup>. The increase in total particle number concentrations begins in the same minute (4th) as the ozone was introduced into the chamber, which is 1-2 min faster than during most of dry conditions experiments and the maximum is reached within 2 min, similarly as under dry conditions. The maximum of total particle number concentration starts to drop immediately after reaching its maximum and drops to around 200 000 particles/cm<sup>3</sup> at the end of the measurement. Total particle mass concentration starts to increase 1 min after ozone introduction into the chamber and gradually increases until 13th minute of the measurement, similarly as under dry conditions. However, maximum total particle mass concentration under humid conditions is around 50–60  $\mu$ g/m<sup>3</sup>, which is five times more than under dry conditions ( $\sim 10 \ \mu g/m^3$ ). After reaching the maximum, total particle mass concentration begins to drop to reach  $\sim$ 35 µg/m<sup>3</sup> at the end of the measurement. Under humid conditions, one can also perfectly notice the main SOA formation driving processes; nucleation within 4-7 min of the measurement indicated by fast total particle number concentration increase, followed by very short period of condensation around 7th min of the measurement, followed by coagulation in 13-16 min of measurement, characterized by decreasing particle number concentration and constant total particle mass concentration.

15 17

Time [min]

13

21 23 25 27

In this set of experiments contour plots allow to observe SOA formation process and particle number and mass concentration changes over time with respect to particle sizes. According to Fig. 7, there is a



Fig. 7. Particle number and mass concentration changes over time as a total concentration and with respect to particle size during experiments under high substrate concentration and humid conditions.

visible burst of particles that starts right after ozone introduction into the chamber in 4th minute of the measurement again indicating new particle formation process. Sharp particle number concentration increase is visible in 5th - 6th min. The maximum particle number concentration is located between 6th and 12th min of the measurement, which is followed by constant particle number concentration decrease until the end of the measurement. One may observe particle mass concentration increase since 5th min for particles of around 30 nm diameter. Particle mass concentration maximum lasts from 9th until 19th min, which is followed by slow decrease. As the particle number concentration begins to decrease, particle mass concentration, similarly as during dry experiments, still has high/moderate values. According to numerical data presented in Fig. 7, changing RH from low to high and keeping high terpene concentration resulted in maximum particle number concentration in a range 5 200 000–6 000 000 particles/cm<sup>3</sup> for particles of diameter 40-54 nm. Humid conditions resulted in the highest particle mass concentration in a range 2–2.5  $\mu$ g/m<sup>3</sup> for ~55 nm particles. Changing experimental conditions from dry to wet resulted in maximum particle number concentration increase ~9 times among all conducted experiments. Elevated RH influenced also maximum particle mass concentration, which was  $\sim 5$  times greater under humid conditions.

To compare our results with other data, we carried out literature research. We found that for particle number concentration, some of the studies, also focused on terpene (such as squalene,  $\beta$ -pinene,  $\alpha$ -pinene, limonene) ozonolysis, claim negative or none effect of RH on particle number concentration (Fick et al., 2003; Rohr et al., 2003; Von Hessberg et al., 2009; Wang and Waring, 2014). On the other hand, some research indicates positive RH influence on yiled of SOA. Zhang et al. determined positive effect of humidity on SOA formation during experiments where SOA was formed by ozonolysis of limonene, 3-carene or  $\alpha$ -pinene separately (Jonsson et al., 2006). Tillmann et al. also indicated that SOA yields were higher under humid conditions during experiments on  $\alpha$ -pinene ozonolysis (Tillmann et al., 2010). Other known to us studies indicating positive RH influence on SOA number concentration consider

SOA formed by e.g. photooxidation of cyclohexane (Liu et al., 2019) or toluene and m-xylene (Chen et al., 2021). However, it should be high-lighted, that different oxidation conitions and different type of VOC (not terpenoid) were applied in those studies.

Regarding particle mass concentration, most of the studies confirms that higher RH increases SOA mass concentration (Boyd et al., 2017; Chen et al., 2021; Jonsson et al., 2006; Tillmann et al., 2010), which can be partially explained by water up-take by organic particles from terpene oxidation, which was previously determined by hygroscopic tandem DMA systems by Cocker et al. and Wirkkula et al. (Cocker et al., 2001; Virkkula et al., 1999). Asa et al. (Jonsson et al., 2006) also suggest that the properties of initially producted cluster can be changed by water, resulting in production of larger fraction of clusters, able to grow beyond their critical size for nucleation. However Zhang et al. (2011) indicates that this happens only up to the maximum SOA growth. While this point is crossed, SOA mass begin to drop. This may be explaind by wall loses, temperature changes, evaporation of organic compounds previously condensed on particles back to the gas phase.

We also carried out experiments aimed at investigation of backgrond aerosol presence and concentration influence on SOA formation. Results are presented and described in supplementary material (Supplement Chapter 2).

### 4. Discussion, conclusions and future trends

By application of PTR-TOF-MS, its dedicated software and statistical analysis, we were able to find 4 new ions appearing at the very beginning of limonene ozonolysis reaction and estimate their formula with over 70% probability: m/z 43 (C<sub>2</sub>H<sub>2</sub>O), m/z 83 (C<sub>6</sub>H<sub>10</sub>), m/z 99 (C<sub>6</sub>H<sub>10</sub>O) and m/z 101 (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>). Presented ions appeared in mass spectra with the same frequency as well-known oxidation products such as m/z 31 (formaldehyde), m/z 47 (formic acid), m/z 59 (acetone) and m/z 61 (acetic acid). We also analyzed data in terms of RH influence on limonene ozonlysis, finding m/z 75 (C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>) and m/z 115 (C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>) formed under dry conditions and m/z 111 (C<sub>7</sub>H<sub>10</sub>O) and m/z 125

 $(C_8H_{12}O)$  formed under humid conditions. This findings suggest that different short-lived oxidation products are formed under dry and humid conditions, which may indicate different pathways of SOA formation and further evaluation under different RH conditions. Data suggest that these newly found oxidation products are either short-lived, very quickly undergoing further reactions or formed in a very small amounts or both. Short-lived compounds would not stay long in indoor air, however they may play important role in mechanisms leading to SOA formation. Those compounds might be another important components in gas and condensed phase changes, thus guiding the direction of reactions and influencing SOA formation and size distribution. Since we did not apply any additional analytical technique to determine chemical structure of determined uncommon products, we have to little information to speculate and propose the formation mechanism of these products.

Our results prove that elevated RH results in elevated particle mass concentration, regardless initial terpene concentration. These results are in accordance with most of the findings (Boyd et al., 2017; Chen et al., 2021; Jonsson et al., 2006; Tillmann et al., 2010). Regarding particle number concentration our results are inconsistent. For experiments with low terpene concentration all our experiments prove that increasing RH causes decrease in particle number concentration. These findings are in accordance with most of the studies claiming more SOA is formed under dry conditions (Von Hessberg et al., 2009), probably because higher water content inhibits stabilized CIs formation, which are correlated with nucleation potential (Bonn et al., 2002). However, for high terpene concentration, our experiments indicate that increasing RH causes particle number concentration increase, which was observed by particle number concentration ~9 times greater under humid conditions. There are some of the studies indicating similar observations. For example, Chen et al. (2021) investigated RH influence on SOA formation from aromatic hydrocarbons, claiming that increasing RH in the system resulted in formation of more low volatility products, promoting SOA formation. Similarly, Liu et al. (2019) indicated enhanced SOA formation under humid conditions, by gas phase soluble components becoming more concentrated on wet particulates surface.

Apart of the RH influence, we would like to focus a bit on the substrate concentration influence on obtained results. There are some literature findings suggesting that initial substrate concentration may influence the RH and SOA formation dependence. Chen et al. (2021) found that SOA mass concentration was increasing from RH  $\sim 2\%$  to reach maximum at RH  $\sim$  50% for both systems and it was decreasing with RH  $\sim$  70% and  $\sim$ 90%, which was in contrary to some previous studies that reported constant positive relationship between RH and SOA yield (Jia and Xu, 2018). Therefore, Chen et al. (2021) suggested that this discrepancies may be caused by lower initial substrate concentration utilized in his study, in comparison to Jia et al. (Jia and Xu, 2018), which in turn can result in different oxidation processes influencing SOA formation (Chen et al., 2019). Seinfeld et al. (2001) also concluded that the RH dependance on SOA formation may be altered by the amount of terpene undergone oxidation by adsorption of non-polarcompound (terpene) on SOA particle surface, which makes SOA particles less hydrophilic. Oxidation of large amount of terpene will result in more aerosol available for coagulation, condensation and gas-to-particle partitioning. We also noticed that different initial substrate concentration may influence the particle size range where, especially, maximum particle mass concentration is localized. For low subtrate concentration the maximum particle mass concentration values were oriented for the particles of 320-380 nm. Increasing initial substrate concentration resulted in maximum particle mass values shift towards smaller particles of 50-60 nm diameter. The influence of initial substrate concentration is not so great on the maximum particle number concentration, which for most of the experiments is around particles of 40-55 nm. Only under low substrate concentration and hunmid conditions maximum particle number concentration is shifted twards smaller particles with diameter around 10 nm.

We would also like to highlight the influence of bachground aerosol presense on limonene ozonolysis induced SOA formation. As it is easier to interprete the results of chamber experiments with no background aerosol, one has to remember that in real environment there always is some background aerosol. Our experiments focused on the very first steps of SOA formation proved that in the presence of background aerosol nucleation process becomes weaker while the main process occurring in the experimental chamber is condensation. The greater the total concentration of the background aerosol the slower the particle formation proces and the less particles are formed, while condensation becomes more dominant proces.

Determination of RH influence on terpene derived SOA formation is a difficult task. It is confirmed by this and other studies that RH has an inflence on SOA formation process, particle number and mass concentration and paritle size distribution changes over time. In this study, we found uncommon limonene ozonolysis products that are characterized by short life time indicating high reactivity. The appearance of some of the described products is characteristic for either dry or humid conditions indicating that RH influence of SOA formation begins in the gas phase. Unfortunately, sampling time for PTR-TOF-MS was 10s, whereas for SMPS it was 60s and due to that it is impossible to directly overlap PTR-TOF-MS and SMPS results. Therefore, we are not able to preset the exact and direct relationship between gas-phase products and SOA. However, it is known that oxygenated compounds (such as our uncommon products) formed by limonene ozonolysis are polar and have lower volatility than precursors, which promotes phase transfer and thus formation of SOA.

However, it is hard to draw clear conclusion since there are other factors highly influencing SOA formation process, such as eg. substrate concentration, which was also confirmed in this study. In our study we applied only one terpene – limonene – and one oxidant – ozone – in defined concentrations ensuring complete consumption of terpene, however, in real environment (and also in another experiments) there can be plenty another scenarios involving reactions with more than one terpene, more or other oxidant, other reactive chemical species like OH radicals etc. Hence, it is important for scientists to precisely define experimental conditions, so that the results are comparable and conclusions are more consistent.

There is plenty of research concerning terpene derived SOA formation and environmental factors influencing these processes, however it is very hard to compare results due to different experimental protocols. Scientists apply different chambers, substrates, environemntal conditions, time of the experiment, etc., which apart of differencec in result comparison, causes also contradictory results that are hard to explain (Pytel and Marcinkowska, 2022). Moreover, most of the research is currently focused on SOA particles of diameter 5.5-800 nm, whereas it is well known that the smaller the particles, the more dangerous they are for human health due to increasing surface-to-volume ratio (Marval and Tronville, 2022). Recent analytical advances allows to stydy SOA partcles also in a range below 5 nm diameter. For example Yang et al., in 2021 for the firt time reported formation of nanocluster aerosols <3 nm formed via reaction of ozone with human skin lipids. Authors indicated that particles with diameter 1.18-1.55 nm are precursors for new particle formation, which is a key phenomenon associated with the develoment of indoor air aerosol (Yang et al., 2021). Therefore, despite current issues with results comparison, application of experimental knowledge in the real environment becomes yet more difficult due to human presence factor, which most commonly is not included in the experimental studies.

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### CRediT authorship contribution statement

Klaudia Pytel: Visualization, Writing - original draft. Bożena Zabiegała: Conceptualization, Supervision, Writing - review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.140854.

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