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Significant OH production under surface cleaning and air cleaning conditions: impact on indoor air quality

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## **Abstract**

We report measurements of hydroxyl (OH) and hydroperoxy (HO<sub>2</sub>) radicals made by laser-induced fluorescence spectroscopy in a computer classroom (i) in the absence of indoor activities (ii) during desk cleaning with a limonene-containing cleaner (iii) during operation of a commercially available ‘air cleaning’ device. In the unmanipulated environment, the one-minute averaged OH concentration remained close to or below the limit of detection ( $6.5 \times 10^5$  molecule cm<sup>-3</sup>), whilst that of HO<sub>2</sub> was  $1.3 \times 10^7$  molecule cm<sup>-3</sup>. These concentrations increased to  $\sim 4 \times 10^6$  and  $4 \times 10^8$  molecule cm<sup>-3</sup>, respectively during desk cleaning. During operation of the air-cleaning device, OH and HO<sub>2</sub> concentrations reached  $\sim 2 \times 10^7$  and  $\sim 6 \times 10^8$  molecule cm<sup>-3</sup> respectively. The potential of these OH concentrations to initiate chemical processing is explored using a detailed chemical model for indoor air (the INDCM). The model can reproduce the measured OH and HO<sub>2</sub> concentrations to within 50% and often within a few % and demonstrates that the resulting secondary chemistry varies with the cleaning activity. Whilst terpene reactions products dominate the product composition following surface cleaning, those from aromatics and other VOCs are much more important during the use of the air cleaning device.

**Keywords:** hydroxyl radical, hydroperoxy radical, air cleaning technology, limonene, indoor air chemical model, indoor air chemistry

## **Practical Implications**

Cleaning is an important part of building operation and a variety of techniques are currently employed, usually with an emphasis on removal of biological pathogens. However, depending on the technique adopted, different chemical species can be produced, some of which may be harmful to health. It is important to understand the implications of different

types of cleaning indoors, to ensure that the removal of biological pollutants does not inadvertently expose occupants to high concentrations of chemical pollutants instead. This could have special relevance for health workers, who may spend many hours in environments where air cleaning devices are operated.

## **1. Introduction**

Indoor air quality is of increasing concern in developed countries, especially given we are estimated to spend 90% of our time indoors. Most of our exposure to air pollution happens indoors rather than outdoors, despite the regulatory focus on the latter. A recent report estimated the total number of deaths due to air pollution each year was 40,000 in the UK alone, with further deaths caused by indoor air pollution.<sup>1</sup> It is therefore of critical importance that the routes to exposure indoors are fully understood, in order to calculate health burdens accurately and to develop policies that reduce overall exposure.

Indoor air is subject to a number of sources of pollution. Outdoor air can ingress to the indoor environment, providing a source of pollutants indoors, such as ozone ( $O_3$ ), nitrogen oxides ( $NO_x$ ) and particulate matter (PM). However, there are also numerous direct sources of pollution indoors, particularly from human activities such as cooking, cleaning, smoking and the use of personal care products.<sup>2,3</sup> These activities produce a wide range of indoor pollutants including PM,  $NO_x$  and volatile organic compounds (VOCs), including oxygenated species such as formaldehyde (HCHO). Indoor activities can lead to higher indoor concentrations of some pollutants than outdoors and provide the basis for reactive chemistry. In addition, evidence in this field suggests that secondary rather than primary pollutants are to blame for adverse health effects that have been reported indoors.<sup>2</sup>

One area of active research indoors is the potential impact on health of using cleaning products, both for occupational cleaners<sup>4</sup> and for domestic use of cleaning products in the

home.<sup>5</sup> Many cleaning products contain limonene,<sup>6</sup> which can be oxidised indoors by ozone to form a range of secondary products, including some that have demonstrated adverse health effects.<sup>5,7,8</sup> Although it remains unclear exactly what causes the adverse health effects, there is compelling evidence that the gas-phase products of limonene-ozone mixtures rather than those in the particle phase are responsible for prominent sensory effects.<sup>7</sup>

A method that is being increasingly adopted to maintain indoor environments is so-called ‘air cleaning’ technology.<sup>9</sup> A variety of instruments adopt one of a number of different techniques, including thermal-or photo-catalytic oxidation, adsorption, filtration (of particles), UV germicidal irradiation, ion generation and electrostatic precipitation.<sup>10</sup> Many of them operate by generating high concentrations of OH radicals, with the aim of removing biological pathogens. However, OH radicals can initiate chemical oxidation indoors, leading to a wide variety of chemically complex products some of which are likely to be harmful to health.<sup>11</sup> Indeed, in a recent review of air cleaning technologies, it was noted that none of the technologies removed all indoor air pollutants and many generated undesirable secondary products.<sup>10</sup> Clearly, it is important to understand what these products are and how they are formed to ensure that those who are exposed on a regular basis to cleaning processes are not adversely affected.

This paper describes a small-scale study in a computer room in the University of Leeds in September 2012 that measured concentrations of OH and HO<sub>2</sub> radicals (known collectively as HO<sub>x</sub>), VOCs and O<sub>3</sub> in indoor air, as well as a range of biological indicators (such as viable counts). The study aimed to explore whether activities that aim to remove biological pathogens, such as the use of surface cleaning and air cleaning technology, could inadvertently increase the concentrations of indoor chemical pollutants within indoor environments. We use a detailed chemical model to attempt to reproduce measured radical

concentrations indoors and then compare the indoor air chemistry that resulted from the different cleaning activities.

## 2. Methods

### 2.1 Description of Room and Activities

The office is situated to the rear of the Chemistry building at the University of Leeds, on the opposite side to a busy road adjacent to the front of the building. Measurements were made over 4 days in September 2012, but the focus of this paper is on September 5<sup>th</sup> when several different activities were carried out within the office. The office is 6.95 m long with a width of 9.35 m and height of 2.9 m, providing a floor area of 65.0 m<sup>2</sup> and a volume of 188.4 m<sup>3</sup>. This includes a small side office with a volume of 33 m<sup>3</sup>. The office was carpeted, with a number of desks and contained 19 new PCs. The room was mechanically ventilated with 6 supply and 4 extract grilles all located on the ceiling. Ventilation flows were measured using a balometer (Airflow instruments) prior to the study. The room was positively pressurised with a total supply flow rate of 1210 m<sup>3</sup>/h and extract 465 m<sup>3</sup>/h. A proportion of this flow was recirculated giving an estimated fresh air ventilation rate of 3.5 air changes per hour. There were also several large windows in the room. The side office was used to locate the radical instrument to minimise the influence of heat from the instrument on the main room.

Several different activities were carried out as described in Table 1. The surface cleaner was a well-known ‘lemon’ scented UK brand listed to contain glutaral, benzisothiazolinone, undisclosed perfumes, citral, citronellol, hexylcinnamal, limonene and linalool and was diluted and applied according to the manufacturer’s instructions. The ACD was a commercially available instrument, which generated ozone internally in the presence of excess limonene to rapidly produce OH radicals. The odour of limonene was detectable close to the instrument.

**Table 1:** Description of activities over the measurement period

Period	Time	Description
1	07:55-10:11	Morning baseline: instruments running, but no perturbations
2	10:12-10:22	Cleaning desks and FAGE inlet with surface cleaner.
3	10:23-11:30	Post-cleaning period (internal door opened at 10:50)
4	11:31-11:45	ACD operational 2m from FAGE
5	11:46-12:10	ACD operational 0.5m from FAGE
6	12:11-12:59	Post-ACD use period 1
7	13:00-16:20	Post- ACD use period 2 (windows were opened at 14:14)

## 2.2 Radical concentration measurements

Fluorescence assay by gas expansion (FAGE) has been well-demonstrated as a powerful tool for atmospheric measurements of HO<sub>x</sub>.<sup>12</sup> OH and HO<sub>2</sub> were monitored using the aircraft-FAGE instrument from the University of Leeds in a ground configuration. The FAGE inlet sampling the radicals was located in the room, with the laser and main instrument rack located outside the room: there is no loss of radicals when sampling with this configuration.

The instrument has been described elsewhere,<sup>13</sup> but a brief description is provided here. The instrument sampled ambient air at a rate of ~ 4 slpm through a 0.7 mm diameter pinhole and the gas flowed through a single detection cell, held at a low pressure of ~ 1.7 Torr, for sequential detection of OH and HO<sub>2</sub>. OH was detected by its on-resonance laser-induced fluorescence following excitation at 308 nm. A reference cell, containing a heated filament used to thermally decompose water vapour to yield OH, was used to identify the wavelength at which the fluorescence of OH at that transition was strongest. Upstream of the detection cell was an injection port for NO, to chemically convert HO<sub>2</sub> to OH, subsequent to detection at 308 nm. The NO flow stabilised within 2 seconds of being switched on,

providing a constant flow of 10 sccm, resulting in complete conversion of ambient HO<sub>2</sub> to OH. Typically, 1 minute of OH measurements (no NO) was followed by 1 minute of HO<sub>2</sub> measurements (NO flow switched on), although this duty cycle was altered throughout the experiments according to priorities. The fluorescence signal during NO injection contained contributions from ambient OH as well as the OH generated in situ from chemical conversion of HO<sub>2</sub>. The ambient OH signal, recorded without NO injection, was subtracted from the OH + HO<sub>2</sub> signal to give the signal due to HO<sub>2</sub> alone. The fluorescence signals were then normalised with respect to the laser power entering the detection cell (typically 10–30mW).

The instrument was calibrated separately for OH and HO<sub>2</sub> in the laboratory before and after the measurements under the same conditions (i.e. laser power, instrument pressure, NO flow) as for ambient sampling. The calibration was performed using the 184.9 nm photolysis of water vapour, whose concentration was measured using a dew point hygrometer, in a flow of synthetic air in a turbulent flow reactor. The product of the photolysis time and lamp flux was determined using an N<sub>2</sub>O (nitrous oxide) actinometer.<sup>14</sup> N<sub>2</sub>O was photolysed in the same flow reactor at 184.9 nm to generate excited state oxygen atoms that react with N<sub>2</sub>O to generate NO in a known yield, which was measured using a chemiluminescence analyser.<sup>13</sup> Although it is also possible to use a method whereby O<sub>2</sub> is photolysed to produce O atoms that recombine with O<sub>2</sub> to form ozone, which can then be detected by a commercial UV Absorption analyser,<sup>15,16</sup> the Leeds NOx analyser is sensitive to 50 pptv of NO (cf. 1 ppb for O<sub>3</sub> detection limit), permitting lower lamp fluxes to be measured and hence lower OH concentrations to be generated.

The calibration yielded mean instrument detection limits of  $6.5 \times 10^5$  molecule cm<sup>-3</sup> and  $6.6 \times 10^5$  molecule cm<sup>-3</sup> for OH and HO<sub>2</sub>, respectively, for an averaging time of 1 min and a signal-to-noise ratio of 2. The  $2\sigma$  uncertainty in the measurements was ~ 30 % for both OH and HO<sub>2</sub>. This measurement uncertainty was calculated as the sum in quadrature of the

uncertainty in the instrument sensitivity (determined by calibration), the standard deviation of the measured OH and HO<sub>2</sub> signals, and the standard deviation in the measured laser power. Calibration uncertainty was determined by uncertainties in the measured concentration of H<sub>2</sub>O vapour, the absorption cross section of H<sub>2</sub>O vapour, the product of the lamp flux and photolysis time determined by chemical actinometry, the slope of the linear fit through the calibration data, measured laser power and laser wavelength. Note that the FAGE HO<sub>2</sub> measurements are likely over-estimated through an interference from RO<sub>2</sub>, particularly when the VOCs are dominated by alkenes.<sup>17</sup> In a recent aircraft campaign using this instrument for similar NO concentrations, the average model-predicted interference in the HO<sub>2</sub> measurements was 14%,<sup>18</sup> hence the reported HO<sub>2</sub> concentrations in this study should be regarded as an upper limit. Some instruments have also reported an interference for OH measurements,<sup>19-21</sup> thought to originate from the decomposition of species within the sampling assembly/fluorescence cell. However, this artificially-generated OH is likely to vary with instrument design and there is no evidence to suggest it affects our reported concentrations.

### 2.3 Other measurements

The concentrations of 22 different VOC concentrations (ethane (2.9 ppb), propane (0.94 ppb), i-butane (1.2 ppb), n- and i-pentane (0.09 and 0.25 ppb respectively), n-hexane (0.09 ppb), n-heptane (0.02 ppb), octane (0.2 ppb), ethene (0.2 ppb), propene (0.08 ppb), 1-, and cis-2-butene (0.003 ppb and below level of detection (LOD) respectively), 1-pentene (below LOD), isoprene (below LOD), 1,3-butadiene (0.007 ppb), acetylene (0.2 ppb), benzene (0.06 ppb), toluene (0.37 ppb), ethylbenzene (below LOD), m-, o- and p-xylene (1.1, 1.3 and 1.1 ppb respectively) and 1,3,5-trimethylbenzene (below LOD)) were determined indoors between 08:00-13:15 h with detection limits between 1-3 ppt.<sup>22</sup> Over this period, 18 samples were

taken at approximately 15-20 minute intervals. The air samples were collected in pre-evacuated canisters and then analysed off-line using gas-chromatography.<sup>22</sup> The samples were not taken frequently enough to determine changes following the various cleaning activities that were performed, and owing to technical reasons, the concentrations of the terpene species (including limonene) were not measured. However, those determined provide some internal VOC concentrations to initialise the model.

Ozone concentrations were determined using an Aeroqual Series 500 Monitor fitted with a low range sensor head. The detection limit was 1 ppb with an accuracy of  $\pm 2$  ppb. Eleven temperature and relative humidity (RH) sensors were placed around the room. Over the period from 08:00-16:00 on the 5<sup>th</sup> September on which this study focuses, the average temperature and RH values in the study room were 20.3°C and 47.7% respectively with standard deviations of 0.9°C and 3.7%.

Outdoor concentrations were not measured as part of this study. However, a regulatory National monitoring network site (Leeds Central) was located ~1 km from the School of Chemistry in Queen Square Court.<sup>23</sup> Outdoor concentrations were 27, 13, 6 and 301 ppb for O<sub>3</sub>, NO<sub>2</sub>, NO and CO respectively averaged over the period from 12:00-16:00 h (unfortunately, no data are available before this time, presumably owing to technical problems with the network instruments). Average PM<sub>2.5</sub> concentrations were 13.4  $\mu\text{g}/\text{m}^3$  for the same period. These concentrations are typical for an urban area: the monitoring site is ~30 m from a frequently congested 4-lane inner city road and 150 m from an urban motorway.

## 2.4 Model

The model used to support this study is a detailed chemical model for indoor air (INDCM) that has been described in detail before.<sup>24,25</sup> It includes terms that describe the exchange of indoor species with outdoor air, photolysis (driven by indoor lighting as well as attenuated

light from outdoors), deposition processes on indoor surfaces and chemical reactions. For the latter, the Master Chemical mechanism v3.2 has been used,<sup>26-29</sup> which is a comprehensive chemical mechanism that describes the degradation of ~140 VOCs common in the ambient atmosphere. The INDCM also includes gas-to-particle partitioning for limonene oxidation products.<sup>25</sup> However, the MCM does not contain degradation schemes for the other terpene ingredients in the surface cleaner, namely linalool, citral, citronellol and hexylcinnamal.

A literature search was carried out for these 4 compounds and rate coefficients for reaction with OH and O<sub>3</sub>, as well as OH yield from the ozonolysis reaction were available for linalool. Therefore, a simple scheme was devised based on laboratory studies of reaction pathways and rate coefficients for oxidation by OH and O<sub>3</sub>.<sup>30,31</sup> It was assumed that reaction with OH proceeded via the addition of the OH group to one of the two double bonds to form two peroxy radicals (LINALAO<sub>2</sub> and LINALBO<sub>2</sub> in Supplementary Information). The ratio was 77:23 in favour of addition to the double bond within the (CH<sub>3</sub>)<sub>2</sub>C=CH- group compared to that within the CH<sub>2</sub>=CH- group.<sup>30</sup> The major fate of these peroxy radicals is then to react mainly with NO or other RO<sub>2</sub> radicals within the peroxy radical pool.<sup>26</sup> Reaction with O<sub>3</sub> was assumed to proceed via addition of the O<sub>3</sub> to the double bond within the (CH<sub>3</sub>)<sub>2</sub>C=CH- group, leading to the formation of acetone, two Criegee intermediates and a hydroxyl-substituted aldehyde.<sup>30</sup> Further decomposition of the Criegee intermediates leads to OH, formaldehyde and acetone as products. Note that the reaction with NO<sub>3</sub> was ignored for simplicity, given the low predicted concentration of NO<sub>3</sub> by the model (<0.1 ppt). Many of the products from these new reactions already exist in the MCM. For new species, simple degradation schemes were created according to the MCM protocol,<sup>26</sup> or analogous compounds used if sensible. This led to 34 new gas-phase reactions (presented in the Supplementary Information section). The absence of schemes for the other terpene species is addressed in the sensitivity study in Section 3.2.

Although the Leeds centre ambient monitoring site was the closest to the measurement location, it is unlikely to be fully representative of the air outside the office, given the location of the office away from the busy street. The ozone concentrations measured inside the office on the 5<sup>th</sup> September were around 20-25 ppb when measurements began, similar to the concentration measured outdoors at the urban centre site 1 km distant. Away from the road, ambient ozone concentrations were likely to have been higher. Therefore, the outdoor concentration of ozone was increased in the model to 40 ppb, in order to produce an indoor concentration in the range of ~20-25 ppb under the observed conditions, to be more in line with the indoor measurements. Note that when the windows were opened at 14:14 h, the indoor O<sub>3</sub> concentration increased to 36 ppb, so this assumption seems reasonable. Outdoor NO and NO<sub>2</sub> concentrations were decreased by the same proportion to be consistent, to ~4 and 10 ppb respectively. This provided indoor NO and NO<sub>2</sub> concentrations of < 1 ppb and ~9 ppb respectively. The impact of these assumptions on the predicted radical concentrations is discussed in Section 3.2.

The measured VOC concentrations were input into the model as constant indoor values over the measurement period. The concentrations of isoprene, cis-2-butene, 1-pentene, ethylbenzene and 1,3,5-trimethylbenzene remained below the detection limit of 1-3 ppt<sup>22</sup> for the entire measurement period and were consequently set to zero in the model. Other VOC species for which measurements were not available were initialised at zero, with the exception of limonene and linalool as explained subsequently. Outdoor formaldehyde (HCHO) and acetone (CH<sub>3</sub>COCH<sub>3</sub>) concentrations were assumed to be 3 and 1 ppb respectively, typical of urban background values.<sup>32</sup>

In the absence of measurements, it was assumed that the light transmitted through the windows was attenuated to 7.5% of that outdoors in the UV and 30% of that outdoors in the visible: indoor lighting was also included in the simulation.<sup>24</sup> Deposition velocities were

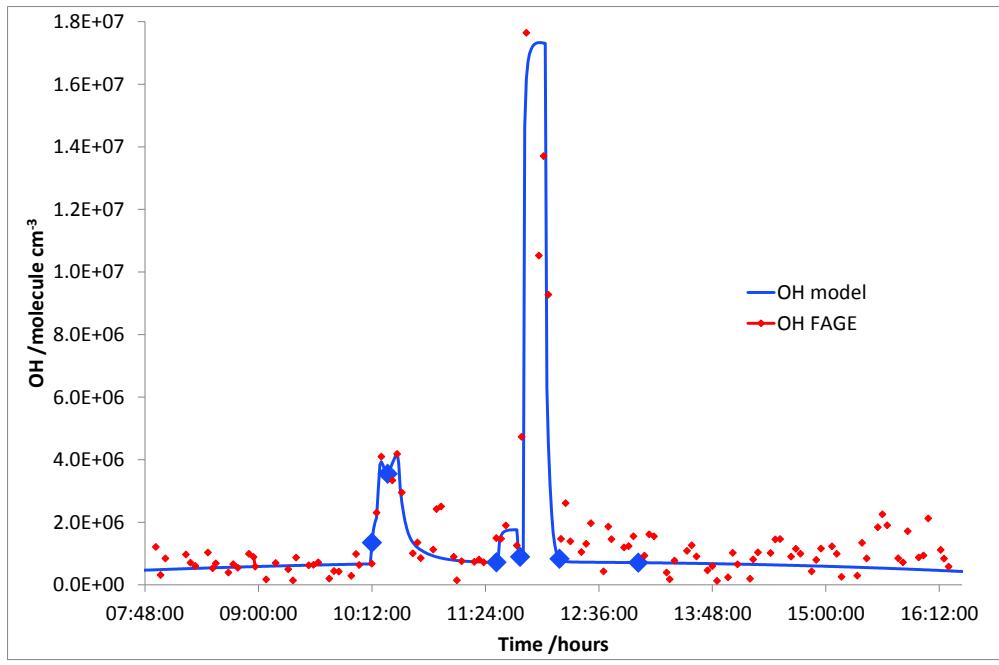
based on a recent estimation of indoor values<sup>25</sup> and the surface to volume ratio was assumed to be  $1.4\text{ m}^{-1}$ , the average value found during a recent campaign to investigate indoor air quality in European offices.<sup>33</sup> The impact of these assumptions on the predicted radical concentrations is discussed in Section 3.2.

### 3. Results and discussion

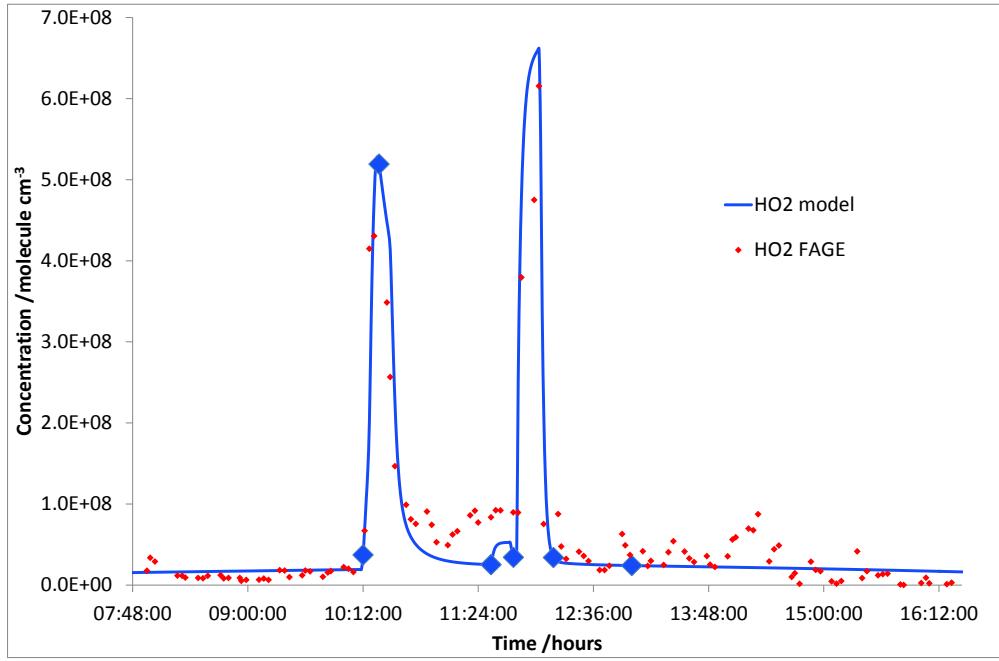
#### 3.1 Measured OH and HO<sub>2</sub> concentrations

Figures 1 and 2 show the OH and HO<sub>2</sub> measurements and model predictions for the ~8 hours of measurements, starting at about 08:00 h. The average concentrations of OH and HO<sub>2</sub> (denoted by [OH] and [HO<sub>2</sub>]) measured in the computer office in the absence of any human activities (period 1) were around  $5.9 \times 10^5\text{ cm}^{-3}$  and  $1.3 \times 10^7\text{ molecule cm}^{-3}$  respectively. The one-minute averaged OH concentrations remained close to or below the limit of detection ( $6.5 \times 10^5\text{ molecule cm}^{-3}$ ) during the measurements in the unperturbed environment. HO<sub>2</sub> remained above the detection limit ( $6.6 \times 10^5\text{ molecule cm}^{-3}$ ), demonstrating that a small, but significant, background concentrations of radicals exists in the room.

At 10:12, cleaning with the surface cleaner began and lasted for about 10 minutes. The measured [OH] increased during this period to  $4.2 \times 10^6\text{ molecule cm}^{-3}$ , whilst the [HO<sub>2</sub>] increased to  $4.3 \times 10^8\text{ molecule cm}^{-3}$ . The concentration of both radicals then decreased until the ACD became operational just before noon. The operation of the ACD generated a large peak in measured [OH] (up to  $1.8 \times 10^7\text{ molecule cm}^{-3}$ ), with the measured [HO<sub>2</sub>] peaking during this period at  $6.2 \times 10^8\text{ molecule cm}^{-3}$ . The measured concentrations of both radicals then decreased when the ACD ceased operation, although remained higher than those determined during period 1.



**Figure 1:** Concentrations of the hydroxyl (OH) radical during the measurement campaign with the FAGE measurements represented by red diamonds (one-minute averages) and the model predictions in blue (see text). Note that the large blue diamonds indicate the demarcation between different periods shown in Table 1.



**Figure 2:** Concentrations of the hydroperoxy ( $\text{HO}_2$ ) radical during the measurement campaign with the FAGE measurements represented by red diamonds (one-minute averages) and the model predictions in blue (see text). Note that the large blue diamonds indicate the demarcation between different periods shown in Table 1.

Few measurements exist in the literature with which to compare our results.  $\text{HO}_x$  radicals were measured in a classroom with natural ventilation in an urban environment,<sup>34</sup> as well as in a classroom in a suburban area in a low energy consumption building with

mechanical ventilation.<sup>35</sup> The photolysis of HONO produced peak concentrations of  $1.4 \times 10^6$  of OH and  $3.7 \times 10^7$  molecule cm<sup>-3</sup> of HO<sub>2</sub> in the naturally ventilated classroom during sunlit periods.<sup>36</sup> For the campaign in the mechanically ventilated classroom, maximum OH concentrations were observed during cleaning ( $3.5 \times 10^6$  molecule cm<sup>-3</sup> and HO<sub>2</sub> of up to  $6.0 \times 10^7$  molecule cm<sup>-3</sup>), though these were for much higher O<sub>3</sub> concentrations of 180 ppb compared to the study described here.<sup>35</sup>

### **3.2. Modelled OH and HO<sub>2</sub> concentrations**

Given the absence of measured terpene concentrations, a sensitivity study was carried out with the model with an aim to reproduce the modelled radical concentrations during the surface cleaning activity. Assuming this aim is achieved, it becomes reasonable to use the model to investigate the chemistry in greater detail. The sensitivity study focused on the first three periods (Table 1): the baseline before cleaning started (1), during cleaning (2) and the post-cleaning period (3). For the model tests described, the root mean square (rms) difference between modelled and measured concentrations for each of the three periods was calculated and normalised to the measured value for that period (so that high/low concentration periods didn't bias the overall agreement). The sum of the normalised rms differences for the three periods then provided an indication of which of the sensitivity tests best described the measured values.

The input values for the model were as described in Section 2. For limonene concentrations during cleaning, a recent study that reported indoor limonene concentrations following surface cleaning was used as a guide for a starting concentration. The average limonene concentrations in the published study were ~ 1 ppb before cleaning, ~13 ppb 0-30 minutes from the start of cleaning and ~3 ppb 30-60 minutes after cleaning started.<sup>6</sup> After correcting for the fact that our study involved a smaller volume, larger AER and shorter

cleaning time, equivalent averages for our conditions were ~0.2 ppb before cleaning, ~3 ppb average between 0-30 minutes and ~0.7 ppb 30-60 minutes after cleaning. The linalool concentration was set at an arbitrary emission rate of 75% that of limonene, such that peak concentrations of the two terpenes during cleaning were 4.5 and 6.2 ppb respectively for the preliminary model run (Run 1). The results of the sensitivity study are shown in Table 2 for the three periods. As well as varying the indoor limonene and linalool emissions, the outdoor concentrations of NO and O<sub>3</sub> were varied, as well as the assumed A/V and photolysis rates.

**Table 2:** Results of sensitivity study to fit modelled surface cleaning peaks of OH and HO<sub>2</sub> to the measurements

		OH concentration (10 <sup>5</sup> molecule cm <sup>-3</sup> )			HO <sub>2</sub> concentration (10 <sup>7</sup> molecule cm <sup>-3</sup> )			RMS for 3 periods
		Period 1	Period 2	Period 3	Period 1	Period 2	Period 3	
	<b>Measured</b>	<b>5.9</b>	<b>32.0</b>	<b>15.8</b>	<b>1.3</b>	<b>30.4</b>	<b>11.0</b>	N/A
1	Baseline	5.9	14.2	11.1	1.7	25.7	10.9	0.243
2	LIM 7.7 ppb	5.9	13.6	10.9	1.7	27.6	11.9	0.243
3	LIM 9.3 ppb	5.9	13.1	10.7	1.7	29.3	12.7	0.244
4	LIM 4.6 ppb	5.9	15.0	11.2	1.7	23.6	10.0	0.245
5	LIM 1.5 ppb	5.9	16.9	11.6	1.7	18.9	7.8	0.259
6	LIM 7.7 ppb; LIN 5.9 ppb	5.9	17.8	12.2	1.7	22.2	8.8	0.236
7	LIM 7.7 ppb; LIN 7.4 ppb	5.9	17.8	12.7	1.7	26.4	10.4	0.220
8	LIM 7.7 ppb; LIN 8.8 ppb	5.9	17.6	13.0	1.7	30.1	11.8	0.215
9	Outdoor NO 108%	5.9	17.9	13.0	1.7	29.5	11.3	0.213
10	Outdoor NO 200%	5.9	20.2	12.8	1.0	20.2	6.8	0.241
11	Outdoor O <sub>3</sub> by 150%	5.9	20.9	13.6	2.4	37.7	14.7	0.226
12	Transmitted vis 150%	5.9	17.8	13.0	1.7	30.1	11.7	0.214
13	Transmitted UV 170%	8.3	20.9	15.7	2.0	30.3	11.1	0.210
14	A/V 70%	5.6	18.3	13.1	1.8	31.7	12.6	0.214
15	A/V 130%	6.0	17.0	13.1	1.7	28.6	11.1	0.219
16	Add terpinene (see text)	5.9	29.7	13.2	1.7	30.3	10.3	0.184

Runs 2-8 explored increasing or decreasing the limonene (LIM) or linalool (LIN) emission rates. The maximum value of the relevant terpene during surface cleaning is reported.

Increasing the limonene concentration actually reduced the [OH] and made the agreement worse (Runs 2 and 3). Decreasing the limonene concentration increased the OH concentration, but also decreased HO<sub>2</sub>, so overall agreement was worse (Runs 4-5). For runs 6-8, the limonene emission was left as for run 2 when the rms error was slightly lower than the baseline value. As the linalool emission rate increased, the overall rms started to reduce up until a maximum linalool concentration of 8.8 ppb when the modelled OH peak during cleaning started to reduce again. Run 8 was therefore defined as a new baseline for the remaining sensitivity tests. Runs 9 and 10 increased outdoor (and hence indoor) NO concentrations. Although this increased the [OH], it decreased the [HO<sub>2</sub>] and made overall agreement worse when it was more than 10% greater than for the baseline run. Note that reducing NO concentrations reduced predicted [OH] and overall agreement worsened. Increasing outdoor (and hence indoor) O<sub>3</sub> (run 11) increased the predicted [OH], but also increased HO<sub>2</sub> to make worse agreement overall.

Increasing the amount of outdoor visible light transmitted through the windows increases OH slightly (run 12), though increasing UV had a larger impact (run 13). However, as this is increased through the whole run, the background values also increase so overall, the agreement tends to worsen for any increase that is large enough to affect the peak values. Finally, A/V was increased or decreased by 30% (runs 14-15). Decreasing the A/V improved the agreement slightly, but not enough to explain the difference with measurements.

None of these sensitivity tests could reproduce the measured values. The predicted [OH] for the surface cleaning period was far too low, no matter what factor was varied. Although some of the tests increased the [OH] for this period (e.g. increasing O<sub>3</sub>, reducing NO), such changes tended to make the HO<sub>2</sub> agreement worse and did not increase the OH concentration sufficiently to agree with the measured values.

With the observed concentrations of indoor OH and O<sub>3</sub>, both linalool and limonene act as net sinks for OH. Taking into account the [OH] of  $4 \times 10^6$  molecule cm<sup>-3</sup> during cleaning, limonene becomes a net OH source when the O<sub>3</sub> concentration is 142 ppb and linalool when O<sub>3</sub> is 83 ppb, much higher concentrations than observed here. Increasing the concentrations of these VOCs reduces [OH], rather than increasing it. Reducing them increases [OH] (but not by enough) and also reduces the [HO<sub>2</sub>] to below that measured.

We therefore searched in the literature for a terpene that was an OH source under these conditions and found that α-terpinene was a possibility. Past studies have found α-terpinene to be present in cleaning products at similar levels to limonene.<sup>37,38</sup> Its rate coefficient for reaction with OH is approximately two times faster than for limonene, but importantly, with O<sub>3</sub> is 100 x faster.<sup>39</sup> Therefore, only 7 ppb of O<sub>3</sub> is needed to make α-terpinene a net OH source. A simple scheme was consequently included in the model mechanism for terpinene. Reactions with OH and O<sub>3</sub> were included with the measured rate coefficients, and the rest of the simplified mechanism proceeded via analogy with linalool. The concentrations of limonene, linalool and terpinene were then varied again to attempt to match the observed peak. The best results were found for maximum concentrations of limonene, linalool and terpinene of 0.7 ppb, 3.9 ppb and 70 ppt respectively. This produced an rms value of 0.184 (Run 16, Table 2).

For the use of the ACD, another sensitivity study was used to investigate which OH emission rate best reproduced the measured [OH] and [HO<sub>2</sub>] in periods 4 and 5. Model agreement was tested with and without a limonene emission, given the odour was detectable close to the ACD unit. The best agreement was found when we assumed that no limonene was emitted from the ACD, but that the OH emission rate was  $8.6 \times 10^7$  molecule cm<sup>-3</sup> during period 5 (corresponding to a direct emission rate from the ACD of  $1.6 \times 10^{16}$  molecule s<sup>-1</sup>).

For period 4, the emission rate was reduced to ~1/20<sup>th</sup> of this value for best agreement, as the ACD was further from the FAGE (2 m distant cf. 0.5 m in period 5).

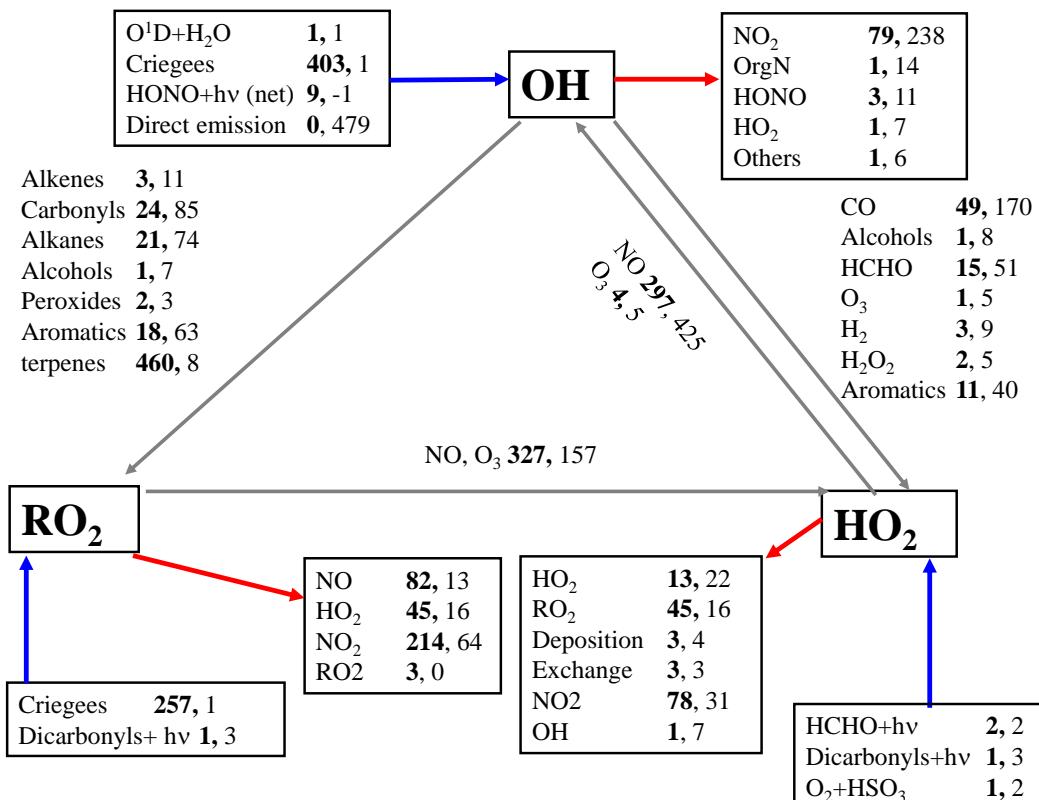
Figures 1 and 2 show the model predictions along with the measured [OH] and [HO<sub>2</sub>]. The model is generally in reasonable agreement, with the main exception being the period between the two cleaning activity peaks, where [HO<sub>2</sub>] is poorly simulated by the model. This is despite the fact that the [OH] is reasonably well reproduced during the same period, but likely reflects the assumptions we have made about the composition of the cleaning liquid. Measured and modelled [OH] and [HO<sub>2</sub>] are within 50% of each other for the duration of the experiment and generally much better: OH is within 7.5% for the cleaning periods. This level of agreement was considered sufficient to explore the chemical composition following each of these cleaning activities in more detail and in particular, to compare secondary pollutant formation following an OH peak driven by terpene emissions with one driven by direct OH emission.

Figure 3 shows a rate of production analysis for OH, HO<sub>2</sub> and RO<sub>2</sub> for the two cleaning activities. Initiation reactions are those that create radicals from non-radical reactants (often photolysis driven, but also includes formation through ozone-terpene reactions via Criegee intermediates), propagation reactions transform one radical to another and termination reactions involve radicals reacting to produce non-radical products.

For OH, the formation was driven by the terpene reactions with O<sub>3</sub> for surface cleaner use and by direct emission during the ACD use. Although HONO was a net source of OH during use of the surface cleaner, during ACD use, the high concentrations of OH meant that HONO was formed much more rapidly through reaction with NO than consumed via photolysis. The HONO concentration was also relatively low at 0.4-0.5 ppb under these conditions. Termination reactions of OH and propagation to HO<sub>2</sub> and RO<sub>2</sub> occurred at rates 3-4 times faster for the ACD compared to surface cleaner use, reflecting the higher OH

concentrations for the former cleaning activity. Reaction with NO<sub>2</sub> was responsible for most OH removal in both cases.

HO<sub>2</sub> initiation was driven by photolysis of carbonyls for both cleaning episodes, whilst termination was from a range of processes, but most important was reaction with NO<sub>2</sub> to form HO<sub>2</sub>NO<sub>2</sub>, followed by reaction with RO<sub>2</sub>. The reaction of ozone with the monoterpenes via Criegees intermediates dominated RO<sub>2</sub> initiation for surface cleaner use, whilst carbonyl photolysis was more important for ACD use. For both cleaning periods, reaction with NO<sub>2</sub> to form PAN-type species dominated termination.



**Figure 3.** Rates of reaction for the major initiation, propagation and termination reactions for OH, HO<sub>2</sub> and RO<sub>2</sub> radicals in units of 10<sup>5</sup> molecule cm<sup>-3</sup> s<sup>-1</sup>. The figure in bold is for surface cleaning and the other figure is for ACD use. Blue arrows denote initiation, red termination and propagation reactions are shown by grey arrows.

### 3.3 Production of secondary species: Impact on indoor air quality

Figure 4 shows the composition of RO<sub>2</sub> radicals during the two cleaning activities, where RO<sub>2</sub> represents the sum of all peroxy radicals in the model excluding HO<sub>2</sub>. This analysis

focuses on the RO<sub>2</sub> formed during the first 2-3 oxidation steps of the parent VOCs and these accounted for 96% of total RO<sub>2</sub> during surface cleaning and ~80% during ACD use. The remainder of the RO<sub>2</sub> concentration, particularly during ACD use, was composed of small contributions from many different RO<sub>2</sub>. The further down the oxidation chain you go, the more likely an individual peroxy radical will have derived from more than one source and so assigning its parent VOC becomes more difficult.

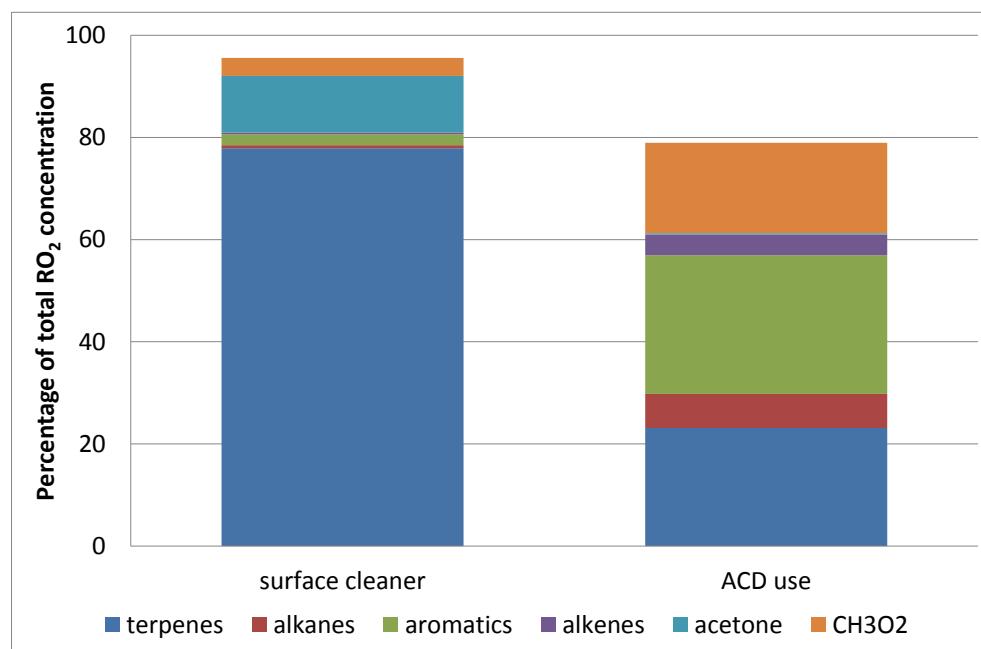


Figure 4: Composition of RO<sub>2</sub> radicals during the two cleaning activities according to the VOC(s) from which it was derived.

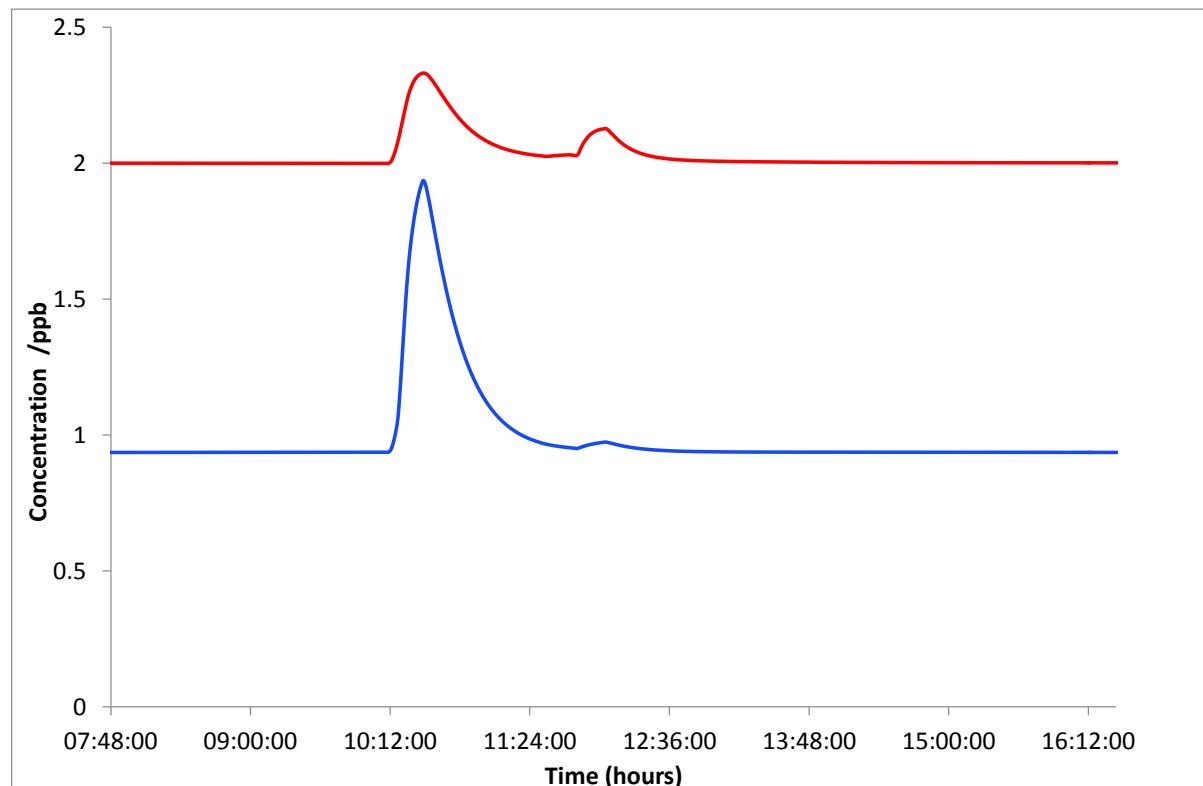
During the use of the surface cleaner, the dominant radicals were those formed from the degradation of the terpenes in the cleaning product (figure 3). The RO<sub>2</sub> concentration peaked at ~70 ppt following the use of the surface cleaner at ~10:20, with a much smaller peak of ~ 17 ppt during the use of the ACD. During the first peak, ~80% of the RO<sub>2</sub> radicals derived from the terpene schemes, with a further 11% from acetone degradation (and numerous smaller contributions from other species). During ACD use, ~23% of the RO<sub>2</sub> derived from terpene oxidation, 27% from aromatic oxidation, 7% from alkanes and 4% from alkenes (figure 3). The CH<sub>3</sub>O<sub>2</sub> radical formed 18% of the total RO<sub>2</sub> during ACD use,

compared with only 4% during surface cleaning, although its absolute concentration during both activities was similar at ~3 ppt. The CH<sub>3</sub>O<sub>2</sub> radical is formed through the oxidation of methane, but it is also the end product of the oxidation of a number of other VOCs, so likely has numerous sources.

It is interesting that the RO<sub>2</sub> from aromatic oxidation increased in prominence during ACD use, both in percentage terms but also absolute terms (from ~1.5 to 4.5 ppt). The aromatic species dominated the measured hydrocarbons in the PC room and their oxidation rates with OH are much slower than for the terpenes. For instance, for an OH concentration of  $1.8 \times 10^7$  molecule cm<sup>-3</sup>, the lifetime of limonene is ~6 minutes whilst that of o-xylene is over an hour. Consequently, the production rate of RO<sub>2</sub> was much lower during ACD use because of the absence of appreciable terpene concentrations. Clearly then, the mode of cleaning can have a large impact on the subsequent indoor air chemistry. Note that the NO<sub>3</sub> concentration remained low during the whole simulation, never exceeding 0.1 ppt. Although it has been suggested that NO<sub>3</sub> concentrations could be as high as 1 ppt indoors,<sup>40</sup> other modelling studies have also predicted low concentrations.<sup>24</sup> Clearly, measurements of NO<sub>3</sub> and speciated RO<sub>2</sub> indoors would be highly beneficial to help validate model predictions.

Figure 5 shows the modelled concentrations of HCHO and CH<sub>3</sub>COCH<sub>3</sub>. Whilst HCHO exhibited distinct peaks during both cleaning activities, acetone showed a more pronounced peak during surface cleaning. HCHO reacts ~50x faster with OH than acetone, so one might have expected the acetone concentration to be higher during ACD use when the OH concentration was highest. However, HCHO is also formed rapidly through VOC oxidation that is enhanced at high OH concentrations, such that it sustained a similar concentration during ACD use to that observed during surface cleaner use. Many of the formation routes of acetone in the mechanism involve RO<sub>2</sub> interactions, particularly permutation reactions. The lower concentrations of RO<sub>2</sub> during the ACD use meant that this

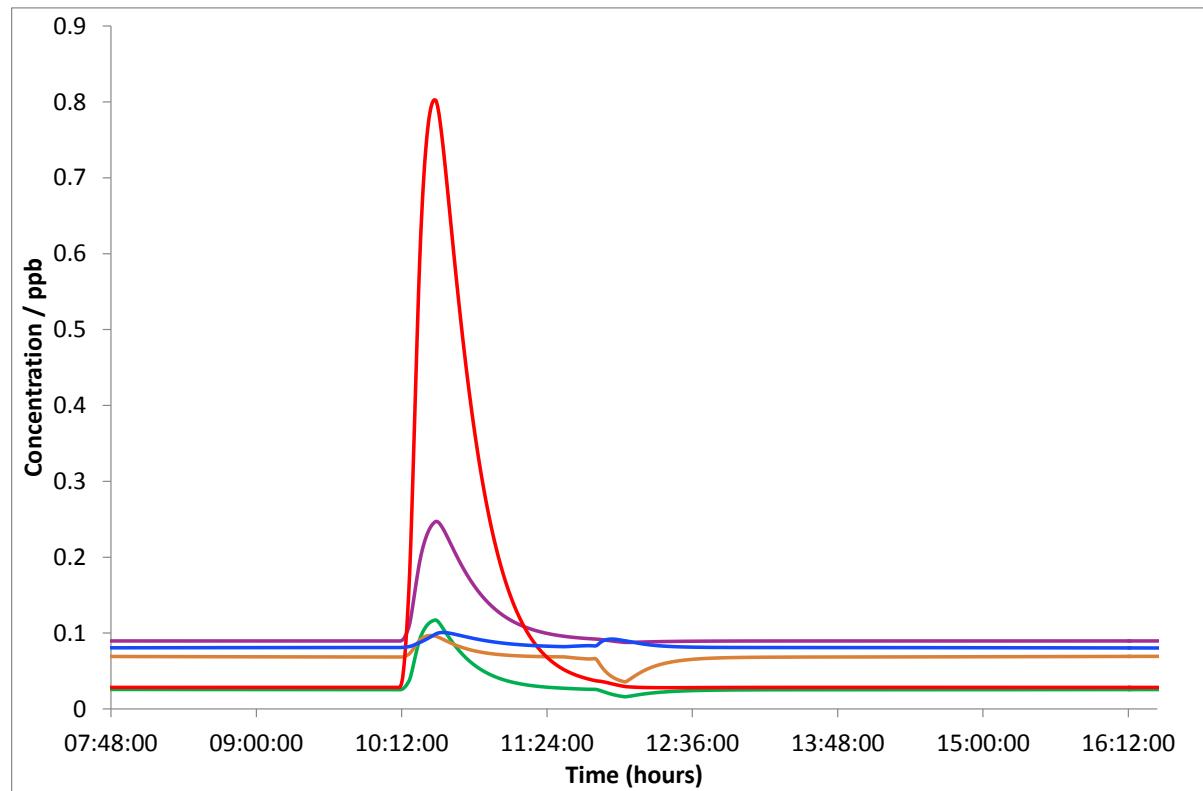
route was suppressed. Also, linalool oxidation is a very efficient way to produce acetone. OH oxidation leads to an acetone yield of 34-51%, with ozonolysis producing 21-35% according to experimental measurements.<sup>29,30</sup> These 2 factors explain the relative heights of the acetone peaks.



**Figure 5:** Concentrations (ppb) of HCHO (red) and CH<sub>3</sub>COCH<sub>3</sub> (blue) during the model simulation.

Figure 6 shows a selection of secondary products formed from the terpene degradation mechanisms in the model (structures are provided in Supplementary Information). With the exception of LMLKET (3-acetyl-6-oxoheptanal), these species showed a more pronounced peak during the use of the surface cleaner when compared to the ACD operation, which isn't surprising given the higher concentrations of the terpenes at that point. LMLKET reacts much more slowly with OH than LIMKET or LIMAL (rate coefficient is  $3.6 \times 10^{-11}$  for LMLKET cf.  $\sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the other two). Presumably, this difference in reactivity with such high OH concentrations permitted the

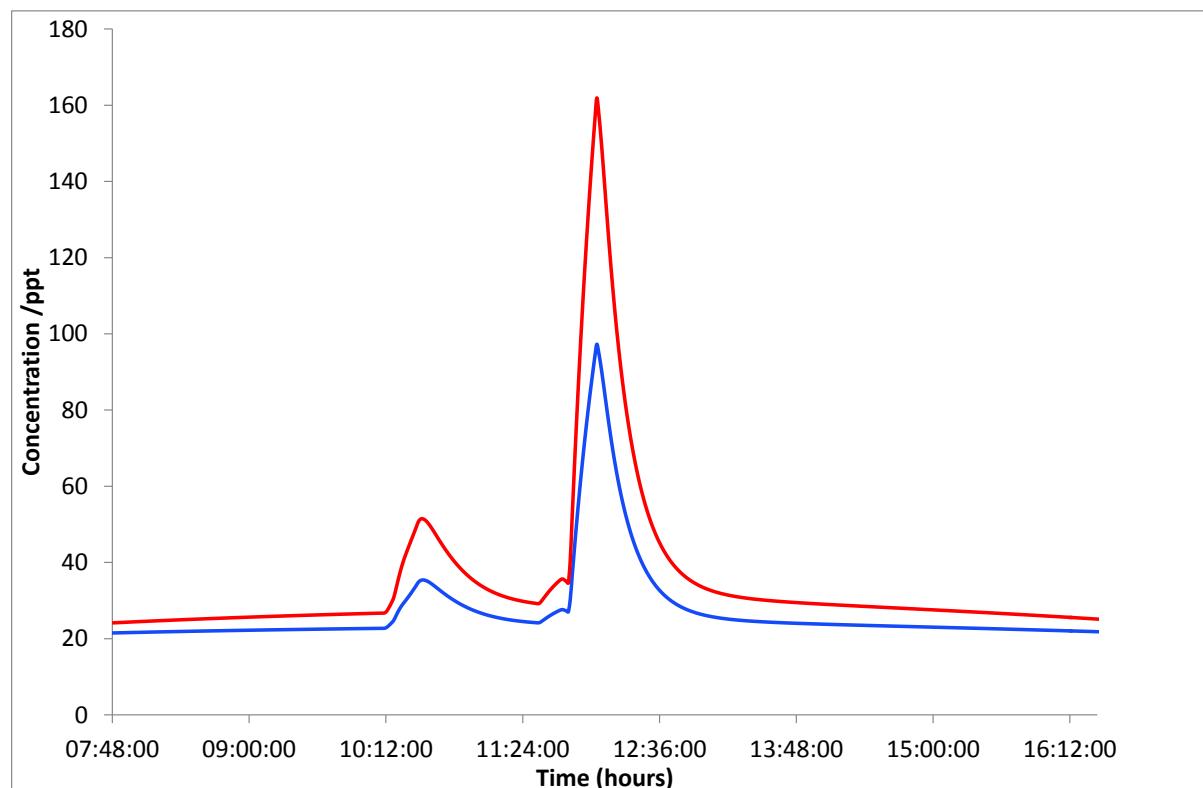
LMLKET concentration to be maintained relative to the other two during ACD use, given the large number of formation routes for this species following limonene oxidation.<sup>41</sup>



**Figure 6:** Concentrations (ppb) of LIMAL (3-Isopropenyl-6-oxoheptanal, green), LIMKET (4-Acetyl-1-methyl-1-cyclohexene, orange), OCT3ONE (3-octanone, purple), C<sub>6</sub>H<sub>13</sub>CHO (heptanal, red) and LMLKET (3-Acetyl-6-oxoheptanal, blue). Names are from the MCM available at <http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm> and structures are shown in Appendix B.

The largest peak was for heptanal (C<sub>6</sub>H<sub>13</sub>CHO), which was derived in this simulation from linalool (and terpinene) degradation chemistry. This was assumed as a surrogate third generation product in the absence of a more detailed mechanism (see Supplementary Information), so its concentration should be viewed as a proxy for linalool degradation in general. LIMAL, LIMKET and LMLKET have been shown to be important in the gas phase following the use of a limonene-containing cleaner in a previous modelling study.<sup>41</sup> The presence of LIMAL and LIMKET was also detected following use of a surface cleaner in a 20 m<sup>3</sup> chamber, with maximum concentrations of around 3 and 0.2 ppb respectively, albeit under higher ozone concentrations and a smaller volume than for the current study.<sup>5</sup>

Figure 7 shows the predicted concentrations of glyoxal and methylglyoxal, with both species exhibiting a larger peak for the use of the ACD compared to surface cleaning. These two species are formed from oxidation of aromatics and also from alkenes. Interestingly, ambient measurements have shown that the ratio of glyoxal to formaldehyde decreases as the composition of VOCs in the atmosphere moves from anthropogenic to biogenic in origin.<sup>42</sup> The same happens indoors with a lower ratio of glyoxal: HCHO for the surface cleaner (0.015) compared to ACD use (0.045). VOC composition was dominated by the terpenes for surface cleaning compared to ACD use where a wider range of VOCs were able to react with OH. This observation is reinforced by the RO<sub>2</sub> composition.



**Figure 7:** Concentrations of glyoxal (blue) and methylglyoxal (red) during the model simulation.

The selection of simulated concentrations presented in Figures 4-7 shows different concentration profiles of secondary species depending on the mode of cleaning. Whilst the indoor air composition following surface cleaning has been investigated through

measurements and modelling studies previously,<sup>5,6,25,41</sup> we believe this represents the first study to measure and model radical concentrations during the use of a commercial ACD and to investigate in detail the resulting chemistry that follows. Clearly, the choice of cleaning method can have a significant bearing on the resulting composition of the air inside a cleaned room and consequently, any subsequent health effects. Although the concentrations of the secondary species shown here do not reach particularly high concentrations, the cleaning activities investigated were both of short duration and with a relatively high air exchange rate of 3.5 ach<sup>-1</sup>. In reality, ACDs would likely be operating for much longer periods than during our study with much higher secondary pollutant concentrations possible. For instance, given the rate at which glyoxal and methylglyoxal concentrations increase during ACD use, it is possible that their concentrations could reach 2 and 3.6 ppb after 8 hours of ACD operation and assuming a supply of VOCs. Given the potentially harmful nature of some of these products<sup>5</sup> and the unknown effects of exposure to mixtures, this is an important area for further research.

## Conclusions

This study has demonstrated that air cleaning devices are able to produce OH concentrations indoors that are higher than those typically observed outdoors on hot, sunny days and also, than those that result indoors following the use of a surface cleaning product. Although such instruments are often marketed as effective removers of biological pathogens, their propensity to form chemical contaminants is a large drawback, but one that is relatively under-investigated. The results from this study show that a range of secondary pollutants can be produced following cleaning and this could be of particular concern where such instruments are operated over long periods. There is a clear need to carry out careful assessments of the effect on human health of air cleaner technology in a range of indoor

environments, so that any gains through biological pathogen removal can be weighed up against the adverse effects that may arise from the formation of chemical contaminants<sup>9,43</sup>.

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## Supplementary Information

### Linalool scheme

The new reaction scheme follows the MCM protocol according to Jenkin et al. (1997). Note that LINALOOL, LINALAO2, LINALBO2, LINALAO, LINALBO, LINALANO3, LINALBNO3, LINALAOOH, LINALBOOH, LINALAOH, LINALBOH, LINALOOB and LINALBOO are all new species, whilst the remainder already exist in the MCM and can be seen at <http://mcm.leeds.ac.uk/MCM/> with references for the generic rate coefficients. Units for rate coefficients are  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  except for KDEC and J41 which have units of  $\text{s}^{-1}$ .

Reaction No	Rate coefficient	Reactants	Products
<b>1a</b>	$1.7 \times 10^{-10} * 0.23$	LINALOOL+OH	LINALAO2
<b>1b</b>	$1.7 \times 10^{-10} * 0.77$	LINALOOL+OH	LINALBO2
<b>2a</b>	KRO2NO*0.772	LINALAO2+NO	LINALAO+NO <sub>2</sub>
<b>2b</b>	KRO2NO*0.228	LINALAO2+NO	LINALANO3
<b>3</b>	KRO2NO3	LINALAO2+NO <sub>3</sub>	LINALAO+NO <sub>2</sub>
<b>4</b>	KRO2HO2*0.914	LINALAO2+HO <sub>2</sub>	LINALAOOH
<b>5a</b>	$9.20 \times 10^{-14} * 0.7$	LINALAO2+RO <sub>2</sub>	LINALAO
<b>5b</b>	$9.20 \times 10^{-14} * 0.3$	LINALAO2+RO <sub>2</sub>	LINALAOH
<b>6a</b>	KRO2NO*0.772	LINALBO2+NO	LINALBO+NO <sub>2</sub>
<b>6b</b>	KRO2NO*0.228	LINALBO2+NO	LINALBNO3
<b>7</b>	KRO2NO3	LINALBO2+NO <sub>3</sub>	LINALBO+NO <sub>2</sub>
<b>8</b>	KRO2HO2*0.914	LINALBO2+HO <sub>2</sub>	LINALBOOH
<b>9a</b>	$9.20 \times 10^{-14} * 0.7$	LINALAO2+RO <sub>2</sub>	LINALBO
<b>9b</b>	$9.20 \times 10^{-14} * 0.3$	LINALAO2+RO <sub>2</sub>	LINALBOH
<b>10</b>	$7.36 \times 10^{-11}$	LINALAOOH+OH	LINALAO2
<b>11</b>	J41	LINALAOOH	LINALAO+OH
<b>12</b>	$6.20 \times 10^{-11}$	LINALANO3+OH	OCT3ONE+NO <sub>2</sub>
<b>13</b>	KDEC	LINALAO	OCT3ONE+HO <sub>2</sub> +HOCH <sub>2</sub> CHO
<b>14</b>	$7.02 \times 10^{-11}$	LINALAOH+OH	OCT3ONE+HO <sub>2</sub>
<b>15</b>	$1.04 \times 10^{-10}$	LINALBOOH+OH	LINALBO2
<b>16</b>	J41	LINALBOOH	LINALBO+OH
<b>17</b>	$6.20 \times 10^{-11}$	LINALBNO3+OH	C <sub>6</sub> H <sub>13</sub> CHO+NO <sub>2</sub>
<b>18</b>	KDEC	LINALBO	C <sub>6</sub> H <sub>13</sub> CHO+HO <sub>2</sub> +CH <sub>3</sub> COCH <sub>3</sub>
<b>14</b>	$6.70 \times 10^{-11}$	LINALBOH+OH	C <sub>6</sub> H <sub>13</sub> CHO+HO <sub>2</sub>
<b>15a</b>	$4.1 \times 10^{-16} * 0.8$	LINALOOL+O <sub>3</sub>	CH <sub>3</sub> CCH <sub>3</sub> OOA+C <sub>6</sub> H <sub>13</sub> CHO
<b>15b</b>	$4.1 \times 10^{-16} * 0.2$	LINALOOL+O <sub>3</sub>	LINALOOB
<b>16a</b>	KDEC*0.5	LINALOOB	LINALBOO+OH
<b>16b</b>	KDEC*0.5	LINALOOB	C923O2+CO+OH
<b>17</b>	$1.20 \times 10^{-15}$	LINALBOO+CO	CH <sub>3</sub> COCH <sub>3</sub>
<b>18</b>	$1.00 \times 10^{-14}$	LINALBOO+NO	CH <sub>3</sub> COCH <sub>3</sub> +NO <sub>2</sub>
<b>19</b>	$1.00 \times 10^{-15}$	LINALBOO+NO <sub>2</sub>	CH <sub>3</sub> COCH <sub>3</sub> +NO <sub>3</sub>
<b>20</b>	$7.00 \times 10^{-14}$	LINALBOO+SO <sub>2</sub>	CH <sub>3</sub> COCH <sub>3</sub> +SO <sub>3</sub>

<b>21a</b>	$1.40 \times 10^{-17}$	LINALBOO+H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>
<b>21b</b>	$2.00 \times 10^{-18}$	LINALBOO+H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub>

Where KRO<sub>2</sub>NO =  $2.7 \times 10^{-12} \times e^{(360/\text{TEMP})}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; KRO<sub>2</sub>NO<sub>3</sub> =  $2.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; KRO<sub>2</sub>HO<sub>2</sub> =  $2.91 \times 10^{-13} \times e^{(1300/\text{TEMP})}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; KDEC =  $1.00 \times 10^6$  s<sup>-1</sup>; J41 is the photolysis rate used for methyl hydroperoxide in the MCM. Over the average conditions of this simulation, the average value is  $2.6 \times 10^{-7}$  s<sup>-1</sup>.

### Chemical structures for key species

